TIRE WASTE AND RECYCLING

Edited by

Trevor M. Letcher, Valerie L. Shulman, Serji Amirkhanian

TIRE WASTE AND RECYCLING

This page intentionally left blank

TIRE WASTE AND RECYCLING

Edited by

TREVOR M. LETCHER
School of Chemistry, University of KwaZulu-Natal, Durban, South Africa

VALERIE L. SHULMAN
ETRA, Brussels, Belgium

SERJI AMIRKHANIAN
The University of Alabama, Tuscaloosa, AL, United States

ACADEMIC PRESS
An imprint of Elsevier

Academic Press is an imprint of Elsevier
125 London Wall, London EC2Y 5AS, United Kingdom
525 B Street, Suite 1650, San Diego, CA 92101, United States
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom

Copyright © 2021 Elsevier Inc. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-12-820685-0

For Information on all Academic Press publications
visit our website at https://www.elsevier.com/books-and-journals

Publisher: Matthew Deans
Acquisitions Editor: Edward Payne
Editorial Project Manager: Rachel Pomery
Production Project Manager: Poulouse Joseph
Cover Designer: Mark Rogers

Typeset by MPS Limited, Chennai, India

Contents

List of contributors xv
Preface xix

Part I Introduction and basic information about tires 1

1 An introduction to tires and recycling 3
Valerie L. Shulman

1.1 Introduction 3
1.2 Beginning of urbanization and advancement toward globalization 4
1.3 The catalyst for change 6
1.4 Sustainable development: the context for recycling 7
1.5 Implementation and progress 11
1.6 Interpretations 13
References 14

2 Tires and the tire market 15
Peter Taylor OBE

2.1 Introduction: the early days of the tire 15
2.2 The global players and their national roots 15
2.3 The economics of tire manufacturing 17
2.4 What we expect from our tires 20
2.5 Tires and the consumer 21
2.6 Future trends 23

3 Global motorization: increasing tire usage 27
Simon Hodson

3.1 Introduction 27

3.2 Demand for mobility 27
3.3 Regional analysis 32
3.4 Changes in motorization 36
References 42

4 Management of end-of-life tires 43
Valerie L. Shulman

4.1 Introduction 43
4.2 The tire: the raw material for recycling 45
4.3 Management of postconsumer tires 46
4.4 Material recycling: treatments and technologies 48
4.5 Material outputs 55
4.6 Traditional and evolving markets 56
4.7 Energy recovery 62
4.8 The future 63
References 65
Further reading 65

Part II Toward a circular economy 69

5 The 4 Rs: reduce, reuse, recycle, and recover 71
Peter Taylor OBE

5.1 Introduction 71
5.2 The European Union Landfill Directive 72
5.3 Producer responsibility and the circular economy 73
5.4 Putting our old tires to good use 74
5.5 Putting reuse + recycling into perspective 76

Part III Material treatments and technologies 79

6 Cryogenic tire recycling 81
Jim Anderson

6.1 A first step: understanding liquid nitrogen 81
6.2 The beginning of the process: the shredder 83

6.3 The freeze chamber 84
6.4 Hammermills 85
6.5 Fine mesh cryogenic system 91
6.6 What to do with cryorubber crumbs 94

7 Regeneration and devulcanization 97

7.1 Regeneration and devulcanization 97
Wilma Dierkes and Sitisaiyidah Saiwari

7.1.1 Introduction 97
7.1.2 Analysis of the devulcanization mechanism 98
7.1.3 Devulcanization versus regeneration 103
7.1.4 Influence of rubber composition on the devulcanization efficiency: tire rubbers 111
7.1.5 Influence of rubber composition on the devulcanization efficiency: fillers 117
7.1.6 Process parameters affecting devulcanization efficiency 120
References 125

7.2 In-product-sorting end-of-life tires for effective recycling by devulcanization 130

Said Seghar and Florian Lacroix

7.2.1 Introduction 130
7.2.2 Existing sorting criteria and their limits 131
7.2.3 Mechanical characteristics of devulcanized materials according to the type of end-of-life tires 132
7.2.4 Analysis of ground tire rubber samples available on the European market 133
7.2.5 Impact of ground tire rubber heterogeneities on the devulcanized material 136
7.2.6 Analysis of ground tire rubber at the industrial scale (case of industrial output) 139
7.2.7 Conclusion 143
References 144

8 Make rubber, sell rubber: building a sustainable industry 145
D. Elroy Fimrite and Carl D. McAfee

8.1 The value proposition 145
8.2 Understanding the problem 146
8.3 Conversion: challenges of processing tires to ground tire rubber 148
8.4 Historical solution model: the reclaim industry 150
8.5 Defining devulcanization 152
8.6 Measuring results 153
8.7 Market opportunities 154
8.8 Building an industry 158
8.9 Thermoset rubber 159
8.10 Polymer-modified asphalts 162
8.11 Conclusions 163
References 163

9 Pyrolysis 165

9.1 Technology update toward recovered carbon black 165

Juan Daniel Martínez, C. Gisèle Jung and Jean Paul Bouysset

9.1.1 An introduction to pyrolysis 165
9.1.2 An overview of the pyrolysis technologies 168
9.1.3 Thermal pyrolysis 172
9.1.4 Microwave pyrolysis 173
9.1.5 Conclusions 174
References 175

9.2 Recovered carbon black: characteristics and properties in compounds 177

Juan Daniel Martínez, C. Gisèle Jung and Jean Paul Bouysset

9.2.1 Carbon black generalities 177
9.2.2 Recovered carbon black (rCB) generalities 180
9.2.3 Impurities contained in the rCB 185
9.2.4 Upgrading of rCB after pyrolysis 186
9.2.5 Conclusions 187
References 188

9.3 Recovered carbon black: potential markets 191

Juan Daniel Martínez, C. Gisèle Jung and Jean Paul Bouysset

9.3.1 Carbon black market 191
9.3.2 Approximation to the recovered carbon black (rCB) market 192
9.3.3 Market price and projections 198
9.3.4 Conclusions 198
References 199

9.4 Recycling of waste tires for silicon carbide production 201

Cesare Freda, Enrico Catizzone and Giacinto Cornacchia

9.4.1 Introduction 201
9.4.2 SiC as a high-added value material 203
9.4.3 Production of silicon carbide from alternative carbon sources 206
9.4.4 The TyGRe project 212
9.4.5 SiC from end-of-life tire pyrolysis streams: a simulation study 216
9.4.6 Conclusion 221
References 222

10 Surface-modified materials 225

Alexander Paasche and Frank Lindner

10.1 Introduction 225
10.2 Why modify? 226
10.3 Physical modification 228
10.4 Chemical modification 230
10.5 Biological treatment 244
10.6 Economic considerations 245
References 247

11 Molding industrial products from tire ground rubber 251

Fabrizio Quadrini, Denise Bellisario and Loredana Santo

11.1 Introduction 251
11.2 Scientific state of the art 252

11.3 New findings in direct molding of ground tire rubber 260
11.4 Conclusion 268
References 270

Part IV Key markets for recycling materials, products, and applications 273

12 Environmental impact of tires used in marine construction 275
K.J. Collins

12.1 Introduction 275
12.2 Marine applications for whole tires 276
12.3 Microplastics 292
References 293

13 Civil engineering applications 297

13.1 Surface modification of crumb rubber by cold plasma for performance enhancement of rubberized asphalt 297

Serji Amirkhanian, Feipeng Xiao and Jin Li

13.1.1 Introduction 297
13.1.2 Materials and methods 300
13.1.3 Surface characteristics of plasma-treated crumb rubber 306
13.1.4 Engineering performance of plasma-treated rubberized asphalt 315
13.1.5 Mechanisms behind performance enhancement 327
13.1.6 Conclusions 333
References 335

13.2 Application of rubberized asphalt mixtures in low-temperature environments 338

Serji Amirkhanian, Feipeng Xiao and Tao Wang

13.2.1 Introduction 338
13.2.2 Mechanism of crack resistance of rubberized asphalt 341

13.2.3 Key factors influenced low-temperature performance of rubberized asphalt 345
13.2.4 Field applications 357
13.2.5 Conclusions 362
References 363

13.3 Application of rubberized asphalt materials: Chinese experiences 371

Feipeng Xiao, Qidi Zong and Xiangdao Hou

13.3.1 Introduction 371
13.3.2 Rubberized asphalt 372
13.3.3 Rubberized asphalt mixture 374
13.3.4 Production and construction processes 381
13.3.5 Typical application of rubberized asphalt mixtures 389
13.3.6 Environmental and economic benefits of rubberized asphalt pavement 402
13.3.7 Conclusions 408
References 408

13.4 Quiet pavements: a novel approach of utilizing rubberized asphalt mixtures 420

Krishna Prapoorna Biligiri

13.4.1 Introduction 420
13.4.2 Asphalt–rubber as a tire/pavement noise mitigation strategy 423
13.4.3 Discussion and way forward 428
Acknowledgments 429
References 429

13.5 Utilization of crumb rubber modifiers in producing polymer asphalt emulsions 432

Amanda Koh

13.5.1 Introduction 432
13.5.2 Crumb rubber-modified asphalt emulsions 439
13.5.3 Conclusions and future directions for CR-modified asphalt emulsions 449
References 451

13.6 Utilization of rubberized asphalt in the Europe 454

Davide Lo Presti, Juan Gallego Medina, Jorge Carvalho Pais, Lily Poulikakos, Moises Bueno, Davide Dalmazzo and Ezio Santagata

13.6.1 Introduction 454
13.6.2 Rubberized asphalt mixtures: an overview of technologies currently used in Europe 455
13.6.3 Experience and lessons learned—Spain 459
13.6.4 Experience and lessons learned—Portugal 464
13.6.5 Experiences and lessons learned—Italy 469
13.6.6 Experience and lessons learned—Switzerland 473
13.6.7 Conclusions 476
Acknowledgments 477
References 478

14 Sports and leisure infrastructure and applications: styrene butadiene crumb rubber infill in artificial turf sports fields 483
Nicolas Evans

14.1 How tire waste and sports infrastructure fit together – the role of artificial turf in football and football development 483
14.2 Outlook and challenges: how will styrene butadiene rubber fit into sports systems down the line? 489
14.3 What is the verdict on the status quo of tire waste application in sports installations? 495
References 497

15 Roads to opportunities 499
Serji Amirkhanian

15.1 Brief history of roads 499
15.2 Introduction 500
15.3 Roads around the world 501
15.4 Impact of road infrastructure on society 502
15.5 Impact of new innovations on roads 506
15.6 A brief introduction: what is rubberized asphalt and why should you use it? 507
15.7 Conclusions 511
References 512

16 Construction: acoustic insulation in buildings and railway applications 515
Valentí Fontserè, Miquel Morata and Joan Peset

16.1 Introduction 515
16.2 Neoballast 515
16.3 The Anagennisi project 524
16.4 Conclusions 544
References 544

17 Reuse of tire constituents in concrete 547
Kyriacos Neocleous, Thomaida Polydorou and Kypros Pilakoutas

17.1 Introduction 547
17.2 Steel fiber-reinforced concrete 547
17.3 Plain rubberized concrete and steel fiber-reinforced rubberized concrete 551
17.4 Textile fiber-reinforced rubberized concrete 558
References 561

18 Tire-derived aggregate applications in civil engineering 565
Armen Amirkhanian and Eleanor Skelton

18.1 Introduction 565
18.2 Retaining walls and bridge abutments 566
18.3 Embankments and engineered fill 570
18.4 Safety and environmental concerns 571
18.5 Summary 576
References 576

Part V The future 579

19 Green public procurement 581
Ettore Musacchi

19.1 General information on green public procurement 581
19.2 Economic aspects 583
19.3 Green public procurement policy 585

19.4 Legal framework for green public procurement 587
19.5 Environmental management systems and green public procurement 588
19.6 Clean vehicles directive and green public procurement 588
19.7 Green public procurement criteria 589
19.8 Postconsumer tires and recycled tire materials in green public procurement 590
19.9 What are the opportunities for tire recycling sector critical and crucial point? 591
19.10 Some successful good practices as opportunities to use recycled tire materials 591
19.11 Circular procurement 598

20 Roads to the future 603
Valerie L. Shulman and Serji Amirkhanian

20.1 Introduction 603
20.2 The context for tire recycling 604
20.3 Market focus—thoughts for the future 608
20.4 The future: getting started 620

Index 623

List of contributors

Armen Amirkhanian
The University of Alabama, Tuscaloosa, AL, United States

Serji Amirkhanian
Department of Civil, Environmental and Construction Engineering, The University of Alabama, Tuscaloosa, AL, United States

Jim Anderson
RTI Cryogenics Inc., Cambridge, ON, Canada

Denise Bellisario
Department of Industrial Engineering, University of Rome "Tor Vergata" Via del Politecnico 1, Rome, Italy

Krishna Prapoorna Biligiri
Civil & Environmental Engineering, Indian Institute of Technology Tirupati, India

Jean Paul Bouysset
Senior Consultant, Rubber Products Pyrolysis and Regeneration (RPPR), Versailles, France

Moises Bueno
Empa—Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Enrico Catizzone
ENEA, Laboratory of Thermochemical Processes for Wastes and Biomass Valorization, Rotondella, Italy

K.J. Collins
Ocean and Earth Science, University of Southampton, Southampton, United Kingdom

Giacinto Cornacchia
ENEA, Laboratory of Thermochemical Processes for Wastes and Biomass Valorization, Rotondella, Italy

Davide Dalmazzo
Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Torino, Italy

Wilma Dierkes
Chairs of Sustainable Elastomer Systems (SES) and Elastomer Technology and Engineering (ETE), Department of Mechanics of Solids, Surfaces and Systems (MS3), Faculty of Engineering Technology, University of Twente, Enschede, The Netherlands

Nicolas Evans
FIFA-Strasse 20, 8044 Zurich, Switzerland

D. Elroy Fimrite
EFG Polymers LLC, Bay City, TX, United States

Valentí Fontserè
COMSA Corporación, Barcelona, Spain

Cesare Freda
ENEA, Laboratory of Thermochemical Processes for Wastes and Biomass Valorization, Rotondella, Italy

Simon Hodson
Astutus Research, London, United Kingdom

Xiangdao Hou
Key Laboratory of Road and Traffic Engineering of Ministry of Education, Tongji University, Shanghai, P.R. China

C. Gisèle Jung
Ecole Polytechnique (EP-4MAT), Université Libre de Bruxelles (ULB), Brussels, Belgium

Amanda Koh
Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL, United States

Florian Lacroix
Laboratoire de Mécanique Gabriel Lamé (LaMé), Université de Tours, Université d'Orléans, INSA Centre Val de Loire, Tours, France

Jin Li
Key Laboratory of Road and Traffic Engineering of Ministry of Education, Tongji University, Shanghai, P.R. China

Frank Lindner
Evonik Operations GmbH, Smart Materials - High Performance Polymers, Marl, Germany

Davide Lo Presti
Department of Engineering, University of Palermo, Palermo, Italy; Nottingham Transportation Engineering Centre, University of Nottingham, Nottingham, United Kingdom

Juan Daniel Martínez
Grupo de Investigaciones Ambientales (GIA), Universidad Pontificia Bolivariana (UPB), Medellín, Colombia

Carl D. McAfee
McAfee Consulting LLC, Kennedale, TX, United States

Juan Gallego Medina
Dpto. Ingeniería del Transporte, Territorio y Urbanismo Universidade Politecnica de Madrid, Madrid, Spain

Miquel Morata
COMSA Corporación, Barcelona, Spain

Ettore Musacchi
President, ETRA, Brussels, Belgium

Kyriacos Neocleous
Department of Civil Engineering and Geomatics, Cyprus University of Technology, Limassol, Cyprus; ERATOSTHENES Centre of Excellence, Limassol, Cyprus

Alexander Paasche
Evonik Operations GmbH, Smart Materials - High Performance Polymers, Marl, Germany

Jorge Carvalho Pais
ISISE, Department of Civil Engineering, University of Minho, Guimarães, Portugal

Joan Peset
COMSA Corporación, Barcelona, Spain

Kypros Pilakoutas
Department of Civil and Structural Engineering, The University of Sheffield, Sheffield, United Kingdom

Thomaida Polydorou
Department of Civil Engineering and Geomatics, Cyprus University of Technology, Limassol, Cyprus; ERATOSTHENES Centre of Excellence, Limassol, Cyprus

Lily Poulikakos
Empa—Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Fabrizio Quadrini
Department of Industrial Engineering, University of Rome "Tor Vergata" Via del Politecnico 1, Rome, Italy

Sitisaiyidah Saiwari
Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani, Thailand

Ezio Santagata
Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Torino, Italy

Loredana Santo
Department of Industrial Engineering, University of Rome "Tor Vergata" Via del Politecnico 1, Rome, Italy

Said Seghar
Phenix Technologies, Sancheville, France

Valerie L. Shulman
The European Tyre Recycling Association (ETRA), Brussels, Belgium

Eleanor Skelton
The University of Alabama, Tuscaloosa, AL, United States

Peter Taylor OBE
Industry Commentator and Secretary General of the UK Tyre Recovery Association, London, United Kingdom

Tao Wang
School of Civil Engineering, Beijing Jiaotong University, Beijing, P.R. China

Feipeng Xiao
Key Laboratory of Road and Traffic Engineering of Ministry of Education, Tongji University, Shanghai, P.R. China

Qidi Zong
Key Laboratory of Road and Traffic Engineering of Ministry of Education, Tongji University, Shanghai, P.R. China

Preface

This book is a response to general interest in tire waste and recycling in the world today. This text looks at the whole spectrum of tires—giving a firm background to tire before launching into the topics of available waste and recycling technologies.

The book is divided into five sections:

- Introduction and basic information about tires
- Toward a circular economy
- Material treatments and technologies
- Key markets for recycling, materials, products, and applications
- The future

The main difficulty in producing this type of book is finding qualified authors to write the chapters. We are very fortunate in this volume to have such a high caliber of authors offering their expertise on such diverse topics. However, there are many other issues that have not been covered in this book.

This volume is unique in the genre of related titles currently available in that each chapter of *Tire Waste and Recycling* has been written by an expert scientist, engineer, or technologist working in the field. As a result, readers not only benefit from the latest research and expertise in tire waste and recycling but also get access to a variety references to the research being done in the field. The authors have been chosen for their expertise in their respective fields and come from countries: United Kingdom, Spain, Portugal, Cyprus, Switzerland, India, South Africa, France, United States, Canada, Germany, Colombia, Thailand, Belgium, Italy, the Netherlands, and China. They have been invited from both developing and developed countries in order to gauge the problem from a worldwide perspective and to encourage global awareness and participation in its solution.

The International System of Quantities is reflected in the book with the use of SI units throughout along with the addition of alternate non-SI units that may be more familiar in certain areas of the world. Where possible, the index notation is used to remove any ambiguity; for example, billion and trillion are written as 10^9 and 10^{12}, respectively.

This book gives readers a thorough understanding of tire waste and tire recycling and the technologies available today. The way we use, recycle, and dispose of tires in the future must take into account many factors including sustainability; the safety and health of the general public; the overall needs of society; the geographical position of each region; and, above all, the alarming rise in tire waste over the past 50 years, which threatens our environment, animal welfare, and even human health.

The aim of this book is to offer readers insight into the crisis of tire waste and recycling and, hopefully, to help solve it. It is also hoped that the book will be a springboard for new developments with contact between readers and authors (e-mail addresses are included in the heading of each chapter).

Governments throughout the world are supporting the war on tire waste, but there is a long way to go before the problem is under control.

The solution to waste tires is the responsibility of not only the government and the tire recycling industry but of the citizens, politicians, and professionals in the field. We hope that not only students, teachers, professors, and researchers of new energy, but also politicians, government decision-makers, heads of industry, corporate leaders, journalists, editors, and all interested readers will heed the book's contents and absorb its underlying message.

We wish to thank all of the authors and coauthors for their cooperation, expertise, and time in writing their chapters. It has been a pleasure working with each and every one of them. We also wish to thank the Rachel Pomery and the staff at Elsevier for their help in getting this volume published.

Trevor M. Letcher
Stratton on the Fosse, Somerset

Valerie L. Shulman
Serji Amirkhanian

PART

Introduction and basic information about tires

This page intentionally left blank

1

An introduction to tires and recycling

Valerie L. Shulman
The European Tyre Recycling Association (ETRA), Brussels, Belgium

1.1 Introduction

Waste management and recycling are neither new concepts nor new activities. In fact, they are among the oldest, most enduring concerns of human communities—throughout the world, from the earliest civilizations until today. Historically, waste management has been inextricably linked with the evolution of communities, population growth, and the emergence and development of commerce.

As communities grew from scattered agricultural areas, to hamlets, and then to villages and larger more densely populated urban areas and eventually city-states with populations in the tens of thousands, the problems of waste management attracted greater attention and active response. Public commentaries on the impact of waste and the extent of its damage to people and to the environment date from over 7000 years ago! Air pollution, arable soil, clean water, sanitation, and deforestation were among the principal early issues of concern. As civilizations expanded, and new trade opportunities were explored, waste management and recycling were increasingly coupled with economic development, population growth, and the movement of people and goods.

Needless to say, the composition and volume of the wastes changed dramatically over time. Nonetheless, a review of the literature shows that the most prevalent waste streams, from about 5000 B.C.E. until today, derive from agriculture, mining and fuel use (still over 40%), household wastes as well as transportation, construction, and industrial wastes—even though tires were not included.

However, although the complexity and volume of the wastes have increased immeasurably over the centuries, the four basic means of managing wastes appear to have remained relatively the same: reuse and recycling (including composting), landfill,

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00029-6
© 2021 Elsevier Inc. All rights reserved.

and incineration. Until the "disposable society" more than three millennia later, it was commonplace for almost all materials to be reused and, once beyond their useable lives, they were reused again in another form—due to recycling.

The earliest landfills can be traced to Crete in 3000 B.C.E., the practice apparently continuing without interruption throughout the millennia. Composting appears to have been introduced early on for many household wastes, with extensive evidence in China dating from earlier than 2000 B.C.E. Material recycling (bronze) had already begun in Europe during the same period, as had organized incineration.

Nonetheless, throughout the ages, the basic issues of waste management appear to have remained the same: what to do with the wastes that arise, how to counteract or respond to their deleterious effects—and, who will pay. Ultimately, the question of how to gain the greatest benefits from natural resources seems to have been resolved pragmatically through reuse, recycling, and energy recovery.

Respect for the environment and specific concerns regarding water management, land use, production residues, and even producer responsibility have all been addressed before. From the earliest times, keen observers have noted the potential devastating effects of natural aberrations (i.e., soil erosion, flooding, deforestation, "acid mists," among others) and have sought to identify the causes and to remediate them. Lessons learned more than 10,000 years ago still appear relevant.

Even the use of supporting legislation is not a new concept. Beginning with Hammurabi circa 2300 B.C.E., and then to Athens in 500 B.C.E., the first legislation on waste management appears—requiring wastes to be transported at least 2000 paces from the homes (+-one mile) for deposit in landfills. And pollution was seen as responsible for illness—smoke from fires, etc. Lead poisoning was well documented.

1.2 Beginning of urbanization and advancement toward globalization

By 500 B.C.E., with a world population of +100,000,000 small rural agricultural areas slowly began to expand, creating more populace communities as newly formed hamlets away from fields. Growth continued, through 1800 A.D. when global population had grown to over +1,000,000,000 with 90% of people living in rural areas[1] and less than 10% in built-up sectors.

[1]Hanna Ritchie and Max Roser. Urbanization, November 2019.

Box 1.1 Four steps to globalization.

1. Silk Roads: The first Global links, 1st Century BCE—5th Century AD: **Rise of the Chinese and Roman Empires**

Beginning with food but later other goods China became a prime producer and hauled goods thousands of miles to the Roman Empire. By 1100, horses were traded for tons of tea in Tibet. These routes then collapsed.

1st Century BCE to 5th Century AD: Mogul Empire—the Black Sea to the Korean Peninsula, fostering trade routes, creating embassies, and encouraging travelers—with the first moves toward Europe.

2. Spice Routes: 7th to 15th Centuries

By the early 9th century Islamic merchants dominated the sea routes of the Mediterranean and Indian ocean trade to Indonesia and west to Moorish Spain—this was the first establishment of East–West trade for spices and other goods.

3. Age of Discovery: 15th to 18th Centuries

Global trade was in force by the end of the 15th century. European explorers tied the East to the West and discovered the Americas and lands in between. The Scientific Revolution began with mechanics, physics, astronomy, and shipping. Portuguese, Spanish, and Dutch and English explorers discovered "new lands" and integrated them into their economies. Not yet a true globalization, the empires created both mercantilist and colonial economies—supported by the slave trade.

4. The first wave of Globalization (19th Century to 1914)

Great Britain led the world geographically and innovatively changing commerce, industry, and production with the steam engine, industrial looms, refrigerated cargo ships, trains, etc., joining world capitols with the telephone and changing how investments were done. The car, plane, and other means of transport opened many new options. It all ended with a major world crisis in 1914.

The World Wars 1914–1945

After World War I, the Great Depression which followed, and World War II, trade as a percentage of world GDP fell to 5% "a level not seen for more than 100 years."

Second and Third waves of Globalization—The Creation of the United Nations

New technologies, evolving in two separate tracks, with the Iron curtain dividing the new world. At its fall in 1989—globalization became one effort.

The progress and developments during these millennia were cogently described by Peter Vanham[2] in his address to the 2019 Davos Economic Forum as a four-phase period of the evolution of globalization from 500 BCE, through the end of World War II and beyond. Box 1.1: *Four steps to globalization* is paraphrased from the document, ending with an acknowledgment of the

[2]Vanham, Peter. A Brief History of globalization. World Economic Forum. Key moments from World Economic Forum Annual Meeting. Economy in Transition. 25 January 2019.

next two waves of globalization. The end of World War II was the catalyst for change in the manners in which global issues could be presented, discussed, and resolved in future.

1.3 The catalyst for change

At the end of World War II, the world was in shambles from every perspective: physically, economically, socially and environmentally. It had been the most pervasive military conflict in human history—over land, on and under the seas, and in the air. Sixty-one countries and many territories on six continents as well as all the world's oceans had suffered devastating damage and long-term social, economic, and environmental impacts. Only the Western hemisphere, parts of the Near East and sub-Saharan Africa, were left unscathed.

Although we are most conscious of the human toll, wars also severely impact the ecosystem and the environment. Lakes, jungles, forests, farmlands and deltas were obliterated—with dangerous wastes left behind. Hundreds of cities were demolished and others rendered virtually uninhabitable—bridges, roads, and railroads were laid to waste—and rendered nonfunctional.

Almost 60 million civilians and military personnel were killed and tens of millions more were seriously injured or permanently maimed. War-induced famines took the lives of 2 million more in Africa and Asia [1]. Millions remained homeless throughout the war-torn world. Thousands more were captive of foreign nations—or at home.

According to the International Registry of Sunken Ships [2], more than 12,500 sunken vessels including battleships, aircraft carriers, destroyers, landing craft, and more than 5000 merchant ships were scattered on ocean floors. Governments estimate that more than 335,000 aircraft were lost, primarily over Europe, Asia, and Africa [3]. Thousands of tons of unexploded ordnance including mines, bombs, and various forms of ammunition litter sea beds, fields, jungles, caves, and even home gardens.

Seventy-five years after the end of the war, experts estimate that it could take another 100 years to clear the detritus and neutralize the hazardous content—which continue to pose dire threats to the environment, humans and creatures in the seas, on land\ and in the air. In addition to military debris, every type of waste imaginable—from natural to synthetic materials—including construction rubble, plastic debris, synthetic rubber, electronic equipment and parts, transistors, microwave materials,

and synthetic fuels, among hundreds of others, became residue of the war—and had to be treated and disposed.

Many of the products created for the "war effort" have become the most common products on the market today—with the same problems and issues surrounding their treatment and disposal. Pesticide formulations such as the organophosphates, owe their basic chemical structures to chemical war agents. Petrochemical products have also grown substantially in response to war efforts. In addition, tires and tracks from tanks and military vehicles, abandoned ammunition dumps, practice ranges, and other military facilities continue to be hazardous waste sites.

1.4 Sustainable development: the context for recycling

In August 1941 the Atlantic Charter defined Allied goals for the postwar world. As early as 1942, signatories to the Charter initiated discussions about an organization that could replace the failed League of Nations. Before the final guns were silenced, world leaders had begun to prepare for the future—one without war, in which disputes could potentially be resolved through discussion and cooperation. The structure and substance of the United Nations was agreed upon with 51 available to sign it into international law.

Signed on June 26, 1945, the UN Charter came into force on October 24, 1945 as an international organization with the mission to provide a platform for dialog and cooperation among nations in order "to save succeeding generations from the scourge of war." Inherent within the Charter is the recognition that equal rights and self-determination are imperative for each sovereign nation—large or small, wealthy or poor, and must be supported. During the next three-quarters of a century, these concepts pervaded all aspects of UN undertakings—from decolonization and economic development to environmental and waste issues.

At its inception, five interactive themes were identified: international law, international security, economic development, social progress, and human rights. The infrastructure provided for six principal organs: the Trusteeship Council, the Security Council, the General Assembly, the Economic and Social Council, the International Court of Justice, and the Secretariat (see Fig. 1.1). Each organization had its own mission and objectives, which have evolved over time to reflect current issues and needs.

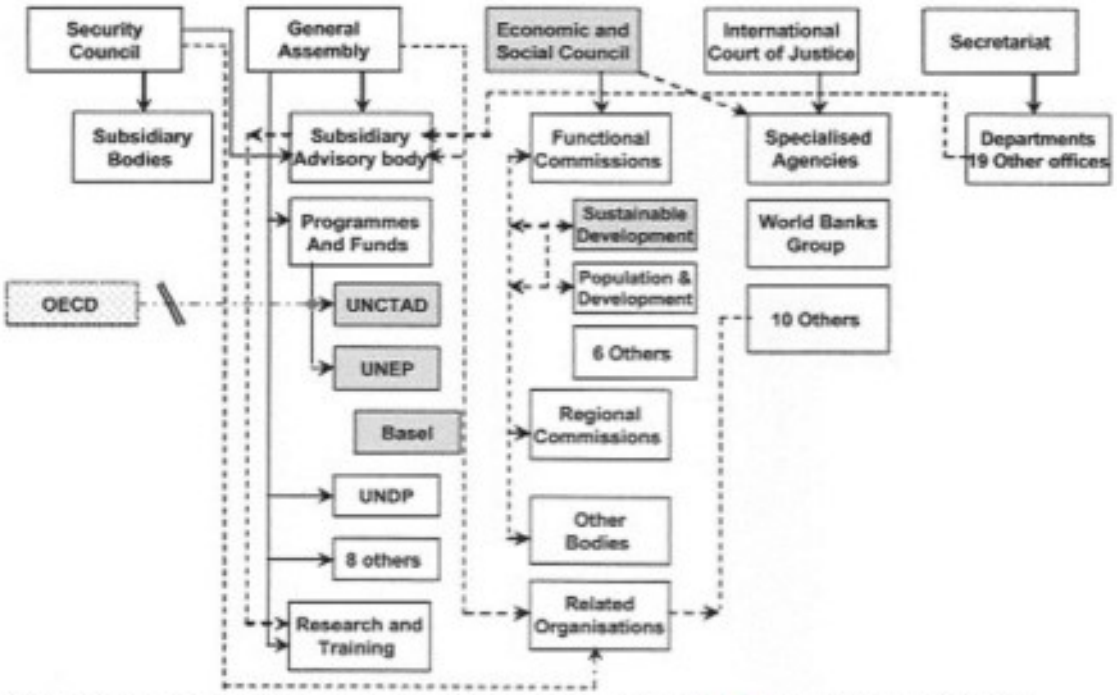


Figure 1.1 United Nations (UN) structure concerning the environment [4] is an adaptation of the UN organization chart to illustrate the relationships between and among the five current organs.

Actions related to the environment, and by extension waste management and movement, can best be described in terms of three broad periods: the postwar period (1945–1970); globalization, scientific, and environmental awareness (1970–1990); and implementation and progress (1990 to the present).

1.4.1 The postwar period

The postwar period can be described as one of far-reaching political, social and economic changes.

- Governments were responsible for assessing war damage—and initiating the clean-up and reconstruction of needed infrastructure, homes, civil institutions, business and industry.
- The Organisation for Economic Cooperation and Development (OECD) was formed in 1960 with 20 members as an independent forum for industrialized democracies to study and formulate economic and social strategies that could involve developing nations. Today, 37 member countries focus on environmental, economic, and social issues to institutionalize and integrate

sustainable development concepts into national policy and strategies. Its projects are diverse, ranging from sustainable materials management to corporate responsibility and climate change.

- By mid-1961, almost 750 million people had exercised their right to self-determination, and more than 80 once-colonized territories had gained independence, including those under the Trusteeship Council. By the end of 1961, a Special Committee on Decolonisation was formed to aid 16 non-Trusteeship countries seeking sovereignty.
- With self-determination came new responsibilities and social commitments requiring interactions between wealthier and poorer nations (often described as "north" and "south"). Self-determination became increasingly important as developing countries sought a stronger role in global economics.
- The United Nations Conference on Trade and Development (UNCTAD) was formed in 1964 as a permanent body of the United Nations dealing with trade, investment, and development issues. It supports the integration of developing countries into the world economy—ensuring that domestic policy and international action toward sustainable development do not clash. It helps to assess the needs of the least-developed countries in trade relationships (e.g., north vs south and producers vs. consumers).

The 25-year postwar period focused on clean-up and rehabilitation of affected areas. Vast quantities of wastes were collected—and often shipped from wealthier to poorer nations for disposal. The concept of self-determination came into play—and by the end of the period, poorer nations began to refuse acceptance of external wastes.

An infrastructure for debate had been created with the formation of the OECD and UNCTAD. A principal outcome was the establishment of a system of organizations that had the capacity to act in unison to establish a worldwide mechanism to attain peace, as well as economic and social responsibility. There was a keen awareness of the relationships between policy, trade, economic development, and environmental impacts.

1.4.2 The period of globalization

The period of globalization after the second world war can be described as one of the rapid scientific and technological innovation, coinciding with the creation of the United Nations Environment Programme (UNEP) and the Basel Convention. Commercial globalization exacerbated many environmental

problems and highlighted the need for global solutions. Together, these bodies have assisted poorer nations to become a driving force in world economic development.

- The UNEP was formed in 1972 to smooth a path for international agreements, with the mission of assisting poorer countries to develop and implement environmentally sound policies and practices, coordinate the development of environmental policy consensus, and keep environmental impacts under review. As awareness of cross-border pollution grew, nations established agreements with neighboring states and instituted a series of treaties, conventions, and protocols for controlling pollution and similar problems that crossed national boundaries. International environment conventions promoting science and information drew great support and helped these nations to work in conjunction with policy, guidelines and treaties—particularly in terms of hazardous materials—transboundary air pollution and contamination of waterways, among others.
- The Basel Convention created in 1989 under the UNEP filled the gap between existing mandates that facilitate and monitor world trade, on the one hand, and those concerned with sound environmental practices on the other. The mission of the Basel Convention is to monitor the transboundary movements and management of wastes to ensure their environmentally sound treatment and disposal and to provide support to governments by helping them carry out national sustainable objectives. In 1999 the Basel Convention published Doc. No. 10 focusing on the guidelines for the identification and management of used tires. Today, it is being reviewed and revised in terms of treatment classifications, which could impact upon the way that tire recycling is viewed (i.e., as a pretreatment or as a full recycling structure).

During the 1970s, 80s and 90s, these organizations undertook an exhaustive awareness campaign to draw support of national and local governments, nongovernment organizations, industry, and the public at large. Transboundary movements of wastes required the development and implementation of environmental management systems to evaluate the quantity and impact of emissions within the environment. New guidelines were created for the import/export of wastes for recovery with OECD support. The focus on the prevention and minimalization of wastes led to the study of the economics of waste to identify barriers and failures as well as facilitators and successes.

1.5 Implementation and progress

During the final years of the 20th century and the first two decades of the new millennium, it became apparent that the unbridled economic growth of the past could not be sustained in the future without irreparable damage to the environment. Discussions initiated during the 1960s culminated in a proposal for change, at the global level.

The Stockholm meeting of the United Nations Conference on Environment and Development (UNCED) in June 1972 is often marked as a critical turning point in the move toward more sustainable growth practices. It signaled a break from the past and the beginning of a new era.

The goals of the conference were limited. They were first, to introduce the concepts and practices inherent in sustainability and second, to provoke sufficient concern and interest for world leaders to make a commitment to delink economic growth from negative environmental impacts.

Simply stated, sustainability requires policies and actions that foster economic and social growth that meet current needs without detriment to the environment. The aim is to not compromise the ability of future generations to meet their own needs.

"Environment" was defined in the broadest sense to include all conditions, circumstances, and/or influences affecting development. The specific issue was the improved management and use of natural resources, concentrating on the prevention and control of pollution and waste.

Delegates adopted the principle and accepted the challenge implementing the sustainable model of development for the 21st century. One of the most immediate results of the meeting was the creation of the UNEP as the global authority on environmental issues. It was envisioned that UNEP would smooth the way for international agreements—including those between the wealthier northern and poorer southern countries.

The global economic and social nature of the plan led to the involvement of other organizations within the UN infrastructure. As described in Box 1.2, these bodies provide the international framework within which intra- and international trade occur, including the movement of wastes.

By the 1992 UNCED meeting in Rio de Janeiro, much of the groundwork had been completed. The infrastructures for both encompassing legislation and actions were in place. The goal of the conference was to propose alternative strategies and actions that could be undertaken in the short, medium, and long terms to ensure that consideration and respect for the

Box 1.2 Organizations within the UN structure.

The ***UNCED*** formulates strategies and actions to stop and reverse effects of environmental degradation and promote sustainable, environmentally sound development in all countries.

The ***UNCTAD*** promotes trade between countries with different social and economic systems and provides a center for harmonizing the trade and development policies of governments and economic groups.

The ***OECD*** is a permanent body under the UNCTAD. It was created to assist in removing restrictions and facilitating trade between and among member and nonmember countries, ensuring that the substances, materials, products, and so on involved do not pose a threat to the environment or humanity in the receiving country.

The ***UNEP*** is the designated authority on environmental issues at the global and regional levels. It was created to coordinate the development of environmental policy consensus and bring emerging issues to the international community for action.

The ***Basel Convention***, under UNEP, is specifically concerned with the control of transboundary movements of hazardous and other wastes and their disposal, from OECD countries to non-OECD countries. Further, it is concerned with the identification of those products and materials that could cause damage to the receiving countries.

environment would be integrated into every aspect of the development process. The Basel Convention provided the common framework for the classification, management, and treatment of waste. Briefly, waste was defined as follows:

> *. . .substances or objects which are disposed of or are required to be disposed of by the provisions under national law.*

Both the Basel Convention and the OECD independently prepared catalogs of the substances, objects, materials, etc., which are defined as waste and separated out those defined as hazardous or dangerous. A final list contains those wastes that are not perceived to pose a risk to the environment or human health. However, it is important to note that the lists are not mutually exclusive and that under certain conditions a "waste" can and often does appear on more than one list. Virtually every conceivable material, product, or residue listed—those that are not specifically named fall under the rubric "other."

The definition and annexes served as a guide for transboundary movements of waste, principally for their environmentally sound management. Examples of recovery and disposal operations were appended. Environmentally sound management was broadly defined as follows:

> *. . .taking all practicable steps to ensure that waste is managed in a manner that will protect human health and the environment against adverse effects which may result from such waste.*

Within the context of the definitions of waste and its environmentally sound recovery and disposal, the OECD laid down the provisions for the transboundary movement and acceptance within and outside the member countries. Each country was invited to prepare a list of those wastes that it would no longer accept to receive for either recovery or disposal due to the lack of appropriate treatment facilities available, or potential risks to human health, among other reasons. Thus procedures were also established for the nonacceptance of wastes and their return when they are delivered in error.

Once the framework was established, various tools were explored to assess their capacity for targeting potential environmental impacts. Life cycle analysis was selected as the most appropriate and effective tool for determining the points at which the greatest environmental impacts occur, thus making possible the suggestion and selection of less damaging options. For example, the approach permitted the evaluation of industrial outputs from the production or extraction of raw materials through the design and manufacture of materials and products, as well as during product use.

The definitions, annexes, and provisions were accepted by the delegates. However, many of the participating countries also adapted the provisions to comply with national policy and priorities.

The most hazardous wastes and the most prevalent sources of pollution were targeted and identified for immediate attention. Five priority waste streams were distinguished. In addition to the more general category of "household waste," postconsumer tires, demolition wastes, discarded end-of-life vehicles, halogenated solvents, and hospital waste were earmarked for action.

1.6 Interpretations

Virtually every industry has come under scrutiny from mining to manufacturing and healthcare. A raft of legislation has been enacted, with the agreement and cooperation of the partners. A horizontal framework was established for waste management, including definitions and guiding principles. Treatment operations were defined vertically—to include the control of landfills, incineration, etc., a body of standards is nearing completion for an ever-expanding range of treatment operations—through the International Standards Organisation, with support from national standards bodies.

During the 60 years since the initiation of the first discussions on sustainable development in the 1960s, legislation and actions have been put into place to ensure that governments

work together with industry and the public at large. Today, the majority, if not all 193 UN member countries have enacted at least basic environment and waste management legislation.

Reuse and recycling are again being integrated into industrial activities. However, as they are interpreted today, the concepts of reuse and recycling are inextricably linked to the production and management of waste, and by extension, to its prevention and minimization.

Reuse and recycling have evolved into two of the four pillars that support improved resource management through the prevention of waste and the reuse, recycling, and recovery of the wastes that do occur to achieve sustainable development goals by reducing reliance on natural resources.

Today, many of the actions taken concerning end-of-life tires (ELTs) are being reviewed with an eye to the future. One of the most critical reviews concerns the Basel Convention treatment classifications, which could have the potential to revise the role of treatment procedures.

ELTs are an excellent example of one of the most successful means of meeting the objectives for sustainable development and the circular economy, fulfilling key goals of the Green New Deal proposed by UNCTAD and the European Union. Although tires are 100% recyclable there are those that cannot be effectively recycled but can nevertheless be recovered through their energy value.

This book illustrates many of the practical ways in which tire recycling can and does contribute to the circular economy by recycling tires in commercially viable ways—either by reusing the tires themselves—or the three principal parts: the rubbers, the metals, and even the textiles in a variety of formats.

Each of the chapters herein has been prepared by an expert who has actually prepared and used these processes, materials, products, or applications in a commercial/municipal setting.

References

[1] D. Reynolds, One World Divisible: A Global History Since 1945, W.W. Norton & Company, New York, NY, 2000.
[2] International Registry of Sunken Ships, Saskatchewan, Canada. http://www.shipwreckregistry.com/, 2010 (accessed 26.07.10).
[3] J. Ellis, World War II: A Statistical Survey: The Essential Facts and Figures for all the Combatants, FACTS ON File, New York, NY 1993.
[4] United Nations History of the United Nations. http://www.un.org/aboutun/unhistory/, 2010 (accessed 26.07.10.).

2

Tires and the tire market

Peter Taylor OBE
Industry Commentator and Secretary General of the UK Tyre Recovery Association, London, United Kingdom

2.1 Introduction: the early days of the tire

An Englishman, John Boyd Dunlop is credited with inventing the first pneumatic tire in the late 1800s. For centuries and indeed millennia before that seminal moment wheels had been made of wood. Interestingly, the word "tire" long predates its modern-day equivalent referring as it did to the metal band or "tie" introduced in the late middle ages to hold together these early assemblies of wooden rims and spokes that replaced earlier and much heavier solid wooden wheels. Those early considerations of weight, performance and load are concerns that still absorb the thinking of today's tire designers everywhere.

Mr. Dunlop's invention soon caught on and quickly attracted other now famous names with brands of their own. Interestingly, many of those product names remain with us today, although ownership patterns in the industry have changed radically as ambition and consolidation have combined to create a clutch of global players who dominate the international tire scene today.

2.2 The global players and their national roots

A summary of the global players and their roots is given in Fig. 2.1.

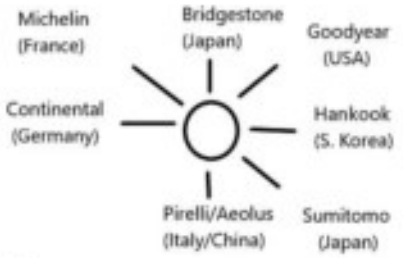


Figure 2.1 Global players and their roots.

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00022-3
© 2021 Elsevier Inc. All rights reserved.

But the scene is changing quickly and many other names are fast emerging, especially from China.

2.2.1 Evolution not revolution

Nevertheless, tire manufacturing remains a rather conservative business where attempts at product diversification have with a few exceptions been modest. Tire making is complex but perhaps not glamorous and for decades these characteristics defined its practitioners and their introspection bred risk aversion at a time when the demand for tires rose exponentially year-on-year as the world became ever more motorized. Technical change too has been evolutionary rather than revolutionary, which made it easy for new entrants to come into the business and they have so in significant numbers, most noticeably in Asia. China is now the world's largest tire maker churning out products not just for its own nascent brands but for most of the legacy players who still dominate the upper rankings today.

Seminal changes to the business have been slow to impact. For example, the one great technical advance in the 20th century, Michelin's radial tire concept, took more than two decades to gain acceptance due to the reluctance of industry traditionalists to grasp the nature of its impact on the market and on their own long-held approaches to investment and to manufacturing techniques. Some of these laggards paid a heavy price for such complacency at the heart of product planning and management. This inwardness on the part of industry leaders also brought with it an overemphasis on the product and on manufacturing to the detriment of good marketing and brand building sometimes, just making them was enough.

Their responses were often piecemeal. On the product front there was an attempt to meet Michelin's radial challenge halfway with the launch of hybrid but technically inferior radial products, which only served to emphasize engineering weaknesses and market blindness. The consequences for many, if not most, was pressure on market share and brand renown resulting in a downward pressure on sales. The easy answer was the creation of subsidiary brands and the acquisition of smaller market players to maintain production volumes but that inevitably sold at lower price levels. So began a very damaging era of brand proliferation and declining margins. For some, the consequences were terminal as they were swallowed up by larger rivals while others somewhat questionably were all too ready to sell manufacturing knowhow to the developing world, often to the very entities that

would soon become more aggressive and much lower cost competitors.

The consequences of this market myopia have been deep and pervasive. The root of much of the market disfunction we see today as market share was all too often bought through acquisition and brand proliferation then lost in short order as managements failed to embrace the new realities of 20th century consumerism. The legacy is still with us today in a marketplace where there are as many brands as there are days in the year and where brand value in particular remains an elusive aspiration for most. It need not have been so. The pneumatic tire is a hugely successful and complex piece of chemistry and engineering quite fundamental to human mobility.

2.3 The economics of tire manufacturing

2.3.1 What goes into a tire?

It is still a popular belief that the pneumatic tire is an injection-molded product. While nothing could be further from the truth such a concept is still seen as an ultimate manufacturing concept by many. From very early days tires were assembled from a variety of components, not just from rubber but from reinforcing materials such as steel wire and synthetic fabrics such as rayon and nylon. Indeed, in the very early days of the product, cotton cord was used but was quickly displaced by these and other better performing man-made materials. Our early tires were comprised entirely of natural rubber but the need for product improvements throughout the 20th century led to the introduction of a whole range of synthetic materials, not just rubbers but fillers and other chemicals aimed at drastically improving the performance characteristics of the product from those early days.

2.3.2 Principal product categories

There are seven main categories of tire each distinguished by function, that is to say their applicability to particular types of vehicle, industrial equipment, and even aircraft. As modern-day tires are manufactured in many thousands of sizes and types, they are best categorized by their design applicability to particular functions ranging from automobile fitment to aircraft landing gear as seen in Fig. 2.2.

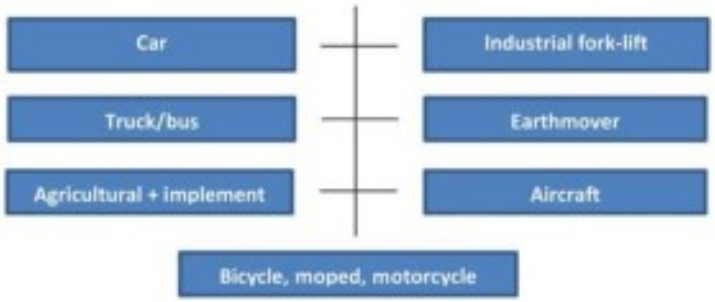


Figure 2.2 Tire types.

Table 2.1 What goes into a tire?

Materials	Proportions	
1. Natural and synthetic rubbers	± 40%–48%	Ratio of natural to synthetic rubber: ± 2–1 truck tires; ± 4–3 car tires
2. Carbon blacks and/or silica	± 22%–27%	A range of carbon blacks of varying sizes, structures, and characteristics are used in different parts of a tire
3. Reinforcing materials	± 5%–25%	
Metals (steel)	+ 15%–25%	In the beads, belts and castings of a truck tire
	+ 11%–13%	In castings and plies of a car tire
Textiles	+5%–10%	Textiles are a basic reinforcing material used in many tire types
4. Facilitators	± 8%–0%	Extender oils, waxes, and plasticizers aid processing; curing systems include sulfur, zinc oxide, stearic acid, and accelerating agents; antioxidants, antiozonants, etc., protect the compound; carbon black/silica increase mechnical properties; clay, whitings, etc., are fillers

Source: Courtesy ETRA, 16 Avenue de Tervueren, 1040 Brussels, Belgium.

The modern-day tire is an amalgam of many materials each designed to optimize its performance capabilities under many different operating conditions so while they may all end up round and black, they will each have the different performance and design characteristics needed for that particular market segment.

The mix of product in a marketplace is also indicative of economic development. In most Western economies it is the car tire that dominates at least in terms of units sold whereas in other developing nations truck and motorcycle and moped tires often feature more strongly in the market mix.

Table 2.1 lists just some of the components of automobile or truck/bus tires.

The material compostion of tires varies by category (i.e., passenger car, utility behicle, truck, off-road, etc.). Although the content may also vary to some extent from continent to continent (Europe, the Americas, Asia, etc.) the ingrdient ratios remain relatively the same – and have negligible impact on use, wearability, or recyclability.

But this is not just a story about rubber polymer + chemicals technology; the supporting carcass of the tire is equally important. Strength, rigidity, and bead construction are all critical to the overall performance characteristics of the particular finished product. This illustrative cross-section of an automobile tire demonstrates its multiple components – see Fig. 2.3.

In the early days of tire making the process was both cost and labor intensive as each tire was assembled component by component by skilled operatives before being cured at high temperatures in molds to produce the product we are all familiar with today. In the 21st century the making of the modern tire is much more automated process but one that still needs to combine those very many same components to deliver the bespoke performance characteristics required for dozens if not hundreds of in-service conditions.

No longer the labor-intensive process it once was our tire factories are capital-intensive and volume-dependant operations

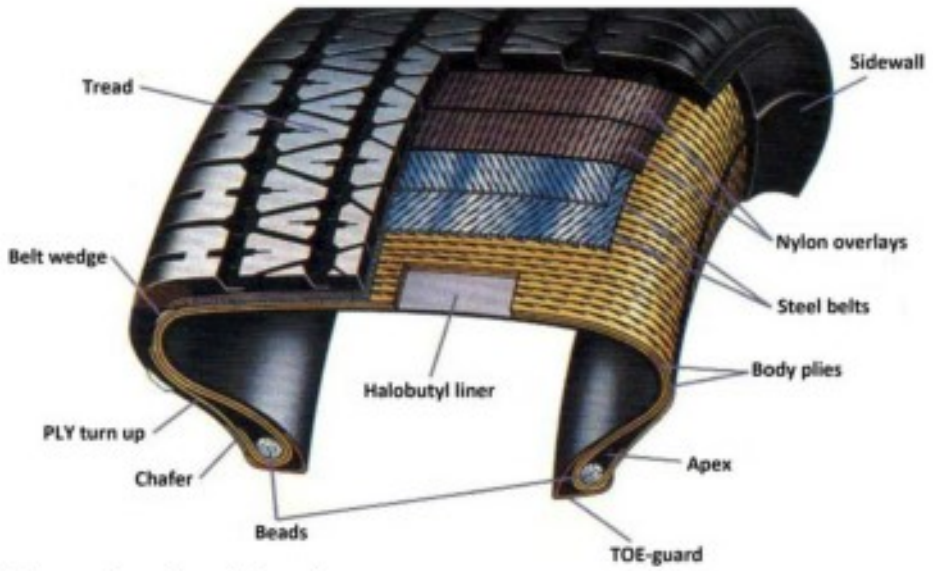


Figure 2.3 Cross-section of a typical car tire.

each capable of producing tens of thousands of units daily for shipment to markets at home and across the world and an absolutely integral part of the global economy. The modern-day tire is expected to meet a wide range of user expectations.

2.4 What we expect from our tires

Our tires are expected to fulfill the demands of very many different applications and operating conditions. Fig. 2.4. lists a few of the things we expect from our tires.

Perhaps the most important of these is durability. A tire must be robust enough to meet the load and operating conditions for which it is intended. A truck tire, for example, needs to be capable of supporting heavy loads at relatively high speeds usually over long distances. Car tires are expected to cope with lesser loads but often higher speeds whereas a tire engineered for fitment to an airplane must support a heavy load, high impact forces as well as short bursts of very high speeds. In all of this the big enemy is destructive heat build-up in the body of the tire so this is perhaps the biggest single challenge for our tire engineers.

Tire design is inevitably a compromise between many competing demands beyond that of intrinsic durability. Tires are required to deliver good traction in a variety of operating conditions from muddy tracks to snowbound roads and can be designed to cope and perform well in such extremes. Grip is another challenge for those who engineer our tires. Whereas the prevailing weather conditions in areas like northern Europe demand tread compounds that perform well in wet pavement this may not be so in the more arid areas of the world. As far as possible manufacturers have to optimize these competing needs. Comfort and quietness are also important consumer requirements and ones that vehicle manufacturers are also insistent on. Noisy tires make for more noisy vehicles and a hard-riding product means driver and passenger discomfort.

Then there is the no small matter of fuel economy, something every vehicle producer is constantly striving to improve. Those who engineer our tires play an important role in designing

Figure 2.4 A few of the things we expect from our tires.

products that optimize rolling resistance between the tire tread and the road surface. There have been large advances over the years in carcass construction, tread design as well as rubber compounding to enable tires to make their own individual contribution to overall vehicle fuel economy but this challenge, like other aspects of tire design, is ongoing and unending.

2.5 Tires and the consumer

2.5.1 Product choice

Despite the domination of a few big names there is still considerable market segmentation. Just like the tadpole it has a large head and very long tail. More than a hundred companies around the world vie to make their mark and to develop and grow to challenge the dominant legacy players. China is the home to many of those but numerous other countries have viewed indigenous tire-making as an early badge of industrial development and automotive progress. This phenomenon has had its consequences. Because brand proliferation is rife and competitive pressures are often overwhelming literally hundreds of brands are on offer to consumers at any moment in time. This is especially true of passenger tires but other market sectors exhibit the same characteristics to greater or lesser degrees. This excessive product choice underpinned by exacting international technical standards has made the purchase choice a superficially easy one.

The role of internationally accepted technical norms and standards is often overlooked. Driven in part by the exigences of a globalized automotive industry tires are built to consistently high levels of conformity and therefore of consumer trust and acceptance. Round black and seemingly ubiquitous "accepted but not demanded" is the familiar retort from advertising and marketing professionals everywhere but surely, few major consumer products can have neglected brand image to the extent many tire manufacturers have done.

There are some exceptions of course; Michelin and its iconic "Bibendum" or "Michelin man" and travel guides, Pirelli and its celebrated calendars but to an extent this is notoriety by association. In the world of tires and its literally hundreds of usually well-performing brands intrinsic product worth is all too frequently less important to the consumer than the price tag. These weaknesses in brand husbandry have had some profound effects in many countries.

2.5.2 The main markets

Traditionally these were "domestic" and "export" markets, but this distinction has largely vanished in what is a global business. New tires find their way onto a vehicle in one of two ways, either as a first fitment by a vehicle manufacturer (this is usually known as Original Equipment, or simply OE) and replacement or aftermarket fitments by tire retailers and others. The requirements of our vehicle producers can be extremely demanding so just being accepted as a supplier is a much-prized badge of brand status. But this badge often comes at a price as vehicle producers use this product fitment opportunity to exact highly competitive prices from the tire-maker. Most still consider this a worthwhile investment; not just because it confers status on the product but because it comes with the hope that the vehicle owner will ultimately replace those tires with the self-same brand that would of course be purchased at a much higher retail price. Although this argument is less persuasive than it once was it does still does hold some validity even in the present context of declining brand loyalty.

2.5.3 The delivery chain

Often known as "routes to market" these have experienced waves of significant changes throughout the 20th century that are still ongoing today. In the early days of the business from the 1920s onward manufacturers were not only quick to build factories at home and abroad but to support these with extensive regional distribution networks in their major markets that in turn delivered products more or less on demand to vehicle manufacturers and to local retailers. However, as it became ever-more costly to sustain these networks were progressively whittled away for the most part in favor of direct shipment to the growing retailer networks or to multibrand wholesalers who took over this function from manufacturers. As a result, manufacturers saved on distribution costs but in many cases became yet more remote from the end user particularly in the consumer-facing passenger tire market. This inexorable trend was driven by a further important factor, tire size proliferation. In less than half a century we have moved from just a small handful of tire sizes accounting for a majority of market needs to a vast explosion in sizes, tires, and brands of tire that only a large wholesaler can service efficiently. As a result, this disconnect between tire producer and ultimate tire user widened yet further.

The consequences of this "distancing" of the brand owner from the ultimate user have been profound and still characterize the retail marketplaces in many countries today. For now at least, power lies in the delivery chain and that means in the hands of our distributors and retailers.

For the everyday car owner therefore and even to some extent the commercial operator the real interface lies less with the tire retailer in whose hands the power of persuasion now largely rests. In Europe, tire labeling requirements requiring retailers to point out product performance characteristics to purchasers of passenger tires have only reinforced the ability of the retailer to influence and steer buyers toward particular types of tires or brands. No doubt our new tire producers had hoped it would be different but the logic of current patterns of distribution have so far determined otherwise.

2.6 Future trends

2.6.1 Product design + manufacturing

For more than a century tire design has followed an evolutionary path. The invention of the pneumatic tire like that of the electric lightbulb was a truly revolutionary event that has yet to be superseded. For decades now the load-bearing and performance characteristics of tires have been the subject of endless refinements at every level, which are ongoing even today. Similarly, the manufacturing process itself has become ever-more automated; factories have grown greatly in size and manufacturing has been rationalized across continents thus reflecting the global nature of the tire business and of its automotive partners. Little of this is likely to change in the short term, although there are signs that the flight of production capacity from West to East may be slowing as the number of Asian producers choosing to invest in Eastern Europe increases significantly.

In terms of the product itself clear signs of revolution have yet to emerge though emerge they almost certainly will. Michelin's nonpneumatic "Tweel" is an early example while Michelin and others have continued their pursuit of other forms of airless and wholly recyclable products.

Before any such possible design revolutions, however, there will be other developments, namely the so-called "intelligent" tire for this is already the age of the sensor and the microchip. Whatever radical new products emerge the age of the tire as a

totally independent automotive component is coming to a close. Tires, wheels, brakes, and other underbody components are and will be increasingly interlinked, will be wired into the DNA of the vehicle, and have the capability not just to diagnose potential faults but to order up replacement items and servicing facilities. This is rather useful in the case of tires with their multiplicity of sizes and types distressingly few of which are instantly available "off the shelf." Such developments may once again bring about a shift in that all-important balance between the tire maker and the tire seller.

Of course, there remains the all-too-likely prospect of further consolidation among producers mirroring the same scenario we have witnessed among vehicle manufacturers. For tire makers though that need is more acute and even more inevitable as dozens of names, literally hundreds of brands and thousands of different sizes and types of product, confront the realities of structural and technical change.

2.6.2 Retailing and distribution

An "atomized" tire market of the kind we see in many Western countries plays to the strength of wholesalers and other intermediaries in servicing the supply lives of retailers and consumers in a way the manufacturers no longer can. As only the largest retailers can take on this role in their own right and not even then in its entirely the role of the wholesaler is key. Some manufacturers themselves now seemingly recognize this and are starting to acquire ownership of major wholesalers to better position and control the flow of their own brands into the marketplace.

This renewed interest in consumer delivery has also led to large investments by some new tire manufacturers in either franchise or wholly owned retail outlets. The acquisition of retail chains by manufacturers has had a long and not always impressive history in many countries but lessons seem to have been learned. In a crowded and oversupplied marketplace like tires the strongest will always be tempted to take steps to protect or even build market share in the face of the many challenges from smaller rivals.

Such pressures are to be found in many product areas and tires are certainly not exempt from them, but technical changes in the product itself coupled with its likely increasing integration into vehicle under-gear systems may have profound implications for retailing patterns generally as the tire becomes less the "standalone" product it has been for so long.

Figure 2.5 The purchase challenge.

Then of course, there is the influence of the Internet, which is already devastating some retail sectors but so far the fear that Internet sales would decimate traditional tire retailing has not been realized and for rather obvious reasons.

The multiplicity of brands coupled with the vast range of sizes and tires of passenger tires in particular inevitably gives rise to widespread consumer confusion made only worse by the relatively weak demand-pull of even the higher profile brand names. The consumer is very frequently perplexed, uncertain, and left feeling disadvantaged at the point of sale for what is a frequently reluctant purchase. Sadly, few drivers buy tires because they want to but simply because they have to.

2.6.3 The purchase challenge

A summary of the purchase challenge is given in Fig. 2.5.

Nevertheless, price comparison websites have sprung up everywhere and fitment-only networks developed by internet traders even in the face of these clear obstacles. However, there are very wide variations in tire markets across the world and it would be unwise to venture too far in market generalizations.

This page intentionally left blank

3

Global motorization: increasing tire usage

Simon Hodson
Astutus Research, London, United Kingdom

3.1 Introduction

Despite the short-term disruption caused by the Covid-19 pandemic, tire demand is expected to maintain its upward trajectory in the longer term. Growth in the global vehicle parc (also known as vehicle fleet, vehicles in use or vehicles in operation [VIO]) will lead to further expansion of replacement tire demand. This is despite changes resulting from a shift toward *Mobility as a Service* (MaaS).

MaaS refers to the trend toward consumers paying for vehicle usage rather than ownership – with concepts such as car sharing and ride-hailing. After continued growth over many decades, some mature markets are believed to be approaching "peak parc," and the changes in how mobility is delivered are expected to result in a decline in the car parc in these markets.

Nevertheless, an increase in aggregate vehicle kilometers traveled is predicted to result in maintained demand for tires. Fleets are expected to account for a larger share of the tire market, a trend that will be reinforced by the development of MaaS.

3.2 Demand for mobility

The ultimate determinant of demand for car tires is aggregate demand for personal mobility, and is itself principally a function of population and income per capita. Long-term trends in both demography and economics have been positive over the past two decades, and are expected to remain so, despite short-term fluctuations and significant variation by country and region.

Fig. 3.1 below shows the long-term development of key indicators of global personal mobility. The global population has risen by a little over 1% per year, from a total of 6 billion people

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00030-2
© 2021 Elsevier Inc. All rights reserved.

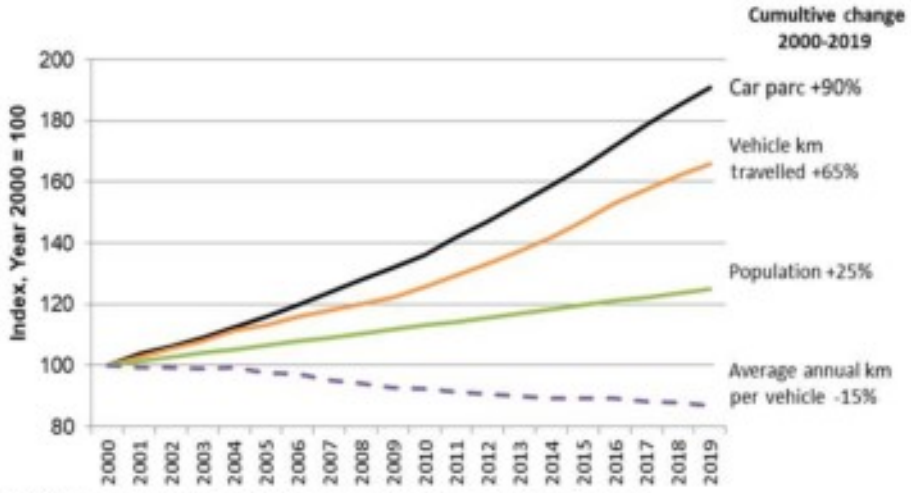


Figure 3.1 Trends in global mobility, indexed 2000–19. Source: Astutus Research.

in 2000 to 7.4 billion in 2019, an aggregate increase of around 25% over the period as a whole. This growth has naturally led to greater demand for transport.

In addition, incomes have risen by more than 50% in the two decades since 2000, significantly increasing per capita demand for mobility. As a result of combined impact of these two factors, the total volume of passenger transportation or "passenger kilometers traveled" has risen sharply, as has the total spending on such services by households.

Increased prosperity also has a significant effect on the mode of travel, and as economies develop there is a trend for modal shift from public transport to private transport. While the car dominates private transport in the most developed economies, elsewhere there is still a far greater reliance on "powered two and three wheel" transport – scooters, motorcycles, and auto rickshaws. This is particularly the case within parts of the Asia Pacific region. While scooters and motorcycles are a niche travel mode in Europe and North America, in markets such as India, Indonesia, Thailand, Malaysia, and Vietnam the number of powered two-wheel vehicles on the road far outnumbers cars and they are the mainstay of personal mobility. With increased incomes, however, comes a general shift toward from two wheels to four wheels and toward the car.

These factors combined have resulted in a significant increase in "light vehicle kilometers traveled," that is, the aggregate distance traveled by all passenger cars and light commercial vehicles. It is this metric that is the key factor determining

tire usage, and in the period 2000–19 it has risen by almost two thirds.

This greater demand for mobility and the modal shift toward the car has resulted in steady growth in the global light vehicle parc (or vehicles in operation) and in vehicle density (vehicles per 1000 of the population). The global vehicle parc has almost risen by 90%, from a little over 700 million cars and light commercial vehicles in 2000 to approaching 1.4 billion units in 2019. This represents an increase in vehicle density from 122 light vehicles per 1000 people to 187 per 1000.

The greater penetration of vehicles has resulted in a gradual long-term decline in the average intensity of vehicle usage. Globally, average annual kilometers traveled per vehicle are around 13% lower than in 2000.

Underlying these global trends are some very significant differences between countries and regions.

Economic and demographic trends are expected to remain broadly supportive for continued growth in demand for personal mobility and therefore the tire market. In the longer term, however, there are expected to be fundamental shifts in how this demand is satisfied.

There are wide disparities in population growth across countries and regions of the world – both historic and forecast. In the period 2000–19, Europe experienced the slowest growth in population (under 5% in aggregate), and within this region there was a decline in population in Central Europe, and very modest growth in Western Europe and Eastern Europe, which includes Russia the former Soviet countries.

North America, South and Central America, and Asia Pacific each experienced moderate growth in population, with an increase of around 20% in each, while the fastest growth has been experienced in the Middle East Africa region (almost 60%). The Asia Pacific region is the most diverse in terms of demographic growth, including Japan with a declining population, South Korea and Taiwan with modest growth through to the India subcontinent and the ASEAN region with rapid growth. China is unique as it has managed to control population growth through its longstanding "one child" policy, which has now been relaxed somewhat.

In addition to absolute growth in population, other demographic factors are also important for motorization including its age structure and size of the "middle class" population that are able to spend more of their income on transportation services. Demand for mobility is greatest among the working age population and lower for children and retirees.

Underpinning future growth in the global tire market is further forecast growth in population. By 2030, the global population is forecast to increase by a further 10%, reaching 8.2 billion. Again, the Middle East and Africa region is expected to show the fastest growth (a 25% increase by 2030), with Asia Pacific, North America, and South America each forecast to rise by between 7% and 8.5% over the period. Meanwhile Europe is expected to show negligible growth (0.5% in total), with declines predicted in most Central and Eastern European nations, including Russia, and also in several large Western European markets such as Germany, Spain, and Italy.

Alongside population, the other key determinant of passenger mobility—and therefore tire usage—is per capita income. On average, the wealthier a nation's population the further they travel (per capita passenger kilometers increases), and growth in per capita GDP has a proportionate impact on growth in passenger transport demand Fig. 3.2. Furthermore wealthier countries tend to have better transport infrastructure, including their road networks.

In North America, per capita GDP is three and a half times the global average while in Europe it is double; this is reflected in mobility patterns. By contrast incomes in sub-Saharan Africa are less than a quarter of the global average and, despite rapid growth in the past two decades, in South Asia they are a little more than a third of the average.

Globally, real per capita incomes have risen on average by almost 2.5% per year since 2000, although with lower growth at

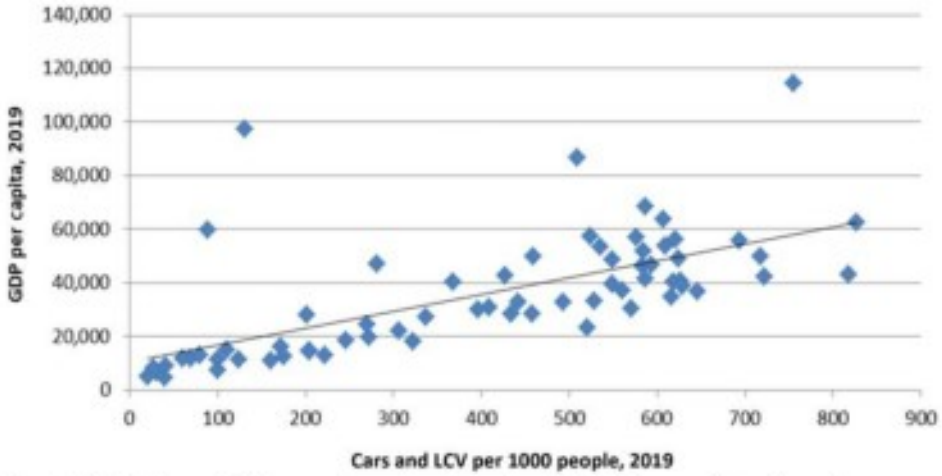


Figure 3.2 Correlation between GDP per capita and vehicle density, 2019. Source: Astutus Research.

the start of the period (2001–02) and during the financial crisis (2008–09). Global per capita incomes declined in only one year through the period, 2009. By 2019, real GDP per capita was 53% higher than in 2000. The aggregate growth in per capita incomes was lowest in North America and South and Central America, somewhat higher in Europe and Middle East and Africa and highest in the Asia Pacific region where the starting point was lower. Some countries have seen far higher levels of economic growth. By 2019 per capita incomes in China were more than four times the level of 2000, and in India they have more than doubled. Several of the former Soviet states, such as oil-rich Kazakhstan, and East Asian nations such as Vietnam are also among nations with the fastest per capita economic growth over the period. These countries were also among those with the greatest increase in motorization and tire demand.

Between 2000 and 2019, the global vehicle parc has continued to increase year on year generally at a rate of between 3% and 4%, and growing from 725 million vehicles in 2000 to almost 1.4 billion in 2019, or an aggregate increase of 90% (Fig. 3.3). The fastest growth since 2000 has been experienced in the regions that had the lowest vehicle density at the start of the period and therefore the greatest potential for catch-up: the Middle East and Africa, South and Central America, and Asia Pacific (Fig. 3.4). Conversely the slowest growth in vehicle parc has been in Europe and North America, regions that had significantly higher vehicle density in the year 2000.

The global passenger car and light truck (PCLT) original equipment (OE) tire market (i.e., tires fitted to newly manufactured

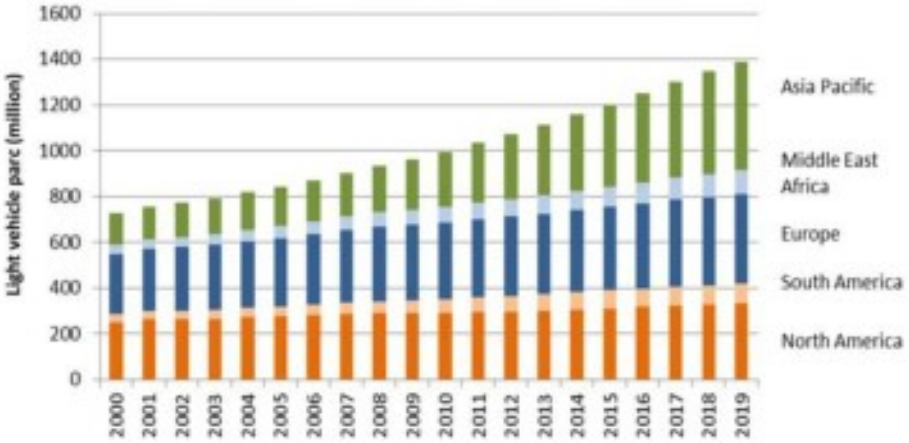


Figure 3.3 Global light vehicle parc (VIO) by region, 2000–19. Source: Astutus Research.

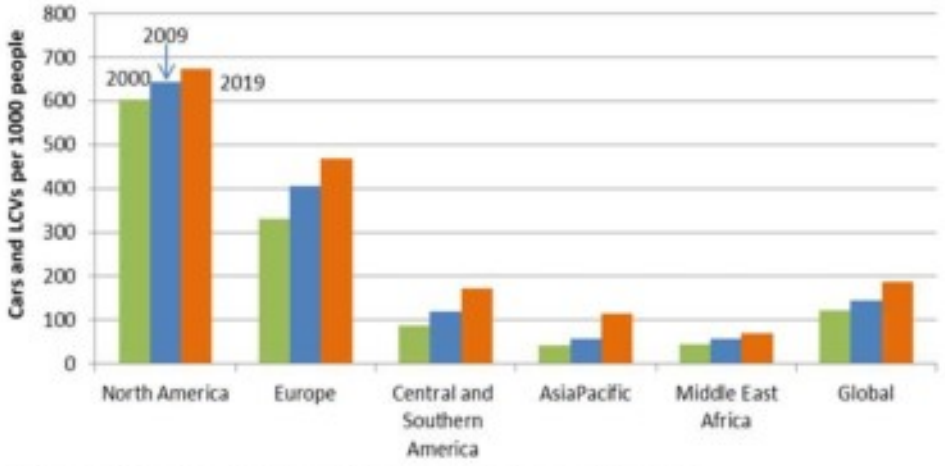


Figure 3.4 Light vehicle parc density by region, 2000–19. Source: Astutus Research.

cars) is projected to increase from 350 million units in 2010 to 430 million in 2025, having peaked at almost 450 million in 2017. Light vehicle production and therefore OE tire sales have been significantly affected by the Covid-19 pandemic, particularly in the first half of the year. Sales are expected to fall by more than 20% in 2020 and are not currently forecast to reach their 2017 peak by 2025. The Asia Pacific region accounts for over half the global market and is expected to lead growth out of the downturn, including resurgence in China after declines in 2018 and 2019.

The global PCLT replacement tire market has grown steadily from a little under 1 billion units in 2010, and is forecast to reach 1.4 billion units in 2025, despite a temporary decline in the market in 2020 resulting from the impact of Covid-19.

The growth in the replacement tire market reflects the change in aggregate vehicle kilometers traveled. Although average kilometers traveled per vehicle have declined as vehicle penetration has increased, trends in replacement tire sales are strongly correlated with parc growth. The regions with the greatest increase in car parc are those with the greatest increase in replacement tire sales. Asia Pacific is projected to see the fastest growth in the forecast period to 2025, with Europe experiencing the slowest growth.

3.3 Regional analysis

3.3.1 Asia Pacific

Over half of all vehicles added to the global light vehicle parc between 2000 and 2019 have been in the Asia Pacific region.

Remarkably, China alone has accounted for over one third of the additions to the light vehicle parc in the period, with a dramatic shift toward car-based mobility in the country as incomes have risen. At the start of the period the country had one of the lowest rates of vehicle density, with less than 9 light vehicles per 100 people; by 2019 vehicle ownership had risen 20-fold, reaching 180 vehicles per 1000. These averages mask significant differences in motorization within the country, as levels of wealth vary significantly. The highest rates of motorization are in the large "Tier 1" cities such as Beijing and Shanghai that have the largest populations. Vehicle penetration rates decline in the smaller "Tier 2," "Tier 3," and "Tier 4" cities that have a successively smaller population and generally have lower average incomes.

Until the late 1990s much of mobility in China was nonmotorized; low average incomes put private motorized transport out of reach for most while schemes to subsidize workers' purchases of bicycles encouraged their use. Sales of motorcycles in China rose through to 2014, but many cities put restrictions or prohibition on their use, citing their role in congestion, road traffic accidents, and pollution; their sales subsequently declined. By contrast, sales of cars have risen dramatically. The Chinese government has strongly encouraged the development of the automotive manufacturing sector; it has also invested huge sums in its road network, and continues to do so.

In 1990 new car registrations in China totaled just 42,000. By 2000 they reached 600,000 but the country remained outside the top 10 new car markets in the world. By 2003 sales exceeded 2 million and China was the fifth largest market behind the UK, Germany, Japan, and the United States. In 2004 sales surpassed those in the UK and in 2006 the total exceeded that in Germany. In 2007 sales in China breached 5 million and were greater than those in Japan for the first time. In 2012 China became the world's largest new car market, surpassing the United States. Sales exceeded 10 million in 2010 and 20 million in 2015, remaining above this benchmark every year since.

Elsewhere in the Asia Pacific region, Australia and New Zealand are the markets with the highest levels of motorization, exceeding 700 and 800 vehicles per 1000 population, respectively, in 2019. Japan is one of the most mature markets, however, and with limited growth in per capita incomes and a declining and aging population the light vehicle parc has now peaked.

By contrast, India and the ASEAN markets of Thailand, Indonesia, Malaysia, and Vietnam are expected to see continued growth in car parc. These are all countries with high penetration rates of motorcycles, in absolute terms and relative to the car

market. Across these markets the unit volumes of tires for powered two and three wheelers have far exceeded sales of car tires.

India is now the world's largest market for new motorcycles, scooters, and three-wheel vehicles; their combined sales have been more than five times those of cars and light commercial vehicles for several years now. In India and Vietnam penetration of cars and light commercial vehicles remains around 30 per 1000 people, although in both cases this represents significant growth: in India the penetration rate has doubled since 2010, and in Vietnam it has doubled since 2014.

3.3.2 Europe

Europe accounted for 20% of the increase in parc between 2000 and 2019. While rates of vehicle ownership have continued to rise in Western Europe, the rate of increase has been relatively slow, from 520 in 2000, to 610 in 2019. The differential in parc density between Western Europe and Central Europe has diminished substantially since 2013, with further convergence forecast by 2025. Rates of vehicle ownership in Central Europe have risen from 210 per 1000 people in 2000 to 480 in 2019. Parc density in the Russia and CIS (Commonwealth of Independent States) region lags significantly behind the rest of Europe, although there are substantial differences within the region, with lower levels of ownership in Uzbekistan, Tajikistan, and Turkmenistan and relatively higher rates in Belarus, Russia, and Georgia.

In Western Europe, light vehicle ownership rates have largely converged at between 520 and 620 vehicles per 1000 people in each country, with Italy an outlier at over 700 vehicles. Parc density in Central and Eastern Europe is more varied, with the Czech Republic and Slovenia having the highest rates at over 600 vehicles, compared with around 180 in the CIS outside Russia. The change in ownership rates between 2000 and 2019 is also more noticeable in the countries of the Central and Eastern Europe region.

The European parc is expected to approach 420 million units by 2025. Within the region forecast growth will be concentrated in the Central and Eastern Europe, with minimal growth for Western Europe as the region approaches "peak parc." While car ownership rates are expected to fall in the longer term, in the current forecast period to 2025, the parc is expected to show slower growth rather than decline.

By 2025 Russia's light vehicle parc is expected to surpass that of Germany, currently the largest in Europe; both countries will

have over 50 million cars and light commercial vehicles on the road. In Russia, this will represent an addition of 9 million vehicles in a decade. Poland and the CIS outside Russia are also forecast to see further substantial growth in the parc, with more than 5 million vehicles added in each between 2015 and 2025. Italy, France and the United Kingdom will each have around 40 million light vehicles by 2025. In Spain, the parc is expected to approach 30 million vehicles by 2025.

3.3.3 North America

North America is the region with the highest penetration of light vehicles. In 2000 there was a density of 600 vehicles per 1000 people, almost five times the global average; by 2019 this rate had risen to almost 675 vehicles. The region accounted for 12% of the increase in the global parc over this period. With already high levels in the United States and Canada, the increase in vehicles in operation in these countries was predominantly driven by rising population; growth in penetration was relatively modest. By contrast, in Mexico the penetration rate more than doubled between 2000 and 2019 (although it remains below 275 per 1000) and in absolute terms the light vehicle parc more than tripled.

Although China has shown very rapid growth in the past two decades, and while its new vehicle sales exceed those of the United States, the United States still has a larger vehicle parc. By 2025, however, it will have also lost this title to China. Because of the large absolute size of the US vehicle parc, despite a relatively low growth rate it will have added more vehicles by 2025 than any other market globally except China.

3.3.4 South and Central America

Vehicle penetration rates in South and Central America have doubled between 2000 and 2019 and at 170 vehicles per 1000 people is now only marginally behind the global average of 190 vehicles. Financial crises have been a periodic feature in markets across the region, hampering even greater catch-up. Once-wealthy Venezuela has experienced a major economic collapse in recent years, while Argentina has suffered from numerous bouts of economic turmoil over the period.

Although national rates of vehicle ownership vary significantly across the region, the trend of a near doubling of penetration in the past two decades is common across the region. Argentina and Chile are current leaders in terms of penetration,

reflecting their higher per capita incomes, while Peru and several of the Caribbean nations lag behind.

Brazil is the dominant market in the region, accounting for almost half the vehicle parc in the whole of South and Central America despite a vehicle density only two thirds that of Argentina. Brazil was the fifth largest global market in terms of vehicles added to the fleet between 2000 and 2019, with an increase of 25 million units.

3.3.5 Middle East and Africa

The Middle East and Africa region includes several of the world's wealthiest counties (concentrated in the oil-rich gulf states), but many of the world's poorest (particularly in sub-Saharan Africa). This diversity is reflected in the varying vehicle densities across the region. The number of vehicles per 1000 people has risen by 50% in the Middle East and North Africa as a whole between 2000 and 2019, although it remains below the global average. It has doubled—albeit from a low base—in North African markets such as Algeria, Morocco, and Egypt. In sub-Saharan Africa, however, the growth in light vehicle parc has only kept pace with population growth—vehicle density has barely risen in absolute terms and has fallen from 17% of the global average in 2000 to just 13% in 2019.

The average age of the car parc in the region is high, reflecting the low level of new car registrations and the fact that the region is a key destination for legal and illegal imports of used cars exported from Europe and Japan.

3.4 Changes in motorization

Although there will be significant differences across geographies, influenced by variation in economic prospects and demography (population growth rates and population density), there are four commonly referenced mega-trends that will impact on future demand for motorization. Personal mobility will be increasingly *CASE*:

- Connected
- Autonomous
- Shared
- Electric

The diagram in Fig. 3.5 shows that under the influence of these CASE mega-trends we expect there to be a disruption to the long-term historic trend of growth in car parc and decline

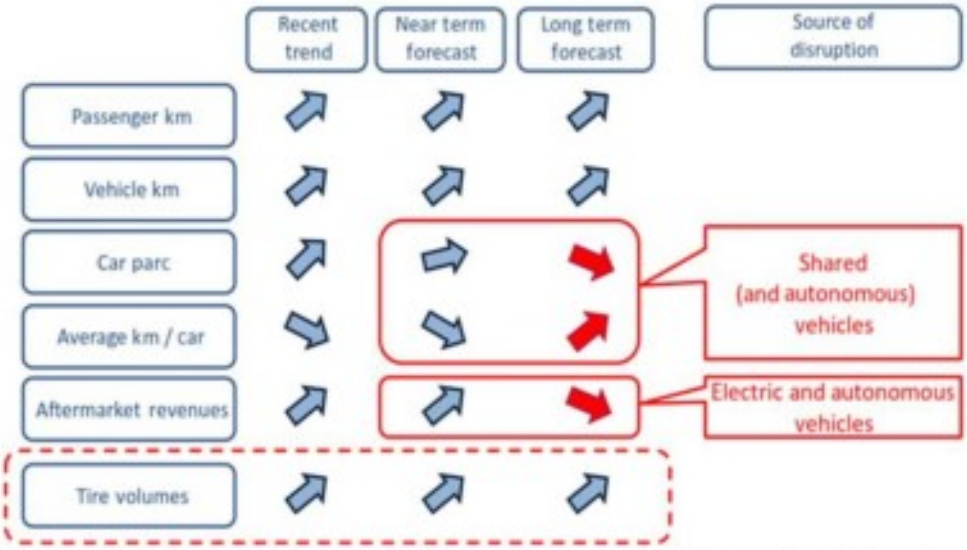


Figure 3.5 Disruptive forces and their impact on indicators of personal mobility. Source: Astutus Research.

in average kilometers traveled per vehicle. This "discontinuity" is expected to be more clearly visible in the later 2020 s and into the 2030 s. Despite these trends, however, the outlook for the tire segment remains positive.

3.4.1 Shared and autonomous vehicles

A significant increase in the popularity of shared mobility (both car sharing and ride-hailing) will ultimately lead to a structural decline in the number of vehicles in operation, with those vehicles used more intensively. Shared-vehicle kilometers currently account for a small proportion of total vehicle kilometers traveled. This is expected to change significantly in the next couple of decades, but with increased demand and more comprehensive service provision.

- While aggregate demand for mobility will continue to increase, a shift from "pay to own" to "pay to use" should result in lower personal car ownership rates, and the growth of MaaS.
- This will result in growth in shared mobility fleets, including rental, car-share, and ride-hailing vehicles.
- Such shared ownership is more attractive in areas of high population density, where supply is more prevalent and average distances traveled are lower; the decline in vehicle ownership rates will therefore be particularly notable in cities. It

is also in cities where legislative attempts to curb vehicle usage or ownership are most prevalent (such as congestion charges).
- While the number of vehicles in operation is expected to decline in the longer term (from the latter half of the 2020 s) vehicles will be used more intensively and average annual vehicle kilometers will rise.
- More intensive vehicle ownership could also reverse the current trend of vehicles being replaced less frequently. A decline in the car parc therefore does not necessarily imply a decline in new vehicle sales.
- The trend toward shared mobility is likely to be accelerated once autonomous vehicles become more widespread (with the concept of robotaxis).

Increased vehicle usage will therefore sustain growth in demand for tires in both the near term and longer term, despite a reduction in the car parc. However, an increased frequency of vehicle replacement could result in some shift in demand from the replacement tire market to the OE tire segment. Furthermore, there will be a shift in demand from private consumers toward concentration in a number of large fleets.

3.4.1.1 Car sharing

The concept of the shared car is not new: there is a very well-developed global short-term rental (or daily rental) market. Rental vehicles are intensively used and regularly replaced; on average, the leading players currently dispose of their cars after 10–12 months.

While the leading players remain focused on renting vehicles by the day, several have also entered the car-sharing (or "micro-rental") market, where vehicles are rented by minute or hour to "members," with vehicles picked up from a street location rather than a rental station. These cars must either be returned to the parcing spot from where they were collected or, under the "free-floating" model, can be left at any location within certain parameters. In the long term, significant growth in car sharing is expected to be one factor resulting in a decline in private car ownership. Enterprise Car Rental and Avis Budget Group (through Zipcar) are leaders in the car-sharing segment among the global car rental companies.

Car-sharing service providers either operate vehicles themselves (car-sharing fleets) or act as an intermediary between individual car owners and renters (peer-to-peer). The peer-to-peer car-sharing model currently has fewer implications for the tire

industry as the vehicles remain owned by individuals. However significant growth of car-sharing fleets will have a far greater impact on the tire sector—a large number of vehicles operated by a small number of providers would ultimately control a large share of the tire replacement market.

The car-sharing fleet is currently relatively small in comparison with the traditional daily rental market. The fleet is expected to continue growing rapidly, driven by increased demand and more comprehensive service provision.

Europcar previously owned a minority stake in the *car2go* car-sharing business but sold this to partner Daimler in early 2018. Europcar has stated that it intended to use the proceeds from the sale to invest in wholly-owned car-sharing activities. Similarly, BMW purchased the 50% shareholding in the *DriveNow* car-sharing business formerly held by its partner Sixt. The rental company has re-entered the market with the launch of *Sixt share*.

BMW and Daimler then proceeded to merge their respective global "urban-mobility" businesses, with the process completing in the first quarter of 2019. This includes *car2go* and *DriveNow*, operating as *SHARE NOW*.

Other vehicle manufacturers have also launched car-sharing schemes, or plan to do so. In Europe alone these include the Volkswagen Group, Renault, PSA, and Toyota. In addition to the strategic operators (vehicle manufacturers and vehicle rental providers), several independent companies have also entered the car-sharing market, such as Lithuania-based Modus Group, which operates in the car-sharing market under the *CityBee* brand.

3.4.1.2 Ride-hailing

In addition to car sharing, there has been a rapid increase in the number of vehicles available on ride-hailing or ride-sharing platforms. While these services have clearly gained business from traditional taxi operators in the geographies where they operate, they have also significantly expanded the "hire with driver" market, at the expense of public transport or self-drive. As these networks attract more drivers in a region they enter a virtuous circle, cutting wait times and reducing fares, increasing the convenience and value offered.

Uber is clearly the most prominent ride-sharing provider globally. The company's ride-sharing offering took gross bookings of almost US$50 billion in 2019, up from $19 billion in 2016, and consumers traveled approaching 30 billion kilometers on its platform. Uber claims to control more than 65% of the

ride-share business in the United States and Canada, Latin America, Europe, Middle East Africa, and Australia and New Zealand. In January 2020 Uber completed the acquisition of *Careem*, the leading ride-share player in the Middle East. Uber has withdrawn from several markets where it faced a major local incumbent, instead folding its operation into a joint venture in which it took a minority stake—*Didi Chuxing* in China, *Grab* in South East Asia, and *Yandex Taxi* in Russia. Other major players in the ride-hailing business include India-based Ola, Lyft in the United States, and Bolt in Europe.

Over time, ride-hailing services are expected to account for an increasing share of the passenger mobility market and account for a greater share of vehicle kilometers. As the ride-sharing fleet grows in importance there are opportunities for rental and leasing companies to provide cars to drivers, further increasing their share of the vehicle parc and tire demand.

Faster growth in ride-hailing is expected to follow the introduction of autonomous robotaxis. Tesla has previously stated that "a custom-made robotaxi capable of running about a million miles using a single battery pack ... should cost less than US$38,000 to produce [1]." The company further states that low vehicle cost, low maintenance cost, and powertrain efficiency should make this it "the most profitable autonomous taxi on the market." The robotaxi concept is already being tested by, among others, Waymo (a sister company of Google) and Cruise, a subsidiary of General Motors.

3.4.2 Electric vehicles

The advance of electric vehicles is expected to have a significant negative effect on the value of the vehicle aftermarket as the electric powertrain requires less maintenance than that on an internal combustion engine (ICE)-powered vehicle.

Tires, however, are an exception. There are specific additional demands on the tires of electric vehicles. For example, Goodyear has stated that traditional tires can wear out up to 30% faster than they would on an ICE-powered vehicle. The leading manufacturers continue to develop tires specifically designed for electric vehicles. At least initially, these tires will be more expensive and this should have a positive impact on average selling prices.

Electric cars are currently heavier than their ICE equivalents, principally due to the weight of the battery, and therefore require tires with a stronger internal structure. They must also be able to withstand the substantial torque associated with

electric vehicles. Furthermore, it is important for the tires to minimize rolling resistance, in order to increase the vehicles' distance between charges, while also providing a smooth ride.

A sharp increase in uptake is expected over the next few years as vehicle manufacturers release a host of new electric versions of their vehicles and the cost relative to ICE vehicles drops dramatically with economies of scale in production. Furthermore, there are plans to rapidly expand charging infrastructure in several countries, and changes to legislation and taxation will also encourage switching.

The switch from manufacturing petrol and diesel cars to electric vehicles is a huge – and disruptive – undertaking for the vehicle manufacturers. It is already leading to realignment of their plant footprint, and by implication for OE, tire markets.

3.4.3 The connected car

New vehicles are increasingly "connected" via mobile Internet technology—the so-called "Internet of things." This is clearly useful for navigation and user comfort (such as in car entertainment), but there are also implications from a vehicle management perspective, including maintenance. This technology is particularly useful for fleet operators, allowing them to remotely track and monitor their vehicles. Predictive maintenance will become increasingly common as a result of this technology, which will also allow the transmission of data on tire status (i.e., temperature, pressure, tread depth, puncture detection). Drivers and fleet managers will be alerted if their tires require attention, with the potential for a direct relationship between tire manufacturer and motorist. Tire manufacturers with controlled distribution could also direct motorists to have their tires changed through their network.

The perceived importance for the tire industry is evident from recent acquisition activity, including the €910 million acquisition of TomTom Telematics (since renamed Webfleet Solutions) by Bridgestone Europe in early 2019, and Michelin's successive purchases of Sascar (Brazil, 2014), NexTraq (United States, 2017), and Masternaut (Europe, 2019).

On acquisition, the TomTom business had an installed base of 860,000 vehicles and Bridgestone stated that combined offering would allow it to cross-sell tires and solutions to a larger customer base.

Michelin's European acquisition, Masternaut, has over 220,000 vehicles under contract. These are mostly light commercial vehicles (LCVs) and primarily located in the UK and

France. The company said that the acquisition will hasten the development of its Services and Solutions business for light vehicles and enable Masternaut to roll out its offering across the whole of Europe using Michelin's geographic coverage.

Regional Definitions

Asia Pacific comprises the Asia and Oceania regions. It excludes the countries that are included in the Middle East grouping (see Middle East and Africa below).

Europe—includes Western Europe, Central and Eastern Europe. Russia, Ukraine and the CIS are included in the Central and Eastern Europe grouping. We exclude Turkey, which is included in the Middle East Africa region. These groupings include the following subregions of West Europe and Central and East Europe:

West Europe—includes Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

Central Europe—includes Baltic States, Bulgaria, Croatia, Czech Republic, Hungary, Poland, Romania, Serbia, Slovakia, and Slovenia.

Eastern Europe—includes Russia, Ukraine, and the CIS nations.

Middle East and Africa comprises the African continent, plus the Middle East region. The Middle East includes Egypt, the states of the Gulf Cooperation Council (including Kuwait, Saudi Arabia, and the United Arab Emirates), Iran, Iraq, Israel, Jordan, and Turkey.

North America—this comprises the United States, Canada, and Mexico.

South and Central America—This comprises the countries of South America, Central America, and the Caribbean, but it *excludes Mexico*, which is included in the NAFTA region.

Reference

[1] Tesla, 2019. First Quarter Update. https://www.sec.gov/Archives/edgar/data/1318605/000156459019012758/tsla-ex991_6.htm.

4

Management of end-of-life tires

Valerie L. Shulman
The European Tyre Recycling Association (ETRA), Brussels, Belgium

4.1 Introduction

Tires are an essential part of the economy of every country that relies on vehicular and/or air transport to move people and/or goods. Frequently imported for use, they are often repaired, retreaded, recycled, and/or recovered locally. They have been "reused" in one way or another since they were first produced in the early 1900s. By 1912 retreading had become a viable means of extending tire life and providing an interim step as an option for long-term reuse and recycling, setting the stage for the circular economy of today. Although the overall rubber sector is small in comparison to others, tires are a significant part of domestic, international, and global trade.

Table 4.1 illustrates the relative consumption of key material and product streams in the European Union (EU). Similar patterns are found through- out the developed world. It is evident that the total quantity of rubber used is relatively small in comparison to others, but the product units are comparatively large, and the resulting wastes are conspicuous and unattractive.

The combined annual global production of natural and synthetic rubber has grown during the past decade by almost a half, to approximately 33,000,000 tons of which +75% is consumed by various divisions of the automotive industries. The preponderance, about 60%, is used for the manufacture of tires for passenger cars, utility vehicles, and commercial trucks. Smaller diverse categories are grouped as "other," which include tires for off-road vehicles (OTRs), such as agricultural, airplane, civil engineering, industrial, and mining, among others as well for smaller ones for bicycles and motorcycles [1]. Hundreds of nontire automotive products including appearance items, belts, hoses, housings, rings, brake components, seals, numerous molded products, and mats, among others, utilize the remaining 15%.

During the past decade, global tire production effectively doubled to an estimated +1,900,000,000 units per year in order

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00027-2
© 2021 Elsevier Inc. All rights reserved.

Table 4.1 Examples of European Union waste streams (in tons).

Product	Use	Subset
Paper	±79,000,000	
Plastics	±37,000,000	
Packaging		±19,980,000
Glass	±15,000,000	
Aluminum	±8,860,000	
Rubber	±5,000,000	
Tires		±3,500,000

to maintain pace with the burgeoning global vehicle demand, which has emerged in many nontraditional regional markets. Typically, passenger car tires account for slightly more than 90% of production while truck and "other" categories constitute the remaining 10%. Annual tire sales are divided into two principal categories: original equipment (i.e., those that are delivered with the vehicle) and replacement (i.e., those that are after-sale purchases). The general rule for annual waste prediction is that for each tire sold, whether newly manufactured, part-worn, or retreaded, one becomes waste.

In 2019, +3,470,000 tons of car, utility, and truck tires, and an additional +470,000 OTR tires were classified as waste in the EU with comparable quantities arising in North America and Asia.[1] Almost simultaneously, as tire production has doubled, indications are that natural rubber production has begun to decline, primarily in Malaysia and India, posing a potential threat to the continued exuberant growth of supplies for the automotive industry. As a result, larger quantities of synthetic rubbers are being used—and indications are that tire manufacturers are beginning to look toward high-quality recycled outputs to fill the impending material gap.

The infrastructure for providing a continuous flow of high-quality recycled tire materials (RTMs) that can be used in substitution of virgin resources is in place in the EU, much of North America, Australia, parts of South America, and Asia and is evolving in many countries around the world.

[1]2020 will show a major decrease in global data for ELT tires treated for the first time since 1994, when annual tire arisings were first systematically analyzed.

4.2 The tire: the raw material for recycling

A pneumatic tire is often described as an engineering marvel. It is basically a large, round, hollow shell filled with compressed air that can support more than 50 times its own weight. While the external features have not changed perceptibly since radial tires were introduced over 70 years ago, numerous internal changes have improved durability, performance, and environmental quality. Many ingredients that improve longevity, resistance to abrasion, etc., during on-road life also contribute to the effectiveness of RTMs downstream in new products and applications.

The material composition of tires varies by category (i.e., passenger car, utility vehicle, truck, off-road, etc.) and nominally from continent to continent (i.e., Asia, Europe, the Americas, etc.), although ingredient ratios remain relatively the same. However, the variations that do occur have negligible impact on use, wearability, or recyclability. Overall, all tires are homogeneous. No matter where they are produced, all tires contain four fundamental material groups: natural and synthetic rubbers, carbon blacks/silicas, reinforcing materials (metals/textiles), and facilitators as shown in Table 4.2.

Once the ingredients are compounded, the tire structure is assembled and vulcanized, which cures the rubber, transforming it into a strong, elastic, rubbery hard state. The final structure is an integrated whole that can withstand continuous abrasion,

Table 4.2 Four material categories.

1. Natural and synthetic rubbers	± 40%–48%	Ratio of natural to synthetic rubber:
		+2–1 for truck tires; +4–3 for car tires
2. Carbon blacks and/or silica	±22%–27%	A range of carbon blacks of varying sizes, structures, and characteristics are used in different parts of a tire
3. Reinforcing materials	+5%–25%	
Metals	+15%–25%	In the beads, belts, and casings of a truck tire
	+11%–13%	In casings and plies of a car tire
Textiles	+5%–10%	Textiles are used in car tire casings
4. Facilitators	+8%–0%	Extender oils, waxes, and plasticizers aid processing; curing systems include sulfur, zinc oxide, stearic acid, and accelerating agents Antioxidants, antiozonants etc., protect the compound; carbon black/silica increase mechanical properties; clay, whitings, etc., are fillers.

Source: ETRA 2020.

Table 4.3 Composition by weight European Union car/truck tires.

Material	Car/utility	Truck
Rubber/elastomers[a]	±48%	±52%
Carbon black and silica	±22%	±22%
Metals	±15%	±25%
Textiles	±5%	±-%
Zinc oxide	±1%	±2%
Sulfur	±1%	±1%
Additives	±8%	–

[a]Natural/synthetic rubber ratio: truck tires +1:2; car tires +4:3.

road rutting, deformations, etc. Table 4.3 is a generic profile of tires produced for the EU market.

Wastes from various production processes are handled separately, including malformed tires. However, once properly fitted and mounted on a vehicle, a tire can reach the end of its on-road life at any point thereafter. Once a tire has been permanently removed from a vehicle without possibility of being returned to the road, it is defined as "waste." From this point forward, the tire enters into a designated management system for nonhazardous wastes. Within the EU many tire management programs are under an "Extended Producer Responsibility" scheme in which the manufacturers groups assume responsibility for the collection and management of arisings. Tires, within and outside of the EU, are considered a "priority waste stream" and must be handled according to local, national, and international legislation.

4.3 Management of postconsumer tires

Management schemes for end-of-life tires vary from continent to continent and frequently from country to country. It is not unusual for management schemes to vary among regions or municipalities as well. Recycling schemes are greatly influenced by two key elements. The first is based on environmental legislation at the international, national, state and, even local level at times. The second focuses on national needs and priorities for the potential benefits that could accrue from the sustainable options available for their treatment and use. Both have had a crucial impact on recycling—and recyclers—from tire sourcing, to the identification and selection of technologies that will be

favored and the types of output materials, products, and applications that can be supported for investment, research, and development. Some communities even define local product or application needs, potential usage, and the means of final disposal for recycling residues.

Table 4.4 briefly describes the "four Rs" of sustainable waste management for tires, which through their use, minimizes waste and reduces reliance on natural resources. The four are reflected in the five-step waste management hierarchy that places material recycling at the top of the list. In the EU the revised Framework Directive on Waste (2008) [2] has also had a critical impact by directing postconsumer tires toward recycling, and away from landfilling. It also provides a definition of "recycling" and offers a means for recycled materials to exit the waste designation:

> *Recycling means any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations.*

Five wastestreams have been identified as "specified wastes (to) cease to be a waste." Each will require that "specific criteria" be prepared: *aggregates, paper, glass, metal, tires, and textiles*. Thus although tires are not the subject of specific waste management legislation—they are frequently identified as among those materials and products that require special consideration and are the focus of distinctive funding schemes.

Table 4.4 Sustainable options.

Reuse: includes the sale of part-worn tires for domestic on-road and other uses as well as for export to countries with less restrictive road-use requirements.
Retreading: remanufactures a tire using as the core, a carefully selected, undamaged casing, which reduces production energy as well as virgin resources.
Recycling: transforms a waste into a raw material that can be reintegrated into the economic stream as a resource to substitute the use of virgin resources.
Recovery: transforms a waste into energy or fuel, which can be reintegrated into the economic stream as a resource to substitute the use of other energy sources.

4.4 Material recycling: treatments and technologies

Tire recycling is somewhat unique in comparison to other recycling sectors for a number of reasons:

- First, it is among the smallest wastestreams;
- Second, tires are 100% recyclable—the rubber, steel, and textile fibers are currently recovered by recycling technologies;
- Third, tires are essentially homogeneous (i.e., all are made from the same materials) using virtually the same generic formulae with nominal variations—worldwide. The principal variation is size;
- Fourth, there is an interim treatment, retreading, which can extend the on-road life of a tire, and which in recent years has been limited to tires other than those for passenger cars;
- Fifth, until recently, tire recycling outputs were not used to produce the same or similar products as the original (i.e., tires), but have become strategic materials in over 100 different market sectors with hundreds of individual products and applications; and
- Finally, under EU legislation, tires, tire pieces and recycling residues cannot be placed in landfills, compelling the development of new options for valorization, including landfill engineering.

Nonetheless, the starting point for tire recycling is the same as for other industries—the sourcing of a continuous flow of raw materials. Historically, end-of-life tires have been separately collected and sorted for two sectors—the part-worn market (secondhand), and retreading, the restructuring of the tire. However, as retreading dwindled, and reuse/export stagnated for a period, before a temporary resurgence, material recycling and energy recovery operations began to absorb a majority of the tires. Many countries with large retreading industries provided the infrastructure for collecting, sorting, and transporting tires and became the means of creating and servicing new markets (i.e., material recycling and energy recovery).

Today, in most EU States, much of the Americas, many parts of Asia, Australia, parts of Africa, and elsewhere, tires destined for recycling are collected under commercial contract from a variety of "regular" sources including garages, retail outlets, and vehicle dismantlers, among others. In some regions, they are also removed from long-standing stockpiles or "mono-fills." It is important to note that any tires that have been involved in a fire, even those that have only been partially consumed, must be removed and cannot be included in recycling treatments.

Generally, prior to delivery to a treatment facility the tires are sorted by category (i.e., car, utility vehicle, truck, other) and then by size. Road-worthy part-worn tires are removed for domestic reuse or export under OECD regulations. Retreadable casings are diverted to appropriate facilities according to industry criteria. Nonretreadable tires are sorted again before delivery to a treatment site. As end-of-life tires are waste, they must be shipped in compliance with the Basel Convention and OECD regulations. However, until now, tires have been classified as nonhazardous waste destined for recovery, thus the documentation and information required is limited.

Once delivered to a treatment facility, the tires come under the jurisdiction of the national and/or local authority(ies) that regulate the quantity limits, location, timeframe, and circumstances under which they may be stored on the premises. Appropriate zoning and land-use permission, as well as permits and licenses must be obtained. Under certain circumstances, and in certain countries, a waste management permit may also be required before the tires can be processed or the materials used.

Prior to processing, the tires are cleaned of debris such as glass, stones, or miscellaneous items. Tires acquired from stockpiles or other long-term storage often must be washed prior to use.

Tire recycling treatments range from the simplest mechanical cutting devices to sophisticated, complex multiphase chemical, mechanochemical, and/or thermal processes, which overcome many of the principal obstacles inherent in the recycling of thermoset rubbers. Specifically, the treatments and technologies that have evolved do not attempt to dissolve or melt the rubber into the virgin compound. Rather, they aim to exploit and enhance selected properties of the compound.

It must be noted that the following discussions refer only to RTMs that will reenter the economic flow for use as ingredients in compounds or materials for use in a wide range of products and applications. They do not include materials that are prepared for use for energy recovery, cement kilns, or other similar purposes—although in some instances the treatments do overlap.

There are four basic levels of treatment. Each can be described in terms of its basic functions, which become increasingly complex as they progress through successive levels. The capabilities of each level can be expanded by linking two or more technologies to operate in tandem in order to produce the desired result. Level 1 and 2 treatments currently produce approximately 75% of all RTMs used today and thus will be the focus of this discussion.

Level 1 treatments: destruction of the structure of the tire

These treatments use car and truck tires as feedstock. They are simple mechanical means that destroy one or more of the physical attributes of the tire (i.e., shape, weight-bearing capacity, and rigidity, among others). They are designed to produce materials that can be directly used for simple products in civil or environmental engineering or as feedstock for further recycling. The most common methods include bead, sidewall, or tread removal; compression; baling; or cutting.

Level 2 treatments: liberation and separation of the elements of the tire

These treatments separate out the principal components of the material (i.e., the rubber, metals, and textiles). The most common technologies are ambient and cryogenic size reduction as well as some newer technologies such as microbes and water jetting, among others, to treat the tires.

Fig. 4.1 illustrates the progressive, often inclusive nature from the "first cut," by mechanical means, through the "higher level," specialized treatments and technologies that add distinctive characteristics or properties to the material outputs. Many of the technologies as well as their outputs (i.e., materials, products, applications) for which the materials are used are discussed throughout this book.

Bead removal is used for car and truck tires as a pretreatment for later recycling. It is a mechanical procedure that removes the rubber-coated steel coil wires by cutting or tearing the points that anchor the bead to the casing. The carcass can be directly used for civil engineering applications or as feedstock for later recycling.

Sidewall removal is used primarily on car tires as a pretreatment for later recycling treatments or the sidewall can be used directly in civil engineering applications. It is a mechanical cutting procedure that frees the strips of tread from the carcass. The tread can be used directly in simple products or as feedstock for later processing.

Baling is used on car and truck tires. It is a mechanical procedure that destroys the structure of a specified number of tires by

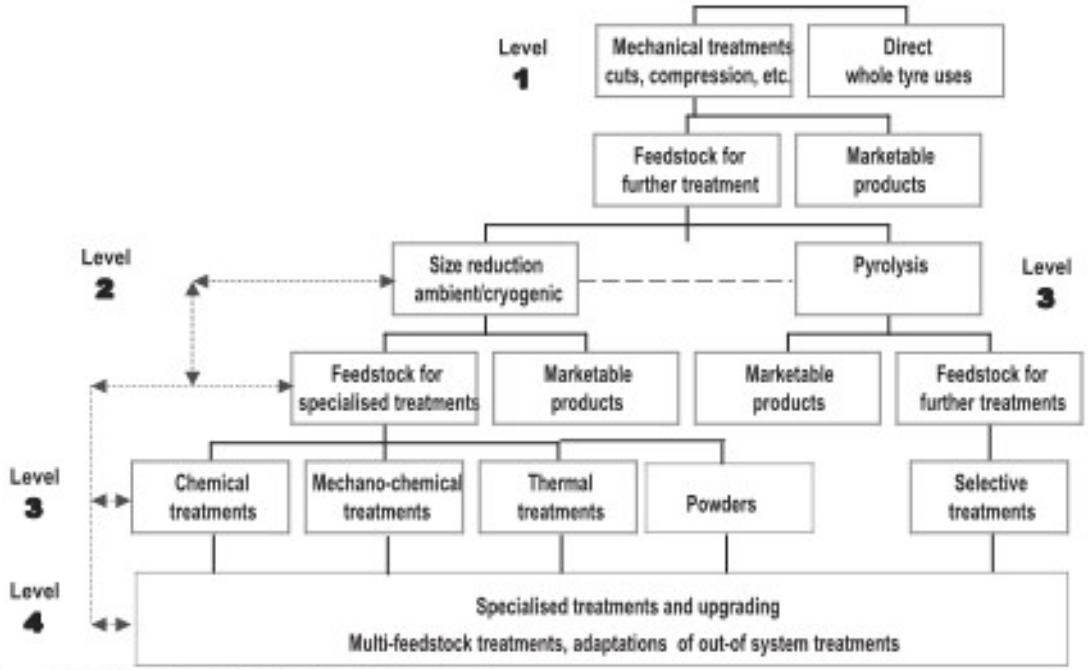


Figure 4.1 Schematic of the four levels of treatment.

placing them in a chamber under high pressure (+65 tons) to permanently deform them into a cube or rectangular solid that is then secured with a defined number of straps at specified points. The number of tires is dependent on the final dimensions of the bale. They can be used directly for a number of civil engineering uses.

Equipment can be stationary or mobile, depending on how the material will ultimately be used. Thus a baler could be placed on-site during an erosion control project. Other than in debeading, neither the bead wires nor the belts are removed prior to or during processing.

As greater quantities of off-road tires (OTRs) have been collected, equipment has become available to cut them into more manageable pieces, often in halves or quarters so that they can be shredded using standard equipment.

Whole tires and Level 1 outputs are generally used as feedstock. The outputs can be used directly in applications or products or as feedstock for Level 3 processing.

Shredding and chipping are used on whole car or truck tires. Shredding is a treatment that uses different technologies to fragment the tire. Most often, a set of knives is used to produce material ±50 to ±300 mm that is irregularly shaped or equidimensional. Neither the bead wires nor the belts are removed prior to, during, or after processing unless it is accomplished as the first step in size reduction processing.

Chipping is generally a second processing of shred that results in material ±10 mm to ±50 mm that is either irregularly shaped or equidimensional. Chips are often used directly in civil engineering applications and often as feedstock for ongoing Level 2 treatments.

Ambient grinding uses whole or pretreated car or truck tires in the form of shred, chips, sidewalls, or treads. Ambient grinding is a multistep technology. Processing takes place at or above normal room temperature. The rubbers, metals, and textiles are sequentially separated out. First, the material is sheared with a system of knives. If the reinforcing and bead wires are not removed prior to processing, the metals are magnetically separated out during the granulation process. The material may continue through one or more sequential granulators to further reduce it in size. The material passes through a series of screens and sifting stations to remove the final vestiges of impurities and ensure consistency of size. During the final phase, the textile residues are removed by air separators.

Cryogenic processing generally uses pretreated car or truck tires as feedstock, most often in the form of chips or ambiently produced granulate. Processing takes place at very low temperature

Level 3 treatments: multitreatment technologies

This group of diverse treatments and technologies further processes the first and second level material outputs to modify one or more characteristics by means of mechanical, thermal, chemical, mechanochemical, or multitreatment procedures. The outputs of Level 2 are most often used as feedstock.

using liquid nitrogen or commercial refrigerants to embrittle the rubber. It can be a four-phased system that includes initial size reduction, cooling, separation, and milling. The material enters a freezing chamber where liquid nitrogen is used to cool it below the point where rubber ceases to behave as a flexible material. The cooling process embrittles the rubber and allows it to be fractured to the desired size resulting in a smooth and regular shape. Because of its brittle state, fibers and metal are easily separated out in a hammer mill. The granulate then passes through a series of magnetic screens and sifting stations to remove the last vestiges of impurities.

Both ambient and cryogenic processing can be repeated to produce finer particles. Increasingly, with their attendant technologies, the two are combined into one continuous system to benefit from the characteristics and advantages of each and to reduce overall costs. An ambient system is generally used in the initial size reduction phases. The cryogenic system is used to further reduce the material in size and then to remove the metal and textiles. The outputs from either or both systems can be used directly or as feedstock for further processing.

Within the past decade, these size reduction technologies have begun to produce sufficiently clean steel and textiles fibers that can be used as input materials for further treatments with commercially viable output results. Thus these recycling residues are no longer wastes, and have begun to enter the economic flow as additional material streams for use in a variety of products and applications.

Level 4 treatments: material upgrading

Level 4 treatments refine, upgrade, modify, or generate specific characteristics or properties in materials produced by Level 3 treatments that most often provide the feedstock. Upgraded reclaim, reactivated, surface modified, or devulcanized materials, upgraded pyrolytic char (carbon products), and new compounds are among the most representative outputs.

Reclaim, pyrolysis, surface modification, and devulcanization are representative examples of the range of treatments used. The outputs can be used directly in applications or products or as feedstock for Level 4 processing.

Reclaim is a two-phase process during which the material is thermally broken down. Part 1 relies on clean, ambiently produced granulate. The second part is plasticizing during which the granulate is mixed with the chemical agents and oils, subjected to heat, then worked mechanically, extruded, and cut into blocks. Key elements that influence the output are the chemical composition of the material used, the duration of the breakdown process, and the ratio of thermal-to-mechanial breakdown. A principal characteristic of reclaim is that it can be modified during processing and customized for specific uses. The vast majority of reclaim is returned to the automotive industry for a range of products—including tires.

Pyrolysis is a two-stage thermal decomposition that heats the rubber in the absence of oxygen to break it into its constituent parts

(i.e., carbon, oil, steel, etc.). The principal stages are primary cracking and postcracking. Depolymerization and primary cracking take place progressively by heating the material at relatively low temperatures while aromatic components are produced at higher temperatures, although both can occur in a one-step furnace. Pyrolysis produces a minimum of three commercializable products including saleable steel, oils, and carbon products. The resulting carbon products have proven viable as a replacement for some types of carbon black for use in inks, toners for photocopiers and printers, paints, and even tires. In-roads have also been made with the production of silicon carbide, which will expand markets into ceramics components, semiconductors, etc.

Devulcanization is a process that can be undertaken by different means including microwaves, ultrasound, biologics, and chemicals, among others. The goal is to reverse the sulfur-carbon cross-links that were formed during vulcanization so that the material can be reformatted and revulcanized. Different processes modify specific properties of the rubber. The system used will determine whether it will be a batch or continuous process. Each devulcanization system begins with a first phase of either cryogenic or ambient size reduction. As an example, chemical processing utilizes a batch processing. The new material can then be used in replacement of virgin resources—including tires.

Surface modification/activation uses buffings or peelings from retreading or ambiently size reduced granulate produced from truck tire treads as its principal feedstocks. Surface modification is a three-phase treatment. In the first phase, the feedstock is ambiently reduced to a fine powder of <0.04 mm from which all metals and textiles are removed. In the second phase the powder is activated by coating it with high-molecular unsaturated polymers in aqueous dispersion with an appropriate curing system. The third phase occurs during vulcanization on a double-belt press that rolls the material at very high pressure. During the curing process, bonds are formed between the polymer chains of the coating and the polymer to which the powders are added. As a result, the rubber particles activated by the coating are bound to the new three-dimensional network. The original rubber properties are retained.

Posttreatments of pyrolytic char include mechanical separation and physical or chemical treatments that can upgrade the char by reducing it in size and separating out impurities. Posttreatments generate materials that have similar characteristics to a variety of different grades of carbon black currently used to produce a broad range of commercial products and are

a valuable resource for technical rubber goods. Resonance disintegration is an innovative example of particle fragmentation using resonance forces to vibrate particles apart. It can take pyrolytic char from a maximum of 600 μm to below 30 μm with 50% below 1 μm after a single processing with a surface area, structure, and dispersion in the rubber compound similar to standard carbon blacks. Other treatments are being used to produce silicon carbide materials that can be used in replacement of virgin materials. A number of posttreatments are currently undergoing standardization with ASTM.

Thermoplastic elastomers (TPE) use granulate and/or powder produced from car or truck tires as feedstock. The treatment requires two feedstocks: rubber and plastic. It is a two-phased reactivation and mixing process that combines the material qualities of the former with the processing behaviors of the latter. The reactivation and mixing occur under high shear forces in a conventional internal mixer. The granulate acts as an elastomeric compound during the rubber phase in cross-linked thermoplastics creating a new compound—not a blend. As a rule, smaller-sized materials retain fewer impurities from metal or textile.

As specialty treatments generally use smaller granulate or powders as feedstock, there is usually no further loss during processing. One of the few exceptions could be the upgrading of pyrolytic char and removal of extraneous ash, etc.

It is important to note that each time the material is processed it loses some of its bulk. Thus the smaller the finished size of the material, the more tire weight will have been lost. The loss is due to production wastes that are generally the result of the casing. The residues include metal and textile fiber separations. Table 4.5 illustrates the amount of waste per ton of product output.

Table 4.5 Percent of processed material per ton.

Material output	+% Product	+% Loss p/t
Shred and chips (unseparated)	95%	+5%
Extended shred (metal/fiber removed)	70%	+30%
Granulate (depends on mm) truck	60%	+40%
Granulate (depends on mm metal/textile out) car	50%	+50%
Powder	30%–40%	60%–70%

4.5 Material outputs

The material outputs from the four levels of treatment are broadly classified into eight categories, six referring to the rubber component: cuts, shred, chips, granulate, powders, and fine powders, as well as two that refer to nonrubber elements: steel fibers and textile fibers.

Each rubber category is comprised of one or more subcategories with different parameters, creating a continuum from less than $\pm 500\,\mu m$ to >300 mm and more. The apparent overlap between the larger granulate and the smaller chips is a function of processing specifications. As an example, granulate is generally characterized by multistep processing during which the metals and textiles are removed, while shreds and chips are characterized by processing that merely fragments the tire leaving the metals and textiles intact. Fig. 4.2 illustrates the continuum of materials that result from the treatments.

Evaluations and standardized testing procedures are used to ensure material consistency (e.g., CEN, EN, ASTM, ISO, etc.). The methods used vary according to material size. Larger materials (i.e., shreds or chips) are generally evaluated visually. For example, attention is paid to the size of the material and the presence of extraneous materials such as glass, free wires, or stones. Other criteria may be agreed between the producer and the user.

With smaller materials (i.e., granulate or powder) more exacting methods are used. As can be seen, each category and subcategory is characterized as a range. However, the fragments in each subcategory are not homogeneous, but constitute a range of different size particles. Thus a sample of 1 mm powder contains particles ranging from less than 0.30 mm to more than 1 mm. The distribution in the sample should show that more than 90% of the particles are within the 0.30–1 mm range.

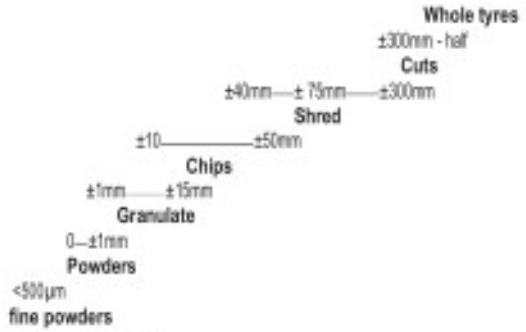


Figure 4.2 The range of recycled tire materials.

Particle distribution is determined with a series of screens. Dependent on the size of the desired material, a set number of screens is generally placed in descending or ascending order (dependent on the test). The material flows through the tier within a specified time. The material that remains on each screen is weighed and expressed as a percentage of the sample. While the size and particle distribution are often critical to the selection of a material, the chemical and physical properties provide information about the material content and how it will react physically in response to certain conditions.

The columns in Table 4.6 compare different material outputs by:

1. *Size:* each material is described as a range of particle sizes (e.g., granulate can be described as a range from ±0.5 mm to ±15 mm, while devulcanizates are described as less than 1 mm). Whole tires are discussed as a unit and bales by the number of tires required to produce a unit.
2. *Key characteristics:* describe some of the principal characteristics of the particular material that can distinguish it from other materials of the same size (e.g., granulate produced ambiently and cryogenically present very different characteristics).
3. *Traditional materials:* lists some of the traditional materials for which particular postconsumer tire materials could be used as substitute for virgin resources.

4.6 Traditional and evolving markets

Organized tire recycling is a relatively young industry. Data on arisings and the predominent valorization routes have been maintained annually for almost 30 years. Under most circumstances, data are maintained by national environment offices and agencies and tracked by recycling organizations and manufacturers. Fig. 4.3 illustrates the steady growth of tire recycling during the period, from only 5% of arisings in 1992 with only 12 EU States, to more than 38% in 2019 when 27 States and Norway contributed.

During the past 30 years tire recycling has made great strides toward fulfilling its mission of producing environmentally sound materials from a priority wastestream so that they can reenter the economic flow to be used in substitution of virgin resources, reducing energy consumption for production as well as CO_2 emissions.

As illustrated above, significant quantities of material are produced annually with indications that capacity could continue to

Table 4.6 Summary of principal material characteristics.

Material	Size	Key characteristics	Traditional materials
Whole tires	unit	Lightweight, low compacted density, high void ratio, good compressibility, water permeability, thermal insulation	Concrete block, clay, quarried aggregate, gravel-filled drums
Construction bale	100–125 tires	Lightweight, low compacted density, good thermal insulation, limited deflection, exceeds specifications for specific gravity, gravity, compressibility, deformation, creep, hydraulic conductivity	Construction block, stone riprap, gravel, packed earth, crushed rock in wire cages or other containers
Shred	±50– ±300 mm	Lightweight, low compacted density ±0.5 ton/m^3, high void ratio with good water permeability between 10^{-1} and 10^{-3} m/s	Crushed rock or gravel, large grain sand, lightweight clay, or light expanded clay aggregate, fly ash from coal burning
Chips	±10–50 mm	Good thermal insulation and compressibility, low earth pressure and high friction road characteristics	
Size reduced		*Dependent on use*	
Ambient	±0.50–15 mm	Cross-linked macrostructure retains same characteristics as the tire; irregular shape; some thermal degradation, temperature stressed. May exhibit nominal degree of reduced cross-linking	Product: Virgin rubbers, EPDM CE: clay, sand, gravel, fly ash from coal burning polyurethane
Cryogenic	±0.5–5 mm	Clean surfaces, regular particle size and shape, glossy, smooth surface, no surface decomposition or thermal stress	
Powder	<1 mm	Dependent on technology: ambient/ cryogenic characteristics as above	Virgin rubber, EPDM, other compounding materials
Fine powder	±0–500 μm	Most often produced by specialized treatments as below	Virgin rubber, EPDM, carbon fillers
Specialty materials		*Dependent on process*	
Reclaim	av.0.360	Some characteristics of virgin rubber, limited aging, and deterioration or flex fatigue; resistance easily modified during processing, improves flow, mold filling, lower die-swell, can be added to virgin rubber and revulcanized	Virgin butyl rubber, EPDM, other commercial rubbers

(*Continued*)

Table 4.6 (Continued)

Material	Size	Key characteristics	Traditional materials
Devulcanizate	<1 mm	Some characteristics of virgin rubber, increased surface reactivity, good fatigue properties, improved tensile strength, reduced cross-links, permanent elongation <50%	Virgin rubber, EPDM
Surface modified	<1 mm	Activated surface gives improved cross-link density, permanent particle modification, return of some virgin characteristics allowing bonding with matrix during revulcanization	Virgin rubbers, EPDM, other commercial rubbers
Pyrolytic char	<0.4–1000 μm	Coarse particles until treated, some structural change possible	Carbon materials, fillers, coal-burning residues
Upgraded materials		*Dependent on process*	
TPE	<1 mm	Mechanophysical characteristics similar to TPEs, about the same shore hardness & polymer base or virgin TPEs	Virgin rubber, TPEs, virgin plastics
Carbon products	>250 nm	Similar size, shape, surface area, structure and dispersion as standard carbon blacks, all particles <30 μm, 50% <1 μm can be used to replace N550, N660, N770	Traditionally produced carbon blacks

grow within the near future once market impacts from the recent corona pandemic have abated. Treatments and technologies have evolved to new levels of sophistication and efficiency that allow the production of finer, cleaner, and more diverse materials, at more competitive prices. In 2018–2019 somewhat more than 1,353,000 tons of tire arisings were materially recycled in the EU bringing the combined total from 1992 to approximately 10,000,000 tons.

During the earliest periods, the primary focus was on the use of larger, more easily produced materials—which only had to meet limited performance requirements (e.g., cuts, shreds, and chips). However, as the inherent performance characteristics became better known, it became apparent that RTMs had a considerably greater value than originally acknowledged. Equipment manufacturers began to work more closely with recyclers and industry representatives to develop more efficient

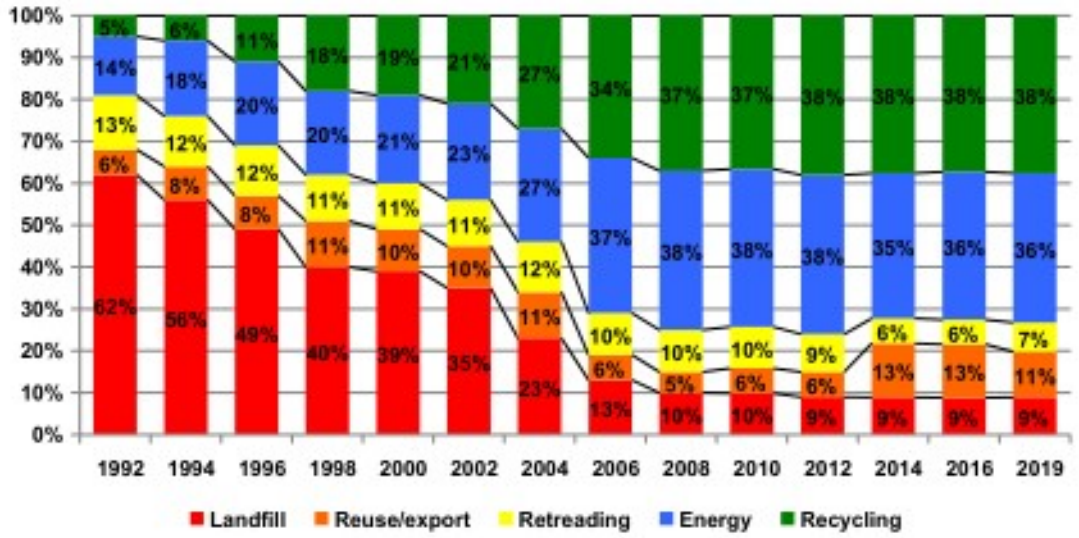


Figure 4.3 European Union recycling capacity 1992–2019 (ETRA 2020).

and more exacting equipment that produce materials with fewer impurities—acknowledged to be +95% free of metal and/or fluff.

Today, there are seven traditional large markets coupled with smaller niche markets that consistently consume more that 80% of the materials produced. Newer niche markets, many of which have the capacity to use increasingly sophisticated technologies are beginning to evolve, albeit very slowly. Until now, production and use have maintained an uneven pace, with some products or applications growing (e.g., automotive), and others beginning to wane (sports field surfaces). There is some expansion into new realms, and there are strong indications that this pattern could continue into the future.

1. *Civil engineering and environmental management.* At the entry level these markets utilize primarily larger materials (e.g., whole tires, bales, shred, and chips). These treatments and applications are especially appropriate for coastal areas, countries/regions with erosion issues, as well as for landfill engineering and road construction bases. These markets have also grown to accommodate communities with small quantities of tire arisings or limited budgets. Development prospects are positive, particularly as motorization continues to expand into new world regions. Civil engineering and environmental management are among the first markets to absorb new arisings. In recent years, smaller materials have

also been added. Many of the applications focus on roads and on earthquake prone areas, particularly noise and tremor management.

2. *Construction* utilizes a wide range of materials from shred and chips to granulate, powders and even steel and textile fibers. During the past decade, construction has become one of the largest markets for RTMs as raw materials, ingredients, and products. Shreds and chips are used for lightweight fill or backfill at construction sites. Granulate is the base for one of the most prevalent products, rubber sheeting made from 90% granulate, for noise and vibration insulation under various types of flooring or concrete screed, as well as roofing. A second group of products uses rubber powder in the production bitumen sheets for roofing underlayments and mastic linings under tiles. Recently, recycled steel fibers have been used as concrete reinforcement for industrial pavements, concrete slabs, and spray concrete. Powders are used in glue mixes for ceramic tiles and plaster.
3. *Sports and leisure infrastructure management (SLIM)* had been a principal market for granulate accounting for large quantities in sport surfaces, playgrounds, and playing fields. International and national bodies provided crucial financial support for these facilities for young and old in urban, rural and isolated areas around the world. The fields reduce isolation and improve socialization, often in war-torn areas. As centers have flourished, SLIM projects have overlapped with other construction including buildings, parking areas, paths, marinas, and pool enclosures. During the past year, the market has declined considerably because of suspected potential problems with the materials—and its use is being discussed and may be banned in a few years.
4. *Manufactured products (MFR)* utilize large quantities of different size materials including granulate and various size powders, as well as specialty powders to produce a wide range of consumer and industrial including technical rubber products. These products, large and small, are supplied to all of the markets currently served from solid wheels for trolleys and trams, to garbage cans, from shoe soles to gaskets and floor tiles, many newly developed automotive products as well as safety products for the sports and leisure sector. MFR are often components for larger product lines.
5. *Automotive products (AU)* currently use a wide variety of granulate, powder, and specialty powders to produce a range of molded parts including hoses, mats, gaskets, connectors, etc., as well as seals, cupholders, etc. It is currently a rapidly

growing market for a broad range of under-the-hood equipment and decorative products. Many products that are currently used in the automotive sector had their beginnings in other industries—including tires.

6. *Urban transport (UT)* uses a wide range of RTMs for different products and applications. Beginning with shreds and chips that are often used in road and rail beds, while granulate and powders are often used in rail housings, coverings, and surfaces. Virtually the same rubberized bitumen is used to pave around the transport area to provide noise and vibration dampening. It is important to note that during the past five years, there has been a major focus on providing UT options—which, due to legislation, must include considerations for noise and vibration reduction.
7. *Materials (ING)* used as ingredients in complex blends, mixes, and compounds including TPE and surface modifications, among others. These materials have become among the most sought after ingredients for rubber alloys, adhesives, plaster mixes, paints, and bitumen additives to name a few. It is important to mention that the steel and textile fibers from the tires have also become products used as ingredients in the cement industry as well for floors, panels, and blocks as well as in spayed-on products.

Table 4.7 illustrates the current quantities of the various classes of materials and the principal sectors in which they are used.

Production and use patterns vary outside of the EU. In Canada, China, Japan, Korea, and the United States, among others, the production of shreds and chips far exceeds that of granulate and powders combined. While civil engineering is more developed in these countries, and consistently consumes vast quantities of tire

Table 4.7 Principal uses of RTMs.

Material/product	%Age	Use	Principal uses/applications
Whole tires	10%	CE, CU, UT	Whole, cut, or in bales for CE and/or construction
Shred/chips	18%	CE, CU, UT	CE, drainage, landfill engineering, horse tracks
Granulate	52%	A, CU, MFR, UT, ING	Molded products, sport /play surfaces,
Powders	11%	AU, CE, CU, MFR, ING	Road surfaces, molded products, sheeting, etc.
Specialty powders	8%	AU, CU, MFR, ING	Pigments, paints, carbon black, tires, TPEs, etc.
Steel and textile fibers	1%	CE, CU,	Concrete, vibration/sound panels, construction

CE, Civil engineering; *CU*, Construction; *EM*, environmental management; *MFR*, manufactured products; *RTMs*, recycled tire materials; *UT*, urban transport.

Table 4.8 Examples of recycled tire material applications.

Application	+Quantity	+Unit of application	Format
Sea embankment	3,000 car tires	500 × 1.5 m high	Whole
Sound barriers	20,000 truck tires	1 km × 3 m high	Whole/cut
Artificial reef	30,000 car tires	1 km × 1 m high	Whole/bale
Drainage culvert bed	50,000 tires	1 km long	Whole/cut/bale/shred*
Coastal stabilization	2,000 bales	1.3 m high × 1 km	Bales
Embankment	1,000,000 car tires	330 × 3 m high	Shred (compacted)*
Backfill	80–100 car tires	1 m^3	Shred (compacted)*
Bridge abutment fill	100,000 tires	1 m wide × 200 mm	Shred (compacted)*
Lightweight fill	2,700–3,600 km m^2	Layer thickness ±1–6 m	Shred (compacted)
Tram rail beds	50,000 tires	1 km	Shred (compacted)*
Equestrian track	15 tires	10 m^2 with 15 mm thick	Shred
Thermal insulation	300,000 tires	0.3 m thick × 10 m wide	chip/shred*
Drainage layer	300,000 tires	0.3 m thick × 10 m wide	chip/shred*
Road surface	70,000 tires	1 km 1lane road	Granulate
Play surface (25mil)	1,400 tires	~500 m^2	Granulate
Asphalt rubber.	3,500 tires	1 km × 12 m × 0.05 m	Granulate
Animal mattresses	18 tires	Unit	Granulate
Sound barriers	20,000 tires	1 km × 3 m high	Granulate
Running tracks	2,700 tires	400 × 7 m	Granulate
Infill for artificial turf	12,200 tires	Normal field	Granulate
Safety tiles	4 tires	1 × 1 × 0.04 m	Granulate
Elastic layers	3 tires	1 × 1 × 0.03 m	Granulate
Mats or sheets	1 tires	1 × 1 × 0.01 m	Granulate
Solid wheels (carts)	±1 ton of tires	±900 units	Granulate/powder
Antistatic shoe soles	1 tire	6 shoe soles (adult)	Powder
Pigments	112 tires	30–50 pigments	Powder

*Tire quantity depends on producer formula or specifications BRRC, BioSafe, ETRA, D. Humphrey, La Sapienza, Amirkhanian.

materials, a large portion of shred and chip production is used as tire-derived fuel (TDF) in energy recovery facilities. Table 4.8 includes examples of the quantities of materials used to construct a broad range of products and applications.

4.7 Energy recovery

While energy recovery is not recycling, it is a crucial part of attaining sustainable development goals. Thus no report on tire recycling would be complete without mentioning energy recovery.

As material recycling, energy recovery is inextricably linked to economic development, and to the prevention and minimization of waste. It is one of the two principal means of valorizing the waste that does occur and, thus reducing its environmental and economic impacts. Together, material recycling and energy recovery offer alternative and complementary means of gaining the greatest sustainable benefit from natural resources and their wastes, thereby reducing the consumption of virgin resources.

Approximately 36% of postconsumer tires in the EU and about 45% in the United States are used as a supplementary nonfossil fuel in some form of energy recovery process in cement kilns or in incinerators to generate electricity, steam, etc., replacing other energy sources. Every country involved in tire recycling has developed at least one technology for incineration with energy recovery. Recent developments that permit the use of mixed feedstock (i.e., tires mixed with other postconsumer or production materials) ensure continued interest.

TDF is a broad rubric that includes whole tires, tire wastes, cuts, shreds, and chips. It is used extensively in developed as well as developing regions around the world. In Japan and the United States, among others, energy recovery is the foremost means of valorization of postconsumer tires and industrial wastes.

In the EU, energy recovery fluctuates between 36% and 38% annually, combining with material recycling at a relatively stable 38%, retreading serving as an interim step at about 7% (primarily for truck tires), bringing the total of tires treated sustainable to 81%—without reuse or export, which is currently 11% of annual arisings. It is important to note that tires are among the most recovered products—accounting for annual, sustainable treatment of its waste arisings at a consistent level of 91%.

4.8 The future

It is apparent that the tire recycling industry has two at times mutually exclusive missions. First, under existing international and EU legislation, it is a waste management industry. As such, it must respond to numerous, and at times onerous regulations that cover every aspect, including permitting, transport, treatment, and use of its raw materials. However, secondly, it is a commercial industry that, in order to prove its worth and success, must be profitable. It must provide materials and products that meet commercial demands and performance specifications, cost-effectively.

From virtually every perspective, the tire recycling industry has made great strides during the past 30 years. By all indications, it is successfully meeting the demands of International and EU legislation and mandates in terms of treating waste in order to produce sustainable and performant, cost-effective, viable materials, and then using the materials in a broad range of products and applications. Further, today, those materials are being produced in an environmentally sound environment and are effectively used to substitute virgin materials for increasingly diverse markets—without substituting quality. In many instances, the characteristics and properties of these materials contribute to improved performance and endurance, often more cost-effectively than those produced with virgin resources. Many have taken their place in the mainstream—even though they are still considered waste. Even recycling residues are treated and used in innovative ways as the fluff and steel.

During the last two decades—1999 through 2019—tire arisings in the 27 EU Member States (and Norway) totaled somewhat more that 10,000,000 tons of materially recycled outputs in an array of materials, products, and applications as discussed herein.

Efficient, effective material recycling produces vast savings in terms of material and energy. Energy in different forms is a crucial part of each phase of a product life cycle—from the production of raw materials, to manufacturing, distribution, and use, through collection during the waste phase, and, finally, for recycling and delivery of sustainable products to market.

In addition to providing clean, cost-effective, environmentally sound, and durable materials for almost 100 industry sectors, the recycling of postconsumer tires contributes to the EU goal of a recycling society, a circular economy with reduced reliance on energy inputs and virgin resources.

Each ton of tires materially recycled equals a savings of an equivalent of +22.3 barrels of petroleum, in energy costs for production alone. While the manufacture of 1 ton of recycled rubber requires only 0.45 barrels or 0.52 toe. The difference in energy use between manufacturing one ton of new tire rubber and recycling one ton of tire rubber is equivalent to 20.86 barrels of petroleum.

In terms of ***energy*** alone, the savings that accrue as a result of the material recycling of +10,000,000 tons of tires, rather than manufacturing the same amount of new tire rubber, or using tires for "energy," is equivalent to +205,000,000 barrels of petroleum. It is anticipated that tire recycling arisings and thus outputs will continue to increase in future.

References

[1] International Rubber Study Group (IRSG) Rubber industry Report, vol. 8, No. 10–12, April – June 2009.
[2] EC, Directive 2008/98/EC Revised Framework Directive on Waste, 2008.

Further reading

G.M.P. Abbot, The use of crumb rubber from end of life tyres in sport and play. Proceedings of the International Symposium on Recycling and Reuse of Used Tyres, Pub. Thomas Telford, 2001, pp. 203–211.
S. Amirkhanian, Utilization of tyres in civil engineering applications. Proceedings of the International Symposium on Recycling and Reuse of Waste Materials, Dundee, 2003, pp. 543–552.
Basel Convention, Technical Guidelines on Hazardous and Other Wastes: Identification and Management of Used Tyres, Basel Convention Series/SBC no: 99/008, Geneva, 1999.
K.J. Collins, A.C. Jensen, J.J. Mallinson, S.M. Mudge, A. Russel, I.P. Smith, Scrap tyres for marine construction: environmental impact, in: R.K. Dhir, M.C. Limbachiyya, K.A. Paine (Eds.), Recycling and Reuse of Used Tyres, Thomas Telford, London, 2001, pp. 149–162.
Conference on Soil Mechanics and Foundation Engineering, Vol. 3, pp. 1617–1620. Humphrey, D.N., Sandford, T.C., Cribbs, M.M., Gharegrat, H., and Manion, W.P., Tire Shreds as Light-weight Backfill for Retaining Walls - Phase I, A Study for the New England Transportation Consortium, Department of Civil Engineering, University of Maine, Orono, ME, 1992.
CWA, Post-consumer tyre materials and applications, CEN Workshop Agreement 14243, European Committee for Standardisation, 2002, internet site: <http://www.cen.eu>.
Deutsch Bank: European Rubber Report, 2000.
EC, Council directive 1999/31/EC of 26 April 199, Jr.9 on the landfill of waste. Official Journal of the European Communities L 182, 16/07/1999, 1999, 19 pp.
EC, Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles. Official Journal of the European Communities L269, 21/10/2000, 2000a, 9 pp.
EC, Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste. Official Journal of the European Communities L332, 28/12/2000, 2000b, 22 pp.
EC, Directive 2006/12/EC of the European Parliament and Council of 5 April 2006 on waste. Official Journal of the European Union, L 114, 27.4.2006, 2006, pp. 9–21.
EEC, Council directive 75/442/EEC of July 1975 on waste, OJ L 194, 25.7.1975, 1975, p. 39.
ERC, The "Recycling Coalition's" reaction to the Commission proposal for a directive on Waste (COM (2005)667 final): the need for a clear recycling definition in the waste directive. 2006, EurActiv, 27 April 2006, internet site: <http://www.euractiv.com>
ETRA, Update on the Recycling Society. ETRA NewsNotes, February 2007, 2007, <http://ww.etra-eu.org>.
European Commission Directorate General XII, The multiple pathway method—a guide to the application of the methodology developed through the research project: a combined methodology to evaluate recycling processes

based on Life Cycle Assessment (LCA) and Economic Valuation Analysis (EVA). Final Report, 1998.
European Topic Centre on Waste and Material Flows, Summary report of main findings, conclusions and recommendations for 2003. DG Environment, Denmark, 2004.
A.B. Hird, P.J. Griffiths and R.A. Smith, Tyre waste and resource management: a mass balance approach. Viridis Report VR2, 2002.
D.N. Humphrey and W.P. Manion, Properties of Tire Shreds for Light ~ veight Fill, Grouting, Soil. Improvement, Geosynthetics, ASCE, vol. 2, 1992, pp. 13441355.
D.N. Humphrey and T.C. Sandford, Tire Shreds as Lightweight Subgrade Fill and Retaining Wall Backfill, Proceedings of the Symposium on Recovery and Effective Reuse of Discarded Materials and By-Products for Construction of Highway Facilities, Federal Highway Administration, Washington, D.C., 1993, pp. 5–87 to 599.
D.N. Humphrey and W.L. Nickels, Jr., Tire Shreds as Subgrade Insulation and Lightweight Fill, 18th Annual Meeting of the Asphalt Recycling and Reclaiming Association, Asphalt Recycling and Reclaiming Association, Annapolis, MD, 1994, pp. 83–105.
D.N. Humphrey and W.L., Nickels, Jr., Effect of tire shreds as lightweight fill on pavement performance. Proceedings of the Fourteenth International, 1997.
D.N. Humphrey, T.C. Sandford, M.M. Cribbs, H. Gharegrat and W.P. Manion, Shear Strength and Compressibility of Tire Shreds for Use as Retaining Wall Backfill, Transportation Research Record No. 1422, Transportation Research Board, 1993, pp. 29–35.
D.N. Humphrey, N. Whetten, J. Weaver, K. Recker and T.A. Cosgrove, Tire shreds as lightweight fill for embankments and retaining walls. Proceedings of the Conference on Recycled Materials in Geotechnical Applications, ASCE, Coral Gables, Florida, USA, 1998, 15 pp.
K.N. Hylands, V. Shulman, Civil Engineering Applications of Tyres, Transport Research Laboratory, Crowthorne, 2003. Viridis Report VR5.
ISWA – Denmark, Recovery of Materials and Energy from Waste Tyres – Present situation and Future Trends, Ed.: Giorgio Bressi, April 1995.
T. Karpetsky, Resonance disintegration of pyrolytic char. Proceedings of the European Tyre Recycling Conference, Brussels, 2004.
S. Kerr, Artificial reefs in Australia: their construction, location and function. Bureau of Rural Resources Working Paper No. WP/8/92. Bureau of Rural Rescues, Canberra. 1992, 34pp.
K. Neocleous, K. Pilakoutas, H. Tlemat, Design issues of concrete reinforced with steel fibres recovered from tyres, ASCE J. Mater. Civ. Eng. 18 (5) (2006) 677–685.
K.A. Paine, R.C. Moroney and R.K. Dhir, Performance of concrete comprising shredded rubber tyres. Proceedings of the International Symposium on Recycling and Reuse of Waste Materials, Dundee, 2003, pp. 719–729.
K. Pilakoutas, K. Neocleous, H. Tlemat, Reuse of steel fibres as concrete reinforcement, Eng. Sustainability 157 (ES3), 2004, 131–138.
V. Shulman, Recycling: the future, Tire Technol. Int. (2000) 50–55. June.
V. Shulman, Tyre Recycling after 2000: Status and Options, The European Tyre Recycling Association (ETRA), Paris, France, 2000.
V. Shulman, Shulman – breaking the mould, Tire Technol. Int. (2001) 12–13. June.
V. Shulman, The status of post-consumer tyres in the European UnionVR3 Transport Research Laboratory Limited, Crowthorne, UK, 2002.

V.L. Shulman, Tyre Recycling. RAPRA Review Report, Vol. 15, No 7, Report 175, ISBN 978-1-85957-489-8, 2004.
V.L. Shulman, Introduction to Tyre Recycling: 2006. European Tyre Recycling Association, Paris. 2007a, Published on internet site: <http://www.etra.eu.org> (January 2007).
V.L. Shulman, Working Together Toawards a Recycling Society. 14th Annual European Conference on Tyre Recycling, Brussels Belgium, 2007b, 21–23 March 2007.
V.L. Shulman, Introduction to Tyre Recycling: 2010. European Tyre Recycling Association, Paris. 2010, Published on internet site: <http://www.etra.eu.org> (January 2010).
M. Talola, Tyre shred civil engineering applications in Finland. Proceedings of the 11th ETRA Conference, 2004.
The recycling industry in the European Union - Impediments and Prospects, 1996. European Joint Research Centre, Institute for Prospective Technological Studies Seville.
H. Tlemat, Steel Fibres from Waste Tyres to Concrete: Testing, Modelling and Design, PhD thesis, Dept. of Civil and Structural Engineering, The University of Sheffield, Sheffield UK, 2004.
H. Tlemat, K. Pilakoutas, K. Neocleous, Modelling of SFRC using inverse finite element analysis, Mater. Struct. (RILEM) J. 39 (2) (2006) 197–207.
H. Tlemat, K. Pilakoutas, K. Neocleous, Stress-strain characteristics of SFRC using recycled fibres, Mater. Struct. (RILEM) J. 39 (3) (2006) 333–345.
Toward Sustainability, A European Community Programme of Policy and Action in relation to the Environment and Sustainable Development, COM(92) 23 final – Vol. 11, Brussels, 27 March 1992.
UNCTAD, September 1996. Draft Statistical Review of International Trade in Tyre and Tyre-related Rubber Waste with Particular Emphasis on Trade between OECD and in non-OECD Countries and Trade among non-OECD countries 1990–1994, Commodities Division Environmental Issues Section.
Urbani, L. and D Andrea, A., 2004. Hot mix asphalt with rubber granulate as anti-vibrating layers in railways and roads. Proceedings of the 11th ETRA Conference.
UTWG, 2004. Sixth report of the used tyre working group. Published on internet site of Used Tyre Working Group: <http://www.tyredisposal.co.uk>, 2004.
D. Vogt, FEAD. The EC experience – tyre recycling: an environment policy issue. Proceedings of the First International Conference on Tyre Recycling, a publication funded under the EEP IV, January 1994. pp. 36–38.
H.R. Wallingford, Sustainable Re-Use pf Tyres in Port, Coastal and River Engineering: Guidance for Planning, Implementation and Maintenance. HR Wallingford, UK, 2004.

This page intentionally left blank

PART II

Toward a circular economy

This page intentionally left blank

5

The 4 Rs: reduce, reuse, recycle, and recover

Peter Taylor OBE

Industry Commentator and Secretary General of the UK Tyre Recovery Association, London, United Kingdom

5.1 Introduction

In most Western consumer societies notions of resource efficiency really took hold in the second half of the 20th century. This growing realization that the resources of our planet were actually finite and could not be plundered indefinitely was further underscored by rapidly growing populations in the world's developing nations who would also demand a share of its natural wealth and limited resources. In short, the accepted practice of "taking-making-wasting" was perceived as unsustainable and needed to be actively reined-in. Scientists, environmental pressure groups, and others all played their part in pressuring governments and regulators to engage much more directly with these issues in order to bring about the changes needed to constrain what was viewed as reckless consumerism. From these concerns emerged the concept of the so-called "Circular Economy," which governs much of our thinking today.

The idea of a circular economy is deceptively simple – it means to return to nature what comes from nature within the life cycle of a product (see Fig. 5.1).

5.1.1 The evolving scenario

In all of this, the countries of Western Europe mostly led the way with new notions of Producer Responsibility followed by the groundbreaking EU Landfill Directive. This Directive was intended to progressively reduce the amounts of wastes put to landfill and in the case of tires to virtually prohibit their disposal in this way altogether.

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00019-3
© 2021 Elsevier Inc. All rights reserved.

Figure 5.1 The circular economy diagram.

5.2 The European Union Landfill Directive

The EU Landfill Directive (sometimes known as the Waste Framework Directive) was a turning point for tire recycling. First, it determined that end-of-life tires (ELTs) were waste and secondly, it banned the disposal of all old tires to landfill no later than 2006 in all member states. It would be up to each to decide the means by which this should take place, but the underlying philosophy would be the concept of Producer Responsibility and what has become known as the "Waste Hierarchy."

5.2.1 The concept of "Producer Responsibility"

This seemingly simple concept comes with many complexities as well as problems of definition. Central to all of these is the question, who really is the producer?

A number of countries took the view that the "producer" was the manufacturer, importer, or other entity who first places the product onto the market. Others, not unreasonably, took a more expansive view deeming that all those in the recovery chain (i.e., manufacturers, retailers, consumers, and ultimately recyclers) were "producers" and adopted a policy of "shared of producer responsibility." However, these simple philosophical differences would ultimately lead to radically different approaches to market organization and to the development of national recycling infrastructures.

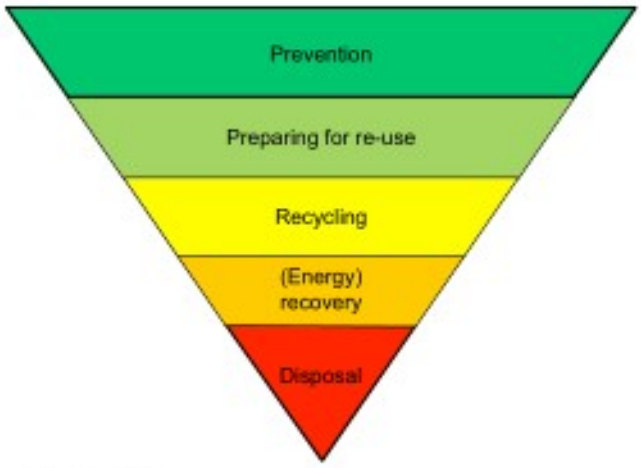


Figure 5.2 The waste hierarchy pyramid.

5.2.2 The waste hierarchy

The concept of the waste hierarchy is simply expressed as an upright or inverse pyramid of preferred outcomes (see Fig. 5.2). A reduction in the overall generation of waste should be our first priority followed wherever possible by reuse. Recycling and other forms of recovery are then our postconsumer options.

5.3 Producer responsibility and the circular economy

The notion of circularity in the management of our natural resources is seductive as it represents a clear step beyond "make-waste-dump" into a realm of renewal where the old can again be remanufactured or reprocessed into something new. However, this idea of a manufacturing closed loop does have some obvious limitations.

5.3.1 Tires and "Circularity"

Not all products readily lend themselves to straightforward renewal and tires are certainly a case in point. Our ambitions in this direction need to be set against what is possible in the context of current technologies and to some extent market demand. In other words, while our ultimate ambition may be fully circular there will remain many product areas where full circularity is unachievable for now, but which still lend themselves to other no less valuable "open loop" recycling options. This is summarized in Fig. 5.3.

Figure 5.3 Tire recovery circular economy.

5.3.2 The limits to recycling — can what goes in always come out?

The unquestioning espousal of the "circular economy" too often fails to understand its current limitations. Many waste streams of which tires are one do not currently lend themselves to wholly closed-loop forms of recycling even though they may represent a valuable intrinsic resource well capable of highly beneficial forms of revalorization. Of course, as product technologies improve it may in time be possible to achieve greater recycling circularity. Until and if this happens the focus must be on beneficial and appropriate forms of valorization actively supported by sound public policy and industry initiatives.

The many ingredients and components that go into making the modern-day tire are then subject to numerous processes and ultimately to vulcanization to provide strength and durability. In that sense they are akin to a "cake" so cannot be unbaked in any normal sense, but that is not to say that tire-derived materials (RTM) do not have many valuable residual uses.

5.4 Putting our old tires to good use

5.4.1 As a fuel source

Tires have a high calorific value not dissimilar to that of coal so are useful as a cofuel in kilns and furnaces. In cement kilns the use of tire-derived fuel contributes to a reduction in NOx emissions and embedded wire in the rubber can help improve cement quality.

5.4.2 As granulate

Granulation in particular is a common and productive form of tire recycling. Granulate is a widely used material in the construction of many types of sports and play surfaces as well as flooring trails and pathways while finer granulates or powders can be widely used in dozens of useful specialist and everyday products.

Granulate/bitumen mixes for road surfacing applications are in widespread use in a number of countries and represent a high-volume use for RTM.

Rubberized asphalt has some obvious advantages over more traditional bitumen mixes including:

1. Flexibility in preventing cracking especially where surfaces are subject to wide temperature variations
2. Noise reduction
3. Grip
4. Reusability and economy – old cover can be lifted, reheated, and relaid. A 1 km lane of highway can require up to 70,000 granulated passenger tires.

There are many other uses for ELT-derived tire shred, granulates, and powders as listed in Table 5.1

5.4.3 Pyrolysis

The use of more efficient and economic forms of continuous flow pyrolysis offers yet more beneficial outcomes for our ELTs. Tires subjected to pyrolysis give off gases, oils, carbon char, and steel, all of which are potentially marketable commodities.

5.4.4 Other technologies

There are a number of other potential useful technologies we should not ignore. Examples such as the use of cryogenics and microwave technology in size reduction already have their advocates as does the use of high-pressure water jetting, which can achieve the same end.

5.4.5 Retreading

Retreading is perhaps the most traditional form of "life" extension and as such is a valuable process. Although the retreading of passenger tires is no longer considered economically viable in most countries the retreading of truck/bus tires is commonplace; aircraft tires are also routinely retreaded. The process is technically precise and can extend the service of the original casing several times over.

Table 5.1 Environmentally and economically sound uses for granulate, shred, and powders.

Application	Quantity	Unit of application	Format
Backfill	80–100 car tires	1 m^3	Shred (compacted)
Lightweight fill	2700–3600/km m^2	Layer thickness ±1–6 m	Shred (compacted)
Tram rail beds	50,000 tires	1 km	Shred (compacted)
Equestrian track	15 tires	10 m^2 with 15 mm thick	Shred
Thermal insulation	300,000 tires	0.3 m thick × 10 m wide	Chip/shred
Drainage layer	300,000 tires	0.3 m thick × 10 m wide	Chip/shred
Road surface	70,000 tires	1 km 1 lane road	Granulate
Play surface (25 mil)	1400 tires	~500 m^2	Granulate
Sound barriers	20,000 tires	1 km × 3 m high	Granulate
Running tracks	2700 tires	400 × 7 m	Granulate
Infill for artificial turf	12,200 tires	Normal field	Granulate
Elastic layers	3 tires	1 × 1 × 0.03 m	Granulate
Mats or sheets	1 tire	1 × 1 × 0.01 m	Granulate
Solid wheels (carts)	1 ton of tires	±900 units	Granulate/powder
Train/rail insulation	6 tires per profile	12 cmW × 18 cmH × 120 cmL	Granulate/powder
Antistatic shoe soles	1 tire	6 shoe soles (adult)	Powder
Membrane	5 tires	100 × 200 × 2 cm	Powder
Pigments	112 tires	30–50 pigments	Powder (rcb)
Automotive parts	2 tires	57 different molded parts	Thermoplastic powder

5.4.6 Other uses for our old tires

Embankment stabilization, coastal and river defenses, and landfill engineering projects are yet more established uses for our postconsumer tires as are many smaller-scale artisanal reuses.

5.5 Putting reuse + recycling into perspective

This myriad of actual and potential uses nevertheless belies a central fact, which is that large markets demand volume solutions. What may be viable and even desirable in countries with relatively small annual arisings of ELTs may not address the challenges of bigger markets where annual arisings may be tens and hundreds of thousands of tons. For those big generators of old tires only big solutions will do. For now, these high tonnage uses must include the use of tires as a derived fuel, rubberized asphalt, and the granulate recovery stream, although pyrolysis as a fully commercialized process may soon also play its part.

5.5.1 Making recycling work

Progress as we know is the art of the possible and in dealing with the many obvious challenges of product recycling there are great distances still to travel. ELTs are no exception, although our particular waste stream has managed to account for virtually all of its arisings at least across the continent of Europe and in doing so has met the fundamental requirement of the EU Landfill Directive.

Likewise, beyond the confines of Europe too, strenuous efforts are being made to develop and introduce robust collection and recycling regimes appropriate to local circumstances.

Clearly, much still needs to be done to better valorize the resources locked into old tires. Simply espousing the virtues of the circular economy does little to deliver its hoped-for reality because this is still a work in progress, which will continue to require constructive engagement.

5.5.2 The role of the regulator

In what is a complex process the challenge is as much one for our regulators as it is for industry itself. For the most part our recyclers are nascent entrepreneurs whose first need is for a benign commercial environment in which to operate and grow. Repeatedly, governments are seen to promote regulation but default on enforcement thus allowing less responsible operators to destabilize the very markets our regulators wish to see develop and grow. Level playing fields are critical to successful market development, but all too often are undermined by an overreliance on regulation to the detriment of effective enforcement. Just as recycling itself comes at a cost so too does enforcement and a recognition of this fact is the often forgotten first essential of a functioning recovery market. Regulation itself has three prime functions: to protect the environment, to favor compliant operators, and to be proactive. Those are essential and symbiotic conditions for successful market development, which we all too often fail to meet.

5.5.3 . . . and of the industry

Because the tire industry itself is a global business it quite naturally seeks to identify global approaches to its perceived problems of which the recycling of its products is clearly one. The intrinsic dangers in such thinking are obvious in that what is viewed as a "problem" clouds the collective thinking thus

obscuring what is a actually an inherent opportunity. The *raison d'être* of the new tire manufacturer is just that, to produce new products rather than to overly focus on the development of opportunities and markets for recyclates. Inevitably, our new tire manufacturers are not always best placed to promote innovation in resource reuse, that may be a role often remains a role for others.

Inevitably the concept of producer responsibility can lead us to this misstep by simplistically placing the sole onus on a product's manufacturer. In reality, all of us in the recycling chain from manufacturer to distributor/retailer, to consumer, and to those who collect and process end-of-life products are producers too. We all share in the responsibilities, interest in responsible recycling and indeed may share too in the opportunities that still and do emerge. It is such opportunities that give rise to entrepreneurial interest, innovation, and investment in tire recycling of the kind we are witnessing right across our world and which we have a duty to nurture and support in the name of market development and resource efficiency.

PART III

Material treatments and technologies

This page intentionally left blank

6

Cryogenic tire recycling

Jim Anderson
RTI Cryogenics Inc., Cambridge, ON, Canada

6.1 A first step: understanding liquid nitrogen

Modern and efficient cryogenic tire recycling is a relatively new technology for the recycling of the rubber, steel, and fiber contained within end-of-life tires. There are many different ways of recycling of tires, with the most popular being the ambient process by way of numbers currently operating. The ambient process, which typically will use granulators or crackermills (or both) to break down the tire into its component parts is flexible in some ways in that it allows for the rubber to be reduced to an approximate desired size by the number of machines in the line. With cryogenic size reduction, there is a variety of sizes of rubber crumb produced all at one time, ranging in size from about 5 mm to as fine as 100 microns. The size range follows a normal curve, with the high point of the normal curve depending on a number of different variables but typically would be in the 20-mesh range, or 0.85 mm average size.

All functioning primary cryogenic systems that are commercially feasible use liquid nitrogen (LN2) as the main vehicle to cool the rubber. Earlier systems used a liquid bath of nitrogen, into which the rubber chunks from a shredder were fed. The shred was then transported through the LN2 bath by way of a stainless-steel conveyor belt. The modern-day primary cryogenic tire recycling system does not use a LN2 bath, but sprays the LN2 onto the chips in a freeze chamber in order to freeze the tire shred. Many more cryogenic systems exist as stand-alone fine mesh systems, using infeed material that has been broken down by ambient systems.

Liquid nitrogen is manufactured at a "liquid air" plant, where the atmospheric air we breathe is compressed by compressors, and as the air gets compressed, it is distilled into its components, which are nitrogen, oxygen, argon, and other minor gases. Nitrogen represents about 78% of air, oxygen about 20%, and argon a bit less than 1%. Other minor gases make up the balance of the composition of air.

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00007-7
© 2021 Elsevier Inc. All rights reserved.

In order to understand the operation of this newer technology, it is necessary to understand some physics.

Firstly, LN2 boils at approximately −196°C (−320 °F). That means that as long as the liquid in the nitrogen tank stays at that temperature, there is very little escape from a liquid to a gas. The modern nitrogen tank is well insulated, and typically vertical, in order to minimize the surface area of the liquid exposed to the atmosphere at the top of the tank. Depending on the pressure maintained in the storage tank, there is typically 3%–4% of the liquid that will escape as a gas over a 24-hour period. The proper pressure for consistent operation of a cryogenic tire recycling system is 4 Bar. Each storage tank, which is always located outside of a building, must have a relief valve on it, so that this nitrogen gas exhaust can escape into the atmosphere, from whence it came. Nitrogen will always gas off, no matter how much pressure it is maintained under. Therefore it is essential to always have a relief valve to allow for the gassing off of the nitrogen gas back into the atmosphere in this size of tank. LN2 stored in smaller vessels can be contained and sealed in a small insulated vessel, but they all have pressure relief valves. The bonds between the two nitrogen atoms in the liquid are so weak that eventual breaking and expansion of the electronic bond is inevitable.

Some have asked if other types of liquid gas would work, and there is not any other that works with the efficiency of LN2. Liquid oxygen won't work, as it is expensive, and when the sparks occur in the hammermill, there would be an almost instantaneous fire. Liquid carbon dioxide will not work, because the boiling point of liquid CO_2 is −78.5°C (−109 °F), which is just at the glass brittleness temperature of tire rubber, so there is no benefit to trying to get the tire chips brittle using liquid carbon dioxide, as they will not get below the glass brittleness temperature.

The other thing about LN2 storage is that the storage tank needs to be close to the release point of the liquid into the freeze chamber, and as has been found, the release point into the freeze chamber should not be too high above the exit point of the storage tank. If it is too high, what is known as two-phase flow can experienced, which means that the liquid turns partially into gas before it gets to the entry point into the freeze chamber. This problem can be corrected with a "subcooler," which will effectively use the coolness in the LN2 to cool the gas that has formed and turn it back into a liquid.

In the process of cryogenic tire processing, the physics of evaporation is used to cool the tire pieces by spraying the nitrogen in liquid form onto the shred, and when LN2 begins to

evaporate (at a temperature of −196°C), there is a heat transfer between the tire shred and the liquid, and the shred then freezes below its glass brittleness temperature as the LN2 evaporates and becomes nitrogen gas. The other issue to consider in the use of LN2 as a coolant is that it expands approximately 700 times in volume from a liquid to a gas. This massive expansion of the LN2 in volume has to be considered in the operation and design of the freezing system, and the extra "air" needs to be directed to its most efficient area of use.

6.2 The beginning of the process: the shredder

Tires are engineered and manufactured to stay together, not to come apart. As with almost all tire recycling processes, the first step is to break the highly engineered tire down into smaller pieces that equipment can handle more easily and more efficiently. This requires a very large shredder, with heavy shafts that can withstand the constant strain of cutting through bead wire that has been made from hardened and flexible steel. It has shown me that any shaft on a twin-shaft shredder that is less than 20 cm (8 inches) will not last any length of time without cracking. If a shaft cracks, it needs to be replaced, which means shutting down the system and replacing the shaft. This is very costly, and time consuming, as typically it will shut down the complete operation unless a stockpile of tire chips has been put in place.

The knives on these shredders must also be able to withstand the constant cutting required, and so are usually made from steel with hardened cutting edges. In most cases, the blades of a shredder when worn will be removed and replaced. If the blades are mounted directly on the shaft of the shredder, then they are taken off the shaft and sent to a machine shop that will do a "hard face" weld buildup on the cutting surface of the blade and then ground down to the proper spec for the machine the blades came from. The blades can be reinstalled back onto the shredder when the set of blades on the machine have worn down. This process can be repeated in most cases about 10 times, until the blades are completely worn through in the hub or the inner sides.

Another type of shredder uses individual cutting knives that are bolted onto a mandrel on the machine, and typically these can be turned so that different surfaces of the blade can be used. The blades cut against a fixed knife, which can be removed, hard-face welded, sharpened, and reinstalled when needed.

Certainly, in cryogenic grinding, it is not wise to let the "spiders" on the tire shred get beyond about 10–12 mm in length (1/2 inch). Spiders are the wire from both the beads and the steel belts that stick out from the shred after it has be shredded. If these are present in shred, excessive entanglement with other shred and inevitable plug-ups result resulting in system shutdowns. As everyone knows who has been involved with tire recycling down to the crumb stage, the margins are not great enough to be able to afford unnecessary shutdowns. The other issue with spiders is that if the shred is left for a period of time, these spiders begin to rust. Rust is not magnetic, and is very fragile, and so it cannot be removed in the process, not even by magnets.

Shredders need a screen or classifier in order to return larger pieces of tire shred back into the cutting chamber of the shredder. In the cryogenic system, the ideal size of shred leaving the shredder is about 5–8 cm in size (2–3 inches). This output from the shredder classifier is then transported via conveyor to a "hopper feeder," a large bin that can catch all of the shred and meter the shred to the next stage of the process in size reduction.

The next stage is the large granulator that can take this shred and cut it down in size to an average of 2 cm (less than 1 inch). During this process, a significant amount of steel is removed usually by an overbelt magnet that lifts the steel out of the stream of granulated tire and deposits it on a belt conveyor for transport to a steel recycling bin.

The hopper feeder feed rate is controlled by the control panel of the granulator, and will typically process about 4.5 metric tons per hour (5 tons/hour). The material from the granulator, which has its own dust collection system and its own fire suppression system, feeds the size -educed material to another hopper feeder, which is the start of the freezing process.

6.3 The freeze chamber

Once the tire has been reduced in size from a whole tire to about 2 cm in size (less than 1 inch), these tire pieces are fed into the variable speed hopper feeder for the freeze chamber; this feeder is controlled by the cryogenic systems control panel. The material is metered into the freeze chamber at one end of the rotating drum, through an air lock. The air lock keeps the nitrogen gas from escaping and allows for the control of many of the variables in order to get an efficient use of the LN2 that is used to freeze the tire pieces below the glass brittleness temperature. During the period in the freeze chamber, the tire material

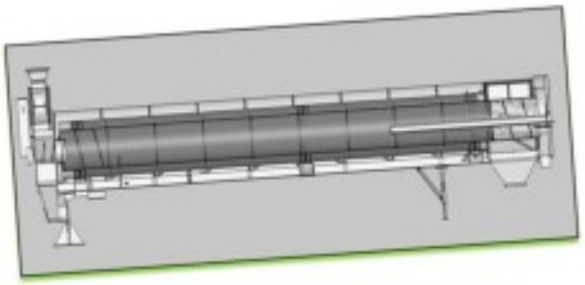


Figure 6.1 The freeze chamber.

gradually gets cooler, from the ambient temperature of the chips (shredded material) down to below −80°C (−112 °F). This temperature is the approximate glass brittleness temperature of rubber from tires, and when this tire material reaches this temperature, it becomes brittle (like glass) and will shatter into many, many pieces when it is hit in the hammermill. At the exit end of the freeze chamber is the nitrogen valve, which meters the liquid nitrogen into the freeze chamber through nozzles fitted to the freeze chamber end. Here the LN2 is sprayed onto the rubber chips so that the LN2 begins to "boil" off immediately. This action creates the effect of vaporization and draws any heat energy out of the rubber chips, rapidly reducing the temperature of the chip below the glass brittleness temperature. The rate of flow of the liquid nitrogen is controlled by the cryogenic control panel through the LN2 valve. This control panel has an HMI interface, with a number of screens that can control different functions. This is a graphic of a freeze chamber for the processing of tire chips (Fig. 6.1).

The freeze chamber is more than 16 m (53 feet) long, with well-insulated walls and ends, in order to be efficient and to keep the cold generated by the LN2 from escaping. Also, with this amount of cold contained in the system, normal steel construction would not withstand the cold and keep its shape. The chamber is constructed of a special steel alloy that resists this tendency to become misshapen, and to change to a "banana" shape. The chamber is driven by a variable speed motor, controlled through the operators control panel HMI, which is usually located very close to the chamber and the hammermills.

6.4 Hammermills

When the frozen rubber chips exit the freeze chamber, they are brittle and drop straight into one of two hammermills

located in a pit under the end of the freeze chamber. This pit is typically about 5 m^2 (approximately 15 feet square and about 3 m deep (10 ft). The mills are identical, and are each powered by a 150 kw (200 HP) DC motor. They are thus variable speed, which is controlled through the control panel for the system. In order to get an efficient and good break on the chips, the tip speed of the hammers in the mill is about 100 m/s (330 ft/s). This speed ensures a clean break of the rubber away from the steel and the fiber in the chip. When the chip is brittle as it is at this point in the process, the breakage happens with one hit. A lot of energy is imparted to the chip in order to break the bonds that exist, and so the rubber starts to warm. Since the rubber is only slightly below its glass brittleness temperature, the rubber rises above that temperature after it is hit once, and there is only time then for one hit. If there were many hits, the temperature of the rubber would rise significantly, and the rubber would not break into as many pieces, and it would also increase the risk of fire in the hammermill from the sparks that are generated by the hammers striking the steel in the tire chips.

Fig. 6.2 is a schematic of one of the hammermills used in the primary tire recycling system.

One of the issues with the hammermill running so fast is that the rotor with all the hammers on it needs to be balanced prior to operating. This can be accomplished by professionals specializing in that sort of thing. Another issue is the generation of sparks in the hammermill, with the steel of the hammers hitting the chips that have steel embedded in them. With these generated sparks, fire is always a concern. However, a built-in fire suppression system, using spark monitors and high-pressure water, keeps the system safe from fires in the hammermill, as well as further down the process in the dust collection system. The fire suppression system has its own control panel, and it is set up by the manufacturer, based on the air velocity to the dust collectors, as the dust collectors are connected to the underside of the hammermills.

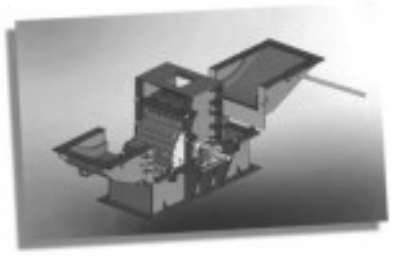


Figure 6.2 A hammermill opened.

One of the major wear points in the cryogenic primary system is in the ambient part of the system at the shredder and the granulator, and then again at the hammermills. Because of the abrasiveness of rubber and the steel, the internal parts of the hammermill wear rapidly, unless special steel is used. The hammers are made of a proprietary type of steel, as well as other parts of the inner hammermill. In fact, the hammermill is basically manufactured as a shell, with all the inner surfaces considered wear surfaces, and these are all replaceable. At least 90% of the total wear maintenance of the complete system is allocated to the shredder, granulator, and hammermills. Maintenance and visual checking on these three pieces of the system are performed every 24 hours, in order to maintain the equipment in efficient operating condition. The total capacity of each hammermill is 2250 kg/hour (5000 pounds/hour) of tire chip. The output from the bottom of the hammermill ranges in size from 5 to 0.6 mm and finer (4 mesh to −30 mesh).

Another determinant of particle size generated is the speed (amount of energy) used to hit the tire chip. The more energy (more speed) put into the hit, the more fracturing that occurs, and thus the size of the resultant particles of rubber generated. Also, the temperature of the tire chip is critical. If the tire chip is too warm, the property of rubber (elasticity) is more prevalent, and the chip will not fracture as much. If the tire chip is too cold, fracturing is plentiful, but then there is a waste of nitrogen, as there are diminishing returns from the extra cost of nitrogen and the resultant smaller sizes of rubber crumb generated.

Other factors that affect the particle size generated by the system are the speed of hammermill rotation, dwell time in the freeze chamber, air flow in the freeze chamber, exit temperature of the air from the freeze chamber, and the amount of LN2 used in freezing the tire chip. Successful operation of the system is dependent on balancing a number of factors in the process, in order to be able to process 4.5 metric tons per hour of tire chip (5.0 imperial tons per hour).

Another factor in the successful operation of the primary cryogenic unit is to be able to remove all of the bead wire and steel belts in the tire. Almost all tires manufactured today utilize steel belts in the process, in order to make them stronger and last longer. Also, in the manufacture of car and truck tires, a combination of many different fibers is used to help keep tires from breaking up while mounted on a vehicle. This material also has to be removed.

In order to remove all of this material, the rubber needs to be broken away from the steel and fiber, and the place where

that occurs is at the weakest point in the rubber, which is that point where a piece of fiber or steel penetrates the material. If the process is able to get the most amount of fracture in the rubber, then the result is the freeing of the steel and fiber from the rubber, and the objective of having clean rubber, with clean steel and fiber as a result, is achieved.

As mentioned, the hammermills are situated in a pit, under the exit end of the freeze chamber. This area also has a concrete block building built around the pit for many different reasons that relate to safety. When the frozen chips drop into the hammermill and get hit by the hammers, they make a very loud noise, way above the safe level for hearing. The second reason for this building is the removal of any gaseous nitrogen that might escape from the hammermills and dust collection system. A separate dust collection exhaust point is located at the bottom of the pit in order to collect any of this excess gaseous nitrogen. One of the characteristics of gaseous nitrogen is that it is heavier than air, so any that escapes from the hammermills will sink to the bottom of the pit, where it can be exhausted outside to the cyclone and filter-house part of the dust collection system.

The picture in Fig. 6.3 shows rubber from a primary cryogenic system, after one pass through the system of tire chips. The right side is a pile of 2 mm (10 mesh) material, and the pile on the left is 0.6 mm (−30 mesh) material. The white particles are the pieces of whitewall tires that are typical of North American tires. These tires are manufactured with a strip of white EPDM (synthetic rubber), and are usually mounted with the whitewall side on the inside of the tire.

Figure 6.3 Tire particles of two different sizes.

The shape of cryogenically ground rubber is different than ambient ground rubber as well. Due to the method of processing, the cryorubber is smooth sided, just like a piece of glass that has been broken. The ambient process rubber tends to be more "ripped" apart, with rough edges and surfaces and appears more spongy. This is beneficial for molding products and asphalt rubber, as there is more surface area on the ambient particle, but one disadvantage of this shape is that this surface keeps the ambient particle afloat in water. This is advantageous for the cryorubber when it is used in artificial turf, as during a heavy rain in this outdoor application, the cryorubber on the turf stays in place, whereas the ambient rubber will tend to float, and need to be raked back into the artificial grass on the field.

After all of the heavy lifting with the freezing and smashing apart, the system needs to separate the components of the tire, since they have all been broken apart, but everything is still intermingled.

Steel can be separated with magnets, and so once the complete mixture is loaded by augers from the underside of the hammermills to the "primary" screen, the separation process begins. This screen is slanted on an angle of about 15 degrees, and the material is dropped onto the top end of the vibrating screen, which is known as a double-deck screen. The rubber, being liberated at this point, mostly falls through the holes in the screen onto the lower deck, along with the steel that has also been liberated. With the fiber that is also in the mix, it tends to "coagulate" from the action of the screen, and stays on the top deck of the screen and floats off to the bottom. Here it is loaded onto a conveyor belt, and moved to the reclaim system. Since there is still some finer rubber in this mix as well as some entangled steel, the first part of the process is to shred this mixture with a small shredder to break the lumps of fiber into small parts, and liberate more steel and fiber, so that the fiber when it is moved to the scrap bin is virtually free of rubber and steel.

At the end of the second deck of this primary screener, there is a "rare earth" belt magnet that removes most of the steel in the rubber and steel stream, and moves that material onto a conveyor belt to be deposited in the scrap steel bin outside. A rare earth magnet is about five times more powerful than a regular magnet, and this is necessary to ensure a clean rubber stream at the end. At this stage the steel is virtually 100% clean of fiber and rubber, and is quite saleable to steel mills for recycling into their products. In order to prevent flashing of this steel once it is dropped into the steel mill furnace, some companies "briquette" the steel so that it is a more compact charge for the furnace.

The other component coming off the lower deck of the screen is the processed rubber, of all sizes. When you pick up a handful of this material, it feels cool and damp, and so the next step in the process is the dryer. Once the rubber hits the air after the hammermills, and begins to warm up, it will attract moisture from the air. This is one of the cryooperator's main physical tests that experience tells him whether there is too much or not enough LN2 being applied to the freeze chamber.

When the rubber is augered into the dryer, after the primary screen, it is usually damp, will stick together if squeezed, and also contains some of the tire dust that is part of the tire chip material that enters the freeze chamber. If scrap tires are being processed, it is impossible to process them without some dust and dirt, unless they are first washed. Washing of the tire chips means more equipment and more resources to clean them, and in the cryosystem that is not necessary, with the way the process is laid out.

In the drying process, a furnace is used to generate heat that is then blown into the dryer from one end. The dryer is a rotating kiln, and the interior is designed so that the rubber is lifted into this heated air stream so that the moisture is driven off, along with any dust and fiber particles. The heated air is then exhausted into the dust collection system. Once the rubber is dry, it is not sticky and flows like very dry sand.

After the dryer, there is another station for the removal of the final bits of steel particles and steel dust. This is a double-drum stainless steel, rare earth magnet, where the dry powder crumb rubber drops on one drum and then a second drum in order to remove this last remaining steel that might still be in the stream of rubber crumb. Most, if not all, processes require clean rubber that is free of steel, in order to manufacture their end product.

From this point, the rubber drops onto another screen separator that gathers all of the plus 5 mm (4 mesh) size material and sends it back to the freeze chamber for reprocessing or on to the fine mesh system (if that is included in the installation) for further size reduction. This amounts to about 5% of the tire rubber that needs to get further reduced in size in either the primary system or the fine mesh cryosystem. Also, this vibrating screen helps to scalp off any fiber that is coagulating on the screen, and takes it through the dust collection system to the cyclone and filter house so that it can be loaded and compressed into the fiber scrap bin outside of the building.

The final process in the primary cryogenic system is the screening and separation of the rubber crumb into different sizes. This is is done on a multideck vibrating screen. The top screen has large-size openings, and screens with progressively smaller openings are

installed at different points below the top screen, with the bottom of the screener, called the pan, receiving all of the finer materials. Typically, a vibrating screen can separate about 4 or 5 different sizes, depending on the market or use of the rubber being produced. If the material is going to continue on to the fine mesh system, this screener might only be a two-deck screener, with a screen for over 600 microns (30 mesh), allowing the minus 600 micron (30 mesh) size to fall through to the pan.

At this point in the process, the rubber is usually blown into bins for storage and bagging. If the rubber crumb is being sold at this point, then there will be 4 or 5 large bins that can hold a couple days of production, so that it can be bagged off into "super saks" or into smaller plastic bags. The super saks will hold up to 1000 kg (2200 lbs), and the plastic bags typically hold 25 kg (55 lbs).

Markets for the rubber crumb determine the next step in the process. If there are good markets with decent margins for the rubber crumb produced at this point, then most likely the rubber will be packaged and sold. The main large markets for cryocrumb at these sizes would be artificial turf, asphalt rubber (finer material), and compression molding. However, none of these markets are huge, so the next step in the process would be to further reduce the size of the rubber crumb by using a cryogenic fine mesh system for that purpose to supply other markets such as tire manufacturing (used as a filler in tire tread), addition to paint for a different effect for the paint, devulcanization of the rubber, and many other possible end uses. One of the end uses that I am familiar with is the blending of the finer rubber (less than 600 microns or finer than 30 mesh) with recycling or virgin plastic to make a thermoplastic elastomer (TPE). This new TPE is made from 100% recycled material, and with no additives to get the chemical bond; it is a 100% recycled material that can replace other virgin TPEs with certain properties, and also other plastics and provide superior properties.

6.5 Fine mesh cryogenic system

The fine mesh cryogenic system uses similar principles for its operation as does the primary system. The physics of LN2 are still the same, and the rubber that is introduced into the system still has a fracture point or glass brittleness temperature of about −80°C. The major difference at this point is that all of the steel and fiber has been removed from the rubber (more correctly the rubber has been fragmented to the point where all of the steel and fiber has been liberated).

The start of the system is again a hopper feeder that has a variable speed drive, that feeds the freeze chamber. One of the benefits of cryogenic rubber is that at this point it flows very much like dry sand, and so the material does not "bridge" in bins, hoppers, or feeders. This is one of the characteristics of cryogenic rubber that differs from ambient rubber in that it will flow easily without causing "bridging." The hopper feeder is controlled from the fine mesh control panel, which controls the complete system through its HMI screen. This control panel also controls the feed rate of LN2 to the freeze chamber, the rotational speed of the freeze chamber, the speed of the hammermill in the system, and the airflow of the dust collection system in the operation.

The material being fed into the fine mesh system should all be larger than 600 microns (30 mesh). If the material is smaller than this size, the mass of the particle is not sufficient to get a good impactful hit on it, and therefore there will not be as much fracturing necessary. One can always increase the speed of the hammermill to try to overcome this situation, but the faster the hammers are rotating in the mill, the more air that is being pushed ahead of the hammers and this tends to push the lighter (less mass) material out of the way, so there is not a direct hit, and therefore not a good fracture of the frozen material.

In the systems that I am familiar with, the finer material from the primary cryogenic system of less than 600 microns (30 mesh), is passed through directly to the end of the process and mixed with the grades from the fine mesh system. As mentioned, this crumb is too small to be further fractured to any degree, and only requires LN2 to freeze it, with very little yield of finer material.

The freeze chamber in the fine mesh system is different from the primary freeze chamber, in that the primary freeze chamber rotates like a cement kiln, whereas the fine mesh freeze chamber is stationary with a screw auger running its length. LN2 is injected into the freeze chamber through nozzles in the top of the chamber, and run approximately 50%–60% of the length of the chamber. Dwell time in the chamber is about 4 minutes. It is insulated to keep the cold inside, and the rubber crumb is cooled to about −100°C (−150°F). Also, on both ends of the freeze chamber, there are airlocks that keep the nitrogen gas inside the chamber, which also helps to keep the rubber cold.

The frozen rubber crumb then drops out of the freeze chamber, through the airlock, and into the hammermill. This is a different style of hammermill again than the one used in the primary

system. The primary mill is a very rugged and heavy-duty mill that is built to withstand the rigors of processing rubber with steel embedded in it. The fine mesh hammermill, however, is smaller and turns somewhat faster. Also, the sizing of the output from this mill can be adjusted by the size of the screen in the mill. There are consequences for that, however, in that the smaller the screen the slower the throughout, because there is more fragmentation required to get through the screen. Also, it takes more LN2, as in this mill, LN2 can be injected directly into the mill chamber in order to keep the rubber frozen as it will get hit more than once at this point, again depending on the output size desired. The extra LN2 aids in reducing the size of the rubber crumb and keeps it from heating up through the continual pounding that it takes in the mill. The setup of the mill directly affects the cost of processing this rubber, but if the mill is set to produce very fine material, such as 100 microns (150 mesh), there will be a high consumption of LN2, and a lot of power required to turn the mill. However, the selling price of finer powder is higher, and hopefully enough to offset the higher cost of processing to the fine powder.

From the bottom of the hammermill, the rubber passes through another air lock, before being transported to the dryer. As in the case of the primary screen, the rubber crumb will attract ambient moisture from the air, and that needs to be driven off by drying, so that a proper classification can be accomplished. It is also essential that the rubber be dry, as most if not all further use of the rubber crumb will require dry material, and the final cleaning of the rubber crumb requires dry material.

Drying rubber crumb of the finer size can be a very tricky proposition. It is so light that if air is passed too rapidly through it, the finer rubber particles get airborne, and would go out in the dust collector vacuum to the cyclone and filter house. Here, the rubber is usually warmed on a vibrating pan that has heat applied to the underside, which allows the moisture in the crumb to be driven off, and the rubber left on the vibrating pan to pass to the next step in the process, which is the final cleaning of the product and then classification into different sizes.

Although the primary cryogenic system removed 99.9% of the steel from the rubber crumb, a double-drum rare earth magnet is used to remove any last bit of steel that might be liberated by the fine mesh hammermill.

The final step before packaging or storage is the classification of the fine mesh product. The set up here will depend on the sizes of rubber crumb being needed for the customers of the operation, or the further value-added processing that will take place using this rubber crumb as a raw material.

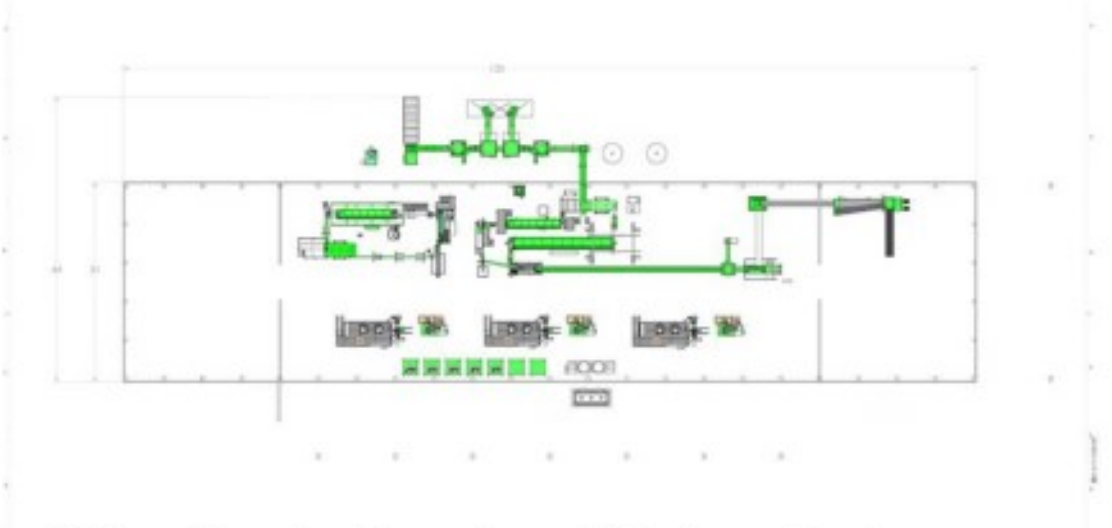


Figure 6.4 The general layout of a typical cryogenic system with both primary and fine mesh systems.

If the final size of material is in the 200–600 microns size (30 mesh to 70 mesh) range, then a simple vibrating screen will perform the job satisfactorily. Usually these are round rotating screens, and they can have multiple decks, depending on the volume of rubber crumb being classified. If the final size required is finer than 200 microns (finer than 70 mesh), then a different type of screening unit is required. Because the rubber crumb at this size is really a powder, it does not have much mass and floats in air very easily. The type of screener necessary for the classification of rubber powder finer than this uses vacuum and brushes to suck the rubber through the different screen sizes. When the final size that is desired for the market is very fine such as 75 microns (200 mesh), it is very difficult to handle and move. The general layout of a typical cryogenic system with both primary and fine mesh systems is given in Fig. 6.4.

6.6 What to do with cryorubber crumbs

As was seen earlier in this chapter, the morphology of cryo-crumb is different than ambient crumb. In some markets, whichever crumb that is available will work without any issues. In other markets, the type and size of crumb is a critical factor in the end results of the product that is being manufactured. As

an example, 2–1.3 mm (10–15 mesh) ambient crumb works well in asphalt rubber, whereas cryocrumb of the same size does not get the same bonding as the ambient crumb. However, if one uses 600 micron cryocrumb, the bonding is as good as the larger ambient crumb, and the resilience of the asphalt mixture is better than ambient crumb. The advantage of the fine cryocrumb is that it can be produced in one pass through the system, whereas the ambient crumb needs to go through a few steps to reach the size required for the end market.

In tire recycling, as with many other recycling industries, there is a problem in finding markets for the end product. In North America, it can be seen that the most successful operations over the long term (over 10 years) have been those recyclers that have incorporated their own value-added processing to their complete operation. Many of the mat manufacturers have their own front-end tire recycling operations to feed the desired size and quality of rubber crumb to their value-added production line. The fine mesh cryosystem added to the primary cryosystem is a value-added technology that enhances the value of the rubber crumb initially produced. This finer material has many different applications such as being used as a filler in the production of new tires. Also, devulcanization has been a growing technology for a number of years now, and in order to get a marketable product, the crumb needs to be fine in order to expose the most surface area to the devulcanization process. This is where the cryosystem has a distinct advantage over the ambient system, both because of throughput capabilities and the manufacturing cost of reaching the desired size.

Another end use for the cryogenically ground rubber is in blending the rubber with recycled scrap plastic to produce a TPE. This is a unique process, now patented and patent pending, that produces a 100% recycled product, with the characteristics of a virgin TPE/thermoplastic polyolefin but is manufactured without using additives such as catalysts or compatibilizers. This process, besides using recycled cryogenic tire rubber, also uses a significant amount of scrap plastic. The specific type of plastic used is polypropylene, high-density polyethylene or low-density polyethylene. The technical values can be altered somewhat, depending on the type of plastic used in the process and the process parameters that are used during the manufacturing process.

Typical applications for this product are in auto parts (e.g., sun visors, door panels, wheel wells, grills, underhood plastics), for artificial lumber, and many other consumer and industrial

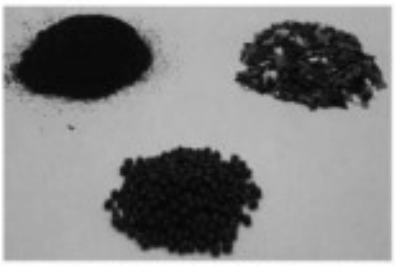


Figure 6.5 The ingredients that make up the input in the blending of rubber and plastic and then the pellets that are produced from that blending process.

Figure 6.6 A car grill that can be chromed or painted.

applications. This material can also be painted, chromed, or produced in a variety of colors other than white.

Fig. 6.5 shows the ingredients that make up the input in the blending of rubber and plastic and then the pellets that are produced from that blending process.

A typical product made from cryogenically ground rubber and scrap plastic is shown in Fig. 6.6.

7

Regeneration and devulcanization

7.1

Regeneration and devulcanization

Wilma Dierkes[1] **and Sitisaiyidah Saiwari**[2]

[1]*Chairs of Sustainable Elastomer Systems (SES) and Elastomer Technology and Engineering (ETE), Department of Mechanics of Solids, Surfaces and Systems (MS3), Faculty of Engineering Technology, University of Twente, Enschede, The Netherlands*
[2]*Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani, Thailand*

7.1.1 Introduction

Material recycling of tire rubber is a well-known technology. Devulcanization is a rather new technology; most conventional technologies are based on grinding and regeneration. However, granulates and powders as well as regenerates face limitations in their application in terms of quality and quantity. The main reasons are:

1. Difference in modulus between matrix and (non-replasticized) recycled rubber particles results in stress concentrations at the interface between new and recycled rubber. As this interface is the weakest spot in such a blend, it is prone to early failure.
2. Breakdown of the polymer network during the regeneration process, which is not selective concerning the type of bonds to be broken, and shorter polymer chains imply lower strength properties.
3. Recombination of chain fragments, which results in uncontrolled network formation and thus a lower degree of devulcanization and reduced properties.

Devulcanization technologies are focused on shifting the balance of crosslink scission to polymer breakdown to the former process, implying that only sulfur-cured elastomers

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00006-5
© 2021 Elsevier Inc. All rights reserved.

can be devulcanized. As this is the case for tire rubber, devulcanization is a process that can be further developed for this material.

In this chapter, the following terms are used for the different types of recycled rubber:

1. Devulcanizate: The main breakdown mechanism is crosslink scission.
2. Regenerate: The main mechanism is random scission with a high percentage of polymer breakdown.
3. Replasticized rubber: The breakdown mechanism is not known; it comprises devulcanization as well as regeneration.

7.1.2 Analysis of the devulcanization mechanism

Replasticization of rubber granules occurs on different levels, on a molecular as well as macroscopic scale:

1. Molecular scale: Distinction between polymer and crosslink scission.
2. Macroscopic scale: Successive removal of devulcanized outer layers of the rubber granules versus homogenous devulcanization within the whole particle.

7.1.2.1 Selective crosslink scission versus random network breakdown

Whenever polymer chains are broken in the regeneration process, a decrease in mechanical properties results. As this is undesirable, a method to analyze the breakdown mechanism is needed. An estimation of the degree of crosslink to random scission is possible using the Horikx–Verbruggen analysis. This method is based on the theory of Horikx [1] on network degradation via two different routes:

1. Selective scission of sulfur crosslinks
2. Random network scission

Horikx based his work on the network theories of Charlesby [2,3]. With a few adjustments, this approach can be applied to devulcanization of sulfur-cured elastomer networks, as described by Verbruggen [4].

In this approach, the soluble fraction of the replasticized rubber – the sol content – is related to the decrease in crosslink density. Horikx derived a theoretical relationship between the soluble fraction generated after degradation of a polymer network and the relative decrease in crosslink density, as a result of either

main-chain scission or crosslink breakage. This treatment of polymer degradation can equally well be applied to rubber regeneration, in which a mix of main-chain scission and crosslink breakage also takes place. When main-chain scission takes place, the relative decrease in crosslink density is given by [5]:

$$1-\frac{\nu_f}{\nu_i}=1-\left[\frac{\left(1-s_f^{1/2}\right)^2}{\left(1-s_i^{1/2}\right)^2}\right] \tag{7.1.1}$$

where s_i is the soluble fraction of the rubber network before degradation or regeneration, s_f is the soluble fraction of the regenerated vulcanizate, ν_i is the crosslink density of the network prior to treatment, and ν_f is the crosslink density of the regenerated vulcanizate. For pure crosslink scission, the soluble fraction is related to the relative decrease in crosslink density by:

$$1-\frac{\nu_f}{\nu_i}=1-\left[\frac{\gamma_f\left(1-s_f^{1/2}\right)^2}{\gamma_i\left(1-s_i^{1/2}\right)^2}\right] \tag{7.1.2}$$

where the parameters γ_f and γ_i are the average number of crosslinks per chain in the insoluble network after and before regeneration, respectively. The values for γ_f and γ_i are determined as described by Verbruggen [6]. Fig. 7.1.1 gives a graphical representation of Eqs. (7.1.1) and (7.1.2). The curves in the figure correspond to the situations when the network is randomly broken (solid curve) and when only crosslinks are broken (dashed curve). In the case of crosslink scission only, almost no sol is generated until most of the crosslinks are broken; only then the long chains can be removed from the network. In the case of

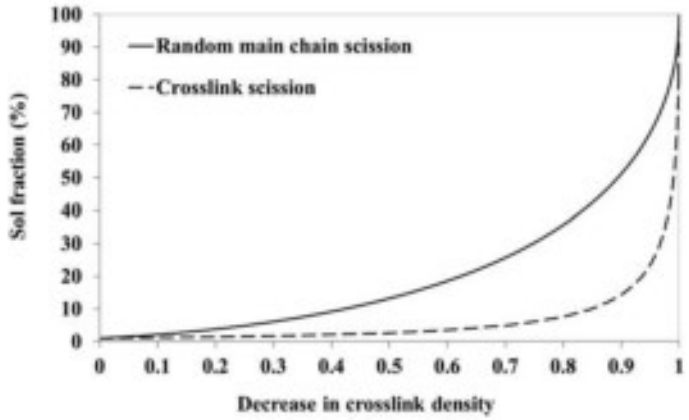


Figure 7.1.1 Horikx–Verbruggen graph to analyze the replasticizing process and determine the degree of crosslink versus random scission. Figure reproduced with permission of Kautschuk Gummi Kunststoffe.

main-chain scission, sol is produced at a much earlier stage, because random scission of the polymers in the network results in small loose network fragments, which can easily be removed [5]. When interpreting these graphs, it has to be taken into consideration that this method is based on a few assumptions and does not give exact percentages. It is a valid tool to show trends, but not precise enough to calculate percentages.

The soluble (sol) fraction of the replasticized materials as shown in the Horikx–Verbruggen plots are measured by Soxhlet extraction for 48 h in acetone to remove polar components followed by an extraction for 72 h in tetrahydrofurane to remove apolar parts. This fraction contains the soluble polymer released from the network by the replasticization process. The samples were dried under vacuum at 40°C. A correction for the oil contained in the original rubber has to be made. The gel fraction is calculated by:

$$\text{Sol fraction} = \frac{\text{weight of rubber dissolved}}{\text{weight of polymer in the compound}} \tag{7.1.3}$$

The crosslink density is in general determined by swelling in toluene for 72 h at room temperature. The weight of the swollen (de)vulcanizates was measured after removal of surface liquid with absorption paper. The crosslink density is calculated according to the Flory–Rehner equation [7], Eqs. (7.1.4) and (7.1.5) [5]:

$$\upsilon_e = \frac{V_r + \chi V_r^2 + \ln(1 - V_r)}{V_s\left(0.5V_r - V_r^{\frac{1}{3}}\right)} \tag{7.1.4}$$

with

$$V_r = \frac{m_r}{m_r + m_r\left(\rho_r/\rho_s\right)} \tag{7.1.5}$$

where υ_e = crosslink density per unit volume, V_r = polymer volume fraction of the swollen sample, V_s = solvent molar volume, m_r = mass of the rubber network, m_s = weight of solvent in the sample at equilibrium swelling, ρ_r = density of the rubber, ρ_s = density of the solvent, and χ = Flory–Huggins polymer–solvent interaction parameter.

This calculated crosslink density is based on the volume of gel in the rubber network after extraction. However, in order to compare these data with the Horikx theory, it has to be realized that the latter defines the crosslink density after devulcanization with the sol fraction still present. During the swelling test, this sol fraction is also extracted and thus needs to be included again in the calculation of the real crosslink density υ_{real} remaining after devulcanization but before extraction. Consequently, in order to obtain

the actual remaining crosslink density of the devulcanizate, the volume of total rubber must be taken into account. Correction for this real crosslink density is made according to [5]:

$$\upsilon_{\text{real}} = \frac{\text{Number of crosslinks}}{\text{Volume of total rubber}} = \upsilon_e \times (1 - \text{sol fraction}) \quad (7.1.6)$$

where υ_{real} = the final corrected crosslink density for the replasticized rubber.

The Flory–Rehner equation is strictly spoken only valid for nonfilled systems. Therefore the Kraus [8] correction for filled compounds is used to give the correct values of the different crosslink densities. In its simplified form, the Kraus correction is given by [9]:

$$\nu_{\text{actual}} = \frac{\nu_{\text{apparent}}}{1 + K + \Phi} \quad (7.1.7)$$

with

$$\Phi = \frac{\text{Weight fraction of fillers} \times \text{density of compound} \times W_b}{\text{Density of fillers} \times W_a} \quad (7.1.8)$$

where ν_{apparent} = measured chemical crosslink density, ν_{actual} = actual chemical crosslink density, K = constant for a given filler, Φ = calculated volume fraction of filler in the specimen, W_b = weight of the specimen before extraction, and W_a = weight of the specimen after extraction.

7.1.2.2 Homogeneity of network breakdown throughout the particles

Homogeneous breakdown of the polymer network results in a successive decrease of crosslink density throughout the particle. This will in first instance result in gel with a reduced crosslink density, but still all polymer chains attached to the network and no soluble part: the horizontal part of the crosslink scission line in Fig. 7.1.1. When the crosslink density further decreases, polymer chains are released from the network with a steep increase in sol content: the vertical part in Fig. 7.1.1. When the network is broken down randomly, sol is generated at an earlier stage, leading to the upper line. These two lines limit the generation of soluble network fragments in one case and polymer chains in the other. However, devulcanization does not occur in all cases according to this mechanism. For some polymers such as butyl rubber (IIR), an overproportioned amount of sol is generated in the early stages of network breakdown. In this case, the data points will be situated far above

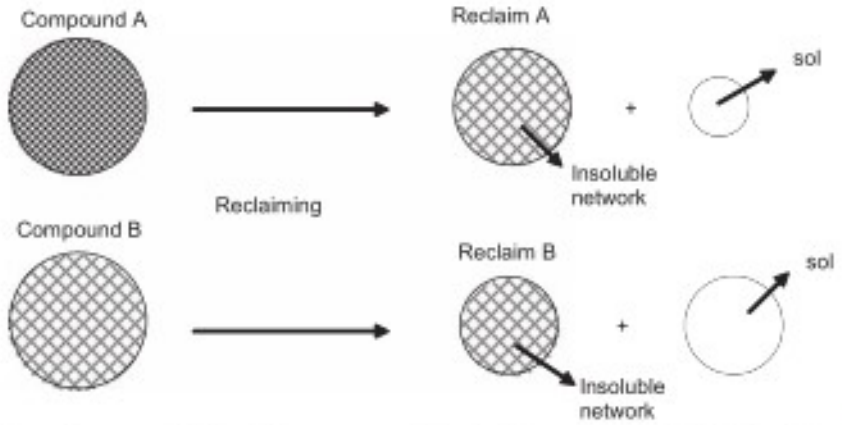


Figure 7.1.2 Schematic representation of homogeneous (top) and inhomogeneous (bottom) breakdown [10].
Figure reproduced with permission of Rubber Chemistry and Technology.

the random scission line. Fig. 7.1.2 shows the two ways of breakdown: In the upper schematic, the polymer network is homogeneously broken throughout the whole particle, resulting in a gel particle with a lower crosslink density over the whole diameter. In the lower case, a gradient in crosslink density is generated, leading to an onion-peeling effect: a lot of sol is generated, while the core of the particle still has a high crosslink density.

Another test method to indicate which type of network breakdown is occurring is the white rubber test (WRA): The replasticized material is blended with a white rubber compound at a concentration of 5 wt.%, and the number and size of remaining particles as well as the shade of gray give an indication to what extent the network within the particles is broken. If the particle size is reduced in parallel with generation of sol content but without significant reduction in crosslink density, an onion-peeling mechanism is predominant.

Fig. 7.1.3 illustrates the two extreme cases of none and complete breakdown of the network of the particles in the upper row, while the bottom row illustrates samples with a different degree of polymer breakdown.

The upper row shows reference samples without, with 10 wt.% ground rubber, and with 5 wt.% completely disintegrated replasticized rubber. The difference in gray-shade as well as size and number of particles is clearly distinguishable. In the bottom row, different samples with a low number of remaining large particles, with a higher number of large particles, and with only small particles and a darker shade of gray due to a more complete network breakdown are shown from left to right.

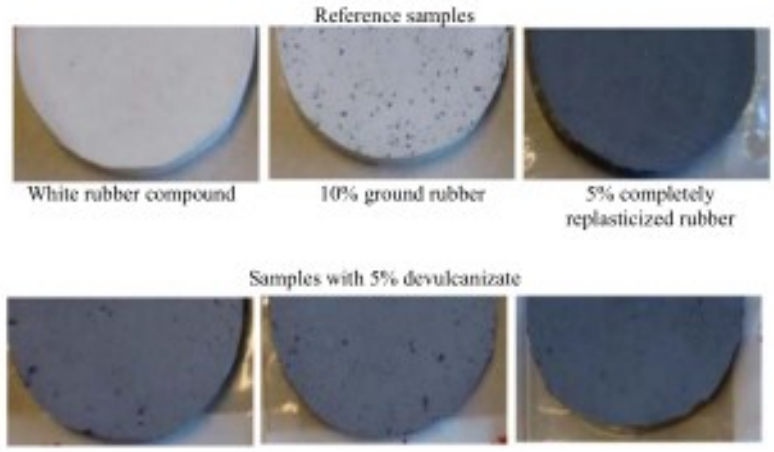


Figure 7.1.3 Samples of the white rubber test.

Table 7.1.1 Energies of the different types of bonds in a sulfur-cured polymer network [11].

	Bonding energy [kJ/mol]
R_3C-CR_3	370
$R_3C-S-CR_3$	310
$R_3C-S-S-CR_3$	270

7.1.3 Devulcanization versus regeneration

Devulcanization in the strict sense of the word is the process of selectively breaking sulfur bonds. Within a sulfur-crosslinked elastomer network, different types of bonds are present as shown in Table 7.1.1.

This difference in bond energy allows some selectivity in breaking of the polymer network. However, chemically attacking the sulfur bonds will have a much higher selectivity and is therefore the method of choice to achieve devulcanization. These chemical reactions require mechanical blending of the rubber with the devulcanization aid and a certain temperature level, but this will lead to mechanical and thermal breakdown of the polymer network as well. The challenge is to shift the balance of crosslink scission and polymer breaking toward the former one.

7.1.3.1 Devulcanization mechanisms

Polymer scission reactions are basically degradation reactions. Fig. 7.1.4 is a schematic depiction of the degradation of

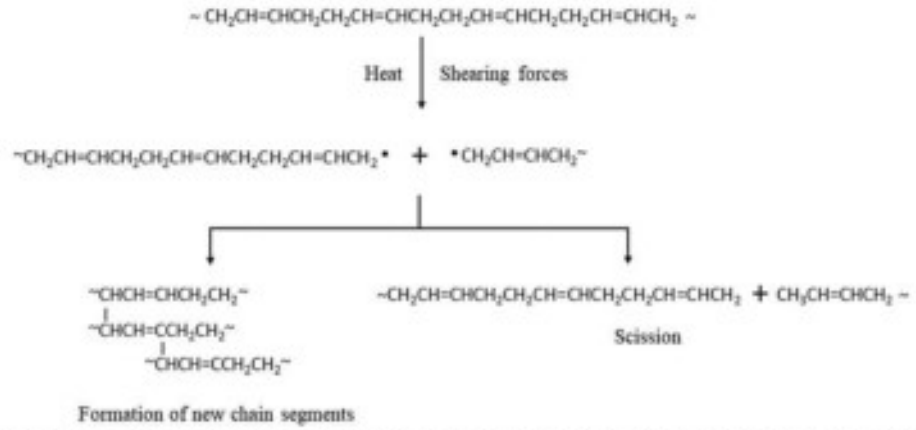


Figure 7.1.4 Simplified reaction scheme proposed for the degradation of polybutadiene and butadiene based polymers.

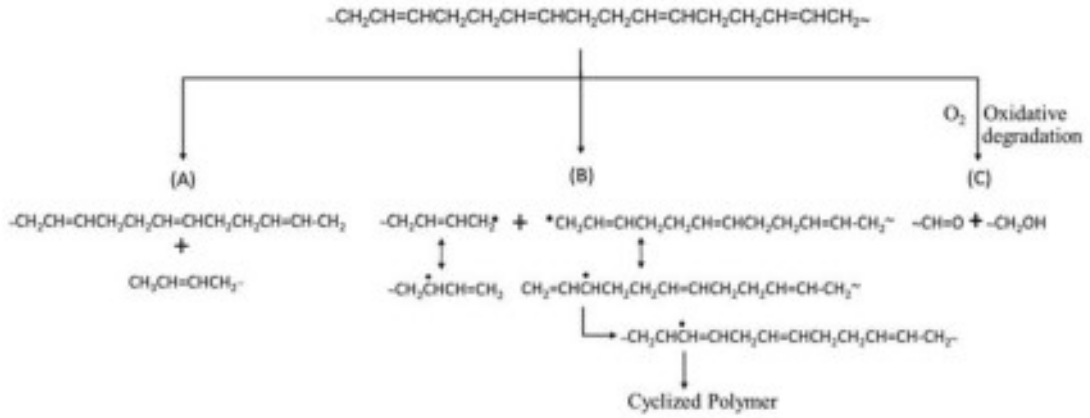


Figure 7.1.5 Polymer scission (A), formation of active bond fragments (B), and oxidative degradation (C) in the specific degradation mechanism of polymers with a butadiene structure.

polybutadiene and butadiene based polymers. Basically, two reactions can occur during degradation of polybutadiene: chain scission and formation of active chain segments. Chain scission occurs when breaking of the C–C bonds (carbon–carbon bonds) in the polymer chains is accompanied by hydrogen transfer [12], and results in polymers with a lower molecular weight. Another reaction, the formation of radically active chain fragments, apparently takes place from three possible reactions as shown in Figs. 7.1.5 and 7.1.6. Reaction (A) in Fig. 7.1.5 is known as a hydrogen transfer reaction. It is initiated by breaking of the C–C bonds in the polymer chains due to physical forces: heat, light, and

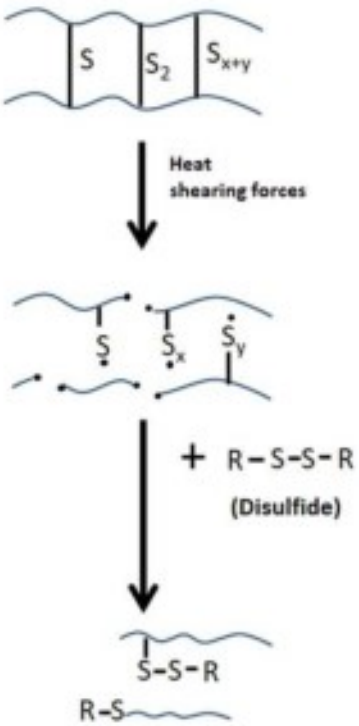


Figure 7.1.6 Simplified reaction scheme proposed for rubber devulcanization using additives with a disulfide moiety.

mechanical forces. It is accompanied by hydrogen transfer which also results in polymer chain scission. However, re-combination of unstable radicals to polymers could possibly take place when scission of C–C bonds in the chain is not accompanied by a hydrogen transfer [12]. It is reported that for degradation in air atmosphere, with the main active component oxygen, hydrogen transfer is less. Therefore the active radicals tend to recombine to a new polymer [5].

Reaction (B) in Fig. 7.1.5 is the transformation reaction. It is associated with thermal isomerization: cis-trans isomerization, cyclization, and volatilization of small fragments [13–15]. These chain rearrangements are enhanced by an increasing temperature and occur with the initial decomposition step of styrene-butadiene rubber (SBR) [5].

Reaction (C) in Fig. 7.1.5 involves generation of active groups derived from the presence of oxygen. The initial predominant attack of aerial oxygen (O_2) takes place at the double bonds. It continues with the generation of hydroperoxide radicals, which then

decompose to give carbonyl (>C=O) functionalities [16]. These reactions typically take place at high temperatures [5]. Accordingly, when carbonyl functionalities are generated, the possibility of creating a rubber soluble fraction is less: the bond energy of C=O (799 kJ/mol) is considerably higher than that of C–C (346 kJ/mol) or carbon hydrogen bonds, C–H (411 kJ/mol) [17].

All three reactions as sketched in Fig. 7.1.5(A)–(C) can conjointly occur in the SBR devulcanization process, particularly at high temperatures. These result in reduction of the sol fraction and increase of the crosslink density above the threshold temperatures as stated above [5].

The degradation of rubber results in radical fragments, thus scavenging of these radicals is of crucial importance to suppress radical chain scission and shift the balance to crosslink scission. Various chemicals can act as radical stabilizing agents; examples are thiols, phenolic compounds and disulfides, which are the most common ones [18–22]. A mechanism that is frequently proposed for the reaction of radical scavengers in rubber replasticization is opening of crosslinks or scission of polymer chains by heat and shearing forces, and the reaction of fragments with disulfide based radicals, which prevent recombination. Okamato [23] suggested that when a vulcanized rubber compound is replasticized by using mechanical shear forces (i.e., milling), free radicals are produced that can further cause the formation of main chain radicals. Chemicals like thiols and disulfides react with these radicals, thus preventing their attack of the polymer chains and recombination [5].

Disulfides are well-known devulcanization aids especially for natural rubber (NR). These aids form radicals with increasing temperature. The radicals then combine with the polymer main chain radicals preventing their recombination. Studies of mechanochemical recycling processes of NR and other tire rubbers indicated that disulfides play an important role in the processes [24,25]. As a result, the mechanical properties (i.e., tensile strength, modulus, and tear strength) of revulcanized disulfide-containing rubber were higher than those of revulcanized rubber obtained without devulcanization aid.

A reaction scheme proposed for the devulcanization of rubber with disulfides based chemicals is shown in Fig. 7.1.6. A mechanism that is frequently proposed for the reaction of radical scavenger devulcanization aids like disulfides for the reaction with sulfur vulcanizates is the opening of crosslinks or the scission of polymer chains by heat and shearing forces, and the reaction of fragments with disulfide based radicals, which prevent recombination.

7.1.3.2 Devulcanization aids and processes

7.1.3.2.1 Chemical devulcanization

Many chemical compounds were considered and tested concerning their effectivity as devulcanization aids. The most common ones are amines and disulfides. In terms of amines, stronger nucleophiles are expected to be better devulcanization aids. Differences in amines that may influence the reclamation reaction are:

1. type of amines (primary, secondary or tertiary)
2. steric hindrance
3. basicity
4. presence of an α- hydrogen

Within the second category, diaryldisulfides (e.g., diphenydisulfide) are often applied [26]. A comparative study on the devulcanization efficiency of three different disulfides, diphenyldisulfide (DPDS), dibutyldisulfide (DBDS), and di(2-aminophenyl)disulfide [5], lead to the conclusion that DPDS and DBDS are even efficient, see Fig. 7.1.7. However, the choice of a devulcanization aid also includes the processing behavior; therefore DPDS is in general chosen. Besides odor, costs and availability have to be considered when choosing a devulcanization aid.

In this study [27], the presence of a stabilizer was also evaluated. A hindered phenolic stabilizer, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Ir1076), was used at a concentration of

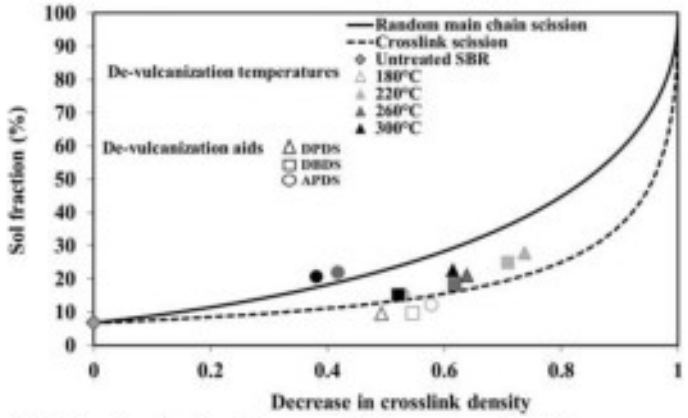


Figure 7.1.7 Devulcanization efficiency of different types of disulfides [diphenyldisulfide, dibutyldisulfide, and di(2-aminophenyl)disulfide]. Figure reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186–232.

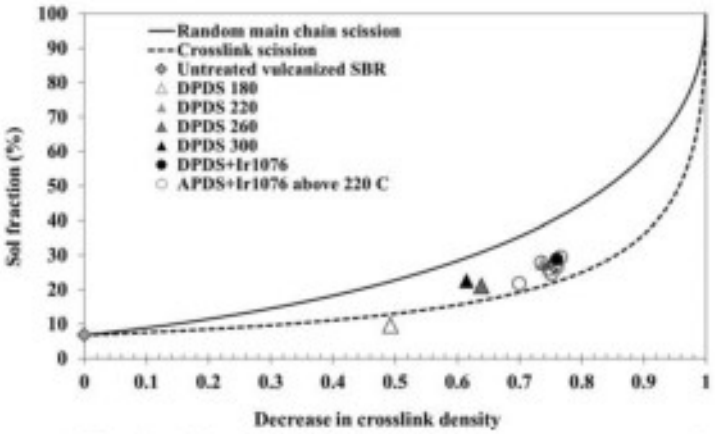


Figure 7.1.8 Devulcanization efficiency depending on temperature, presence of stabilizer (Ir1076), and devulcanization aid. Figure reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186–232.)

1 wt.% in a SBR compound. DPDS was used as devulcanization aid. Fig. 7.1.8 shows that the devulcanization efficiency does not significantly change with temperature; even at high temperatures, when SBR otherwise tends to recombine, network recombination does not occur. Stabilizers thus allow to increase the devulcanization temperature, accelerating the reaction. It was also tested, if the stabilizer supports the devulcanization reaction. The results shown in Fig. 7.1.9 indicate that this hindered phenol does not have any effect on the network breakdown.

Table 7.1.2 gives an overview of different additives described as devulcanization aids.

7.1.3.2.2 Physical devulcanization

Supercritical gas like spCO_2 [16,50,51] is used as a medium to swell a devulcanization aid into the rubber particles. It is also used as the sole devulcanization additive [52]. Besides, the supercritical gas also results in mechanical breakdown of the rubber particles when the material exits the extruder by the sudden expansion due to the pressure loss.

Another approach to breakdown of crosslinked rubber is ultrasonic treatment [53]. This type of radiation is claimed to break by preference the sulfur bonds by cavitation within a few seconds, making it possible to use an extruder with the advantage of a continuous process. A detailed investigation on the extruder

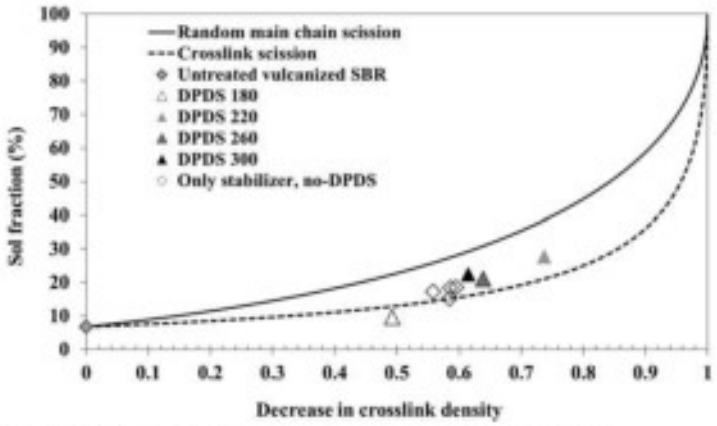


Figure 7.1.9 Devulcanization efficiency with stabilizer and without devulcanization aid, compared to DPDS as devulcanization aid. Figure reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186–232.

Table 7.1.2 Different devulcanization aids.

Devulcanization aid	References
Ionic liquids	[28]
Nitric acid and benzoyl-peroxide	[29–31]
Thiobisphenols, e.g., 4,4-dithiobis(2,6-di-t-butylphenol)	[32]
Bis(3-triethoxysilyl propyl)tetrasulfide (TESPT)	[33,34]
N_2O in organic solvents	[35]
Benzoyl peroxide	[36]
Alcohols/amines and transition metal complex catalysts	[37]
Triphenylphosphine and 1,8-diazabicyclo[5.4.0]undec-7-ene	[38]
Photoactive substances (e.g., semiconducting nanocrystals) in combination with radiation treatment	[39]
Secondary imines	[40]
Amines or sulfides, organic acid or anhydride, oxidant and metal oxide	[41]
Proton donor, metal oxide, organic acid, vulcanization inhibitor and friction agent	[42]
Reactive hydrogen source and catalyst	[43]
Disulfides	[44]
Vegetable product with disulfide as major component	[45,46]
Tetramethyl thiuramdisulfide	[47–49]

settings for an efficient ultrasonic devulcanization is reported in [54]. Certain technologies additionally use devulcanization aids such as eutectic solvents based on, for example, blends of choline chloride and urea or zinc chloride [55].

Microwave treatment is another technique used to devulcanize elastomers. One example is the microwave treatment of a blend of whole-tire powder with a maximum particle size of 500 μm, 6 parts of 2-mercaptobenzothiazole (MBT), and 10 parts of virgin SBR. Prior to blending, the tire powder was oxidized with $KMnO_4$ and peroxide. This blend was irradiated for 150 s at 1000 W [56]. Gamma rays [57] and dielectric fields [58] are also described for physical devulcanization. For all these radiation devulcanization methods it is not well described whether it is indeed devulcanization rather than regeneration.

7.1.3.2.3 Biological devulcanization

Bacterial breakdown of sulfur bonds is another technology [59–61]; this is probably the only devulcanization process in the strict sense of the word. Bacteria that can transform bound sulfur into elemental sulfur and sulfuric acid are, for example, Sulfolobus acidocaldarius [62]. However, disadvantages of this process are that it is very time- and space-consuming, and the devulcanized material has to be dried after the devulcanization process.

7.1.3.3 Process technology

Many devulcanization processes are performed in an extruder with the advantage of a continuous process and a more homogeneous product. Extruder types used for this purpose are, for example, twin screw extruders (TSE), of which a typical setup is shown in Fig. 7.1.10. Planetary roller extruders (see Fig. 7.1.11) are also suitable machines for replasticization and devulcanization [63,64]. General rules for running an extruder in a mode to avoid polymer breakdown as much as possible are low temperatures and limited shearing forces. The critical parameter of an extruder process is the residence time, which generally is too short for complete devulcanization. This can be overcome by using a prolongated extruder die, for example.

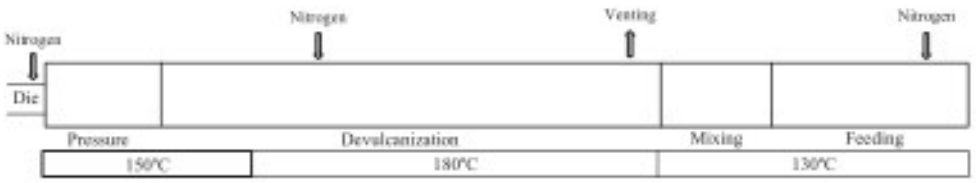


Figure 7.1.10 Twin-screw extruder setup for devulcanization using a devulcanization aid.

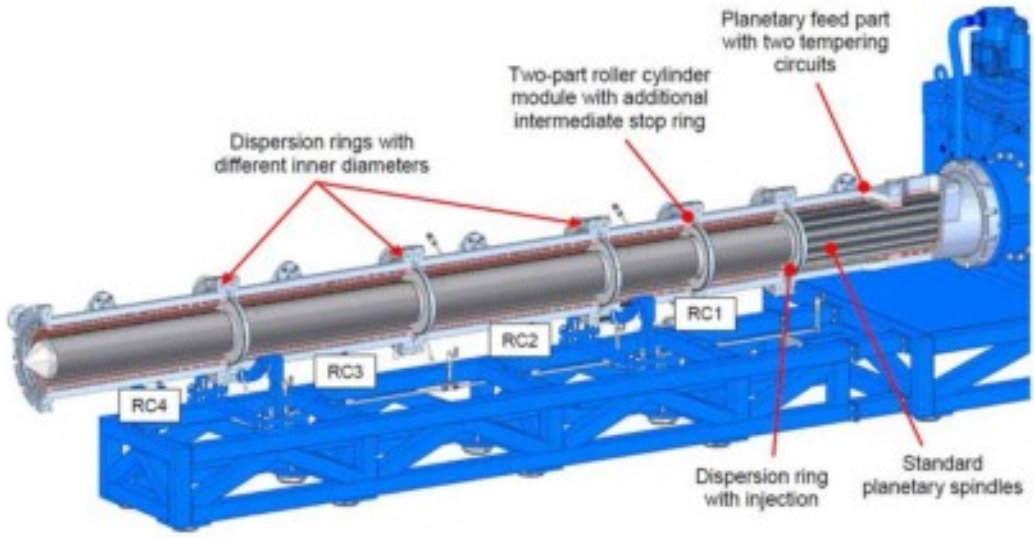


Figure 7.1.11 Planetary roller extruder. Figure reproduced with permission of Entex; Entex, Technical Information Issue 57: Process Technology Information for the Processing of Rubber With the Planetary Roller Extruder, Part 3: Devulcanising Extrusion Processes.

Table 7.1.3 Polymers in different tire parts.

	Apex	Bead	Belt	Cap-ply	Carcass	Innerliner	Sidewall	Tread
Natural rubber	X	X	X	X	X		X	X
Styrene-butadiene rubber	X				X			X
Butadiene rubber	X			X	X		X	X
Butyl rubber (IIR, CIIR, BIIR)						X		

7.1.4 Influence of rubber composition on the devulcanization efficiency: tire rubbers

Tires are an assembly of different type of compounds, which contain a blend of two or three polymers and different fillers, besides other additives such as, plasticizers, curatives and protecting agents. The main polymers used in tires are NR in larger size tires such as trucks and SBR in passenger car tires. Other polymers are butadiene rubber (BR) and butyl rubber (IIR). The latter can be modified with chlorine or bromine, chlorobutyl rubber (CIIR) and bromobutyl rubber (BIIR). Table 7.1.3 shows the presence of these polymers in different tire parts.

The polymers in the blends differ in structure, and - depending on the curing system - the blends differ in the type of crosslink network. The ratio of mono to di- and polysulfidic bonds significantly influences the devulcanization efficiency due to the differences in bond strength of the sulfur bridges and reactivity toward the devulcanization aid [65].

7.1.4.1 Devulcanization of styrene–butadiene rubber [5]

SBR is the most critical polymer in replasticization, as it is prone to recombination resulting in a branched structure and new links between the polymer chains. An extensive study first elaborated a devulcanization process for this polymer in an unfilled model compound, and applied this process to the other three polymers (BR, NR, CIIR) [66]. Fig. 7.1.12 shows the results of the thermochemical devulcanization of sulfur-cured SBR using DPDS as devulcanization aid. Temperature is a crucial parameter: At a temperature of 260°C, compared to the lower temperatures, a significant increase in crosslink density of the devulcanizate is observed. DPDS as devulcanization aid was added in order to scavenge radicals formed during the regeneration process and thus to avoid secondary reactions of the polymer parts; however, this works only at lower devulcanization temperatures. At high devulcanization temperatures, extensive generation of reactive radicals occurs. These lead to formation of new inter- and intramolecular bonds [12] resulting in a decrease of the rubber sol fraction and renewed increase in crosslink density, proving the abovementioned recrosslinking of the polymer during devulcanization at higher temperatures.

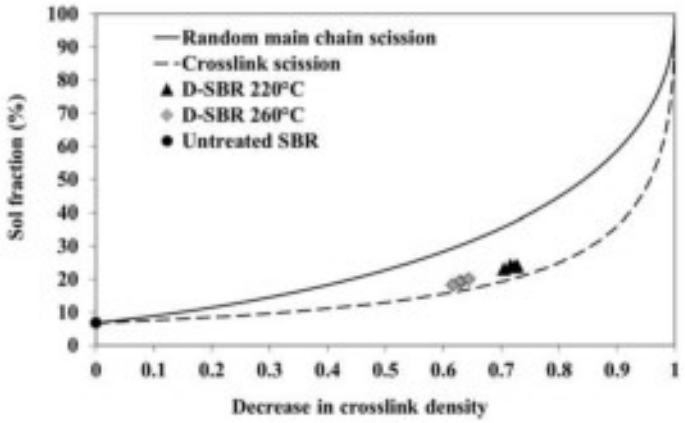


Figure 7.1.12 Relative decrease in crosslink density versus sol fraction of styrene-butadiene (SBR) devulcanizates (D-SBR: devulcanized SBR).
Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31–42.

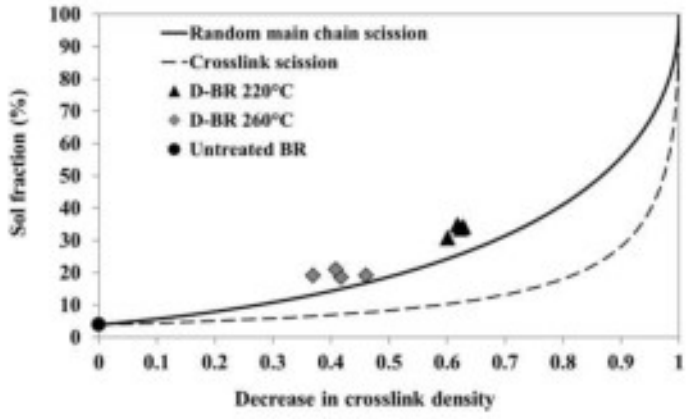


Figure 7.1.13 Relative decrease in crosslink density versus sol fraction of butadiene rubber (BR) devulcanizates (D-BR: devulcanized BR).
Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31–42.

7.1.4.2 Devulcanization of butadiene rubber

The sol fraction of BR devulcanizates as a function of the relative decrease in crosslink density according to Horikx–Verbruggen is shown in Fig. 7.1.13. With increasing temperature within this range, the crosslink density increases. This means that for this polymer, a devulcanization temperature of 220°C is more effective than a temperature of 260°C, as the percentage of soluble polymer is higher and the final crosslink density is lower. However, a considerable amount of main chain scission occurs in both cases, as the sol content is rather high. Degradation of polybutadiene and other butadiene-based polymers follows a unique pathway due to the specific chemical structure of the polymer [12]. In this degradation process, network breakdown occurs, but at the same time network recombination takes place. For this polymer as well, the devulcanization temperature should be as low as possible.

7.1.4.3 Devulcanization of natural rubber

NR is easily devulcanized as seen in Fig. 7.1.14, resulting in a material with relatively good properties. It is rather forgiving in the sense that the devulcanization conditions do not drastically influence the quality of the material.

For NR, the network density can strongly be decreased at temperatures above 170°C [67]. Moreover, DPDS was reported [68,69] to be an effective devulcanization aid for NR. Temperature is the main governing factor, and addition of DPDS can significantly enhance the effects. Using the process parameters as developed for SBR, the NR devulcanizate is completely soluble; not many network connections are remaining between the polymer

molecules. For this polymer, the devulcanization temperature is not critical within this temperature range, as long as the polymer chains do not thermally degrade to a large extent. However, the latter has to be taken into consideration, as NR starts to degrade in the presence of oxygen at about 150°C.

7.1.4.4 Devulcanization of chlorobutyl rubber (CIIR)

The relative decrease in crosslink density of a CIIR model compound is shown in Fig. 7.1.15. At a temperature of 220°C, the data points are far above the random scission line: In spite of a low decrease in crosslink density, the sol content is rather high. This is one example of the onion-peeling devulcanization mechanism discussed above. When the temperature is increased to 260°C, the polymer is degraded, as it is completely soluble.

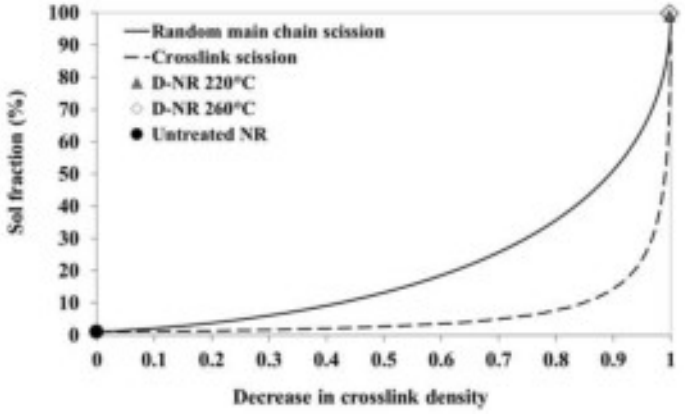


Figure 7.1.14 Relative decrease in crosslink density versus sol fraction of natural rubber (NR) devulcanizates (D-NR: devulcanized NR).
Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31–42.

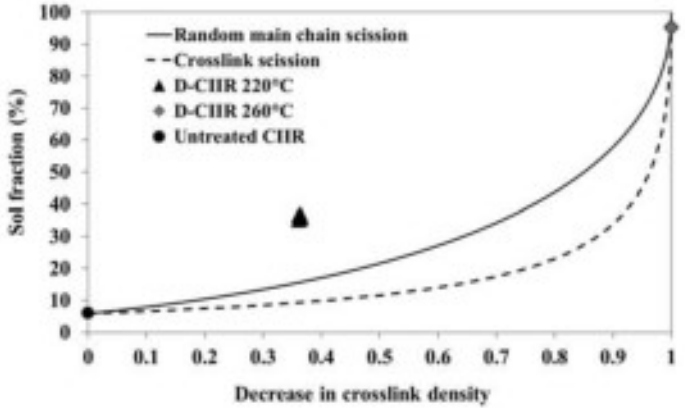


Figure 7.1.15 Relative decrease in crosslink density versus sol fraction of CIIR devulcanizates (D-CIIR: devulcanized CIIR).
Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31–42.

7.1.4.5 Devulcanization of whole-tire rubber

Many different techniques are applied for the devulcanization of ground tire rubber (GTR) from passenger car tires. The main characteristic of these processes is that they can only be a best compromise for the devulcanization efficiency and material quality. In Table 7.1.4, a few of these processes are summarized. Devulcanizates resulting from different processes are evaluated in a review [70].

7.1.4.5.1 Application studies of whole-tire devulcanizate

In general, devulcanized rubber is used to replace a part of a virgin compound. A few studies included such an application case.

The microwave treatment of a not further specified whole-tire powder resulted in a decrease of the crosslink density between 38.6% and 48.5%, depending on the additional treatment of the rubber powder: oxidation and/or MBT addition. According to a Horikx–Verbruggen analysis, the network breakdown was mainly caused by random scission, thus this process cannot be classified as devulcanization. The mechanical properties of a blend of 15 phr devulcanizate with a virgin SBR–silica compound without silane could slightly be improved by the additional treatment [56].

Cryogenically ground truck tire granulate with a maximum particle size of 0.4 mm was treated with supercritical carbon dioxide ($spCO_2$). Fig. 7.1.16 shows the stress–strain curves of blends of a virgin compound (Ref) with vulcanized rubber powder (GTR) and blends with $spCO_2$ devulcanized GTR (T–GTR) [51]. From this graph it can be concluded that the $spCO_2$ treatment does not result in significantly better properties than the untreated rubber powder.

Devulcanizates from different processes based on cryogenically ground whole tire rubber with a maximum particle size of 0.4 mm are compared in terms of mechanical and dynamic properties. The devulcanizates are tested in a NR compound (Ref–NR), to which 10 phr of devulcanizate was added. The fillers are 15 phr silica without silane, 37 phr carbon black in the reference compound, and 34 phr in the blends with recycled rubber. Compared were untreated ground rubber, $spCO_2$ and DPDS treated material, ultrasonically treated material, and samples prepared by bacterial breakdown [59]. Relative to the original compound, the mechanical properties of the blend are negatively influenced: strength is reduced by about 20%–25%, and the $spCO_2$-treated sample with the highest DPDS concentration gives the lowest value. The maximum strain is reduced by 10%. No further significant differences can be observed

Table 7.1.4 Overview of different devulcanization processes.

Process/Devulcanization aid	Process conditions	Properties of the cured vulcanizate as such[a]	Properties of a blend with devulcanizate[b]	References
Thermomechanical	220°C, 30 rpm	–	NR/SBR/15 phr[c] app. 14 MPa/ app. 350%	[71]
	180°C, 120 rpm	12.9 MPa/351%	–	[72]
	180°C, 250 rpm	app. 4.25 MPa/ app. 140%	NR/50/50 2.76 MPa/ 325%	[73]
Mechanochemical		10,9 MPa/289.4%	–	[74]
Mechanochemical/ pentachlorothiophenol hydrazine zinc chloride	150°C, 30 rpm	app. 3.1 MPa/ app. 350%	NR/70/30 14.7 MPa/ 450%	[75]
Ultrasonic	120°C, 20 rpm, 3000 W, 20 kHz	10.5 MPa/250%	–	[76]
	120°C, 20 rpm, 3000 W, 20 kHz	10.5 MPa/250%	–	[77]
	120°C, 20 rpm, 3000 W, 20 kHz	8.7 MPa/217%		[78]
Microwave/diphenyl disulfide	900 W, 3 min, 240°C, 2000 MHz	10 MPa/226%		[79]
Mechanochemical/thiobisphenols	200°C	5.85 MPa/app. 325%		[42]
Mechanochemical/1,8-Diazabicyclo (5.4.0)Undecane-7 (DBU)/ triphenylphosphine (PPh3)	30 rpm	13.6 MPa/390%		[39]
Mechanochemical/2-butanol	30°C, 40 min, 10 MPa	–	SBR/BR 85/15 15.4 MPa/738%	[80]
Mechanochemical/supercritical water/peroxide/alkylphenol polysulfide	200°C, 1.6 MPa	–	SBR app. 20.45 MPa/ app. 710%	[81]
Mechanochemical/supercritical water	200°C, 1.6 MPa	–	SBR app. 15 MPa/ app. 645%	

BR, butadiene rubber; NR, natural rubber; SBR, styrene-butadiene rubber.
[a]Tensile strength/elongation at break.
[b]Polymers in masterbatch/concentration devulcanizate tensile strength/elongation at break.
[c]Parts per hundred rubber.

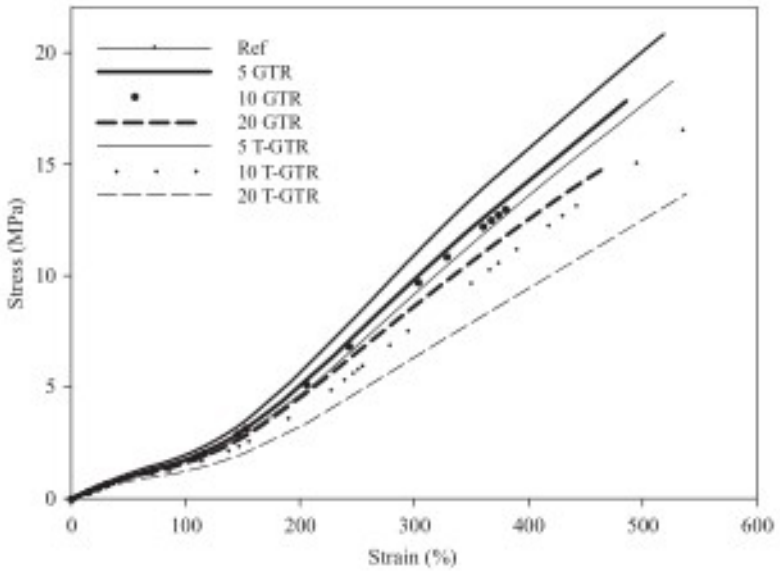


Figure 7.1.16 Stress–strain curves of blends of virgin rubber with rubber devulcanized using supercritical CO_2.
Figure reproduced with permission of Elsevier; I. Mangili, E.M. Collina, M. Anzano, D. Pitea, M. Lasagni. Characterization and supercritical CO_2 devulcanization of cryo-oground tire rubber: influence of devulcanization process on reclaimed material. Polym. Degrad. Stab., 102, 2014, 15–24.

between the different types of devulcanizates. Dynamic properties were also measured: tan δ as indication of rolling resistance showed an increase for all samples containing devulcanizate. The highest level was measured for the spCO_2–DPDS devulcanizate in the blend, the lowest for the bacteria-treated one [59].

In another study, devulcanized whole-tire rubber from different types of tires was treated in a microwave process at 800 W for 1–5 min. The material temperature after the microwave treatment was up to 370°C. The devulcanizates were added to a SBR compound in concentrations of 10, 30, and 50 phr. The only adjustment of the formulation was a reduction of the carbon black content from 67.75 to 63.25 phr. The trends given in Table 7.1.5 were measured on the blended materials [82].

7.1.5 Influence of rubber composition on the devulcanization efficiency: fillers

Devulcanization efficiency and material quality depend significantly on the type of tires used as feedstock, thus on the rubber composition. Besides the polymers discussed above, other ingredients also influence the devulcanization process and material properties. The most important ones are the filler systems.

Carbon black is often used as reinforcing filler in tires since it plays an important role in improvement of the mechanical

Table 7.1.5 Rheological and mechanical property changes by addition of microwave-devulcanized tire rubber to a virgin rubber compound.

	Increasing concentration of devulcanizate	Increasing degree of devulcanization by variation of treatment time
Delta torque (M_H-M_L)	↓	o
Scorch time t_{s2}	↓	o
Curing time t_{90}	↓	↓
Tensile strength	↓	o
Elongation at break	↓	o
Modulus at 100% elongation	o	o
Hardness	↑	o

o: no clear trend.

properties such as abrasion resistance, modulus, and fatigue life. A study of the influence of carbon black loading on the devulcanization of NR-based tire compounds using DPDS as devulcanization aid has shown that the presence of this filler resulted in a decrease in devulcanization efficiency [83]. Addition of carbon black to an elastomer causes adsorption of the polymer molecules onto the filler surface and anchoring in the carbon black structure, resulting in segmental mobility loss. The reactivity of the DPDS for trapping the sulfide radicals stemming from the network breakdown was decreased: these radicals have a high probability to be attached to carbon black and thus are inactivated.

The most problematic component in tire rubber is a silica–silane filler system. This filler forms strong covalent bonds with the polymer by the silane, while carbon black forms physical bonds, which are rather easy to break. But as the additional silica–silane–polymer network results in a low hysteresis, thus lower rolling resistance, silica is more and more replacing carbon black in treads of passenger car tires.

The secondary filler–polymer network in silica-filled rubber is difficult to break, as it contains mainly monosulfidic bonds. Fig. 7.1.17 shows the devulcanization efficiency of a silica–silane-filled SBR compound. The devulcanization conditions were in first instance optimized for a nonfilled SBR rubber. For the latter compound, a devulcanization efficiency of 70%–80% was achieved; for the silica-filled rubber, the efficiency was about 20%–40%. This is caused by the monosulfidic bonds formed by the silane, bis-(3-triethoxysilylpropyl) disulfide.

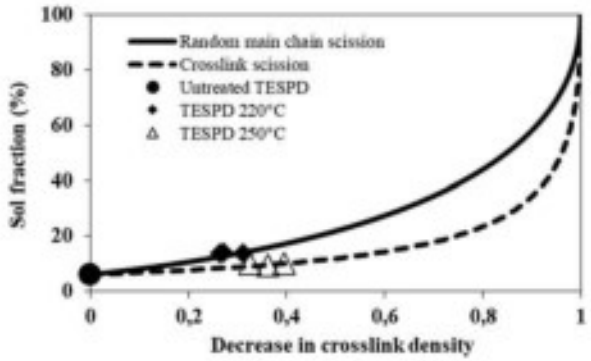


Figure 7.1.17 Devulcanization efficiency of silica–silane reinforced styrene-butadiene rubber.

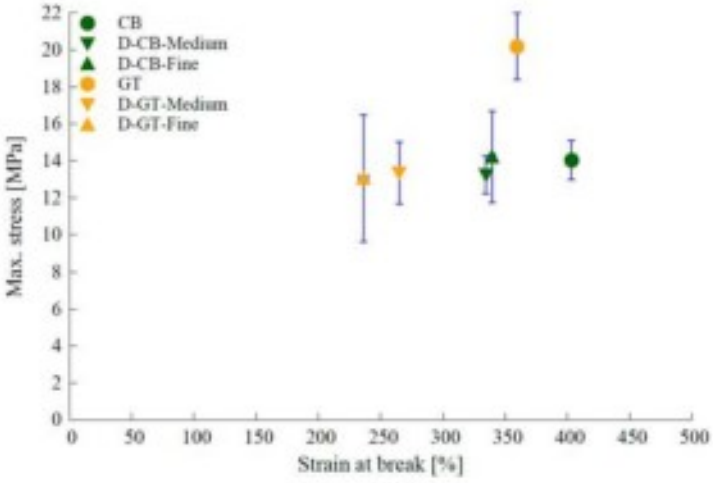


Figure 7.1.18 Stress–strain properties of a carbon black (CB) and silica (GT)-filled rubber before and after devulcanization and revulcanization (D–CB, D–GT) (medium and fine classify the granulometry of the feedstock).

Fig. 7.1.18 illustrates the difference between carbon black and silica filled rubber: the loss in properties after de- and revulcanization of the silica-filled rubber is significantly higher compared to the loss in properties of the carbon black filled material: the filler–polymer network in the latter is easier to be broken, as the filler–polymer bonds are rather weak.

Another new type of compounding ingredients are resins. They are added to mainly passenger car tread compounds in order to improve wet grip. The devulcanization study of this type of compounds was performed using 2-2'-dibenzamidodiphenyldisulfide as devulcanization aid. The resins were polyterpene- (resin A), hydrocarbon- (resin B), and terpene-phenol-(resin C) based. They were blended into a silica–silane passenger car tire tread formulation, in which 20 phr of oil was replaced by the same amount of resin. The

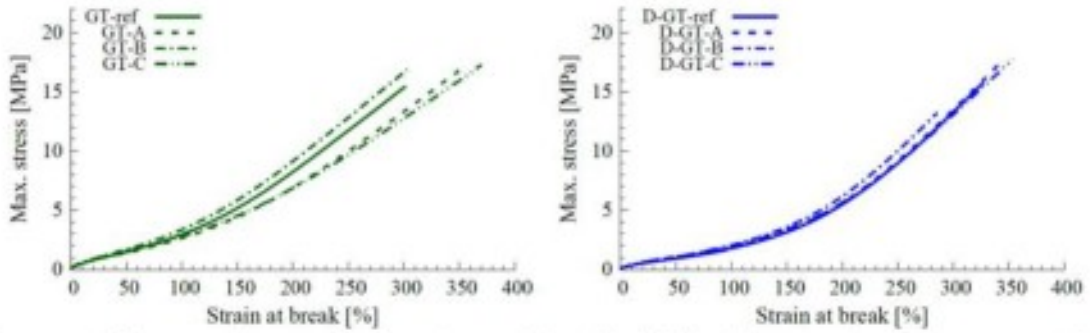


Figure 7.1.19 Stress–strain properties of a resin-containing rubber (left), and the properties of the same material after de- and revulcanization (right) (GT–ref: SBR–silica–silane reference compound; GT–x: SBR–silica–silane compound with resin x; D–GT–ref: reference compound after de- and revulcanization; D–GT–x: SBR–silica–silane compound with resin after de- and revulcanization).

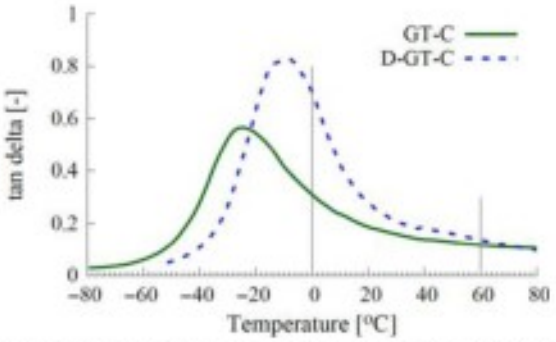


Figure 7.1.20 The correlation between loss angle and temperature for a SBR-based silica-silane compound (GT–C: original compound; D–GT–C: compound with resin C after de- and revulcanization).

stress–strain properties of the original and the devulcanized and revulcanized rubber do barely differ: The presence of resins does not significantly influence the strength properties of the devulcanizate (see Fig. 7.1.19). In terms of tire performance indicators, the loss angle around 0°C was increased significantly, while the value at 60°C was not influenced (see Fig. 7.1.20). The presence of resins thus has a positive influence on the wet grip properties when devulcanizate is added to the compound.

7.1.6 Process parameters affecting devulcanization efficiency

Not only the material composition and devulcanization aid, but also the processing parameters influence the devulcanization

efficiency. A study in an internal mixer on small scale in order to optimize the process conditions is reported [84]. This study shows that the time to swell process oil and devulcanization aid into granulate, concentration of the process oil, presence of oxygen as well as devulcanization time and temperature have an influence on the devulcanization efficiency. In this study, 30 mmol DPDS per 100 g compound were used, and a protective gas (nitrogen).

Fig. 7.1.21 shows that the concentration of the process oil, treated distillate aromatic oil (TDAE), has a considerable effect due to the plasticization of the material and thus less mechanical energy input in the internal mixer used in this study: higher concentrations reduce the devulcanization efficiency. Fig. 7.1.22 shows that an increasing devulcanization time beyond 6 min results in an increase in crosslink density, as the balance between chain scission and recombination of active chain segments shifts to the latter process. It is crucial to achieve a

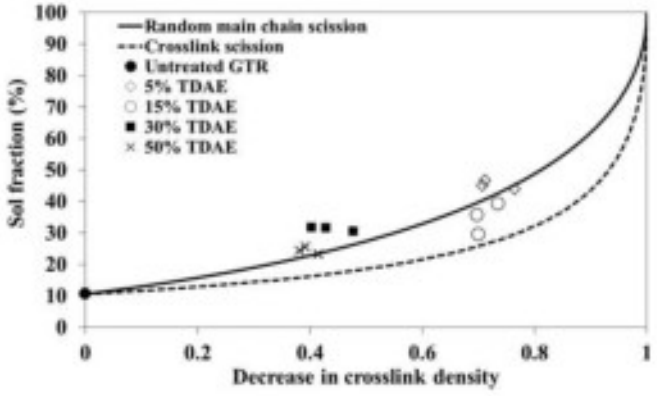


Figure 7.1.21 Influence of concentration of process oil on the devulcanization efficiency. Figure reproduced with permission of Kautschuk Gummi Kunststoffe; S. Saiwari, W. K. Dierkes, J.W.D. Noordermeer. Devulcanization of whole passenger car tire material. Kautsch. Gummi Kunstst., 66 (8), 2013, 20–25.

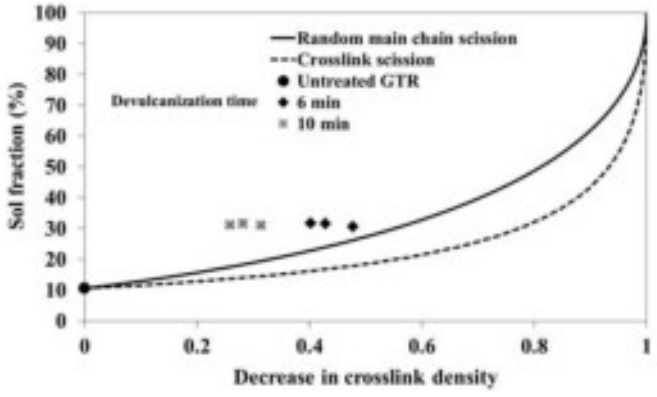


Figure 7.1.22 Influence of devulcanization time on the devulcanization efficiency. Figure reproduced with permission of Kautschuk Gummi Kunststoffe; S. Saiwari, W. K. Dierkes, J.W.D. Noordermeer. Devulcanization of whole passenger car tire material. Kautsch. Gummi Kunstst., 66 (8), 2013, 20–25.

breakdown of the network as far as possible before reformation of polymer–polymer bonds from active chain fragments becomes the prevailing reaction.

Fig. 7.1.23 illustrates the influence of oxygen during devulcanization and cooling of the sample. In this series of experiments, no devulcanization aid was used; therefore the degree of devulcanization is rather low. From Fig. 7.1.23(A) it is obvious that the combination of high temperatures with oxygen presence results in a high degree of recombination: the crosslink density of the material after devulcanization is even higher than the density of the starting material. This does not occur to such an extent when less oxygen is present; see Fig. 7.1.23(B) and (C): The absence of oxygen during devulcanization (B) and additionally during cooling (C) does reduce the degree of recombination, but does not significantly influence the final degree of devulcanization; to improve this, a devulcanization aid is needed. The stress–strain properties of the revulcanized rubber after devulcanization at 220°C for 6 min do not differ significantly depending on the presence of oxygen (Fig. 7.1.24).

Fig. 7.1.25 shows the influence of time, temperature, and screw speed on the devulcanization efficiency of passenger car tire rubber in a TSE using DPDS as devulcanization aid [85]. With increasing temperature, the data points move upward to the random scission line: higher temperatures result in a higher degree of nonselective thermal breakdown of the network. However, the recrosslinking seen in an internal mixer [Fig. 7.1.23 (A)] does not occur here, as the devulcanization was performed in a protective gas atmosphere. Residence time in the extruder also plays a role: when increasing the time from 1 to 3 min, the degree of network breakdown gets considerably higher. Another increase to 6 min enhances the devulcanization efficiency as well, but to a lesser extent. The influence of screw speed is not clear, as here the influence of the shearing forces on the temperature also plays a role.

A similar study [71] showed that the percentage of devulcanization was depending on shear stress, and that the barrel temperature was the most important parameter in changing the sol fraction.

In the study of Fig. 7.1.25, the following trends in terms of mechanical properties were found:

1. Temperature: Samples devulcanized at a maximum temperature of 180°C show higher tensile strength values than those devulcanized at 220°C.
2. Amount of the devulcanization aid (DPDS): There was no significant difference in tensile strength between samples

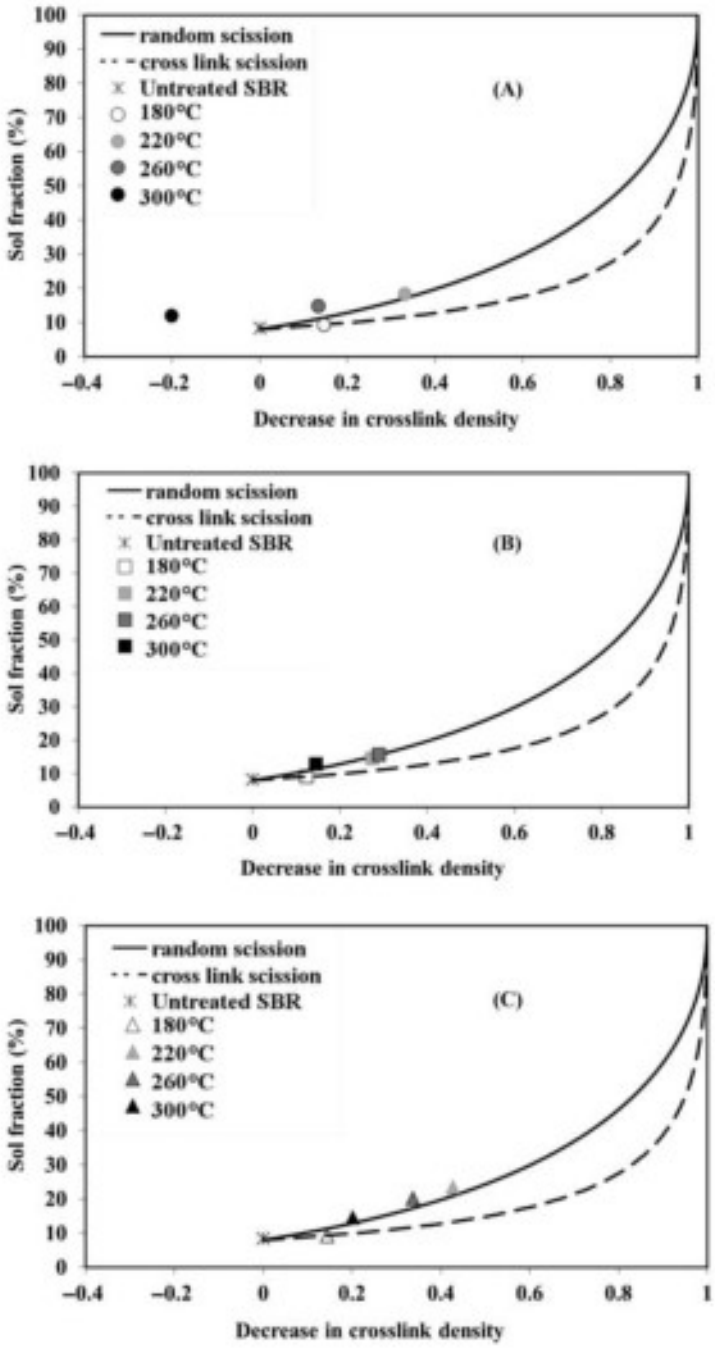


Figure 7.1.23 Influence of the presence of oxygen on the devulcanization efficiency [(A) with oxygen; (B) no oxygen during devulcanization; (C) no oxygen during devulcanization and cooling of the sample]. Figure is reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186–232.

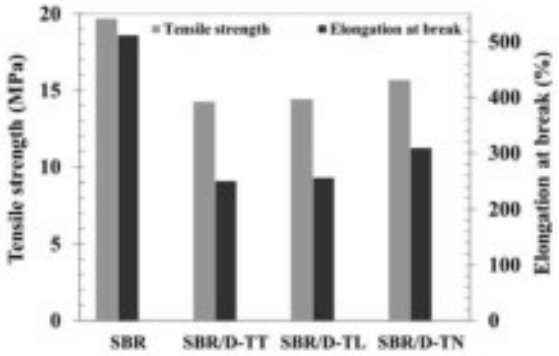


Figure 7.1.24 Stress–strain properties of styrene butadiene (SBR) rubber devulcanized with and without oxygen (SBR/D–TT: with oxygen; SBR/D–TL: no oxygen during devulcanization; SBR/D–TN: no oxygen during devulcanization and cooling of the sample).

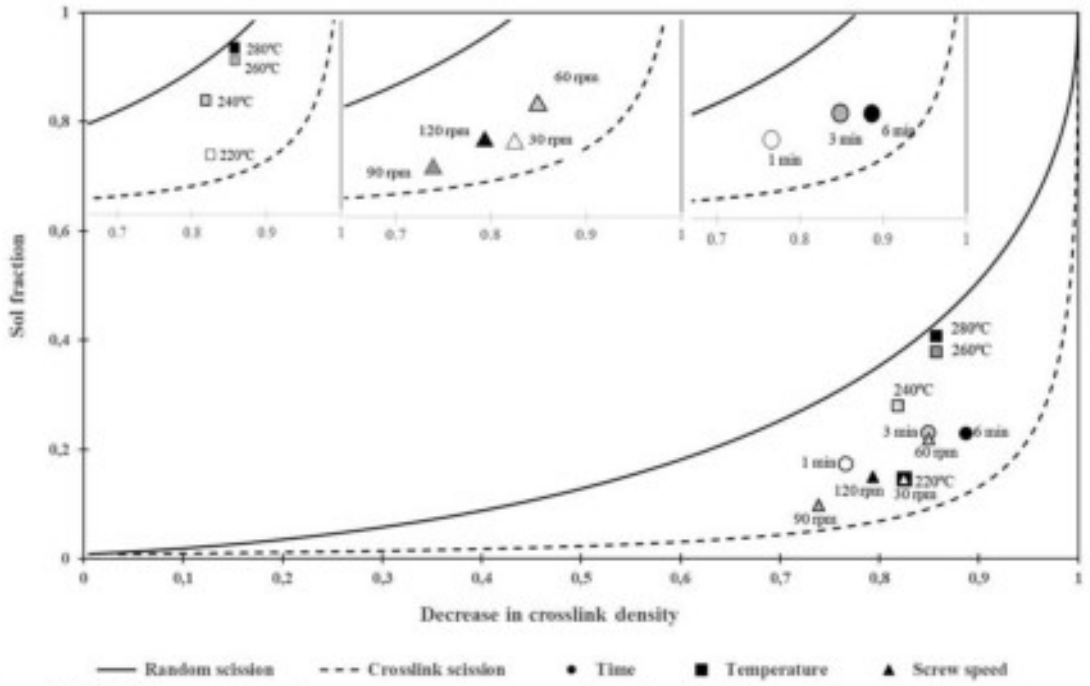


Figure 7.1.25 Influence of time, temperature, and screw speed on devulcanization efficiency in a twin-screw extruder.

devulcanized with 3.9 wt.% and with 6.85 wt.%. A higher amount of devulcanization aid is not necessarily beneficial.

3. Screw speed: As for the degree of devulcanization, the influence is not clear.

4. Amount of process oil: Combined with a low screw speed, high oil concentrations resulted in low tensile strength values.

From this study, it was concluded that the best conditions for the devulcanization of whole passenger car tire rubber in a twin-screw extruder are low shear forces and a devulcanization time of 6 to 7 min at a devulcanization temperature of 180°C. However, the relatively long residence time needed for the devulcanization limits the capacity of the extruder, as the length-to-diameter ratio needed for a reasonable throughput leads to impractically long screws. Due to the required low shear, a delaying influence of additional mixing elements in the screw to increase residence times cannot be used in this devulcanization process. Possible adaptions are the use of an elongated die and, with limitations, an increase of the length-to-diameter ratio. A posttreatment on a mill with friction at a temperature of 60°C improves the morphology and properties of the devulcanizate.

References

[1] M.M. Horikx, Chain scissions in a polymer network, J. Polym. Sci. 19 (1956) 445–454.
[2] A. Charlesby, Solubility and molecular size distribution of crosslinked polystyrene, J. Polym. Sci. 11 (6) (1953) 513–520.
[3] A. Charlesby, Gel formation and molecular weight distribution in long chain polymers, Proc. R. Soc. London, A 222 (1151) (1954) 542–557.
[4] M.A.L. Verbruggen, L. Van Der Does, W.K. Dierkes, J.W.M. Noordermeer, Experimental validation of the Charlesby and Horikx models applied to de-vulcanization of sulfur and peroxide vulcanizates of NR and EPDM, Rubber Chem. Technol. 89 (4) (2016) 671–688.
[5] S. Saiwari Post Consumer Tires Back into New Tires, De-Vulcanization and Reutilization of Passenger Car Tires (Thesis). University of Twente, Enschede, 2013.
[6] M.A.L. Verbruggen, L. Van Der Does, J.W.M. Noordermeer, M. van Duin, H.J. Manuel, Mechanisms involved in the recycling of NR and EPDM, Rubber Chem. Technol. 72 (1999) 731–740.
[7] P.J. Flory, J. Rehner, Statistical mechanics of cross-linked polymer networks II. Swelling, J. Chem. Phys. 11 (1943) 521–526.
[8] G. Kraus, Swelling of filler-reinforced vulcanizates, J. Appl. Polym. Sci. 7 (3) (1963) 861–871.
[9] M. Porter, Structural characterization of filled vulcanizates part 1. Determination of the concentration of chemical crosslinks in natural rubber vulcanizates containing high abrasion furnace black, Rubber Chem. Technol. 40 (1967) 866–882.
[10] K.A.J. Dijkhuis, I. Babu, J.S. Lopulissa, J.W.M. Noordermeer, W.K. Dierkes, A mechanistic approach to EPDM devulcanization, Rubber Chem. Technol. 81 (2008) 190–208.
[11] E. Finazzi, A. Gallo, P. Lucci, Using a co-rotating twin screw extruder-use of a co-rotating twin screw extruder in the continuous process for production of rubber compounds, Rubber World 243 (8) (2011) 21–81.

[12] S.L. Madorsky, Thermal degradation of organic polymers, in: H.F. Mark, E.H. Immergut (Eds.), Polymer Reviews, Interscience Publishers, New York, 1964.
[13] M.D. Sarkar, P.G. Mukunda, P.P. De, A.K. Bhowmick, Degradation of hydrogenated styrene-butadiene rubber at high temperature, Rubber Chem. Technol. 70 (1997) 855–870.
[14] M.A. Golub, Thermal rearrangements of unsaturated polymers, Rubber Chem. Technol. 51 (4) (1978) 677–685.
[15] M.A. Golub, Thermal rearrangements in 1,2-poly(1,4-hexadiene)s, J. Polym. Sci. Polym. Lett. Ed. 16 (1978) 253–260.
[16] J.R. Shelton, Review of basic oxidation processes in elastomers, Rubber Chem. Technol. 45 (2) (1972) 359–380.
[17] <http://www.wiredchemist.com/chemistry/data/bond_energies_lengths.html>; (accessed 23.07.20).
[18] L. Asaro, M. Gratton, S. Seghar, N.A. Hocine, Recycling of rubber wastes by devulcanization, Resour. Conserv. Recycl. 133 (2018) 250–262.
[19] M. Kojima, M. Tosaka, Y. Ikeda, S. Kohjiya, Devulcanization of carbon black filled natural rubber using supercritical carbon dioxide, J. Appl. Polym. Sci. 95 (2005) 137–143.
[20] K. Jiang, J. Shi, Y. Ge, R. Zou, P. Yao, X. Li, et al., Complete devulcanization of sulfur cured butyl rubber by using supercritical carbon dioxide, J. Appl. Polym. Sci. 127 (2012) 2397–2406.
[21] J. Shi, K. Jiang, D. Ren, H. Zou, Y. Wang, X. Lv, et al., Structure and performance of reclaimed rubber obtained by different methods, J. Appl. Polym. Sci. 129 (2013) 999–1007.
[22] I. Mangili, M. Oliveri, M. Anzano, E. Collina, M. Lasagni, Full factorial experimental design to study the devulcanization of ground tire rubber in supercritical carbon dioxide, J. Supercrit. Fluids 92 (2014) 249–256.
[23] H. Okamoto, Mechanochemical reclamation of comminated tyre scrap using vulcanization accelerators. International Polymer Science and Technology, 7, 1980, T/59.
[24] G.K. Jana, C.K. Das, Devulcanization of natural rubber vulcanizates by mechanochemical process, Polym. Plast. Technol. Eng. 44 (2005) 1399–1412.
[25] G.K. Jana, C.K. Das, Devulcanization of automobile scrap tyres by a mechanochemical process, Prog. Rubber Plast. Recycl. Technol. 21 (4) (2005) 319–331.
[26] S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer, Inventors: A Method of Devulcanizing a Rubber Vulcanizate. WIPO Patent WO2014084727. 2014 Jun 05.
[27] S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer, Recycling of individual waste rubber (Green chemistry series no.59) in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi (Eds.), Rubber Recycling: Challenges and Developments, The Royal Society of Chemistry, Croydon, 2019, pp. 186–232.
[28] S. Seghar, N. Aït Hocine, V. Mittal, S. Azem, F. Al-Zohbi, B. Schmaltz, et al., Devulcanization of styrene butadiene rubber by microwave energy: effect of the presence of ionic liquid, Express Polym. Lett. 9 (2015) 1076–1086.
[29] R.R. Rios, M. Gontijo, V.P. Ferraz, R.M. Lago, M.H. Araujo, Devulcanization of styrenebutadiene (SBR) waste tire by controlled oxidation, J. Braz. Chem. Soc. 17 (2006) 603–608.
[30] C. Temram, K. Wattanakul, Investigation the degradation and devulcanization reaction of thermoplastic vulcanizate using peroxide compound, AIP Conf. Proc. 1482 (2012) 246–251.
[31] S. Rooj, G.C. Basak, P.K. Maji, A.K. Bhowmick, New route for devulcanization of natural rubber and the properties of devulcanized rubber, J. Polym. Environ. 19 (2011) 382–390.

[32] X. Zhang, P. Saha, L. Cao, H. Li, J. Kim, Devulcanization of waste rubber powder using thiobisphenols as novel reclaiming agent, Waste Manage. 78 (2018) 980–991.
[33] G. Soumyajit, K.J. Arun, R. Madhusudan, D. Amit, D. Debapriya, Tuning of accelerator and curing system in devulcanized green natural rubber compounds, Polym. Test. 69 (2018) 133–145.
[34] S. Ghorai, S. Bhunia, M. Roy, D. Debapriya, Mechanochemical devulcanization of natural rubber vulcanizate by dual function disulfide chemicals, Polym. Degrad. Stab. 129 (2016) 34–46.
[35] K.A. Dubkov, D.P. Semikolenov, D.P. Ivanov, D.E. Babushkin, G.I. Panov, V.N. Parmon, Reclamation of waste tyre rubber with nitrous oxide, Polym. Degrad. Stab. 97 (2012) 1123–1130.
[36] M. Sabzekar, M.P. Chenar, S.M. Mortazavi, M. Kariminejad, S. Asadi, G.H. Zohuri, Influence of process variables on chemical devulcanization of sulfur-cured natural rubber, Polym. Degrad. Stab. 118 (2015) 88–95.
[37] J.G.A. Juventino, E.R. Raymundo, Inventors. Devulcanization of Rubber Waste by Hydrogen Transfer Reactions. Mexican Patent MX2017007774. 2019, Feb 08.
[38] L.R. Vorobyev, B.V. Bosnik, Inventors: Rubbintec LLC, Assignee. Method of Devulcanization of Sulfur-Cured Rubber. United States Patent US2018148560. 2018, May 31.
[39] J. Kalliopuska, S. Holm, T. Holm, Inventors. Method and Related Arrangement For Devulcanization of Vulcanized Rubber. United States Patent US20150005400. 2015, Jan 01.
[40] L. Vorobyev, Inventor. Composition for Devulcanization of Sulfur-Cured Rubber and Method of Devulcanization Using This Composition. European Patent EP2796491. 2014, Oct 29.
[41] L. Beirakh, Inventor: Green-Gum Rubber Recycle Ltd., Innovert Investments A L Ltd., Assignee. Method and Chemical Composition for Reclaiming of Cured Elastomer Materials. United States Patent US2013096216. 2013, Apr 18.
[42] V. Goldshtein, M. Kopylov, Inventors. Method and Composition for Devulcanization of Waste Rubber. South African Patent ZA200401640. 2004, Nov 18.
[43] R.A. McFarlane, R.K. Lott, H. Huang, Inventors: Alberta Innovates Technology Futures, Assignee. Catalytic Devulcanization of Rubber. United States Patent US20060116431. 2006, Jun 01.
[44] M. Myhre, D.A. Mackillop, Rubber recycling, Rubber Chem. Technol. 75 (3) (2002) 429–474.
[45] D. De, S. Maiti, B. Adhikari, Reclaiming of rubber by a renewable resource material (RRM) II. Comparative evaluation of reclaiming process of NR vulcanizate by RRM and diallyl disulfide, J. Appl. Polym. Sci. 73 (14) (1999) 2951–2958.
[46] D. De, B. Adhikari, S. Maiti, Reclaiming of rubber by a renewable resource material. Part 1. Reclaiming of natural rubber vulcanizates, J. Polym. Mater. 14 (4) (1997) 333–342.
[47] D. De, A. Das, D. De, B. Dey, S.C. Debnath, B.C. Roy, Reclaiming of ground rubber tire (GRT) by a novel reclaiming agent, Eur. Polym. J. 42 (2006) 917–927.
[48] D. De, D. De, Processing and material characteristics of a reclaimed ground rubber tire reinforced styrene butadiene rubber, Mater. Sci. Appl. 2 (5) (2011) 486–496.
[49] D. De, D. De, G.M. Singharoy, Reclaiming of ground rubber tire by a novel reclaiming agent. I. Virgin natural rubber/reclaimed GRT vulcanizates, Polym. Eng. Sci. 47 (7) (2007) 1091–1100.

[50] L. Asaro, M. Gratton, S. Seghar, N. Poirot, N. Ait Hocine Devulcanization of waste rubber using thermomechanical method combined with supercritical CO_2. Presentation presented at: International conference on waste management, recycling and environment; 2018, Mar 5–6; Rome, Italy.
[51] I. Mangili, E.M. Collina, M. Anzano, D. Pitea, M. Lasagni, Characterization and supercritical CO_2 devulcanization of cryoground tire rubber: influence of devulcanization process on reclaimed material, Polym. Degrad. Stab. 102 (2014) 15–24.
[52] T. Costas, Inventor. Method of Devulcanizing Crosslinked Rubber. Canadian Patent CA2500372. 2003, Apr 10.
[53] A.I. Isayev, Recycling of rubbers, in: J.E. Mark, B. Erman, M. Roland (Eds.), The Science and Technology of Rubber, fourth ed., Elsevier Academic Press, Cambridge, MA, 2014, pp. 697–764.
[54] I. Mangili, M. Lasagni, K. Huang, A.I. Isayev, Modeling and optimization of ultrasonic devulcanization using the response surface methodology based on central composite face-centered design, Chemom. Intell. Lab. Syst. 144 (2015) 1–10.
[55] R. Saputra, R. Walvekar, M. Khalid, K. Shahbaz, S. Ramarad, Effective devulcanization of ground tire rubber using choline chloride-based deep eutectic solvents, J. Environ. Chem. Eng. 7 (3) (2019) 103–151.
[56] O. BuitragoSeuscún, R. Britto, Devulcanization of ground tire rubber: thermooxidation followed by microwave exposure in the presence of devulcanizing agent, Iran. Polym. J. 29 (2020) 553–567.
[57] K.E El-Nemr, H.A. Raslan, M.A.M. Ali, Innovative γ rays irradiated styrene butadiene rubber/reclaimed waste tire rubber blends: a comparative study using mechanochemical and microwave devulcanizing methods, J. Polym. Eng. 40 (3) (2020) 267–277.
[58] M. Marc, Inventor: Novation IQ LLC, Assignee. Devulcanization of Rubber and Other Elastomers. United States Patent US20130259762. 2013, Oct 03.
[59] I. Mangili, M. Lasagni, M. Anzano, E.M. Collina, V. Tatangelo, A. Franzetti, et al., Mechanical and rheological properties of natural rubber compounds containing devulcanized ground tire rubber from several methods, Polym. Degrad. Stab. 121 (2015) 369–377.
[60] G. Straube, E. Straube, W. Neumann, H. Rueckauf, R. Forkmann, M. Loeffler, Inventors. Method for Reprocessing Scrap Rubber. United States Patent US5275948. 1994, Apr 01.
[61] G.G. Bohm, G.N. Stephanopoulos, Inventors. Method of Microbial and/or Enzymatic Devulcanization of Rubber. United States Patent US20110301302. 2011, Dec 08.
[62] R.A. Romine, M.F. Romine, Rubbercycle: a bioprocess for surface modification of waste tyre rubber, Polym. Degrad. Stab. 59 (1998) 353–358.
[63] M.W. Batton, H. Rust, Adhesive Processing Using a Planetary Extruder. (n.d.). <https://www.pstc.org/files/public/Batton_Mike.pdf> (accessed 29.06.20).
[64] Entex, Technical information issue 57: Process technology information for the processing of rubber with the planetary roller extruder, Part 3: Devulcanising extrusion processes (2020).
[65] K. Dijkhuis, Recycling of Vulcanized EPDM-Rubber. (Thesis), University of Twente, Enschede. 2008.
[66] S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer, Comparative investigation of the devulcanization parameters of tire rubbers, Rubber Chem. Technol. 87 (85) (2014) 31–42.
[67] V.V. Rajan, W.K. Dierkes, J.W.M. Noordermeer, R. Joseph, Comparative investigation on the reclamation of NR based latex products with amines and disulfides, Rubber Chem. Technol. 78 (5) (2005) 855–867.

[68] V.V. Rajan, W.K. Dierkes, R. Joseph, J.W.M. Noordermeer, Recycling of NR based cured latex material reclaimed with 2,2′-dibenzamidodiphenyldisulphide in a truck tire tread compound, J. Appl. Polym. Sci. 102 (5) (2006) 4194–4206.
[69] A.R. Jalilvand, I. Ghasemi, M. Karrabi, H. Azizi, An investigation on the EPDM devulcanization in co-rotating twin screw extruder by response surface methodology, Progr Rubber Plast. Recycl. Technol. 24 (1) (2008) 33–46.
[70] L. Bockstal, T. Berchem, Q. Schmetz, A. Richel, Devulcanisation and reclaiming of tires and rubber by physical and chemical processes: a review, J. Clean. Prod. 236 (2019) 117574.
[71] H. Yazdani, M. Karrabi, I. Ghasmi, H. Azizi, G.R. Bakhshandeh, Devulcanization of waste tires using a twin-screw extruder: the effects of processing conditions, J. Vinyl Addit. Technol. 17 (1) (2011) 64–69.
[72] G. Tao, Q. He, Y. Xia, G. Jia, H. Yang, W. Ma, The effect of devulcanization level on mechanical properties of reclaimed rubber by thermal-mechanical shearing devulcanization, J. Appl. Polym. Sci. 129 (5) (2013) 2598–2605.
[73] K. Formela, M. Cysewska, Efficiency of thermomechanical reclaiming of ground tire rubber conducted in counter-rotating and co-rotating twin screw extruder2014 Polimery 59 (3) (2014) 231–238.
[74] X. Zhang, C. Lu, M. Liang, Properties of natural rubber vulcanizates containing mechanochemically devulcanized ground tire rubber, J. Polym. Res. 16 (2009) 411–419.
[75] A.A. Yehia, M.N. Ismail, Y.A. Hefny, E.M. Abdel-Bary, M.A. Mull, Mechanochemical reclamation of waste rubber powder and its effect on the performance of NR and SBR vulcanizates, J. Elastom. Plast. 36 (2) (2004) 109–123.
[76] A.I. Isayev, J. Chen, A. Tukachinsky, Novel ultrasonic technology for devulcanization of waste rubbers, Rubber Chem. Technol. 68 (2) (1995) 267–280.
[77] A.I. Isayev, A. Tukachinsky, D. Schworn, Devulcanization of waste tire rubber by powerful ultrasound, Rubber Chem. Technol. 69 (1) (1996) 92–103.
[78] J. Yun, J.S. Oh, A.I. Isayev, Ultrasonic devulcanization reactors for recycling of GRT: comparative study, Rubber Chem. Technol. 74 (2) (2001) 317–330.
[79] M. Molanorouzi, S.O. Mohaved, Reclaiming waste tire rubber by an irradiation technique, Polym. Degrad. Stab. 128 (2016) 115–125.
[80] D.A. Benko, R.N. Beers, Inventors: Goodyear Tire and Rubber Co, Assignee. Surface Devulcanization of Cured Rubber Crumb. United States Patent US6387965B1. 2002, May 14.
[81] X. Wang, C. Shi, L. Zhang, Y. Zhang, Effects of shear stress and subcritical water on devulcanization of styrene–butadiene rubber based ground tire rubber in a twin-screw extruder, J. Appl. Polym. Sci. 130 (3) (2013) 1845–1854.
[82] F. Karaborg, A. Akdemir, E. Pehlivan, Characterization of styrene butadiene rubber and microwave devulcanized ground tire rubber composites, J. Polym. Eng. 34 (6) (2014) 2191–2340.
[83] A. Worlee, S. Saiwari, W.K. Dierkes, S.S. Sarkawi, C. Nakason, Influence of filler network on thermo-chemical devulcanization efficiency of carbon black filled natural rubber, J. Met. Mater. Min. 29 (3) (2019) 76–81.
[84] S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer, Devulcanization of whole passenger car tire material, Kautsch. Gummi Kunstst. 66 (8) (2013) 20–25.
[85] S. Saiwari, J.W. van Hoek, W.K. Dierkes, L.E.A.M. Reuvekamp, G. Heideman, A. Blume, et al., Upscaling of a batch devulcanization process for ground car tire rubber to a continuous process in a twin screw extruder, Materials 9 (9) (2016) 724.

7.2

In-product-sorting end-of-life tires for effective recycling by devulcanization

Said Seghar[1] and Florian Lacroix[2]

[1]*Phenix Technologies, Sancheville, France* [2]*Laboratoire de Mécanique Gabriel Lamé (LaMé), Université de Tours, Université d'Orléans, INSA Centre Val de Loire, Tours, France*

7.2.1 Introduction

The European Commission Directive of September 18, 2000 (Directive 2000/53/EC) deals with the management of end-of-life products. The purpose of this directive is to recover end-of-life waste in order to make a new raw material out of it.

In addition to the environmental issue caused by the storage of huge quantities of waste materials and the inevitable long-term shortage of certain raw materials, major economic developments such as the rapid development of certain countries (such as India and China) have caused an increasing demand and also tensions concerning waste materials.

End-of-life tires (ELTs) are a source of secondary materials for all countries with strong growth and especially for countries with few natural resources, such as European countries. Thus, End-of-Life tires (ELT) can constitute a strategic economic stake for raw material producers and rubber compounders.

However, as with the recycling of other used materials, the recycling of ELTs by devulcanization is generally difficult because of the association with other different materials that may be incompatible with each other. Therefore there is a need to study and improve existing sorting methods in order to provide the recycling industry with clean products that meet demanding specifications.

Currently, it is estimated that 49% of ELTs are incinerated mainly in cement plants and 46% are recycled as secondary material, mainly used in the manufacture of objects and recycled rubber. However, this mode of recycling is principally focused on the creation of objects bonded with polyurethane and only a small part is devulcanized for further processing and reuse after formulation and vulcanization.

The recycling of ELTs as new material by devulcanization involves four processing phases: collection, granulation, devulcanization, and marketing.

By using homogeneous and clean tire granulates ground tire rubber (GTRs) can be used to produce a higher quality devulcanized material. Efficient sorting and separation of ELT waste is therefore necessary, especially when it concerns waste composed of different gums whose formulas have different devulcanization kinetics, such as styrene butadiene (SBR), natural rubber (NR), and polybutadiene (BR).

Today, there are no separation technologies available that can separate rubber according to its nature or formula; it is impossible to separate, for example, SBR from NR or SBR from BR.

It has been found that the waste tire recycling industry by devulcanization is not in tune with the technical realities of the sorting processes used by ELT granulators. In order to further develop this industry, it is necessary to review and improve these sorting techniques by imposing further criteria and more relevant rules that should be defined.

7.2.2 Existing sorting criteria and their limits

ELTs are generally sorted before the shredding stage. For economic reasons, the only criterion applied in sorting ELTs is based on tire dimensions.

ELT granulation professional mainly classify tires according to their size. They can be divided into three categories: ELTs from passenger cars are all small tires, ELTs from trucks are those of larger sizes, and OTR (off-the-road) tires are even larger or tires from construction machinery and the agricultural world are mixed. However, this size criterion is completely subjective and does not ensure an effective, real, and optimal sorting (a sorting that takes into account the nature of the different elastomers composing each tire and not only the size of the tires.) so that the granulated material is destined for the devulcanization industry.

In fact, some large tires contain layers of rubber used in the manufacture of small tires (LV) such as SBR, for example, which can be found in some truck tires. Medium-size tires (e.g., light truck tires) are also sometimes listed with truck tires and other times with light truck tires. The criteria used so far have been satisfactory as long as the use of the GTR concerned sports fields or the manufacturing of objects using polyurethane

compounding. For these applications, transformers often use truck/light truck mixtures without any problems.

However, these criteria are no longer sufficient when it comes to developing good-quality recycled products (high added value). Indeed, devulcanization is much more sensitive to variations in the input material and this sensitivity manifests itself in several ways:

1. Heterogeneity of the devulcanized material: presence of devulcanized and nondevulcanized parts.
2. Variation in the mechanical characteristics of the devulcanized material.
3. Nonrepeatability of the devulcanization process.

This makes it difficult to integrate the devulcanized material into production processes, which limit its commercialization.

7.2.3 Mechanical characteristics of devulcanized materials according to the type of end-of-life tires

We can classify the devulcanized material in three categories (in terms of mechanical behavior) according to the source (the origin of the treated material):

- *Truck tread*: product composed mainly of NR and BR. Truck tread aggregates are generally clean and homogeneous because they are the result of selective sorting. Indeed, these aggregates are the result of retreading truck tires selected according to a more precise criteria. Generally, the mechanical characteristics of tire tread can reach maximum stresses of 14–15 MPa and strains up to 400%.
- *The whole truck tire*: when properly sorted, truck tires are relatively homogeneous because, as mentioned above, a truck tire is essentially made up of NR and BR. The heterogeneity of this product is greater than the previous category for two reasons: firstly, the formulae of the different parts of the same tire are different and secondly, the formulae differ from one range of tires to another and from one brand to another. The mechanical characteristics of devulcanized whole truck tire revulcanizates vary from 8 to 12 MPa for ultimate stresses and from 200 to 300% for ultimate deformations.
- *VL tires*: VL tires contain NR and SBR. These two products have very varied devulcanization kinetics, which cause problems during devulcanization. The mechanical characteristics obtained with this product fluctuate between 5 and

8 MPa at maximum stress and can reach up to 200% maximum deformation in the best of cases (Table 7.2.1).

The heterogeneity of granulates, when it is important, limits their use as feedstock (input material) for the devulcanization industry because the resulting products are often of very poor quality. In order to reduce these fluctuations, sorting will have to be further refined by finding other means and selection criteria in order to obtain the purest possible products.

7.2.4 Analysis of ground tire rubber samples available on the European market

This study was carried out at Phénix-Technologies located in Sancheville (France). Four big-bags of GTR produced from truck tires were purchased from five different European manufacturers, specialized in the granulation of ELTs.

A protocol was set up to statistically analyze the composition of the different GTRs. It was based on the assumption that the truck tires contained only NR and BR.

This protocol is based on Fourier transform infrared (FTIR) analysis of granulate samples randomly recovered from each big-bag. Each sample is composed of approximately 500 granulates (five batches of one hundred grains each), the goal being to identify SBR-containing granules. Thermogravimetric analyses (TGA) were also conducted to identify the various components.

Three types of gums were identified by FTIR (Fig. 7.2.1). Two of the spectra (types 1 and 2) identified are those of NR and BR. The third spectrum is that of SBR (type 3), recognizable by its characteristic peaks, first at 967/cm, which corresponds to the vibration of the 1.4-trans, the peak at 911/cm corresponds to the vibration of the 1.2-Vinyl bond, and the peak at 699/cm, which corresponds to the vibration of the styrene bond [9].

At the same time, thermogravimetric analysis carried out under nitrogen, with a temperature ramp from 50°C to 550°C at 10°C/min, was performed on each type of granule identified by FTIR (Fig. 7.2.2).

The results of the thermogravimetric analyses (Fig. 7.2.2) confirm that the big-bags do contain three types of gum: natural rubber (degradation temperature under these conditions is 371°C); styrene-butadiene (degradation temperature of 413°C); and finally polybutadiene (degradation temperature of 453°C).

Table 7.2.1 Summarizes some examples of the mechanical characteristics obtained on revulcanizates of different types of used tires.

Process	Type of end-of-life tyre	Process parameters	Properties of revulcanizate	References
Thermomechanical	50% Trucks 50% Passenger	*Screw speed*: 50, 100, 150, 200, and 250 rpm, feed rate: 5 kg/h, *T*°: 180°C	*Stress at break*: 3–6.5 MPa, strain at break: 110%–180%	[1]
	Undefined	*Screw speed*: 80, 100, 120, 140, and 160 rpm, *T*°C: 160°C, 180°C, 200°C, 220°C, 240°C, ratio feed rate/rpm = 1.4	*Stress at break*: 5.62–12.5 MPa, strain at break: 337%–356%	[2]
Microwave	Passenger	900 W for 3 min, *T*° = 240°C, diphenyldisulfide as devulcanization agent	*Stress at break*: 10 MPa, strain at break: 226%	[3]
Ultrasonic	Unclassified (mixed tread and side walls of passenger and trucks)	120°C 20 rpm 3000 W 20 KHZ	*Stress at break*: 3–8.7 MPa, strain at break: 110%–217%	[4]
			Stress at break: 10.5 MPa, strain at break 250%	[5]
			Stress at break: 4.38–7.74 MPa, strain at break 131%–183%	[6]
Mechanical chemical	Nonclassified	Chemical devulcanization agent	*Stress at break*: 12.3–13.6 Mpa, strain at break: 330%–390%	[7]
	Tread from tire of heavy trucks	Internal mixer: 45 rpm 180°C and 200°C	*Stress at break*: 4.2–6.5 MPa strain at break: 220%–340%	[8]

It should be noted that the three gums identified above were found on all the big-bags received. A statistical analysis to estimate the proportion of each gum was carried out on the 500 granules analyzed for each batch. The results of the distribution of these different gums according to each batch are shown in Fig. 7.2.3.

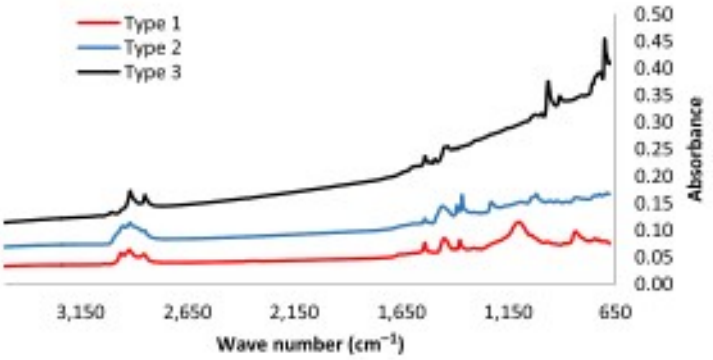


Figure 7.2.1 Fourier transform infrared spectra identified in the granules.

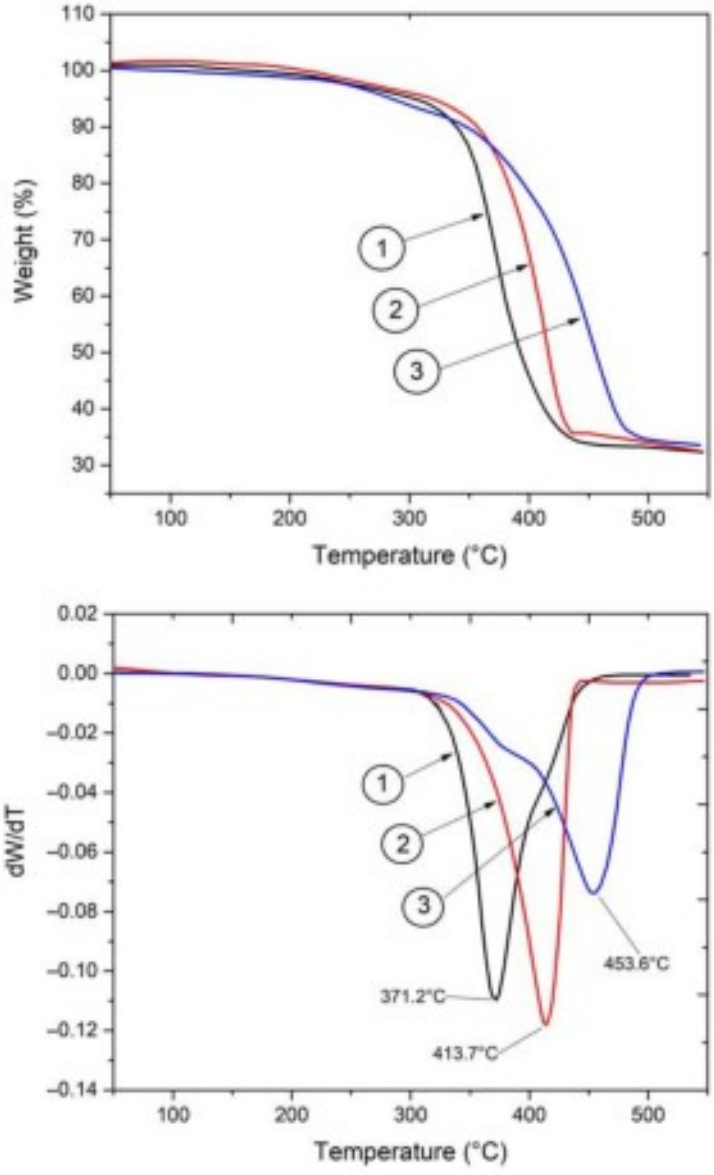


Figure 7.2.2 Thermogravimetric analyses of the three types of gums detected by Fourier transform infrared.

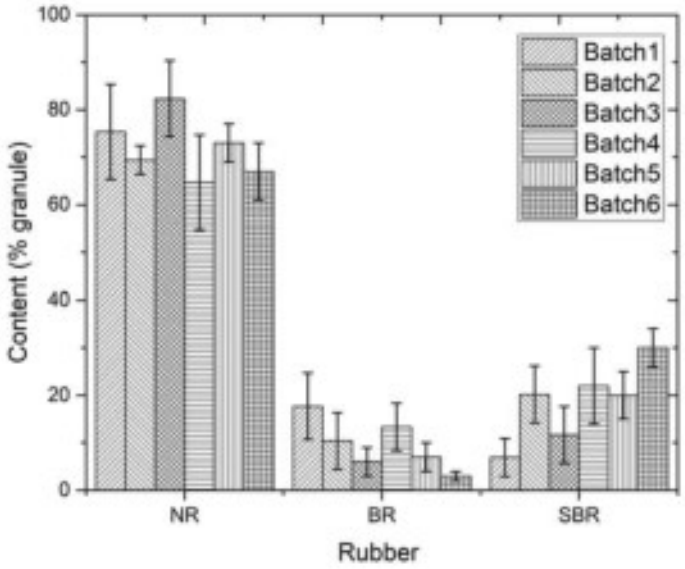


Figure 7.2.3 Distribution of the different gums by batches received and analyzed.

A very large dispersion of the proportion of SBR in each batch (Fig. 7.2.3) was observed, although truck tires are not supposed to contain this type of rubber. This proportion is estimated to be around 7% in batch 1 and 20% in batch 2, although the supplier is the same and the only difference is the delivery date of the two batches. In some cases, the proportion of SBR can be higher than 30%, as in the case of batch 6. What conclusion can be drawn from this situation?

7.2.5 Impact of ground tire rubber heterogeneities on the devulcanized material

In order to understand the effect of this dispersion on the quality of the devulcanized products, a sample from batch 1 and another sample from batch 2 were devulcanized and analyzed. To do so, the thermomechanical devulcanization process was used, under the same conditions, using a twin-screw extruder, corotating with a screw profile designed specifically for rubber devulcanization.

Visually, as can be seen, firstly, the strips extruded from the two batches (1 and 2) exhibit different morphologies (Fig. 7.2.4). Indeed, the strip obtained from batch 1 with an SBR proportion of about 7% is relatively smooth in appearance, in contrast to

Figure 7.2.4 Visual aspect of the two batches.

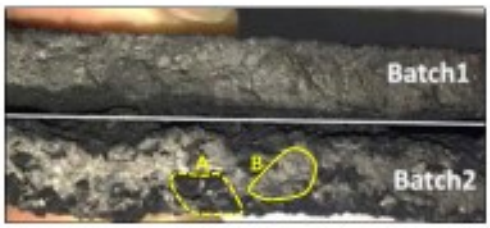


Figure 7.2.5 Extruded bands of two batches.

the aspect of the strip obtained from batch 2 with an SBR proportion of about 20%, which is more wrinkled and granular.

The cross-sectional view of two strips (batch 1 and 2) is shown in Fig. 7.2.5. Depending on the batch, the results showed significant material heterogeneities. Indeed, the general appearance of the band obtained from batch 1 is smooth, shiny, and homogeneous while that of the band from batch 2 is heterogeneous, with smooth domains resembling the smooth part of batch 1 (circled continuously – zone B) and granular domains (circled dashed – zone A).

Pieces of material were picked from both domains (A and B) of batch 2 and were analyzed according to the same procedure used for granule analysis (Fig. 7.2.1), using Fourier Transformed Infrared (Fig. 7.2.6) and Thermogravimetric analysis (Fig. 7.2.7).

FTIR analysis (Fig. 7.2.6) of the two domains observed on the faces of the two extruded bands (domain A and B) shows two very distinct spectra very similar to the spectra already obtained on the pellets.

In fact, the spectrum of zone A, corresponding to the granular domain, is characterized by three wave numbers, firstly that at 967/cm, which corresponds to the vibration of 1.4-trans; then the peak at 911/cm of the vibration of the 1.2-vinyl bond; and finally the peak at 699/cm, which corresponds to the vibration of the styrene bond. This spectrum indicates that this is the spectrum of the SBR. The smooth and devulcanized part, Part B, showed vibration peaks of natural rubber.

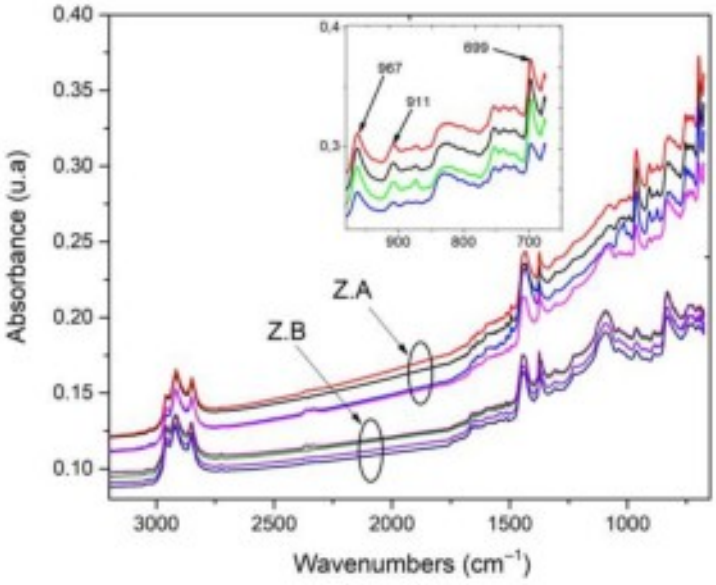


Figure 7.2.6 Fourier transform infrared analysis of zones A and B.

These observations are confirmed by TGA analyses (Fig. 7.2.7), which also shows that the smooth and glossy material (Part B) degrades at 373.4°C, which corresponds to the degradation temperature of NR. Concerning the material from zone A, its degradation temperature is about 420.8°C, almost corresponding to the thermal degradation temperature of SBR.

The presence of the nondevulcanized material domains is probably related to the difference in the devulcanization kinetics of the two gums (NR and SBR) after thermomechanical devulcanization using extruders.

It is therefore clear that the proportion of SBR plays a significant role in the devulcanization of NR/BR. Indeed, the increase of the SBR fraction from 6% to 20% changes the appearance of the devulcanized material, leading to the appearance of nonvulcanized material domains and reduces the mechanical characteristics (stress/strain).

Finally, a sample of each devulcanizate was formulated and then vulcanized to study their mechanical characteristics. For this purpose, the two samples were formulated with 4 phr ZnO (Zinc oxide), 2 phr stearic acid, 1 phr CBS (n-cyclohexyl -2-benzothiazole sulfenamide), and finally 1 phr sulfur (S). The mixture was processed on a cylinder mixer, then calendered (rolled), and finally vulcanized into a 2 mm thick plate.

The mechanical characteristics of the two products are very different. Indeed, a breaking stress of about 12 MPa and a

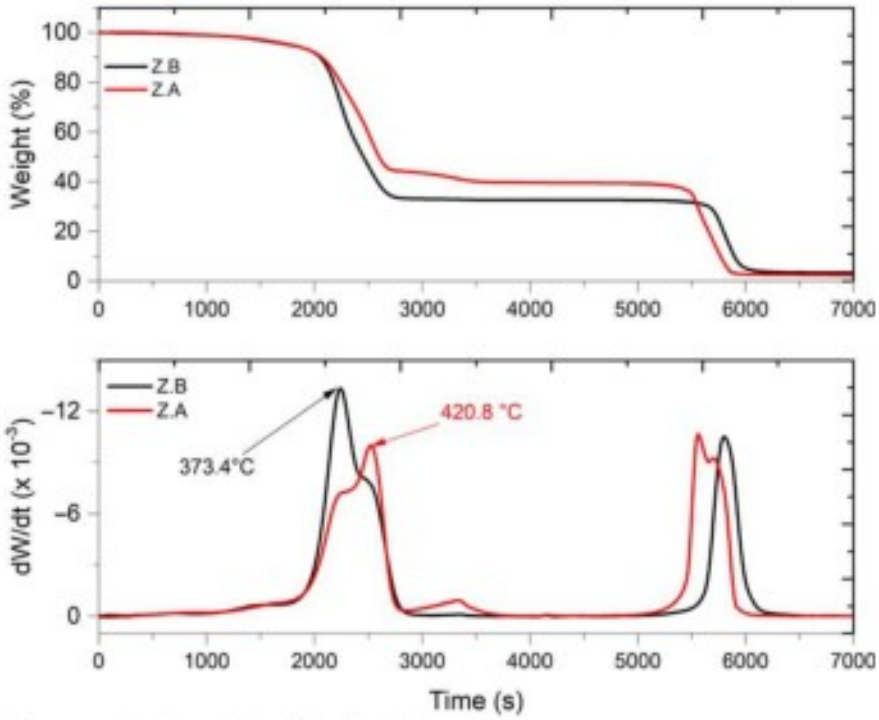


Figure 7.2.7 Thermogravimetric analysis of Part A and B.

breaking deformation of about 350% were obtained on the devulcanized material from batch 1 in comparison to 7 MPa and about 150% deformation for the material obtained from batch 2.

7.2.6 Analysis of ground tire rubber at the industrial scale (case of industrial output)

7.2.6.1 Analysis of the incoming material (aggregate or feedstock)

The industrial-scale FTIR analysis of a delivery of GTR-truck tire was carried out on 18 tons of powder with a granular size of between 1 and 4 mm, delivered in a single batch and by the same granulator, in 18 big-bags of one ton each. An analysis following the protocol described above was carried out on all the big-bags received. Fig. 7.2.8 shows the SBR ratios measured in each big-bag.

The average of the percentage of FTIR spectra containing SBR measured over all big-bags is around 23%, however, there is quite a large dispersion from one big-bag to another. Indeed, this

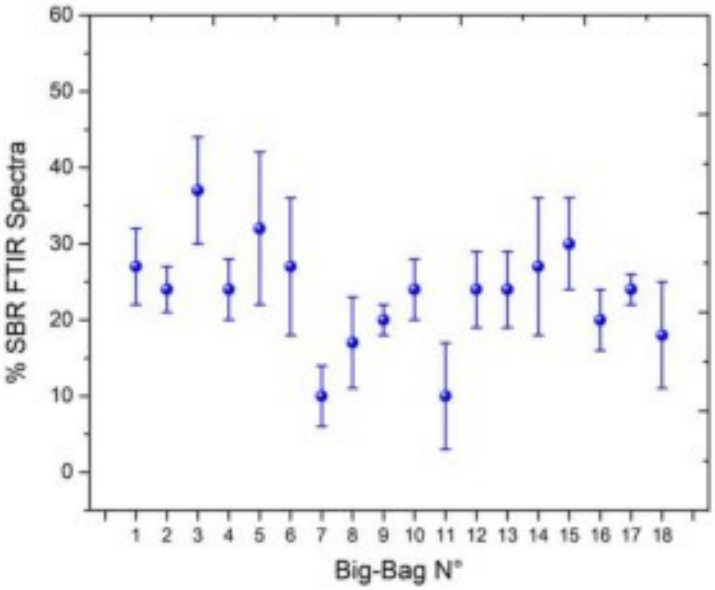


Figure 7.2.8 Statistical analysis of styrene butadiene in the different big-bags.

percentage varies from 10% in some cases to more than 30% in others. Moreover, the standard deviation measured in some cases in the same sample (i.e., in the same big-bags) is very large, which means that the protocol adopted is not very representative of the reality of a big-bag but only gives an idea of its heterogeneity.

Once the material was characterized, quantities of granules from each big-bag were devulcanized by the thermomechanical process using a 40 mm corporate twin-screw extruder (Leist Ritz Maxx40) with the same parameters for all the big-bags.

Devulcanization took five weeks at a rate of 70 kg/hour (i.e., approximately 700 kg/day). Three times a week (Monday–Wednesday and Friday of each week), samples were retrieved from the devulcanization line for analysis.

All samples recovered were analyzed; first to determine their viscosity, then to determine their mechanical characteristics after they were formulated and vulcanized (sulfur, zeno, CBS, and stearic acid).

7.2.6.2 Effect of the feedstock heterogeneity on the viscosity of obtained devulcanized rubber

Viscosity measurements were carried out throughout the production of the devulcanized material, which lasted almost a month. These measurements are shown in Fig. 7.2.9.

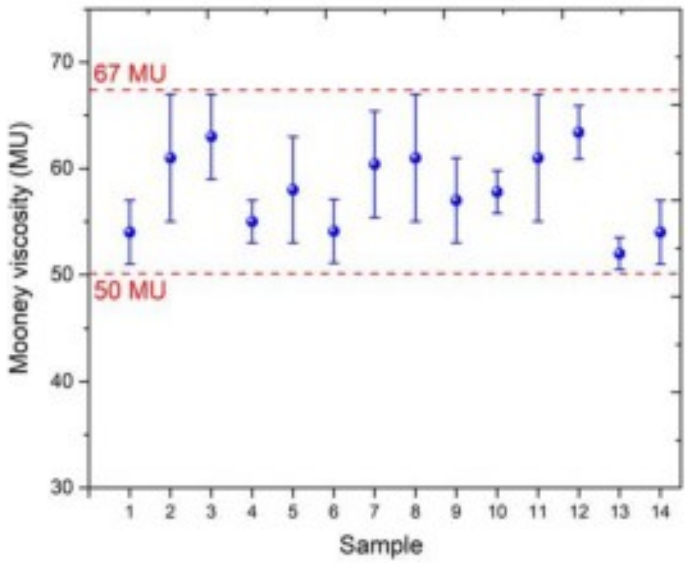


Figure 7.2.9 Viscosity of the different batches devulcanized along the production period.

The average viscosity over all samples is about 58 Mooney, however, it varies considerably from one big-bag to another. Indeed, the range of viscosity obtained varies from 50 to 67 Mooney. These variations are the consequence of the feedstock variation.

7.2.6.3 Effect of the feedstock heterogeneity on the mechanical properties

Throughout production, samples were collected, sulfur-accelerated, and vulcanized into 2 mm thick plates. H2 dumbbell type specimens were cut and tested according to the ISO37 standard and angular specimens were cut to perform tear tests according to the NFT 46-007 standard.

The results of these mechanical tests show the changes in stress at break (Fig. 7.2.10A), strain at break (Fig. 7.2.10B), and tear resistance (Fig. 7.2.10C).

As with viscosity, the mechanical characteristics of the devulcanized material vary greatly depending on the big-bags but also within the same big-bag. Variations ranging from 7.5–10.5 MPa are measured in terms of stress at break, from 150% to 245% in terms of deformation at break and finally from 16 to 22 N/mm in terms of tear resistance.

Again, the variation in the mechanical characteristics of the devulcanized material is strongly related to the variation in the homogeneity of the input material.

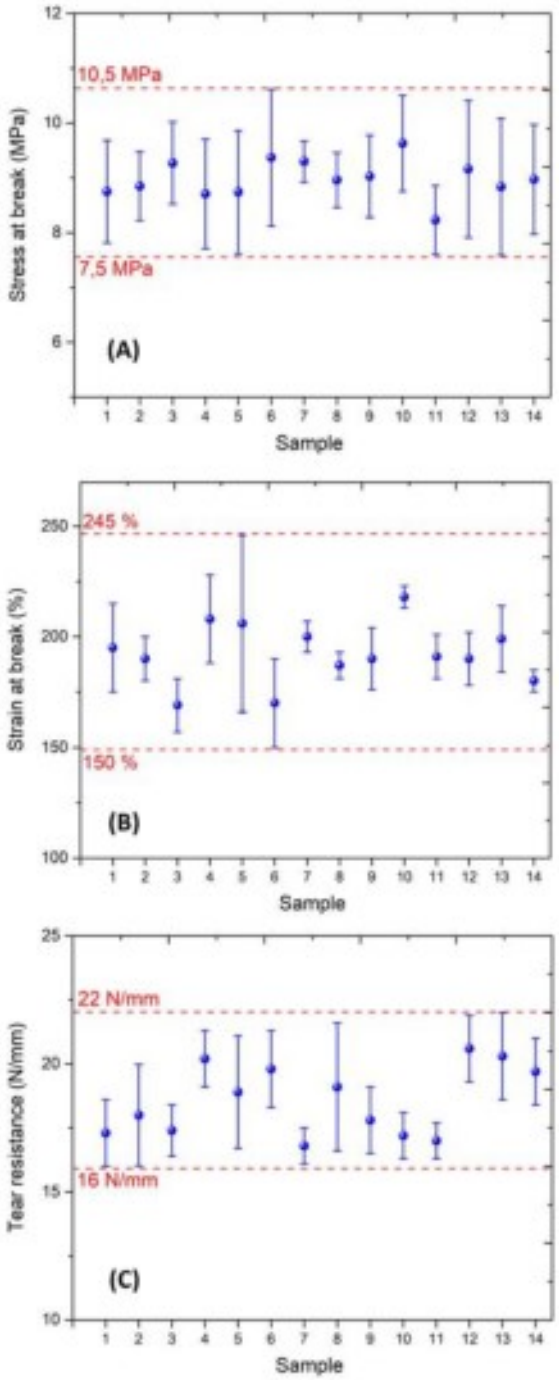


Figure 7.2.10 Stress at break (A), strain at break (B), and tear strength (C).

These variations have led some devulcanization manufacturers to provide only the minimum stress and minimal deformation on the technical data sheets of their products on sale; often, these characteristics are given with very wide standard deviations, a sign of very high dispersion.

7.2.7 Conclusion

New type of sorting other than the one existing or currently practiced must be implemented by used tire granulators to provide the devulcanization industry with cleaner, more homogeneous products. This would make it possible to avoid problems with the stability of the devulcanized material and also to stabilize and control the processes. These issues are a real obstacle to the development of the market for devulcanized material.

The improvement of the sorting condition should make it possible to reduce the heterogeneity of the GTR granules, thus reducing fluctuations in the characteristics of the devulcanized material and thus improving the mechanical characteristics once the material has been devulcanized, since the quality of the output material (devulcanized) depends essentially on the quality of the input material. This will enable the devulcanization industry to provide the rubber industry with more stable products with optimal mechanical characteristics.

Improving the homogeneity of the input material (feedstock) will also help the devulcanization industry to control the devulcanization processes because they will be more stable, more repeatable, and easily industrialized.

These conditions of process stability, repeatability, and ease of use are necessary for the devulcanization industry to produce a secondary raw material that can be valorized and for the rubber industry to be able to use it on a large scale in many industries.

The improvement of the sorting criteria will generate an additional cost for the granulation industry because it will require either additional investments or a larger and more qualified workforce. However, this additional cost can quickly impact on the devulcanization industry because it will allow them to have a more stable and easier to control process. Furthermore, they will also be able to offset part of this additional cost on their customers because they will be able to provide better quality and repeatable products.

References

[1] K. Formela, M. Cysewska, Efficiency of thermomechanical reclaiming of ground tire rubber conducted in counter-rotating and co-rotating twin screw extruder, Polimery/Polymers 59 (2014) 231–238. <https://doi.org/10.14314/polimery.2014.231>.
[2] G. Tao, Q. He, Y. Xia, G. Jia, H. Yang, W. Ma, The effect of devulcanization level on mechanical properties of reclaimed rubber by thermal-mechanical shearing devulcanization, J. Appl. Polym. Sci. 129 (2013) 2598–2605.
[3] M. Molanorouzi, S.O. Mohaved, Reclaiming waste tire rubber by an irradiation technique, Polym. Degrad. Stab. (2016). <https://doi.org/10.1016/j.polymdegradstab.2016.03.009>.
[4] A.I. Isayev, J. Chen, A. Tukachinsky, Novel ultrasonic technology for devulcanization of waste rubbers, Rubber Chem. Technol. 68 (1995) 267–280. <http://rubberchemtechnol.org/doi/pdf/10.5254/1.3538741>.
[5] A. Tukachinsky, D. Schworm, A.I. Isayev, Devulcanization of waste tire rubber by powerful ultrasound, Rubber Chem. Technol. 69 (1996) 92–103.
[6] A.I. Isayev, T. Liang, T.M. Lewis, Effect of particle size on ultrasonic devulcanization of tire rubber in twin-screw extruder, Rubber Chem. Technol. 87 (2014) 86–102. <https://doi.org/10.5254/RCT.13.87926>.
[7] B. Vorobyev, R. Leonid, Method of devulcanization of sulfur-cured rubber, 9982107, 2018. <http://www.freepatentsonline.com/9982107.html>.
[8] X. Zhang, P. Saha, L. Cao, H. Li, J. Kim, Devulcanization of waste rubber powder using thiobisphenols as novel reclaiming agent, Waste Manage. 78 (2018). <https://doi.org/10.1016/j.wasman.2018.07.016>.
[9] S. Das Gupta, R. Mukhopadhyay, K.C. Baranwal, A.K. Bhowmick, Reverse engineering of rubber products, 2013. <https://doi.org/10.1201/b15435>.

8

Make rubber, sell rubber: building a sustainable industry

D. Elroy Fimrite[1] **and Carl D. McAfee**[2]

[1]*EFG Polymers LLC, Bay City, TX, United States* [2]*McAfee Consulting LLC, Kennedale, TX, United States*

8.1 The value proposition

"*A waste tire solution that is sustainable using market price economics.*"

Objective: The purpose of this chapter is to provide readers with a nontechnical understanding of the devulcanization of tires and other rubber waste and the economic value of the end products thereby derived. The purpose of this book is to assist governmental and other responsible parties, who must deal with waste rubber and tires, in determining sustainable solutions for the arisings in their jurisdiction. To accomplish this goal, this chapter will address the capture and conversion of waste tires to a valuable new material. We will further address the scope and scale of market opportunities for the new material and the economic matrix of the available market. Our goal is to contribute an understanding of the scale, efficiencies, properties, advantages, disadvantages, market opportunities, market barriers, technical challenges, and the historical performance of devulcanization as a global solution to the waste tire problem. We will define the "value proposition" of devulcanization.

Limitation: This chapter will not explore the processes of achieving devulcanization. Numerous research papers [1–4] and various patents [5,6] filed are available to those seeking a deeper understanding of available technologies. Instead, we will provide a roadmap for building a sustainable devulcanization industry into which any new or existing devulcanization technology can participate and contribute to solving the waste tire challenge. References will be included in this chapter to EFG–SBE, devulcanized styrene butadiene

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00009-0
© 2021 Elsevier Inc. All rights reserved.

elastomer produced by EFG America LLC at their Bay City, TX facility. Properties and applications may differ between EFG–SBE and other manufacturers' devulcanized products.

8.2 Understanding the problem

Volume of waste rubber: It is important to understand the magnitude of the waste tire problem and to do so we must first understand that very little of the available statistical data generated anywhere in the world is accurate. Estimates of new tires produced per year total around 1.6 billion and estimates of waste tires arising are typically about 1.0 billion per year [7], which would mean that tires in usage increase about 600 million per year. Obviously, there is a disconnect between these numbers. Published data variously includes or omits aircraft tires, agricultural tires, mining tires, heavy equipment tires, and solid wheels such as forklift tires. In addition to tires, each automobile manufactured contains a myriad of other rubber parts. Historically, tires and automotive are estimated to consume about 75% of virgin rubber, which means that about 25% of global rubber consumption is in products and applications about which very little data is generated and very little recycling effort is focused.

Notwithstanding the various types of rules and regulations, tires continue to accumulate in large numbers around the world. Some large tire dumps, captured by satellite images [8] over the years, are the following:

Tire Pits: Site 120 Acres Each Pit Approx. 100 ft. by 300 ft.-Hudson Colorado.[1]

[1]Hudson Colorado Images: Sep 1999 Google Earth, US Geological Survey; Oct 2005 Google Earth USDA Farm Service Agency; Sep 2019 Google Earth.

Tire Pits and Tire Pond, Cottonport LA.[2]

Sulaibiya Tyre Graveyard, Kuwait. New pits at right covered with Sand.[3]

Alternative approach: Another approach to determining the volume of waste rubber is an analysis based on the global volume of natural and synthetic rubber produced and consumed. For most of the past ten years, the production and consumption of natural and synthetic rubber has exceeded 25 million metric tons per year or over 25 billion kg/55 billion pounds per year [9]. With typical rubber compounds containing over 50% polymer, the rubber compounds generated therefore are about 45 billion kg/100 billion pounds per year. With current global population of about 7.8 billion people, we generate/consume, conservatively, over 5 kg/12 pounds of rubber for every human being each year.

Nature of rubber waste: Rubber is a uniquely resilient material; our modern world could not operate without the versatility and unique properties of rubber. Vulcanized rubber will not rot, rust, dissolve, leach, evaporate, or even substantially change its properties over time. Fortunately, because vulcanized rubber is so resilient, it also does not poison the environment unless

[2]Cottonport Images: Jan 1998, Google Earth US Geological Survey; Jun 2006, Google Earth USDA Farm Service Agency; Nov 2019, Google Earth.
[3]Sulaibiya Images: Google Earth, 2020 Maxar Technologies

burned. Each rubber product is composed of rubber polymer and other ingredients designed to deliver specific physical and chemical properties. This poses unique recycling problems, as solutions for one type of rubber may be ineffective for other types of rubber. There are multiple different types of rubber compound in each tire and a myriad of types of rubber compound in a single automobile. Collectively, the various rubber components of an automobile are referred to as S.K.O.R., an acronym for "Some Kind of Rubber."

Beyond tires: We are all familiar with the problems we face with waste tires. The reality is that this is only part of the waste rubber problem. In addition to all of the end-of-life tires and other rubber products, we also generate considerable waste in the manufacture of rubber products. Complicating matters further, some of the factory scrap is vulcanized, some is partially vulcanized, and some is not vulcanized. Unvulcanized waste may be "productive/loaded" with curing agents and ready for vulcanization and some is "nonproductive" compound, rubber compound with no curing/vulcanization ingredients.

In summary, the rubber waste problem appears to be very large; the real rubber waste problem is even bigger than it appears. The wastestream of rubber is very diverse and the rubber materials are very difficult to process due to the multiple compounds and the stage of processing at which the waste is generated. Tires are highly engineered products designed to be indestructible so do not easily convert to a feedstock. About one third of the rubber in a tire is carbon with a hardness of 5 Mohs, and carbon black is very hard on tire recycling equipment and cutting edges.

8.3 Conversion: challenges of processing tires to ground tire rubber

In any recycling business, receiving the waste, sorting, separating, cleaning, and applying primary processing is the most difficult challenge faced. For many postconsumer products, contamination is a significant recycling challenge. With tires chemical contamination is not typically a problem, but contamination with dirt, rocks, rims, nails, screws, glass, rodents, and insects are all factors. If undetected and not removed, these foreign materials are detrimental to the feedstock, dangerous to the workers, hard on processing equipment, and difficult to remove if passed through the recycling process. The second challenge is streaming of the type and size of tire when most

sources of waste tires generate, and expect a waste processor to take, all types and sizes of tires.

Scrap tire recycling technologies: Almost all "ambient" tire recycling equipment is similar in process and generally involve the following stages and equipment type:

1. Primary shredder: For most truck, light truck, and passenger car tires, the primary shredder simply uses brute force to grab and rip the tire into 4–6 inch/10–15 cm pieces with no separation of any component of the tire.
2. Secondary shredder: This stage takes the primary shred materials and further reduces the tire rubber to 1 inch/25 mm nominal material. In this stage steel belting and beads are often removed magnetically, usually with significant rubber still attached to the steel.
3. Primary granulation systems reduce typically 1–2 inch/25–50 mm material to a ½ inch/12.5 mm minus and most residual wire is removed.
4. Secondary granulation systems include a variety of processing technologies including cracker mills, depending on the system and operators design product. Size reduction typically produces a ground tire rubber (GTR) mix of particle sizes between 10 mesh/2.0 mm and 60 mesh/0.25 mm.

A wide variety of supplemental equipment is used for removing bead wire, sidewall cutting, screening, fiber removal, etc. The bulk of the tires that are recycled currently are only processed through part of these stages as the markets the processor is serving do not require smaller particulate and the smaller the particle the higher the processing cost. The largest market is for tire derived fuel (TDF) with users requiring anything from whole tires to 1 inch/25 mm material.

Alternative processing systems: In some configurations, cryogenic size reduction systems replace some phases of processing and in production of very fine granulate/powder wet-grind mills are also used. Ultrafine granulation specialty systems, with extensive processing and expense, process GTR in size ranges from 60 mesh/0.25 mm to 200 mesh/0.074 mm.

Scrap tire recycling dysfunctions and inefficiencies: Tire recycling equipment often evolved from auto and scrap steel shredding systems and have not improved significantly because most of the product produced has low value. Tire derived fuel, mulch, sports field infill, and civil engineering applications do not use the rubber as rubber. Even in asphalt rubber, molded goods, and automotive/tires, the use of GTR is as a filler or aggregate and does not serve as an active polymer. It can be encapsulated in asphalt, polyurethane, or a new rubber compound, but is not bonding at a molecular level because it is still vulcanized. The morphology of

particulate may have differential benefits and high natural rubber (NR) versus high styrene butadiene rubber (SBR) GTR may be preferred by some customers. The effect of this is as follows:

1. Brute force with large consumption of energy is typical in most processing equipment.
2. Separation of materials is typically limited to separate processing of passenger, truck, and off-road tires.
3. Little or no effort is made to separate different segments/compounds within a type of tire such as separation of the butyl rubber inner liner, sidewalls, carcass, and tread.
4. The combination of poor economics, low-quality markets, and difficulty of processing rubber due to carbon black content means that equipment maintenance is neglected and GTR with residual contaminants, fiber, or steel results.
5. Other factors, emerging in the constant evolution of tires, are not reflected with processing technology advances such as the introduction of Kevlar in tires.

8.4 Historical solution model: the reclaim industry

Reclaim industry: The rubber waste disposal problem was created by the invention of vulcanization in 1839. In the 1880s, the first rubber recycling technology called "reclaiming" was invented. Reclaim technologies successfully dissolve the sulfur bonds formed in the vulcanization process, but also sever bonds within the rubber molecules and thus significantly diminish the properties of the resulting reclaimed rubber. By 1942, rubber reclaim volumes in the United States exceeded 350,000 tons per year [10]. To help solve the shortage of rubber during WWII, several large reclaiming operations were established in North America, the last of which, U.S. Rubber Reclaiming Inc., ceased operations in 2010. The reclaiming technology continues to be used, mainly in China and India. However, the processes are inefficient, require large amounts of labor, energy, machinery, and produce useable, but poor quality, devulcanized rubber. Notwithstanding these problems, there are about 1000 reclaim plants in operation in China with production capacity in excess of 6 million metric tons per year. Many of the Chinese plants use coal tar-derived softener and other high pollution ingredients [11]. Products produced with reclaim from these sources increasingly cannot meet the environmental standards for export.

Solution roadmap: While the quality of reclaimed rubber severely restricts its product applications, the previous structure

and approach of the reclaim industry participants provide a roadmap for the structuring of a new devulcanization industry. In 1956, the Rubber Reclaimers Association, Inc. published the "Manual of Reclaimed Rubber," edited by J.M. Ball [12]. In the manual, the chapter titles were as follows:

1. What is Reclaim?
2. Advantages of Reclaimed Rubber
3. Types of Reclaimed Rubber
4. Compounding of Reclaimed Rubber
5. Commercial Uses of Reclaimed Rubber
6. Appendix
   - Laboratory Test Methods
   - Chemical Analysis
   - Miscellaneous Items (S.A.E. −ASTM Specifications)

This information and instructions for reclaimed rubber is precisely the information producers of devulcanized rubber need to produce today to market their product in the conventional rubber industry. Additionally, the structure provides a guide for investors, lenders, or other stakeholders to evaluate the viability of proposed new devulcanization technologies.

Establishing benchmarks: The previous North American and European Reclaim industries and the current Indian and Chinese Reclaim industries are proof that the scale and market opportunity exists for recycling rubber back into conventional rubber products. Depending on the properties achieved by a particular devulcanization technology, this can include tires, which means market opportunities with potential usage volumes that can solve the scrap tire and rubber waste problem. To achieve that solution and scale, the new devulcanization industry has to overcome the technological and environmental problems that precludes the reclaim technologies from becoming the global solution. The problems that must be overcome are as follows:

1. The product must have chemical and physical properties that support inclusion at significant ratios in new rubber goods including tires.
2. The production of the product must meet US and EU environmental standards.
3. The product must not have an offensive odor.
4. The product must be safe for employees manufacturing or using the product.
5. The feedstock used must be consistent in size, compound type, and ratio of polymer to nonpolymeric components.
6. The feedstock must be clean and free from contaminants.
7. The production process must be scalable to produce very large volumes of product.

8. The form of the end product, slab, or particulate must be suitable to existing customer material management systems.
9. The product must have complete product and safety data to facilitate shipping and handling.
10. The producer must have adequate facilities to ensure reliable deliveries.
11. The producer must have operational premises consistent in cleanliness with customer expectations.
12. The producer must have quality assurance monitoring and enforcement suitable to customer standards.
13. The product must have sufficient shelf-life without reversion to facilitate shipping time and a reasonable storage time prior to usage.

8.5 Defining devulcanization

A challenge of devulcanization technology is the definition. What exactly constitutes devulcanized rubber? The answer is in the end result of the product. If it is elastomeric in nature, then it is in essence "devulcanized." Otherwise, the material is just a powdered polymeric filler that has been reduced in size from a tire to a small particle powder. For devulcanized materials, the extent of the devulcanization is determined by the measurement technique or test, which defines the degree of devulcanization or the amount of bonding sites that are available for bonding. For the purposes of this chapter and discussion, devulcanization is defined as at least 75%–80%. As a point of reference, the EFG polymer material has been tested and determined to be "devulcanized" or to possess a "crosslink density measurement" of at least 85% by the solvent swelling method (ASTM D6814-02). This method is indicative of the amount of crosslinking.

Other methods that are often described as repurposing are chemical and mechanical shear methods, microwave and ultrasonic methods, and various other extrusion-based methods. For the record, there are no official ASTM-based methods for "degree of devulcanization." From a practical perspective, a method that EFG polymers use to determine devulcanization efficiency is to take 100% of the reprocessed material and add a general-purpose cure package to the material on a two-roll mill. The cure is added to the material and the resulting rubber compound is cured in a compression mold. If the resulting cured rubber sheet has physical properties at or above a minimum

threshold, the material is deemed "devulcanized" and ready for use as a repurposed rubber elastomer. This method is also deemed effective as a quality control procedure for the product.

8.6 Measuring results

When considering testing and measurement approaches to differentiate the various recycled technologies, one must consider the full aspect of formulating, mixing, processing, molding, performance, and economic perspectives. To this end, the authors have prepared a series of rubber mixes that compare the various recycling technologies to a standard SBR/carbon black reinforced rubber compound.

For this data set the formulation from ASTM D3191, which uses a standard SBR material at 100 phr and a standard carbon black at 50 phr with associated process oils, metal oxides, and curatives, was employed. The various recycled technologies used in the comparison were:

1. ambient grind GTR;
2. cryogenically ground GTR;
3. recovered carbon black from pyrolysis (rCB); and
4. devulcanized rubber EFG−SBE (styrene butadiene elastomer) recovered/devulcanized from the EFG proprietary devulcanization process.

The above materials were mixed, molded, tested, and evaluated with a design of experiments statistical analysis for a complete evaluation of the respective technologies.

For the complete data set and technical analysis, the authors refer the reader to their paper that was presented at the International Elastomer Conference, on October 19−23, 2020 [13], given virtually due to the CoVid-19 protocols set in place by the organizing committee. An executive summary is given for the purposes of this book chapter. The various mixes were prepared and molded into test specimens for the corresponding tests.

Physical properties: From a physical property perspective, the following were measured: (1) tensile; (2) tear; (3) elongation; (4) 100% Modulus; (5) cure properties of Ts2, Ts50, Ts90, and Ts100; (6) maximum torque, MH; (7) Minimum Torque ML; (8) Mooney viscosity; and (9) Goodyear rebound.

Processability: From a processing perspective the samples were evaluated with the Alpha Technologies Rubber Process Analyzer (RPA) via the ASTM D6204 test method. This test method is used to measure viscoelastic properties of raw rubber

as well as unvulcanized rubber compounds. These viscoelastic properties give an indication as to factory processing behavior.

Dynamic properties: From a dynamic perspective the samples were also tested on the RPA via the ASTM D6601 test method. This test method is used to give dynamic properties of G' (modulus), n* (polymer viscosity), and tangent delta (a measure of heat buildup) in a dynamic application.

The final test was the Payne effect via the ASTM D8059 on the RPA. This test gives an indication of the polymer/filler interaction. The higher the polymer filler interaction, the more elastomeric the compound, which in turn gives a more rubbery or dynamic material. Lower values are deemed "less desirable."

8.7 Market opportunities

There is no point making dog food if the dog will not eat it.

The market opportunities for recycled/repurposed materials are endless. Considerations must be made for: (1) product performance, (2) processing, (3) physical properties, and (4) economic value. If all of these conditions are met, then the material has a high degree of probability for commercial success. Current markets that are being successfully pursued are: (1) thermoset rubber, (2) thermoplastic elastomers, (3) thermoplastic olefins, (4) polymer-modified asphalt roofing, and (5) polymer-modified asphalt paving. For the purposes of this chapter, the above markets can successfully use from 20% to 100% replacement of existing materials. These applications are beginning to illustrate the potential volumes of appropriately devulcanized rubber as a potential solution for end-of-life tires.

Advantages of devulcanized rubber: Tire rubber devulcanized by different technologies will have different properties. However, the core ingredients are the components of tires and thus will include reinforcing fibers, processing oils, antioxidants, antiozonants, accelerators, and residual curing elements. Devulcanization does not remove any constituents and thus these ingredients contribute their beneficial properties to any product made with the devulcanized rubber.

Thermoset rubber market:

The true test of recycling is returning materials to their original application. Devulcanized rubber can do that plus contribute additional properties that may yield beneficial properties originally noted in documentation of reclaim rubber [12] including:

1. *Attractive price:* The devulcanized rubber typically contains about 50% rubber polymer and 50% other

ingredients so price comparisons must include the respective costs of all of the ingredients contributing to the new compound.

2. *Stable price:* The market prices of virgin synthetic and natural rubber are subject to significant market volatility while devulcanized rubber is very stable due to the lack of alternative markets for the waste tires, thus enabling long-term supply contracts.
3. *Uniformity:* Providing that the manufacturer of devulcanized rubber manages the selection of feedstock, the devulcanized rubber will be uniform from shipment to shipment.
4. *Short mixing time:* The prior mechanical working combined with the prior inclusion of additives typically will shorten the mixing time for devulcanized rubber compared to new rubber.
5. *Low power consumption:* The requirement for less mechanical working reduces the power consumption.
6. *Low heat development in processing:* Devulcanized rubber develops less heat in processing, which reduces scorch in high carbon black-loading compounds.
7. *Fast processing:* Devulcanized rubber will typically process faster during extrusion and calendaring than new rubber.
8. *Low thermoplasticity:* Devulcanized rubber will typically be less thermoplastic than new rubber and is therefore less affected by continued milling. It will contribute to holding a product's shape during processing and curing of a compound.
9. *Reduce swelling and shrinking:* The addition of devulcanized rubber to a compound can improve dimensional stability and minimize swelling of extruded products.
10. *High rate of cure:* Devulcanized rubber included in a product can significantly increase the rate of cure contributing to savings in energy and reducing cure time, thus freeing up mold capacity.
11. *Minimizes reversion:* Compounds including devulcanized rubber are typically less susceptible to reversion, a softening of a rubber vulcanizate that results in stickiness and loss of properties.
12. *Ages well:* The detrimental affect of ageing on rubber products results from oxidation of the rubber and contributes to hardening, cracking, or loss of elastic properties. Devulcanized rubber is more resistant to aging that most new rubber compounds.

Not all devulcanized rubber compounds will provide all of the above benefits as the quality, nature, consistency, and

polymeric content of the feedstock as well as the type of devulcanization process will yield different results.

New market opportunities: The size, diversity, and history of the conventional thermoset (vulcanized) rubber industry is typically the target market for devulcanized rubber. Over the past three decades several new markets have emerged that offer large and potentially very profitable market opportunities for devulcanized rubber including the following:

1. *Thermoplastic polyolefins:* The emergence of families of polymers that are solid at ambient temperatures but are thermoplastic have grown extensively in the past 40 years. TPEs are used extensively in the automotive appliance and roofing industries. These markets have huge opportunities for the application of devulcanized rubber. In this market sector, devulcanized elastomers have been developed and shown to perform as follows:
   - Formulations have been developed to replace SBR and SBS in numerous thermoplastic products.
   - Provides a shear viscosity stabilized formulation that mimics TPOs.
   - Formulations developed at ratios of 5%–50% of the compound.
   - Qualifies to be compounded with recycled plastic to achieve structural component requirements.
   - Qualifies for usage in composite railroad ties, composite structural lumber, and other composite applications by increasing melt viscosity and providing valuable carbon black as a reinforcing agent to end products.
   - Offers higher coefficient of friction in composites due to the presence of carbon black, which reduces spike and nail removal, which is desirable in structural applications.
   - Qualified for marine applications as it will not rot or be susceptible to insects or biologics due to internal zinc-based soaps.
2. *Polymer-modified asphalt roads:* In most of the world, the construction of roads using a polymer modifier in the asphalt has become necessary to improve the performance of the pavement. The most common polymer used for road asphalt modification is SBS (styrene butadiene, styrene), a synthetic polymer. In Kuwait EFG–SBE was successfully tested to replace 100% of the virgin polymer and was installed in a test hot-mix application successfully. EFG–SBE was successfully used as modifier in over 15 projects in Arizona in 2018 including replacing SBS in PMAR (polymer-modified asphalt rubber) projects as follows:

- High Volume FAST (Chip and Fog Seal) projects
- Low Volume FAST (Chip and Fog Seal) projects
- Low Volume FAST (Chip and PPM Seal Coat) projects
- Rubberized Asphalt Scrub Seal project
- HV FAST SAMI and Hot-Mix Overlay project

The applications have all performed as expected from installation to the present time. The applications and testing in this market segment have established that devulcanized rubber, EFG–SBE, can replace up to 100% of the virgin polymer with the following results:

- Replaces virgin polymers currently approved for polymer-modified asphalt resulting in considerable cost savings and stability of pricing.
- In hot mix applications can achieve targeted PG 76–22 or even PG 82–22 if needed due to high-temperature location.
- Blends easily without shear mill and maintains mix stability for extended storage time.
- Applied in ratios of 5%–15% depending on binder properties.
- Maintains stable viscosity in bitumen solution, and operators find it easier to work with than SBS.
- Installed in hot-mix application, formulations developed for subbase, base, and wear courses.

3. *Polymer-modified asphalt roofing:* The EFG–SBE devulcanized rubber has been tested for the replacement of virgin polymers SBS and SEBS in various roofing asphalt products with the following results:
   - Accepted for replacement of SBS in roofing shingles
   - Accepted for replacement of SBS in sheet roofing
   - Formulations developed, tested, and accepted for replacement of 50% of SEBS in built-up roofing asphalt
   - Adds additional high-value carbon black and antioxidants at no extra cost
   - Provides enhanced viscosity stabilization over a broad temperature range
   - In BUR applications, can be heated to much higher temperature than SEBS in installation without performance failure
   - Provides additional heat stability safety during the application process

The introduction of a new product or new material is always a challenge; users do not like to change but will do so if there is a demonstrable economic, legal, or operational value to them. They must be comfortable with the viability of the supplier and must do sufficient testing to ensure there are

no downstream problems that will result. The diversity of markets and the size of each of the markets available for devulcanized rubber will create the opportunity for new devulcanization technologies to capture a significant segment of the virgin polymer marketplace and create jobs and value out of waste tires.

8.8 Building an industry

New material: It is important to recognize the devulcanized product as a new material. Producers of any new material must first conduct sufficient testing to prepare a comprehensive "Safety Data Sheet" as without an SDS product cannot be produced, shipped, tested, stored, or sold. In addition, proponents of each different process or technology for achieving devulcanization must ensure that any additional chemicals or ingredients added in to the waste rubber as part of the process do not negatively impact users of the product. As a "new material," it is important to not restrict the examination of market opportunities to the industries or applications from which the feedstock was generated.

Commercial technology: As we consider the steps required to build an industry to repurpose "end-of-life tires," we must evaluate the business model. For successful regeneration/devulcanization, the EFG polymer commercial process begins with GTR (ground tire rubber) of approximately 30 mesh particle size. Technology exists and sufficient companies are in place to supply this material in quantity. However, as the devulcanization industry evolves, the separation of different rubber compounds and blending to ensure a consistent polymeric profile will improve the end products and add additional value. The chemical and physical processes required to convert the GTR into regenerated/devulcanized material also exist and are in place to provide sufficient material in large quantities. The EFG Polymers Bay City, TX plant has annual capacity of 15,000 MT per year with the current two production lines. This system is easily scalable to become 30,000 MT or 50,000 MT per year. The plant has established critical criteria for commercial production, with the ability to produce large volumes of consistent product with marketable elastomeric properties at a low cost, relative to market prices of competitive elastomers. The selling of a new material is a technical process and the

producer must have the technical support team to work with introduction of the material into customer formulations. The marketing challenge is to find appropriate industries with receptive leaders and scientists willing to test and evaluate the material on an overall approach. With appropriate technical support, consistency, competitive properties, large volume availability, patience, and a favorable price, the market opportunity is infinite.

8.9 Thermoset rubber

To successfully incorporate this technology into thermoset rubber applications, it is critical to not just use one set of parameters like tensile strength. All properties must be considered for the successful implementation. For the thermoset rubber market, they are: (1) physical properties, (2) processing properties, (3) performance properties, and (4) economic properties. The overall "balance of all properties" has to be the answer for the overall technical and economic success of the approach. Fig. 8.1 illustrates the various physical properties of the different mixes. Rubber compounds are generally specified based on certain physical property requirements (i.e., hardness, modulus, elongation, cure time, etc.). Fig. 8.4

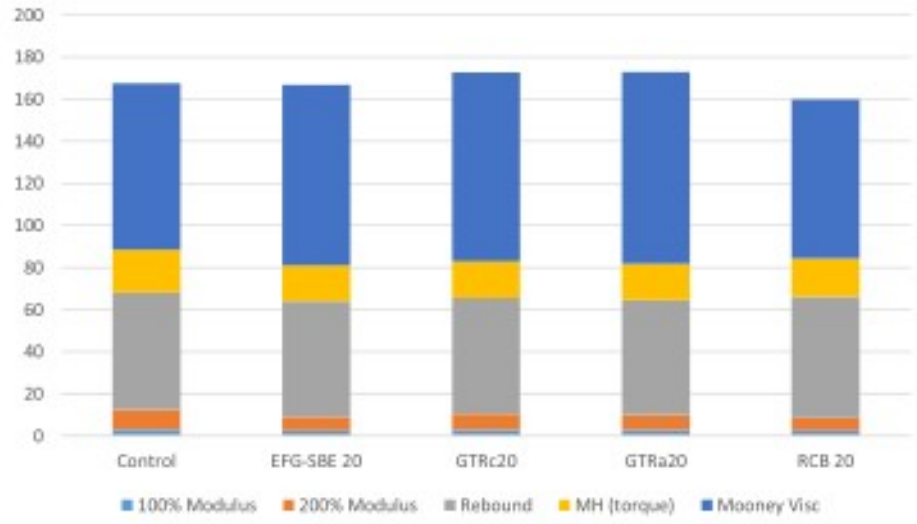


Figure 8.1 Physical properties of various mixes.

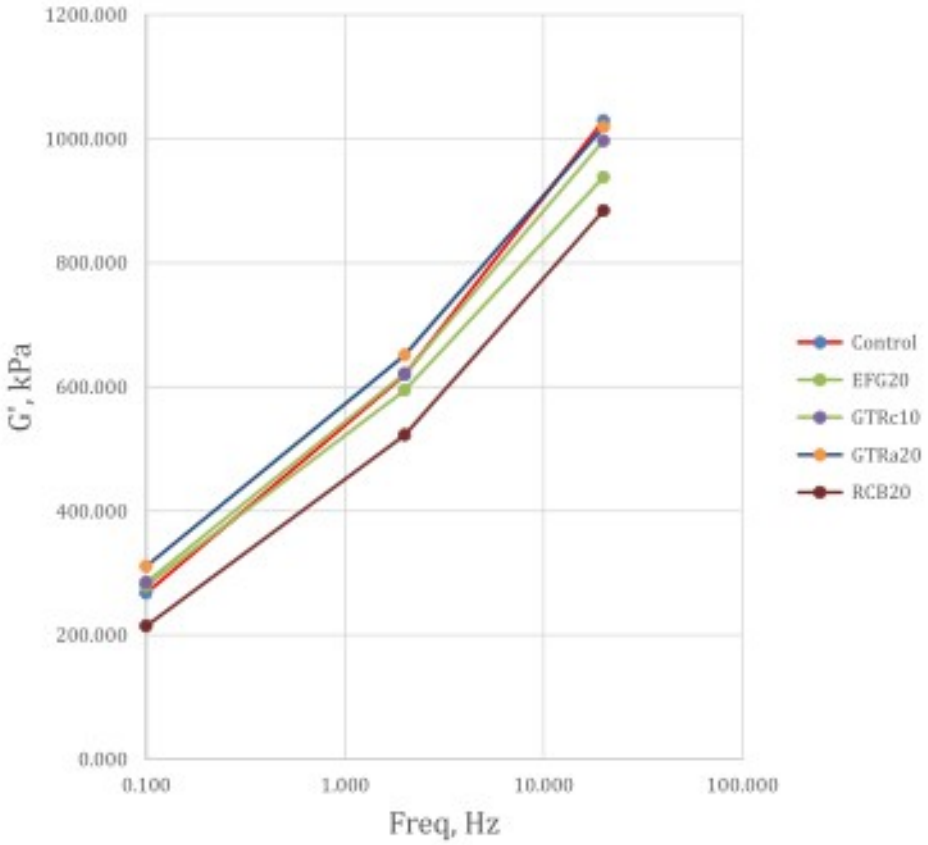


Figure 8.2 Processing ability of various mixes via ASTM D6204.

illustrates the Payne effect of the various mixes. This test focuses on the polymer/filler interaction. A desired result is one that is closest to the control. Too high or too low a value is not desirable. Fig. 8.2 illustrates the compounds processing capability in the uncured state. Again, a result closest to the control is desirable. If the uncured viscosities are too high then molding and shaping the compound for the final product is difficult. If viscosities are too low, the final part struggles to maintain shape until cured (Fig. 8.3).

Balance of properties: Fig. 8.5 shows the desirability function result from a statistical software program that uses a series of linear equations based on the data set to optimize multiple differing criteria [14,15]. The resulting answer is a

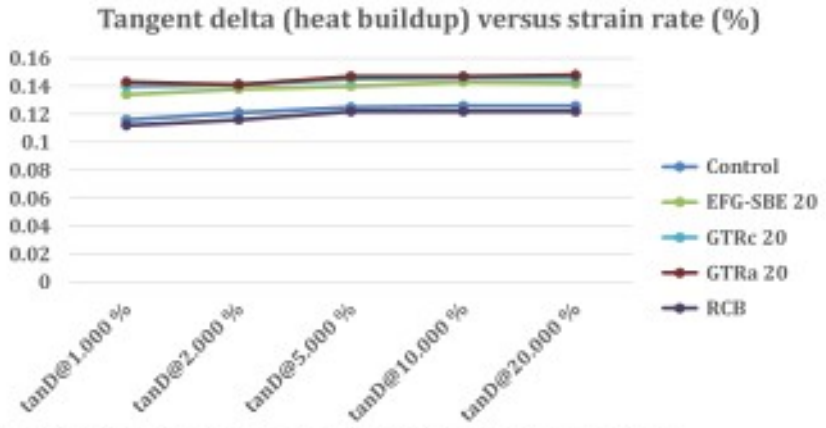


Figure 8.3 Dynamic properties of tangent delta (heat buildup) versus strain rate (%).

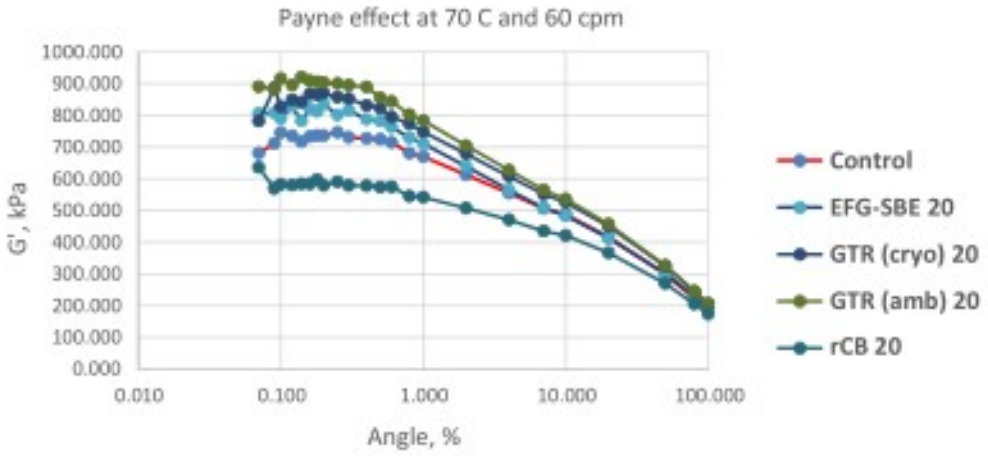


Figure 8.4 Payne effect (polymer/filler interaction) of various mixes via ASTM D8059.

number from 0 to 1 where a higher number is deemed more desirable based on the input criteria (Fig. 8.4).

The desirability function is a mathematical approach to using data to help select the "best balance of all properties." This approach tends to help the user eliminate emotion from the decision-making process (Fig. 8.5).

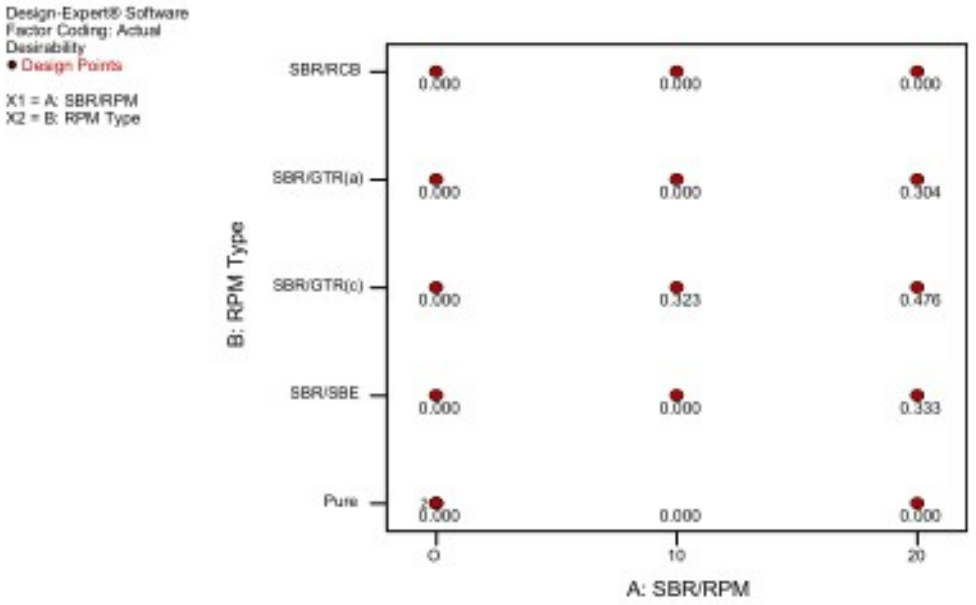


Figure 8.5 Desirability function results of various approaches based on set criteria.

8.10 Polymer-modified asphalts

To successfully incorporate devulcanized rubber into polymer-modified asphalt formulations, effort and consideration must be made for mixing and incorporating the devulcanized rubber into the asphalt matrix. Current systems and formulations use various SBS (styrene butadiene styrene) and SEBS (styrene ethylene butadiene styrene) thermoplastic elastomer block copolymers for the asphalt modification. Successful formulations have used 50% replacement values of the EFG—SBE devulcanized rubber for SBS- and SEBS-based formulations. These efforts have resulted in not only significant cost savings, but the additional values of increased viscosity stabilization, increased thermomechanical properties, and increased polymer stability at elevated temperatures. All of these benefits are the result of the devulcanized nature of the material and the increased molecular weight of the materials. Other benefits not yet fully realized are the antioxidants, antiozonants, and antidegradants that are remaining in the rubber from the highly engineered tire formulations. As this application is further developed and the economics are further realized, more and more products will be moved this direction.

8.11 Conclusions

- Devulcanization is a viable technology that can be implemented in multiple markets immediately.
- The more companies that achieve commercial production of devulcanized rubber, the easier it will be to grow the marketplace.
- Devulcanized rubber can bring long-term supply and price stability to the volatile natural and synthetic rubber markets.
- Devulcanized rubber will always have better economics than alternative uses of GTR in other nonpolymeric applications.
- Ultimately, a robust devulcanization industry can recycle all rubber waste and solve a significant environmental problem while creating jobs and generating profits without government assistance or subsidies.

References

[1] A.M. Joseph, K.N. Madhusoodanan, A. Rosamma, B. George, Incorporation of devulcanized rubber in fresh rubber compounds: impact of filler correction on vulcanizate properties, Prog. Rubber Plast. Recycl. Technol. 33 (4) (2017) 281–301.
[2] Carl D. McAfee, M. Grubb, Ultrafine scrap tire rubber in novel TPO, Rubber World 237 (6) (2008) 31–34.
[3] C.D. McAfee and J. Celura, Ultrafine particle size ground elastomers in novel applications, Paper Presented to PolyComm, Galveston, TX, 2008.
[4] C.D. McAfee, Tire pyrolysis black – a carbon black alternative, Paper Presented to Carbon Black World, Fort Worth, TX, 25 May 2015.
[5] Liang and Shafie, US Patent 8,680,166, filed March 25, 2014.
[6] Benko and Beers, US Patent 6,992,116, filed January 31, 2006.
[7] Global Tire Recycling Market Report, Edition 2020, Goldstein Market Intelligence, 2020-05-15, < http://www.goldsteinresearch.com >, Abstract.
[8] Google Earth Pro, Google Earth Screen Capture, all images.
[9] Malaysian Rubber Board, Natural Rubber Statistics, 2019.
[10] Rubber, Right Under Our Noses, Time Magazine, June 8, 1942.
[11] China releases new standards on reclaimed rubber, Jane Ho, Rubber & Plastics News, May 18, 2015.
[12] Manual of Reclaimed Rubber, Rubber Reclaimers Association Inc, 1956.
[13] EPG Polymers LLC paper to be presented to the International Elastomer Conference on 21 October 2020 virtually in Nashville, TN by C.D. McAfee.
[14] E.C. Harrington, The desirability function, Ind. Qual. Control. (1995) 494–498.
[15] G.C. Derringer, A balancing act: optimizing a product's properties, Qual. Prog. (1994) 51–58.

This page intentionally left blank

9

Pyrolysis

9.1

Technology update toward recovered carbon black

Juan Daniel Martínez[1], C. Gisèle Jung[2] and Jean Paul Bouysset[3]

[1]Grupo de Investigaciones Ambientales (GIA), Universidad Pontificia Bolivariana (UPB), Medellín, Colombia [2]Ecole Polytechnique (EP-4MAT), Université Libre de Bruxelles (ULB), Brussels, Belgium [3]Senior Consultant, Rubber Products Pyrolysis and Regeneration (RPPR), Versailles, France

9.1.1 An introduction to pyrolysis

Among the different recycling methods, pyrolysis is considered as an effective and environmental friendly recovering process for end-of-life tires (ELT) because useful gaseous, liquid, and solid products are obtained [1]. The interest in this process focuses on the resulting products, which can be used in various industries as raw material, closing the ELT loop while minimizing the use of natural resources. For this and other reasons, pyrolysis can be regarded as a roadmap toward a circular and sustainable economy for ELT [2].

Pyrolysis is a thermochemical process aimed at the breakdown of feedstock into smaller and less complex molecules. Depending on the particle size, temperature, heating rate, and both vapors and solid residence time, pyrolysis can be categorized as slow, intermediate, fast, and even flash, which define the yields and characteristics of the products [3,4]. Unlike other chemical recycling processes such as gasification, pyrolysis operates under an oxygen-free atmosphere at moderate temperatures (between 400°C and 700°C). This means that heat must be brought to the reactor to raise the feedstock to the reaction temperature and also to sustain the reaction progress. Hence, pyrolysis requires indirect heating from its

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00028-4
© 2021 Elsevier Inc. All rights reserved.

surroundings. The way to conduct this task depends on the characteristics of each pyrolyzer, which in turn, strongly influences the yield and the quality of the end products.

To explain how pyrolysis works when applied to ELT, it is worth briefly mentioning what tires are made up of. Roughly speaking, tires are mainly composed of natural rubber, synthetic rubber, different grades of carbon black (CB), steel, some organic and inorganic fillers, and textile fibers. Thus pyrolysis of ELT releases the volatile part of the natural and synthetic rubbers leading to the production of liquids and gases. Therefore all the rubber ends in condensable and noncondensable hydrocarbon compounds, herein named tire pyrolysis oil (TPO) and tire pyrolysis gas (TPG), respectively. In addition, a solid fraction herein named recovered carbon black (rCB) is obtained, in which all CB and minerals included in the tire are trapped. For this reason, pyrolysis of ELT can be understood as a deconstruction or decomposition process because it enables the separation of the rubber from all the CB and all inorganic compounds used in tire manufacture (Fig. 9.1.1).

The aforementioned products, TPO and TPG, can be considered as fuels and petrochemical substitutes. The rCB comprises a valuable source of carbon, almost the same as found in virgin CB, but with different properties. For this reason, pyrolysis can

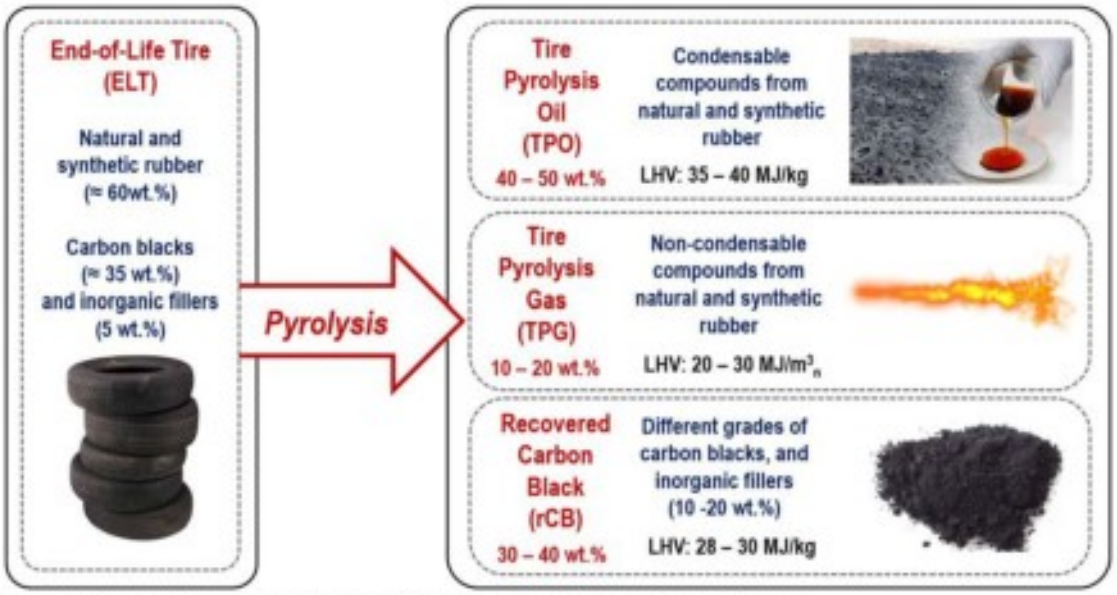


Figure 9.1.1 Schematic representation of the pyrolysis of ELT on a steel-free-basis.

be regarded as an energy and material recovery process able to support circular economy strategies since the "end-of-life" concept is replaced with recovering materials in production/distribution and consumption processes. In this context, the tire cycle is closed and the use of natural resources is minimized reducing the burden on current and future generations [5].

Both the TPO and the rCB are the main and most valuable products produced in pyrolysis of ELT [6]. On a tire steel-free basis, the TPO usually makes up of between 40% and 50% of tire weight. It contains aliphatic, aromatic, heteroatomic, and polar fractions [7], and it can be considered as a mixture of unrefined hydrocarbons. Hence, petroleum-like products such as gasoline, kerosene, and diesel can be obtained after distillation and the adjustment of some properties. The rCB accounts for between 30% and 40% of the tire weight. It exhibits a carbon content higher than 80 wt.%, while ash and undesired carbon deposits represent the remaining 20 wt.%, depending on the technology and the feedstock. The carbon deposits come from extra carbon compounds formed during the pyrolysis process that must be minimized in order to achieve a high value rCB. Depending on its application, the rCB could require further upgrading processes: mechanical posttreatment is recommended for applications in the rubber industry as well as chemical posttreatment to reduce the ash content and to improve surface activity. Finally, the TPG usually makes up between 10% and 20% of tire weight, containing H_2, C_1-C_4 hydrocarbons, CO_2, CO, and H_2S. After the removal of sulfur compounds, the TPG has enough energy to drive the pyrolysis process and also to produce additional heat and power [8].

While both TPO and TPG can be valorized without major complications, in many cases, there are challenging barriers regarding the final market of the rCB. Roughly speaking, the rCB needs more attention since it is more important than the TPO in terms of physical-chemical properties to overcome marketing barriers [9]. Even so, it should be emphasized that posttreatments of pyrolysis products do not necessary imply an unprofitable business. For the same reason, crude oil and the virgin CB would not be either, and it is well-known that they also need refining steps including sometimes complex and expensive operations. The rCB is mainly composed of many CB grades because each type of tire (truck, passenger, or motorcycle) and brand contain different CB grades. Hence, the rCB does not show the same properties as virgin CB. As can be inferred, the rCB quality strongly depends on the feedstock. In addition, some rCB can exhibit a nonsuitable surface activity (surface

area and surface chemistry) because not all pyrolyzers follow the best technical and environmental practices, etc.

9.1.2 An overview of the pyrolysis technologies

From an industrial-scale standpoint, the pyrolysis of ELT can be carried out using fixed-beds, batch-rotary kilns, vertical reactors, as well as using auger or continuous rotary kiln reactors [7]. At this point, it is worth mentioning that currently rotary kilns can operate in either batch or continuous formats. Although fluidized bed reactors (both bubbling and circulating) show interesting characteristics for pyrolysis processes and are able to deal with large flow rates of feedstock, practical experiences at industrial-scale are in development. The same occurs with spouted bed reactors. As fluidized beds, they produce a remarkable yield of TPO (higher than 60 wt.%) due to the fast conditions employed (very high heat transfer conditions and rapid removal of the products from the reaction). However, little is known about their use for ELT pyrolysis at a commercial-scale.

A schematic representation of the industrial-scale pyrolyzers mentioned above is shown in Fig. 9.1.2; detailed information about the main operating characteristics is found elsewhere [6,7,10–13]. All these pyrolyzers have advantages and disadvantages from different points of view, including the necessity of using: (1) whole tires, chips, or granulate; (2) carrier gas (nitrogen or steam, or neither); (3) positive or negative pressure; and (4) catalysts, among others; influencing not only the operational format (batch or continuous) but also the yield and quality of the products. The target of any pyrolysis process, regardless the technology of the pyrolyzer, is to achieve a balance between a high TPO yield and good physical-chemical properties of the rCB. This is very important in order to ensure both the technical and the economic feasibility of the pyrolysis of ELT.

Pyrolysis of ELT can be classified depending on the operation mode (i.e., batch or continuous). Table 9.1.1 summarizes some characteristics of the pyrolysis technologies according to this classification. Batch processes are performed by using the fixed-bed reactor (also known as the static bed reactor) or the batch-rotary kiln, which are probably the best known and simplest configurations. In this case, the ELT can be processed whole or shredded, depending on the specifications of the pyrolyzer. Both technologies exhibit capacities from 5,000 to 20,000 t/year, and for higher throughput, additional modules can be

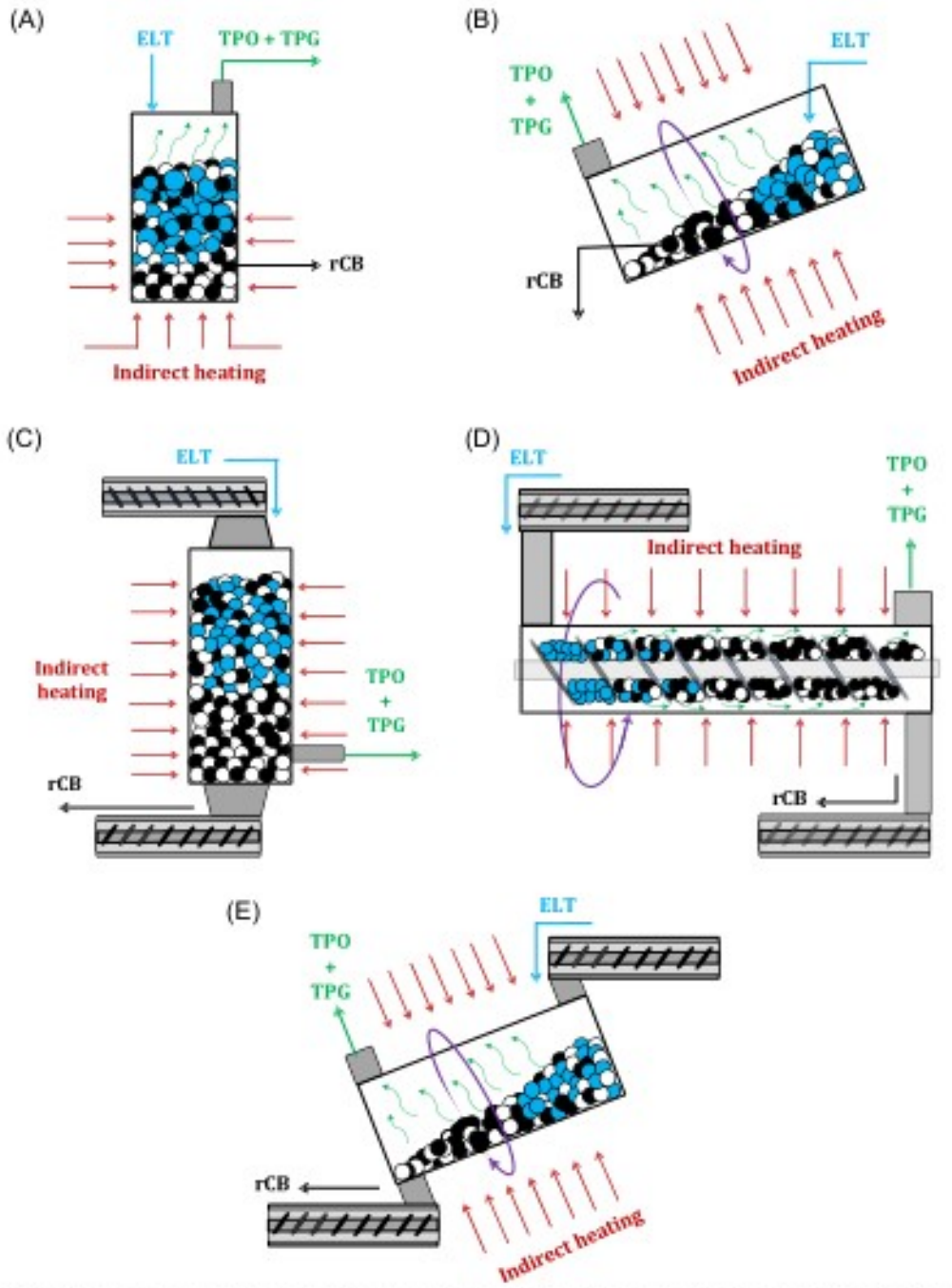


Figure 9.1.2 Schematic representation of different pyrolysis technologies for ELT using thermal indirect heating: (A) fixed-bed; (B) batch-rotary kiln; (C) vertical reactor; (D) auger reactor; (E) continuous-rotary kiln reactor.

Table 9.1.1 Some characteristics of pyrolysis technologies according to the operation regime.

Characteristic		Batch	Continuous
Financial	CAPEX	Low	High
	OPEX: Operational Expenditure	High	Low
Operational	Feedstock	Flexibility regarding size and shape	An appropriate sorting of the feedstock regarding size and shape is needed
	Residence time	High (hours)	Very low (from seconds to minutes)
	Heating rate	Low (<20°C/min)	High (>100°C/min)
	Temperature inside the reactor	Between 400°C and 500°C	Between 500°C and 700°C
	Thermal fatigue	High	Low
	Longevity of the reactor	Low (3–4 years)	High (10–12 years)
	Time for steady state	High (hours)	Very low (from seconds to minutes)
Pyrolysis products management	TPO and TPG	Continuously swiped out from the reactor	Continuously swiped out from the reactor
	rCB	It remains into the pyrolyzer until the batch is finished	It is continuously removed from the pyrolyzer

CAPEX, Capital expenditure; *OPEX*, operational expenditure; *rCB*, Recovered carbon black; *TPG*, tire pyrolysis gas; *TPO*, tire pyrolysis oil.

added. Although some suppliers claim the possibility of having higher capacities in a single reaction module, severe heat transfer limitations are expected, affecting the pyrolysis performance. Generally speaking, the residence time for batch processes can last up to 9 h, and the temperature inside the reactor is usually lower than 500°C, for those technologies using thermal indirect heating. In addition, these processes scarcely use inert carrier gas and the heating rate is lower than 20°C/min. The ELT needs a fixed time inside the pyrolyzer and the rCB takes a non-negligible time to be unloaded from the pyrolyzer, at least in those plants without automated systems. Therefore the selection of these technologies must be conducted carefully, backed by considerable confidence in the pyrolyzer's provider, adequate risk analysis, and also a reliable and successful model business.

Examples of commercial and semicommercial scale pyrolyzers based on these technologies are detailed elsewhere [13].

On the other hand, continuous processes are conducted through vertical reactors (also known as column type), auger reactors, and continuous rotary kilns. These pyrolyzers appear to be able to manage ELT amounts between 5,000 and 10,000 t/year in one single module. Commonly, continuous pyrolysis requires reducing the ELT size (in the order of centimeters and millimeters) to favor heat transfer conditions. Although the embedded steel is frequently extracted, an extra capital investment is required for chipping and granulation machines. After removing the steel, the rubber pieces or granulate are continuously fed into the pyrolyzer. The pyrolyzer is only opened for maintenance. However, there are some reports claiming the possibility of pyrolyzing whole ELT [7].

Continuous operation is important for large-scale implementation since the ELT is valorized constantly and the resulting products are immediately obtained. These reactors usually lead to more efficient operation and a better control of both temperature and residence time as compared to the batch reactors. Moreover, the ease of operation, consistent product characteristics, low labor cost, compact design, and flexibility in adjusting processing conditions are worth noting [14]. After achieving steady state conditions, the temperature inside the reactor is between 500°C and 700°C, and the heating rate is usually higher than 100°C/min for those technologies using indirect thermal heating.

Recently, the pyrolysis of ELT has experienced important growth because of the development of different technologies focusing specifically on rCB production with excellent physical-chemical properties. These features for both batch and continuous pyrolyzers must be interpreted carefully since each technology/supplier offers different specifications. The temperature profile inside the reactor, the heating rate of the ELT, and the residence time of solids and vapors can differ with each technology. The technological maturity differs with different suppliers, and it is possible to find batch pyrolyzers claiming highly efficient operation including excellent control of the operational variables of the process. Currently, there are many domestic pyrolyzers that unfortunately are associated with harmful emissions as well as health and fire hazards.

It is important to note that each pyrolyzer leads to different yields and properties for the TPO, the TPG, and the rCB, since each one operates in a different way. Therefore it is worth taking into account that the degree of control over the process including the feedstock sorting drastically influences the yields and characteristics of the pyrolytic products. As a result, not all

pyrolysis technologies with ELT input do lead to products with the same characteristics. For instance, the misconception that all the rCB are the same, regardless of the pyrolyzer and ELT type, has hindered its incorporation in the market as alternative to virgin CB. The use of ASTM standards to characterize rCBs issued from different technologies is important and is widely discussed in Part 9.2.

In addition to batch or continuous classification, the pyrolysis process can be defined by how the pyrolysis is assisted, or rather, how the process is induced in terms of heat transfer. In this context, it is possible to talk about thermal pyrolysis and microwave pyrolysis. The former uses heat to drive the pyrolysis in a combined process involving conduction, convection, and radiation, while the latter uses merely electromagnetic radiation.

9.1.3 Thermal pyrolysis

Also called conventional pyrolysis, this is the most commonly studied and reported pyrolysis route not only for ELT but also for other feedstock such as biomass and plastic wastes. Here, the feedstock is heated indirectly through the reactor walls by a heat source [3]. For the ELT case, indirect heating employs either the TPG released in the pyrolysis process or an auxiliary fuel to generate the heat needed to drive the chemical reactions involved in pyrolysis. It is also possible to carry out indirect heating using electrically, even at industrial-scale plants. In some cases, the technology is using the TPG in a combustion engine to produce the electricity required. In any case, thermal pyrolysis needs heat exchange surfaces to support the contact of the ELT with the walls and to promote the pyrolysis process.

This heating method has some drawbacks as a result of the uneven rate and also distribution of the heat inside each particle. From the heat transfer point of view, the central portion of the pyrolyzed feedstock gradually reaches the desired temperature by heat conduction. As a result, the process becomes strongly dependent on the pyrolysis time and the temperature profile of both the feedstock and the surroundings. These conditions are determined by the technological level of the pyrolyzer and its intrinsic characteristics. Thermal pyrolysis can be found in either batch or continuous processes. Each pyrolyzer offers different heat transfer conditions and performance

features and hence each one leads to very specific products in terms of yields and properties.

9.1.4 Microwave pyrolysis

Microwave-driven pyrolysis is based on the interaction of an electromagnetic field with the microwave-absorbing material, leading to rapid heating including the possibility of even distribution [15]. Microwave heating represents the transfer of electromagnetic energy to thermal energy and appears to offer an enhanced heat transfer into the ELT and better conditions for an isothermal operation in the reactor. In theory, the center of the feedstock is heated first, instead of the exterior, as occurs in thermal pyrolysis. For this reason, microwave heating favors reactions involving devolatilization or heterogeneous reactions. This characteristic helps to minimize the occurrence of undesired secondary reactions and hence the resulting rCB shows low carbon deposits onto its surface. Despite the low thermal conductivity, ELT could be heated very quick and uniformly, with short reaction time. The high carbon content in ELT (higher than 80 wt.%) enables the quickly absorption of the microwave radiation.

Although microwave pyrolysis looks to be a very promising technology, scientific data on microwave pyrolysis of ELT is rather limited with most reports referring to laboratory-scale operations [16]. In addition, temperature control seems to be a difficult issue, both for the measurement side and the uniformity issue, during the operation [17,18]. Furthermore, microwave heating can lead to "hot spots" inside the pyrolyzer. Because the heat transfer can exceed the rate of transmission of its surroundings, some parts of the ELT can heat faster than others leading to undesired reactions.

Microwave pyrolysis also needs to make important provisions for safety from exposure to microwave radiation; this can be solved by using cavity seals. It is worth considering the radiation emission limits for new and used ovens (1 and 5 mW/cm^2, respectively), and the necessity to avoid any kind of interference from cellular phones and bluetooth operations [15]. Further, microwave pyrolysis seems to be very challenging for both continuous operation and for the scaled-up to industrial throughputs [11]. Up to 2017, pilot-demonstration plants few and far between in Europe [19]. Although the general conception is that pyrolysis by microwave is costly from the large-scale

standpoint, promising growth and development is expected in the near future [16].

The interest in microwave pyrolysis lies mainly in the quality of the rCB. If this product can be marketable as a substitute of virgin CB, the process will become popular. Many technologies and suppliers in Europe and the United States have recently appeared to claim novel processes showing interesting advantages in terms of the rCB quality. Some of these suppliers claim very small or even null residues on the rCB surface, including carbonaceous deposits, inorganic compounds, and polycyclic aromatic hydrocarbons (PAH). However, the scientific literature shows that this is not necessarily true, and these impurities have been found in microwave pyrolysis with volatile matter and ash content in the resulting rCB of around 1.7 and 7.9 wt.%, respectively, with Fe and Zn being the most abundant metals found inside the rCB particles [20]. Generally speaking, there is still insufficient understanding of large-scale equipment, continuous production, and system mechanisms [21].

9.1.5 Conclusions

Besides batch and continuous processes, the pyrolysis of ELT can be defined by how the process is induced in terms of heat transfer. Thermal or conventional pyrolysis is the most commonly studied and reported pyrolysis route. The majority of the current technologies available at industrial-scale are based on this heating transfer. Single modules exhibit capacities from 5,000 to 20,000 t/year including batch and continuous processes. The proper selection of these technologies must be conducted carefully, backed by the pyrolyzer's provider, adequate risk analysis, and also a reliable and successfull model business. The technological maturity is also a key aspect and differs with different suppliers. It is important to take into account that not all pyrolyzers lead to the same product characteristics, since each one operates in a different way. The degree of control over the process including the feedstock sorting drastically influences the yields and characteristics of pyrolytic products.

Pyrolysis of ELT can also be conducted by microwave heating, which unlike thermal pyrolysis, uses merely electromagnetic radiation and seems to offer notable advantages in terms of quality of the resulting rCB. Because the center of the ELT is heated first, microwave heating seems to minimize the occurrence of undesired secondary reactions, lowering the amount of

carbonaceous deposits on the rCB surface. Currently, pyrolysis by microwave is seen as costly and more research is needed to move forward in the development of large-scale plants.

References

[1] M. Betancur, C.N. Arenas, J.D. Martínez, M.V. Navarro, R. Murillo, CO2 gasification of char derived from waste tire pyrolysis: kinetic models comparison, Fuel 273 (2020) 117745.

[2] J.D. Martínez, F. Campuzano, N. Cardona-Uribe, C.N. Arenas, D. Muñoz-Lopera, Waste tire valorization by intermediate pyrolysis using a continuous twin-auger reactor: operational features, Waste Manag. 113 (2020) 404–412.

[3] F. Campuzano, R.C. Brown, J.D. Martínez, Auger reactors for pyrolysis of biomass and wastes, Renew. Sustain. Energy Rev. 102 (2019) 372–409.

[4] C.G. Jung, A. Fontana, Production of gaseous and liquid fuels by pyrolysis and gasification of plastics: technological approach, in: J. Sheirs, W. Kaminsky (Eds.), Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels, John Wiley & Sons, 2006.

[5] J. Kirchherr, D. Reike, M. Hekkert, Conceptualizing the circular economy: an analysis of 114 definitions, Resour. Conserv. Recycling 127 (2017) 221–232.

[6] J.D. Martínez, N. Puy, R. Murillo, T. García, M.V. Navarro, A.M. Mastral, Waste tyre pyrolysis—a review, Renew. Sustain. Energy Rev. 23 (2013) 179–213.

[7] W.M. Lewandowski, K. Januszewicz, W. Kosakowski, Efficiency and proportions of waste tyre pyrolysis products depending on the reactor type—a review, J. Anal. Appl. Pyrolysis 140 (2019) 25–53.

[8] J.D. Martínez, R. Murillo, T. García, A. Veses, Demonstration of the waste tire pyrolysis process on pilot scale in a continuous auger reactor, J. Hazard. Mater. 261 (2013) 637–645.

[9] J.D. Martínez, N. Cardona-Uribe, R. Murillo, T. García, J.M. López, Carbon black recovery from waste tire pyrolysis by demineralization: production and application in rubber compounding, Waste Manag. 85 (2019) 574–584.

[10] N. Antoniou, A. Zabaniotou, Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery, Renew. Sustain. Energy Rev. 20 (2013) 539–558.

[11] M. Arabiourrutia, G. Lopez, M. Artetxe, J. Alvarez, J. Bilbao, M. Olazar, Waste tyre valorization by catalytic pyrolysis—a review, Renew. Sustain. Energy Rev. 129 (2020) 109932.

[12] I. Hita, M. Arabiourrutia, M. Olazar, J. Bilbao, J.M. Arandes, P. Castaño, Opportunities and barriers for producing high quality fuels from the pyrolysis of scrap tires, Renew. Sustain. Energy Rev. 56 (2016) 745–759.

[13] P.T. Williams, Pyrolysis of waste tyres: a review, Waste Manag. 33 (2013) 1714–1728.

[14] K.M. Qureshi, A.N. Kay Lup, S. Khan, F. Abnisa, W.M.A. Ashri Wan Daud, A technical review on semi-continuous and continuous pyrolysis process of biomass to bio-oil, J. Anal. Appl. Pyrolysis 131 (2018) 52–75.

[15] E. Athanassiades, Waste tyre pyrolysis: Sustainable recovery and reuse of a valuable resource. PhD Thesis. Imperial College London, UK, 2013.

[16] K. Formela, A. Hejna, Ł. Zedler, X. Colom, J. Cañavate, Microwave treatment in waste rubber recycling—recent advances and limitations, Express Polym. Lett. 13 (6) (2019) 565–588.
[17] M. Bartoli, M. Frediani, C. Briens, F. Berruti, L. Rosi, An overview of temperature issues in microwave-assisted pyrolysis, Processes 7 (2019) 658.
[18] A. Undri, S. Meini, L. Rosi, M. Frediani, P. Frediani, Microwave pyrolysis of polymeric materials: waste tires treatment and characterization of the value-added products, J. Anal. Appl. Pyrolysis 103 (2013) 149–158.
[19] H. Punkkinen, A. Oasmaa, J. Laatikainen-Luntama, M. Nieminen, J. Laine-Ylijoki, Thermal conversion of plastic containing waste: a review, VTT Res. Rep. (2017). N° D4.1-22, Hels.
[20] A. Undri, B. Sacchi, E. Cantisani, N. Toccafondi, L. Rosi, M. Frediani, et al., Carbon from microwave assisted pyrolysis of waste tires, J. Anal. Appl. Pyrolysis 104 (2013) 396–404.
[21] J. Xu, J. Yu, J. Xu, C. Sun, W. He, J. Huang, et al., High-value utilization of waste tires: a review with focus on modified carbon black from pyrolysis, Sci. Total. Environ. 742 (2020) 140235.

9.2

Recovered carbon black: characteristics and properties in compounds

Juan Daniel Martínez[1], C. Gisèle Jung[2] and Jean Paul Bouysset[3]

[1]Grupo de Investigaciones Ambientales (GIA), Universidad Pontificia Bolivariana (UPB), Medellín, Colombia [2]Ecole Polytechnique (EP-4MAT), Université Libre de Bruxelles (ULB), Brussels, Belgium [3]Senior Consultant, Rubber Products Pyrolysis and Regeneration (RPPR), Versailles, France

9.2.1 Carbon black generalities

Roughly speaking, carbon black (CB) is the most commonly used reinforcement filler and pigment in rubber and plastic products and in printing inks. It is usually produced by the partial combustion or thermal decomposition of liquid or gaseous hydrocarbons under controlled conditions with a carbon footprint around 2.4 kg of CO_2 per kg of CB [1]. The carbon concentration increases to 99 wt.% or more depending on the manufacturing process. In this sense, thermal black, furnace black, and channel black are the three main processes used for CB production. Since the middle of the 20th century, most CB has been produced by the furnace black process [2], which also delivers the most used CB by far for rubber manufacture. The main advantage of this process is the great variety of CB types that can be produced. Furnace black occupies almost 95% of the total market, 70%–80% of which is used in tire manufacture and also in the rubber and plastic industries.

As observed in Fig. 9.2.1, CB exhibits a hierarchy of morphological features: particles (primary particles or nodules), aggregates, and agglomerates [2,3]. CB is considered a nanostructured material made up of tiny and mostly spherical carbon fusing together in clusters by covalent bonds referred to as aggregates [4]. These aggregates are robust assemblies and represent the true primary units of CB because primary particles rarely exist isolated (except for some N900 grades). Hence, the aggregates are the smallest dispersible units of CB, and define one of the main properties of any CB, namely structure. This property relates to some extent the aggregation degree. A highly structured degree in a CB indicates a

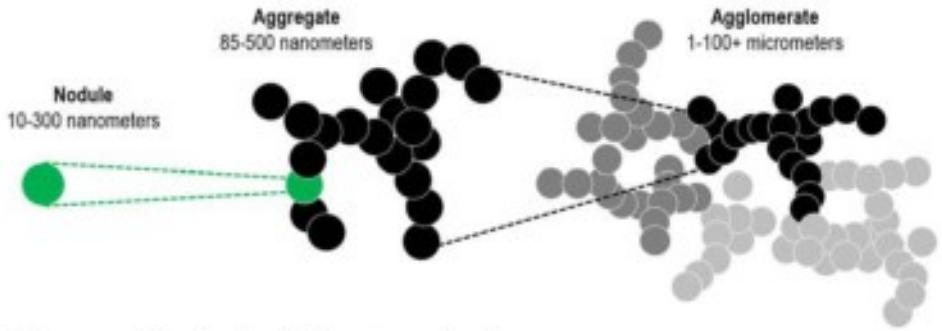


Figure 9.2.1 Sequence of carbon black (CB) structure development.

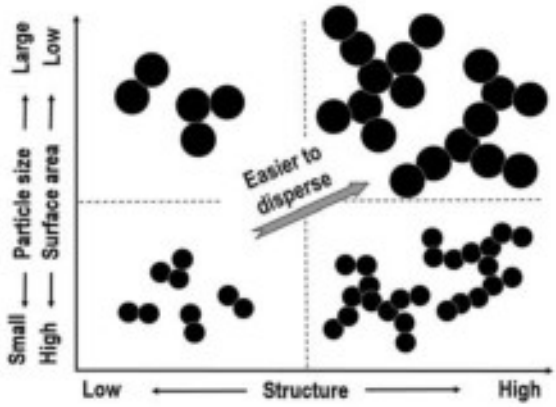


Figure 9.2.2 Relation of particle size and surface area with structure and resulting effect on dispersion.

high number of primary particles per aggregate, while a low structure degree exhibits only a weak aggregation. As observed in Fig. 9.2.2, the structure in a CB changes with the particle size and surface area, strongly affecting the overall dispersion quality and batch consistency in a compounding process [5,6]. Frequently, the tendency to form aggregates decreases with increasing primary particle size.

The aggregates may form agglomerates linked by van der Waals interactions, which break up during the rubber mixing process. Agglomerates are hard to measure correctly because they break apart when shear forces are applied [2]. Sometimes the term agglomerate is confused with aggregate or primary structure formed in the furnace reactor. Agglomerates or secondary structures do comprise a large number of aggregates, which are physically held together unlike the continuous graphitic structure that connects the particles in aggregates [4]. The ability to break up these

agglomerates into aggregates in order to ensure adequate dispersion is critical for achieving a desirable CB performance in composite materials, as for example, rubber formulations. Detailed information about the proper terminology relating to CB is found in the standard ASTM D3053.

CB is composed essentially of an amorphous carbon core and quasicrystalline shell with graphitic carbon stacks [7–9]. The carbon atoms in the aggregates are found in overlapping graphitic layers, also called scales, that locally present a quasicrystalline turbostratic structure with an approximately 0.35 nm interlayer spacing [1] and average lateral extensions of up to 3 nm [8]. At this scale, the CB surface seems to be rough and even fractal [10] and consists of graphitic planes (site I), amorphous carbon (site II), crystallite edges (site III), and slit-shaped cavities (site IV) [11]. The acidic functional groups are preferably located at the edges of the graphitic basal planes or at the crystallite edges (i.e., at sites I and III, respectively) [11]. The presence of these groups (carboxyl, phenol, lactones, and quinonic groups) determine the active sites of the CB. They are considered as being essential during the curing time in many vulcanizing systems [1] to achieve an important reinforcement degree in a composite material [12]. This surface chemistry gives to the CB the condition to be more than just a filler [13]. The presence of these chemical groups on the CB surface determines their applications not only in the rubber industry (reinforcement in rubber bonding) and the plastic sector, but also in the paint industry. The surface chemistry is considered the most important property that influences the physical-chemical properties of CB such as wettability, catalytic activity, electrical and chemical reactivities [4].

To summarize, in order to be efficient, the CB should have four fundamental properties to strengthen the rubber and aid abrasion resistance. The four properties are:

1. Fineness (particle size and particle size distribution)
2. Structure (aggregates, size, and shape)
3. Porosity (specific surface area)
4. Surface chemistry, also called surface activity

The ASTM have well-established procedures to characterize the CB in terms of these properties. The standard ASTM D6556 describes the method for determining the total and external surface area by nitrogen adsorption (m^2/g), which can be related to the particle size. The iodine number (ASTM D1510) is used to estimate the surface area, but the presence of volatiles, surface porosity, or extractable matter does influence the results (measured in g of iodine per kg of CB). The standards ASTM D2414 and D3493 provide the methodology for determining primary structure

Figure 9.2.3 Carbon black (CB) grades in a tire.

(aggregates) and secondary structure (agglomerates), respectively, which also gives a general idea about the surface area. Structure is also connected with both the oil absorption number (OAN) (ASTM D2414) and the oil absorption number of compressed sample (COAN) (ASTM D3493), which are related to the processing and vulcanizate properties of rubber compounds containing CB. This is a very helpful example of how one single test is not enough to properly characterize the CB. Lastly, impurities and poorly dispersed agglomerates may act as initiator to both tear and fatigue and are determined by the standard ASTM D2663. The standard ASTM D1765 provides a general classification of the CB grades, which are commonly recognized in terms of surface area and structure. In this regard, Fig. 9.2.3 shows a general description of different CB used in tires, while Table 9.2.1 presents some of the main properties.

9.2.2 Recovered carbon black (rCB) generalities

According to the ASTM standard D8178, it is important to differentiate the "raw rCB" from the "rCB." The former often exhibits

Table 9.2.1 Main carbon black (CB) grades and characteristics.

Name/process	Acronym	ASTM NR	Particle size (nm)	N_2 adsorption (m^2/g)	OAN ($cm^3/100\ g$)
Super abrasion furnace	SAF	N110	20–25	145	113
Intermediate SAF	ISAF	N220	24–33	119	115
High abrasion furnace	HAF	N330	28–36	83	105
Fast extruding furnace	FEF	N550	39–55	42	120
General purpose furnace	GPF	N660	49–73	35	90
Semireinforcing furnace	SRF	N770	70–96	29	70
Fine thermal	FT	N880	180–200	9	33
Medium thermal	MT	N990	250–350	19	33

poor reinforcing properties when used in rubber compounding, while the latter is free of both wire and fabric, and usually leads to semireinforcing properties in rubber after milling. Also, it is worth mentioning that "char" refers to carbonaceous residues formed during carbonization of organic compounds (i.e., to the carbonaceous deposits discussed above).

The CB is widely used in the manufacturing of several products such as inks and coatings, plastics, construction and metallurgy materials, resins, paints, different rubber products and, of course, tires. Generally speaking, anything black-colored and made out of any kind of plastic contains CB [14]. Depending on the application field, the CB cost varies between 800 and 1500 €/t, for those within series N700 and N100, respectively. These prices are subject to important fluctuations according to the feedstock oil price. Among others, these facts suggest that the most straightforward rCB application is as a substitute for virgin CB [15]. Although this usage can lead to a sustainable and attractive market, the rCB strongly depends on the physical-chemical properties, according to the type of ELT pyrolyzed, the operational conditions, and technological level of the reactor, as noted above, as well as upgrading technologies to be discussed later.

As stated earlier, the rCB contains virtually all the inorganics compounds used in the manufacture of tires (ZnO, SiO_2, SO_3, CaO, Fe_2O_3, and Al_2O_3, among others) as well as several virgin CB grades. Consequently, the ash content in the rCB is considerably higher (between 10 and 20 wt.%) than that of virgin CB (less than 0.5 wt.%). Typical European tire tread compound results in a higher ash content (due to the

utilization of silica filler) as compared to that derived from a North American tire tread [16]. In addition, the rCB frequently shows a wide particle size distribution (i.e., multimodal in nature) and therefore exhibits a structure that varies widely between low and medium.

Furthermore, solid carbonaceous residues can be present on the rCB surface reducing not only the surface area but also the surface activity and can reach up to 20 wt.% [17]. These carbonaceous residues are amorphous in nature and seem to be chemically bonded rather than absorbed [16]. In addition, they lead to the formation of hard-to-break agglomerated particles affecting the structure. As repeated throughout this text, the exact composition and concentration of these residues depends on the composition of the feedstock and how the pyrolysis was conducted. For example, alkylated benzenes and alkylated naphthalenes compounds as well as polycyclic aromatic hydrocarbons (PAH) have been found in these carbonaceous residues [18]. The presence of PAH is considered a threat to human health as a result of its carcinogenic properties. Virgin CB generally consists of less than 1 wt.% extractable organic compounds, including PAH [2]. Similarly, more than 45% of the surface can be covered by these carbonaceous deposits, as reported by Zhang et al. [19]. Fig. 9.2.4 shows a schematic representation of the rCB including the above characteristics.

On the basis of the above, the rCB may exhibit different surface characteristics not only among the several rCB produced from the different pyrolysis technologies and pyrolyzed feedstock, but also when compared to those established for virgin CB. Therefore it is really difficult to provide a correct classification for rCB, although some similarities between a number of rCB and virgin CB can be found in terms of surface area, as shown in other works [20–22]. For instance, some rCB have

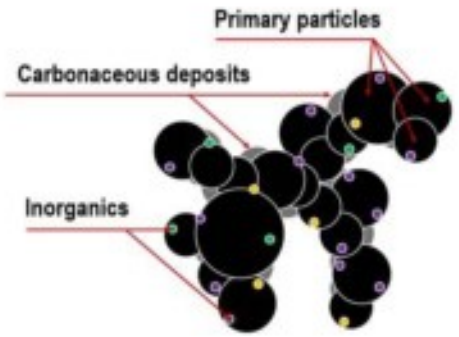


Figure 9.2.4 Schematic representation of rCB aggregate.

been classified in a category close to the commercial N300 series [23,24]. Furthermore, the colloidal properties suggested a reinforcing potential between the N330 and N550 series (assessed using standards for virgin CB), while the in-rubber performance data indicated that they are closer to the N700 series, as demonstrated by Norris et al. [16]. In this sense, Fig. 9.2.5 illustrates two classification windows for rCB within the framework of some virgin CB grades. As observed, the rCB show different patterns before and after its use in rubber formulations, which has been attributable to the carbonaceous residues on the CB surface reducing both surface activity and dispersion [16]. Therefore conventional CB tests do not seem to effectively predict rCB performances. Under this context, it is not surprising to find several and different conclusions regarding the potential applications of rCB in rubber manufactured products.

The above comments point to the need to establish appropriate standards for rCB. Pyrolysis is a capital-intensive activity and standardizing rCB properties not only ensures the safety and high performance of the manufactured products, but also attracts the interest of investors/entrepreneurs [25]. The pyrolysis of ELT failed for many years because most pyrolyzer suppliers and manufacturers have claimed the direct application for "raw rCB" as for virgin CB. In this sense, it is worth mentioning the progress conducted by the ASTM D36 committee, which approved the ASTM D8178 standard for rCB terminology as well as some CB standards used to characterize rCB (Table 9.2.2). Although this is an important step for companies involved in

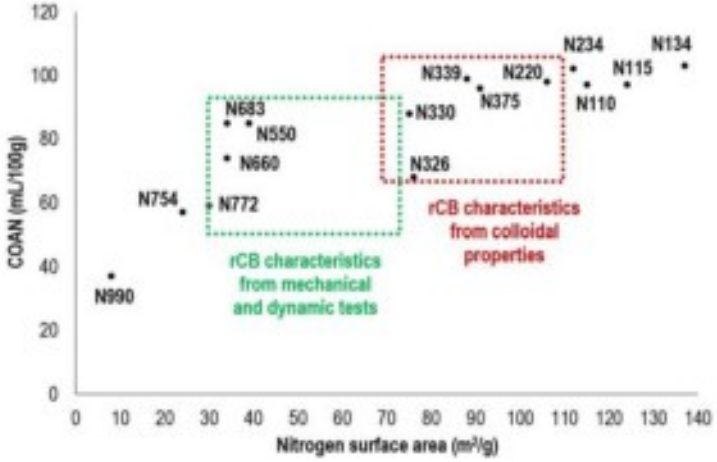


Figure 9.2.5 Representation of the colloidal properties of virgin carbon black (CB) grades and recovered carbon black (rCB).

Table 9.2.2 Recognized standards by committee D36 for their use in the recovery carbon black industry.

Scope	ASTM Standard	Goal
Pellet properties	D1508	Pellets fines and attrition
	D1509	Heating loss
	D1511	Pellet size distribution
	D1513	Pour density of pellets
	D1937	Pelleted — mass strength
	D5230	Automated individual pellet hardness
Sampling and statistical tests	D1799	Sampling package shipments
	D1900	Sampling bulk shipments
	D4122[a]	Evaluation of an industry reference black
	D4821	Validation of test method precision and bias
	D5817	Pelleted-reduction, blending and drying of gross samples for testing
	D6915[a]	Evaluation of standard reference blacks
Analytical tests	D1506[a]	Ash composition
	D1512	pH value
	D1618	Transmittance of toluene extract
	D1619	Sulfur content
	D7771	Determination of benzo-α-pyrene (BaP) content
Rubber tests	D2663	Dispersion in rubber
	D3191	Recipe and evaluation procedures in styrene-butadiene rubber
	D3192	Evaluation in natural rubber
Other tests	D1514	Sieve residue
	D3053	Terminology
	D3843	Morphological characterization using electron microscopy

[a]Currently under discussion and deeper analysis.

ELT pyrolysis to improve the management and logistics associated with rCB, new characterization methods are needed to predict properly rCB performance. Similarly, this committee did not approve the use of conventional CB characterization methods based on structural and surface area measurements for products made from rCB, as they do not seem to correlate in the same way with the in-rubber performance. On the other hand, Table 9.2.3 shows the standards currently under development and revision by different subcommittees attached to D36, for

Table 9.2.3 Standards in development for characterizing recovered carbon black.

Technical subcommittees	Goal
D36-10: Recovered carbon black (rCB)	Thermogravimetric analysis (TGA) and rCB composition test method
	Ash content
	Particle size
	Future development of reference samples
D36-20: Coproducts	Round robin testing on rubber derived liquids (TPO)
D36-30: Terminology	Terminology
D36-40: Environment safety and sustainability	Shelf-life assessment
	Life cycle assessment

rCB characterization including key properties such as ash content, particle size, and thermogravimetric analysis (TGA) for composition analysis, among others.

9.2.3 Impurities contained in the rCB

Carbonaceous deposit is probably the most undesirable characteristic hindering the performance of rCB in rubber formulations. The concentration of inorganic compounds (i.e., the ash content) can also be considered as an important factor, although to a lesser extent compared to the char layers resulting from unwanted reactions occurred during pyrolysis. These impurities may also appear in the manufacturing process of virgin CB (less than 0.5 wt.%), but not in the same concentrations as found in the rCB (between 10 to 20 wt.%). Inorganic residues of refractory material, rust and metal particles, and char, commonly known as "grit," may be formed during the CB synthesis [3,6]. All these factors have a negative influence on the quality of CB and, even at low levels, can have a significant deleterious effect on dynamic applications, affecting the stability of the CB-filled polymer system [3,6].

The presence of carbonaceous deposits can be avoided as long as the pyrolysis process is carried out properly (i.e., by using the right pyrolysis conditions on a high-performance pyrolyzer). These residues behave like a sticky resin [17] and are generally located in the void between the primary particles of an aggregate, blocking a portion of their surface [26]. As a result,

these residues not only affect the surface area available to the polymer matrix, but also structure and surface chemistry. Unlike the carbonaceous deposits, the presence of inorganic compounds in the rCB is practically unavoidable during the pyrolysis of ELT because they are not volatile at these temperatures (between 400 and 700°C); thus they mainly remain trapped in the rCB [27]. The decrease in mineral content has been widely studied for solid fuels such as coal by using successive treatments with acid and basic reagents [28,29] and to minor extent for rCB [13,15,23,30]. While these treatments have proven effective in reducing the ash concentration in the rCB and even significantly improving the surface chemistry through this addition of acidic functional groups, the economics of the process have not been yet established. However, some virgin CB, mainly those produced by furnace black process, contains small amounts of oxygen-containing functional groups on the surface, compromising their final application [24]. Oxidation treatments including HNO_3 and mixtures of NO_2 and air, O_3, or NaClO solutions can be carried out industrially with very positive results for special CB grades [24,31].

9.2.4 Upgrading of rCB after pyrolysis

In general, it was found that rCB can be used in several rubber applications. There is a general consensus that some mechanical properties are reduced and therefore the rubber product does not have the same performance as that offered by a virgin CB [32]. The rCB is generally difficult to disperse in the polymer matrix. This is due to: (1) the presence of agglomerates that are difficult to break; (2) its low-medium structure; and (3) the presence of the carbonaceous residues, as discussed above. However, Norris et al. [16] observed that the undispersed rCB domains appear to be closely related to the agglomerate size. For this reason, intensive milling is strongly recommended (hammer mill, but preferably jet-mill) to improve rCB performance. Milling is an important aspect when using rCB in rubber compounding, and for this reason, the ASTM standard D8178 highlights as "rCB" the solid fraction derived from pyrolysis of ELT free of metal and fabric and properly milled to eliminate the hard agglomerates. Even the best CB can lead to unexpected results if is not properly dispersed increasing the viscosity of the vulcanized material and therefore possible process problems including low tear resistance and crack initiation and propagation. In addition to milling, pelletizing is the other

operation that enables a "physical upgrading" of the rCB. In this process, a relatively large number of agglomerates is converted into pearl-like pellets having a size of a few millimeters in diameter. Pelletizing enables packaging, transport, handling, and preparation of compounds, specifically for rubber and plastics applications. Furthermore, pelletizing rCB allows the control of the fluffy dust to become a free-flowing product. Once pelletized, the final dust-free product is more suitable for shipment. In summary, the pelletization of rCB does improve the physical appearance but also their market value.

The carbonaceous residues, which are responsible for the formation of hard-to-break agglomerated particles, can be also reduced by using postheating treatments. Thus any additional organic material not included in the common composition of a virgin CB is released. This upgrading step can be performed after the production of the "raw rCB" in a secondary stage at moderate temperatures ($>600^{\circ}C$) with the need for an oxygen-free atmosphere in order to avoid possible oxidation of the rCB. This postheating leads not only to a decrease of the volatile matter content of the rCB, but also to an increase of the surface area. In addition, possible strong odors accompanying the rCB is also expected to be reduced. However, this type of posttreatment strongly penalizes the energy efficiency of the whole process, and consequently, its economic feasibility.

Lastly, the so-called "chemical upgrading" implies the use of acid-base washing leading not only to the ash reduction in the rCB but also to a significant addition of oxygen-containing acidic functional groups on the surface of the rCB. This improves the surface chemistry properties such as wettability, catalytic activity, electrical and chemical reactivity, among others. In addition, the presence of oxygen-containing acidic functional groups on the CB surface determines their practical application in the rubber and plastic sector. Thus the rCB surface functionalization can open practical applications in the rubber and plastic industries. Furthermore, better interfacial adhesion characteristics of the rCB with the polymer is to be expected. Plasma and ozone treatments are new procedures both showing promising results regarding the in-rubber performance [33].

9.2.5 Conclusions

Although it seems to be a very hard task, sorting the ELT types (i.e., passenger car tires, motorcycle tires, truck tires) and

even brands helps to produce a more homogeneous rCB regarding structure and silica content. This is an important factor to be considered because passenger car tires in Europe have more silica in the tread section and therefore a higher ash content is expected in the rCB. CB users are looking for suppliers that can produce large volumes of rCB (commercially proven capacities), ensuring homogeneity, consistency, and stability. These are likely the most desired characteristics of the rCB in order to favor its use as substitute of virgin CB.

The rCB is regarded as the profit core of the pyrolysis of ELT and hence the optimization in terms of the rCB properties is a key issue. Ensuring a minimal amount of carbonaceous deposits in the rCB surface, milling, and further pelletization seem to be the basic refining processes to be implemented. Milling can provide a particle size distribution typically between 1 and 10 μm. By using a jet mill, it is possible to reach particle sizes below 10 μm, even around 2 μm. A hammer mill is commonly used for virgin CB given the presence of weak agglomerates instead of hard agglomerates. For this reason, a hammer mill could be to some extent tricky, although it could reach acceptable milling limits depending on the features of the rCB agglomerates. Pelletizing notably improves handling and increases dispersibility in the rubber or plastic matrix.

References

[1] Y. Fan, G.D. Fowler, M. Zhao, The past, present and future of carbon black as a rubber reinforcing filler - A review, J. Clean. Prod. 247 (2020) 119115.
[2] International Carbon Black Association (ICBA). Carbon Black User's Guide. Safety, Health, & Environmental Information (www.carbon-black.org), 2016.
[3] T. Patnaik, B. Brown. Carbon black: why quality matters. Rubber & Plastic News, December 13, 2010.
[4] J.B. Donnet, R. Bausal, M. Wang (Eds.), Carbon Black, Science & Technology, 2nd edition, Marcel-Dekker, New York, NY, 1993.
[5] S. Ahn, Y. Kim, K.J. Kim, T.H. Kim, H. Lee, M.H. Kim, Development of high capacity, high rate lithium ion batteries utilizing metal fiber conductive additives, J. Power Sources 81–82 (1999) 896–901.
[6] M.E. Spahr, R. Rothon, Carbon black as a polymer filler, in: R. Rothon (Ed.), Polymers and Polymeric Composites: A Reference Series, Springer, 2017, p. 489.
[7] N.R. Ostyn, J.A. Steele, M. De Prins, S.P. Sree, C.V. Chandran, W. Wangermez, et al., Low-temperature activation of carbon black by selective photocatalytic oxidation, Nanoscale Adv. 1 (2019) 2873–2880.
[8] M. Pawlyta, J.-N. Rouzaud, S. Duber, Raman microspectroscopy characterization of carbon blacks: spectral analysis and structural information, Carbon 84 (2015) 479–490.
[9] J.B. Donnet, Fifty years of research and progress on carbon black, Carbon 32 (7) (1994) 1305–1310.

[10] G. Heinrich, M. Kluppel, T.A. Vilgis, Reinforcement of elastomers, Curr. Opin. Solid. State Mater. Sci. 6 (2002) 195–203.
[11] T. Mathew, R.N. Datta, W.K. Dierkes, W.J. van Ooij, J.W.M. Noordermeer, T.M. Gruenberger, et al., Importance of fullerenic active sites in surface modification of carbon black by plasma polymerisation, Carbon 47 (2009) 1231–1238.
[12] J.B. Donnet, Nano and microcomposites of polymers elastomers and their reinforcement, Compos. Sci. Technol. 63 (8) (2003) 1085–1088.
[13] A. Chaala, H. Darmstadt, C. Roy, Acid-base method for the demineralization carbon black of pyrolytic, Fuel Process. Technol. 46 (1996) 1–15.
[14] N.J. Hardman, The new carbon black and its role in the United States manufacturing renaissance, Reinforced Plast. 61 (2017) 145–148.
[15] J.D. Martínez, N. Cardona-Uribe, R. Murillo, T. García, J.M. López, Carbon black recovery from waste tire pyrolysis by demineralization: production and application in rubber compounding, Waste Manag. 85 (2019) 574–584.
[16] C.J. Norris, M. Hale, M. Bennett, Pyrolytic carbon: factors controlling in rubber performance, Plastic, Rubber Compos. 43 (2014) 245–256.
[17] F. Cataldo, On the characterisation of carbon black from tire pyrolysis, Fullerenes, Nanotubes Carbon Nanostructures 28 (5) (2020) 368–376.
[18] F. Cataldo, Further insight into some properties of pyrolytic carbon black obtained from scrap truck tires, Fullerenes, Nanotubes Carbon Nanostructures (2019). Available from: https://doi.org/10.1080/1536383X.2020.1789592.
[19] X. Zhang, T. Wang, L. Ma, J. Chang, Vacuum pyrolysis of waste tires with basic additives, Waste Manag. 28 (2008) 2301–2310.
[20] J.D. Martínez, N. Puy, R. Murillo, T. García, M.V. Navarro, A.M. Mastral, Waste tyre pyrolysis - A review, Renew. Sustain. Energy Rev. 23 (2013) 179–213.
[21] N. Antoniou, A. Zabaniotou, Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery, Renew. Sustain. Energy Rev. 20 (2013) 539–558.
[22] P.T. Williams, Pyrolysis of waste tyres: a review, Waste Manag. 33 (2013) 1714–1728.
[23] C. Roy, A. Chaala, H. Darmstadt, B. Caumia, H. Pakdel, J. Yang, Conversion of used tires to carbon black and oil pyrolysis, in: S.K. De, Al Isayev, K. Khait (Eds.), Rubber Recycling, CRC Press Taylor & Francis Group, 2005.
[24] M. Voll, P. Kleinschmit, Carbon, 6. Carbon Black, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co., 2010.
[25] A. Zabaniotou, N. Antoniou, G. Bruton, Analysis of good practices, barriers and drivers for ELTs pyrolysis industrial application, Waste Manag. 34 (2014) 2335–2346.
[26] D. Pantea, H. Darmstadt, S. Kaliaguine, C. Roy, Heat-treatment of carbon blacks obtained by pyrolysis of used tires. Effect on the surface chemistry, porosity and electrical conductivity, J. Anal. Appl. Pyrolysis 67 (2003) 55–76.
[27] J. Yang, C. Roy, A new method for DTA measurement of enthalpy change during the pyrolysis of rubbers, Thermochim. Acta 288 (1996) 155–168.
[28] P. Meshram, B.K. Purohit, M.K. Sinha, S.K. Sahu, B.D. Pandey, Demineralization of low grade coal–a review, Renew. Sustain. Energy Rev. 41 (2015) 745–761.
[29] M. Rahman, D. Pudasainee, R. Gupta, Review on chemical upgrading of coal: production processes, potential applications and recent developments, Fuel Process. Technol. 158 (2017) 35–56.

[30] X. Zhang, H. Li, Q. Cao, L. Jin, F. Wang, Upgrading pyrolytic residue from waste tires to commercial carbon black, Waste Management Research 36 (5) (2018) 436–444.
[31] M.-J. Wang, C.A. Gray, S.A. Reznek, K. Mahmud, Y. Kutsovsky, Carbon black, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc, 2003.
[32] N. Cardona, F. Campuzano, M. Betancur, L. Jaramillo, J.D. Martínez, Possibilities of carbon black recovery from waste tyre pyrolysis to be used as additive in rubber goods—a review, IOP Conf. Series: Mater. Sci. Eng. 437 (2018) 012012.
[33] J. Yu, J. Xu, Z. Li, W. He, J. Huang, J. Xu, et al., Upgrading pyrolytic carbon-blacks (CBp) from end-of-life tires: characteristics and modification methodologies, Front. Environ. Sci. Eng. 14 (2) (2020) 1–17.

9.3

Recovered carbon black: potential markets

Juan Daniel Martínez[1], C. Gisèle Jung[2] and Jean Paul Bouysset[3]

[1]Grupo de Investigaciones Ambientales (GIA), Universidad Pontificia Bolivariana (UPB), Medellín, Colombia [2]Ecole Polytechnique (EP-4MAT), Université Libre de Bruxelles (ULB), Brussels, Belgium [3]Senior Consultant, Rubber Products Pyrolysis and Regeneration (RPPR), Versailles, France

9.3.1 Carbon black market

Carbon black (CB) is one of the most commonly used chemical commodities and is among the top 50 chemical products produced worldwide. As discussed in the last two chapters, CB is a unique and irreplaceable component of the rubber and plastics industry and is also used in pigments, inks, and coatings. CB is used to improve the quality of different products in terms of strength, conductivity, ultraviolet protection, and weatherability. The most dominant CB application is for tire manufacture. The global consumption of CB in 2019 was estimated to be around 13.7 Mt, with 74% used in the tire industry, while nontire products (conveyor belts, hoses, etc.) accounted for 19%. The remaining 7% was used in pigments and other special applications [1]. The demand for CB in 2020 is estimated to be 10.5 Mt, representing a year-on-year drop of 23% [1]. This is largely due to the Covid-19 pandemic and the slump in crude oil prices.

The market price of CB is strongly dependent on the feedstock cost, contributing around 60% of the total manufacturing cost [2]. The furnace process, which produces practically the entire world's production, uses heavy fuel oils of high aromaticity, free of suspended solids, and with minimum concentration of asphaltenes and low sulfur content. These fossil resources are very sensitive to crude oil prices. In addition, as any industry consuming petrochemical feedstocks, the manufacturing process of CB has been questioned about its emissions of CO_2 as well as SOx, NOx, and particle matter during CB manufacture. Polycyclic aromatic hydrocarbon (PAH) compounds are also released in the CB production with potential human health risks. As a result, these issues are leading to strict environmental and safety regulations, increasing the costs associated with CB production.

Recently, the petrochemical industry including the CB sector is facing another serious challenge because of the need to minimize the amount of waste related to the production of items such as tires, hoses, gaskets, cables, conveyor belts, and black-colored housing for cellular phones and computers. The replacement of fossil fuel-based feedstocks by alternative resources obtained from recycling of wastes is considered as one of the most reasonable ways to ensure a sustainable and circular economy. Hence, the use of the recovered carbon black (rCB) as a substitute for virgin CB not only positively enhances the overall feasibility of the pyrolysis process, but also paves the way for a high-performance efficiency of the tire industry from a sustainability standpoint. Many resources are used to produce tires, and a large amount of CO_2 is emitted. As a result, many large tire producers have ambitious targets of incorporating renewable and recycled materials in tire manufacturing. Depending on how the rCB is produced and refined, its use as a substitute for virgin CB can reduce the overall carbon footprint associated with the commercial CB production up to 80%. In short, between 0.6 kg and 0.8 kg of CO_2 is released per 1 kg of rCB. In other words, each kg of rCB used over the virgin CB is projected to save up to 2 kg of crude oil.

9.3.2 Approximation to the recovered carbon black (rCB) market

The use of rCB is expected to grow in the coming years because of the growing demand for environmentally friendly and sustainable materials in rubber applications. A key economic advantage of rCB compared to virgin CB is that the production price is not related to fluctuating oil prices. The rCB is derived from an abundant feedstock that is commonly regarded as a serious waste disposal problem. Developed economies such as the United States and the European Union (including Norway, Serbia, Switzerland, and Turkey) are generating around 4.0 and 3.9 Mt of ELT per year, respectively [3]. As a result, the amount of ELT generated in these economies can produce around 1.2 and 1.17 Mt of rCB every year and hence the need for virgin CB in those regions could be considerably reduced. For instance, in 2017 the approximate demand for CB in the European Union was 2 Mt. Although this picture requires a significant number of industrial-scale pyrolysis plants and assumes that all the rCB is the same in terms of properties, it serves as preliminary point to illustrate the potential market of rCB.

The numbers here provide a basis for the demand of CB in Europe. As shown in Table 9.3.1, the applications include (1) rubber

Table 9.3.1 Estimated European carbon black (CB) market per sector in 2017.

Market sector	Amount (kt/year)	Share (%)
Tire	1360	68
Nontire	400	20
Plastics	100	5
Printing inks	80	4
Coating/paints	20	1
Others	40	2
Total	2000	100

Table 9.3.2 Estimated European carbon black (CB) market per grade in 2017.

Series	Amount (kt/year)	Share (%)
N100	60	3
N200	280	14
N300	780	39
N500	320	16
N600	240	12
N700	200	10
N900	40	2
Others	80	4
Total	2000	100

products (tire applications and nontire applications); (2) plastics; (3) printing inks; and (4) coatings/paints. The rCB can potentially be used in the aforementioned areas so long as the rCB exhibits the properties described in Part 9.2. For comparative purposes, Table 9.3.2 presents the estimated European market of different CB grades. Here, it is worth mentioning again that these characteristics are determined from the whole pyrolysis process chain, from picking the feedstock to adjusting the pyrolysis parameters, as well as correctly conducting the refining process, which includes milling and pelletization. In other words, the rCB should be consistent in terms of quality in order to match customer requirements.

9.3.2.1 Rubber industry

9.3.2.1.1 Tire parts

As shown in Table 9.3.1, the tire sector presents the higher CB demand. So, the most wanted and challenging application

of rCB is possibly the use in tire parts. This application has a market size of around 1360 kt/year in Europe. This sector utilizes practically all the range of CB grades (more than 30 types of compounds in a tire). Furnace CB are generally classified into two categories: one for those having a surface area between 75 and 140 m^2/g and known as "hard grades" (series N100/N200/N300) and the other for those exhibiting a lower surface area, between 25 to 50 m^2/g, known as "soft grades" (series N500/N600/N700). This classification is made by using ASTM (American Society for Testing of Materials) standards, namely D3037 and more recently D6556, dedicated to virgin CB. Using the same ASTM standards to measure rCB surface area, the values obtained are between 70 and 85 m^2/g, depending on the feedstock and the process used in their manufacture. This result suggests classifying the rCB in the "hard grades" range (N330). However, as mentioned in Part 9.2 (Fig. 9.2.5), the results show that the rCB performance in rubber compounds has to be compared to that of "soft grades" (N660/N770). Consequently, there is a need to develop new ASTM standards to evaluate rCB colloidal properties to properly predict performance in the rubber industry.

In addition to surface area, other characteristics such as particle size distribution, structure, ash content, sieve residue, and surface activity must also be taken into account as discussed in Part 9.2. Although these properties can be matched, marketing strategies should be conducted in order to introduce rCB material, because this industry is extremely traditional, and confidence and safety are likely the most important factors. Finally, if upgrading processes are successfully implemented, rCB could be considered in less sensitive tire applications; inner liners, for instance, use CB of the N600 series and the rCB can offer similar characteristics depending on the refining efficiency.

9.3.2.1.2 Nontire products

Nontire products make up the second market in size after the tire industry, with 400 kt/year in Europe. Rubber goods also require a broad range of CB grades, and extruded and molded compounds are the two main sectors. The first sector involves products such as hoses, profiles, gaskets, pipes, and cables. This industry demands a CB with a high structure and low sieve residue in order to obtain a smooth and regular extruded controlled profile. A very high purity is also needed to avoid frequent "pluggings" at the extruder head sieve and nonschedule production stops. These requirements can be addressed using rCB

blended with virgin CB of high structure for example involving N550 or eventually with some from the N300 series.

The second sector involves compounds of a high technical level, commonly used in the automotive and aeronautical industry such as gaskets, belts, seals, brake cups, and special pieces for engines. The high quality requirement for these products could compromise the use of rCB unless upgrading processes are successfully implemented. Nevertheless, nontechnical compounds can offer an interesting application for rCB since the mechanical requirements are less severe. For example, these applications include the fabrication of bumpers for cars, vessels, ports, parking, trains, railcars, wheels for caddies, wheelbarrows, and trolleys. Mats for cars, trucks, and products for residential and commercials areas such as floor tiles surfaces for steps. Small rubber parts for the furniture industry can also be included.

Two other important sectors to be considered in the exploration of the rCB market are rubber compounder/custom mixing compounder and masterbatche producers. These sectors do not produce finished products but instead ready mix-rubber compounds usually in sheets or granular form. The production route can be one of two routes:

1. highly concentrated compounds that are then diluted by the final customer's own compound (masterbatch), and
2. compounds directly used by the customer in line with its specifications (readymade compounds/tailor made compounds).

These compounders are working sometimes in helping large companies who are temporarily facing problem of too small mixing capacities. They are using a wide range of CB grades and are selling products based on finished compound properties (i.e; tensile strength modulus, hardness, etc.). In consequence, they are more versatile and flexible as they know the conditions to look for new raw materials, less expensive than the traditional ones. The above characteristics make this sector a straightforward application of rCB. For that reason, the rCB has to be presented in pellets and not in powder due to equipment used in the rubber industry. These compounders generally have internal mixers (Banbury, Werner, etc.) that are operated exclusively by using pellets, although some companies can have continuous screw mixers enabling the use of rCB in powder form.

In summary, rCB could be used as partial or full replacement of N600/N700 series, with no significant deterioration of physical properties of the final compound for semi- or low reinforcement

filler or in rubber compounder. For these applications, a nonnegligible part of the total market (440 kt/year, Table 9.3.2) is potentially accessible to rCB.

9.3.2.2 Plastics industry

The application of rCB in plastics is more convenient in nontechnical products since high technical and conductive plastics require: ash contents below 0.5 wt.%, very low sieve residues, high surface area, and/or high structure for conductive plastics. Plastic parts for different nontechnical applications such as films for agriculture and garbage bags (mainly for ultraviolet protection), among others, offer a possibility to incorporate rCB. Molded products exhibit more advantages than extruded products since they can tolerate the presence of impurities depending on the applications. There is also a possible market for plastic compounders (ready-mix compounds and high concentration masterbatches), a promising development in line with the evolution of this technology.

9.3.2.3 Printing inks and toners

Generally speaking, pigment requires special CB that disperses properly and quickly with large surface area, adequate surface chemistry, and practically zero impurities (very low ash content). However, rCB can show acceptable performance in specific sectors such as for newspapers (newsinks) and packaging (i.e., in those applications requiring less strict properties, in particular with regard to jet application and color shading). A high content of ash can lead to potential problems of excessive abrasion in the industrial equipment principally due to the presence of silica. Toners or "solid inks" can be used in "low cost" printers, particularly due to their "gray shade."

9.3.2.4 Coating/paints

Pigments are important in the printing inks and coatings/paints industries. This application demands not only a specific tinting strength and blackness value, but also proper dispersion for water or solvent-based systems and thixotropic characteristics. These characteristics hinder the use of rCB in this sector and for this reason the potential market of rCB in this sector seems to be limited at the present time.

9.3.2.5 Others applications: markets in development and potential markets

9.3.2.5.1 Hybrid particles vs. virgin carbon black/recovered carbon black

Producers of virgin CB and rCB collaborate in order to produce hybrid material by blending virgin CB and rCB at different stages of virgin CB production (i.e., furnace reactor, pelletizer, dryer, or in a silo system; Patent 9676943 [4]). This strategy is an interesting option to reduce the production costs of virgin CB and to improve the sustainability of the process.

9.3.2.5.2 Asphalt pavement-road fillers

Important R&D has been made with pilot-scale experiments in the production of agglomerate filler materials in asphalt compositions using rCB (Patent 8394189 [5]). The resulting material presents consistent particle size and binding affinity with asphalt binders. Potential use of rCB in pavements, even in small percentage as modifier in asphalt mixtures, have shown interesting results in the improvement of rutting resistance, as well as in the prevention of cracks. Today, interesting developments in asphalt/concrete mixtures, asphalt seals, shingles, and roofing using CB are being introduced [6,7], which are expected to be extended to rCB.

9.3.2.5.3 Concrete and cement, among others

Commercial CB has also been used in self-sensing concrete cracks and to diagnose damage to concrete beams [8,9]. This has paved the way for further rCB applications. Similarly, semi-industrial evaluation has been made for concrete and brick coloration in replacement of metallic oxides, and more specifically for manganese oxide (economical advantage). Also, the use of rCB as a partial replacement of natural fine aggregate for lightweight concrete has also shown promising results [10].

9.3.2.5.4 Active carbon

Active carbon is principally produced by biomass pyrolysis and the most important market is the production of filters for air and water purification. Intensive research at lab and pilot stages has been carried out by several laboratories in order to increase the rCB surface area [11–16]. Interesting technical results show surface areas between 400 m^2/g and 1200 m^2/g and a predominantly mesoporous structure. Until now, due to high production costs (burn-off of 50% or more), this application has not been

successful. Nevertheless, it is an interesting route with possible technical improvements for the future.

9.3.2.5.5 Lithium-ion batteries

Recently, there has been an interesting field for the rCB in energy-storage applications, for example, for anodes in Li-based batteries [17–19] and for preparing supercapacitor electrodes [20]. These applications appear to be promising in energy-storage systems, where materials with moderate cost and high energy density are critically needed.

9.3.3 Market price and projections

So far, rCB has been considered as a low-priced substitute for virgin CB (around 60%–70% below the virgin CB price). It has been reported that rCB can be sold for from USD 0.5 to 0.7 per kg [21]. However, the final price strongly depends the rCB specifications including origin and final presentation such as pellets or powder. In this sense, the price of high-quality rCB can range between 500 to 700 €/t, while low or medium rCB without technical information can be offered around 300 €/t or less. Some positive projections state that the market size for rCB is estimated to grow to USD 491 million by 2023 [22].

9.3.4 Conclusions

The use of rCB as a substitute for virgin CB has paved the way for enhanced efficiency of the tire industry from a sustainability standpoint. Depending on how the rCB is produced and refined, its use as a substitute for virgin CB can reduce the carbon footprint associated with commercial CB production by up to 80%. Another key advantage of rCB compared to virgin CB is that the production price is not related to fluctuating oil prices. These two factors are expected to be the major driving forces that increase rCB demand in the short and medium term.

The application in rubber industry for tire parts is possibly the most interesting and challenging application of rCB. According to the surface area, the rCB can be used as substitute (total or partial) of those CB grades frequently used in medium-low reinforced compounds (series N500/N600/N700). However, marketing strategies should be conducted in order to introduce rCB in this industry since consistency and safety are likely the most distinguished factors when selecting raw materials. If

upgrading processes are successfully implemented, the rCB can be considered for less sensitive tire applications that commonly use CB of the N600 and N700 series.

The most straightforward application of rCB is in nontire products such as (1) semi- or low reinforcement filler and (2) in rubber compounders/custom mixing compounders and masterbatch producers, as a substitute of N600/N700 series and blended with reinforcing grades. The final price of rCB material strongly depends on the specifications provided by the supplier and these include origin, analytical data, material safety data as well as the final presentation of pellets or powder. In this way, the price of high-quality rCB can range between 500 and 700 €/t, while low or medium rCB (raw rCB with no technical information) can be offered at around 300 €/t or even lower.

References

[1] Focus on Pigments. Notch forecasts a 23% drop in world carbon black demand in 2020, July 2020.

[2] M.-J. Wang, C.A. Gray, S.A. Reznek, K. Mahmud, Y. Kutsovsky, Carbon black, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc, 2003.

[3] World Business Council for Sustainable Development (WBCSD). Global ELT management – a global state of knowledge on collection rates, recovery routes, and management methods, 2018.

[4] Process for producing hybrid carbon black particles. United States Patent 9676943. Application granted: 06/13/2017.

[5] Asphalt composition using pyrolysed carbonaceous material. United States Patent 8394189. Application granted: 12/3/2012.

[6] R. Casado-Barrasa, P. Lastra-González, I. Indacoechea-Vega, D. Castro-Fresno, Assessment of carbon black modified binder in a sustainable asphalt concrete mixture, Constr. Build. Mater. 211 (2019) 363–370.

[7] X. Wu, S. Wang, R. Dong, Lightly pyrolyzed tire rubber used as potential asphalt alternative, Constr. Build. Mater. 112 (1) (2016) 623–628.

[8] Y. Ding, Z. Chen, Z. Han, Y. Zhang, F. Pacheco-Torgal, Nano-carbon black and carbon fiber as conductive materials for the diagnosing of the damage of concrete beam, Constr. Build. Mater. 43 (2013) 233–241.

[9] Y. Ding, G. Liu, A. Hussain, F. Pacheco-Torjal, Y. Zhang, Effect of steel fiber and carbon black on the self-sensing ability of concrete cracks under bending, Constr. Build. Mater. 207 (2019) 630–639.

[10] F. Ali, M.A. Khan, M.A. Qurashi, et al., Utilization of pyrolytic carbon black waste for the development of sustainable materials, Processes 8 (2) (2020) 174.

[11] N. Antoniou, G. Stavropoulos, A. Zabaniotou, Activation of end of life tyres pyrolytic char for enhancing viability of pyrolysis—critical review, analysis and recommendations for a hybrid dual system, Renew. Sustain. Energy Rev. 39 (2014) 1053–1073.

[12] M. Betancur, C.N. Arenas, J.D. Martínez, M.V. Navarro, R. Murillo, CO2 gasification of char derived from waste tire pyrolysis: kinetic models comparison, Fuel 273 (2020) 117745.

[13] E. Mui, D. Ko, G. McKay, Production of active carbons from waste tyres—a review, Carbon 42 (2004) 2789–2805.
[14] R. Murillo, M.N. Navarro, J.M. López, et al., Kinetic model comparison for waste tire char reaction with CO2, Ind. Eng. Chem. Res. 43 (2004) 7768–7773.
[15] A. Zabaniotou, P. Madau, P.D. Oudenne, C.G. Jung, M.-P. Delplancke, A. Fontana, Active carbon production from used tire in two-stage procedure: industrial pyrolysis and bench scale activation with H_2O-CO_2 mixture, J. Anal. Appl. Pyrolysis 72 (2) (2004) 289–297.
[16] A. Zabaniotou, P.D. Oudenne, C.G. Jung, A. Fontana, Active carbon production from char issued from used tyres pyrolysis: industrial improvement, Erdoel Erdgas Kohle 121 (4) (2005) 160–162.
[17] Y. Li, M.P. Paranthaman, K. Akato, et al., Tire-derived carbon composite anodes for sodium-ion batteries, J. Power Sources 316 (2016) 232–238.
[18] A.K. Naskar, Z. Bi, Y. Li, et al., Tailored recovery of carbons from waste tires for enhanced performance as anodes in lithium-ion batteries, RSC Adv. 4 (2014) 38213–38221.
[19] B.-C. Yu, J.-W. Jung, K. Park, J.B. Goodenough, A new approach for recycling waste rubber products in Li-S Batteries, Energy Environ. Sci. (2020). Available from: https://doi.org/10.1039/C6EE02770A.
[20] M. Boota, M.P. Paranthaman, A.K. Naskar, Y. Li, K. Akato, Y. Gogotsi, Waste tire derived carbon–polymer composite paper as pseudocapacitive electrode with long cycle life, Chemsuschem Commun. 8 (2015) 3576–3581.
[21] The California Integrated Waste Management Board (CIWMB). Technology evaluation and economic analysis of waste tire pyrolysis, gasification, and liquefaction (Publication #620-06-004), 2006.
[22] Markets and Markets. Recovered carbon black (rCB) market by application (tire application, nontire rubber application, plastics application, coatings application, and inks application), and region (North America, Europe, Asia Pacific, RoW) - global forecast to 2023. https://www.marketsandmarkets.com/Market-Reports/recovered-carbon-black-market-239229065.html. Last access: 16/08/2020.

9.4

Recycling of waste tires for silicon carbide production

Cesare Freda, Enrico Catizzone and Giacinto Cornacchia

ENEA, Laboratory of Thermochemical Processes for Wastes and Biomass Valorization, Rotondella, Italy

9.4.1 Introduction

Waste tires are no longer suitable for use on vehicles due to wear or irreparable damage. These tires are a challenging source of waste, due to the large volume produced, the durability of the tires, and the components of the tires, which are ecologically problematic. Currently, the total collection of end-of-life tires (ELTs) in the EU is estimated at more than 3.2 million tons per year (Mt/a), representing one of the most critical environmental issues to be addressed. Because tires are exceptionally durable and nonbiodegradable, they can take up valued space in landfills [1]. On the other hand, waste tires have a relatively high heating value in the range of 30–40 MJ kg^{-1} making waste tires a possible fuel in thermal treatments such as incineration, cocombustion with coal, and cocombustion in cement kilns or in thermal power plants [2,3]. In fact, in Europe about 30% of collected ELT is used as an energy source (especially in cement kiln), 20% is retreated and reused, and about 39% is recycled. In the United States 43% of waste tires is burned as fuel with cement manufacturing being the largest user; another 24% is used to make ground rubber, 8% is used in civil engineering, 17% is disposed of in landfills, and 8% has other uses (only 13% of US ELT was sold in the secondhand market) [4]. After retreading and reuse, the recycling (i.e., the process of converting waste tires into new materials and objects) undoubtedly is a environmental friendly strategy compared to energy recovery for heat and power production. Rubber, steel, and textile fibers are mainly recovered from recycling of ELTs that are used in many different products and applications. In particular, ELT-derived rubber is reduced to granulate and powder and then recycled as components for molded rubber products, as well as flooring filler for playgrounds, artificial turf and asphalt for road

surfaces, etc. Some markets have significantly expanded in recent years, such as the sport sector, so much so that the market seems almost saturated. Other areas where waste tires are used, such as roads, public works, and construction, have not grown enough to create a stable demand [5,6]. Therefore other recycling scenarios have to be explored in order to increase the recycling level of ELTs.

It is well known that tires are composed mainly of rubbers (e.g., natural, stirene-butadiene, and butadiene polymers) accounting for about 50 wt.%; silica or carbon black at 20 wt.%; metals 15 wt.%; 5 wt.% textiles; and the rest are additives (ZnO, sulfur, clays, etc.). Nearly 74%–76% of a tire is made of a carbon-based material [7]. The elemental analysis of a waste tire shows that the carbon content is dominant with nearly 85–90 wt.%, followed by hydrogen with 6–8 wt.%, minor amount of oxygen (1–4 wt.%); sulfur (0.8–1.9 wt.%); chlorine (up to 1 wt.%); and nitrogen (0.3–0.5 wt.%) [8,9]. Therefore waste tires could be a good source of carbon for carbon-based products or elemental carbon for chemical synthesis.

Several studies have investigated and developed processes to produce recovered carbon black and activated carbon from waste tires via pyrolysis followed by upgrading of the char [10–13]. Recovered carbon black has an economical advantage compared to virgin carbon black, as its production price is not related to fluctuating oil prices, because it is recovered from waste tires. It partially replaces virgin carbon black in commercial rubber applications [14]. Activated carbon is used in a wide range of industrial applications, including gas and air cleaning. Activated carbon is also being used in the treatment of water, including drinking water, groundwater, service water, and wastewater [15]. The oil derived from the pyrolysis of tires represents about 30%–40% of the output streams in the case of slow pyrolysis, and is usually sold at a low price due to its high sulfur content, although it contains C_5–C_{16} hydrocarbons with low oxygen content, similar to light and medium distillates produced from crude oil, with a high heating value of >40 MJ kg^{-1}. The obtained gas stream mainly consists of syngas and light hydrocarbons, and is usually burned to sustain the pyrolysis process. Nevertheless, the economic viability of pyrolysis recycling technology is hampered by the fact that the selling price of the output products (especially oil) often fails to justify the process costs. Therefore new strategies need to be developed at an industrial level for profitable transformation of ELT pyrolysis products into higher valuable materials. The streams produced

from ELT pyrolysis process might be used as intermediates for the production of silicon carbide, a high-added value product whose market is growing, as it is a key component in high-tech electronics.

9.4.2 SiC as a high-added value material

Silicon carbide (**SiC**), also known as carborundum, is a ceramic engineering material containing silicon and carbon that has gained a considerable amount of interest because it has attractive properties such as high hardness and strength, chemical and thermal stability, high melting point, oxidation resistance, high erosion resistance, semiconductivity, etc. All these characteristics make SiC a high-performing material for abrasion and cutting applications as well as for applications in high-power, high-voltage, and high-temperature electronic devices [16–19]. Furthermore, SiC is expected to replace conventional metallic silicon as semiconductors in electronics, especially in high-power applications [20]. The main advantages of SiC, as compared to silicon in electronics, are: (1) superior performance and voltage operation (e.g., lower power loss, higher energy efficiency, high thermal conductivity); (2) higher operating frequency; (3) higher operative temperature; (4) simpler design and smaller size; and (5) higher reliability. Metallic silicon is considered a critical raw material of high importance for the EU economy. China is the main global producer of metal silicon (61%), followed by Brazil (9%), Norway (7%), United States (6%), and France (5%) [21]. Furthermore, China's production is expected to increase over the next few years due to recurrent dumping practices. As a result, in order to increase the sustainable access to raw materials, alternative strategies may be adopted, especially for high-tech applications. To date, electronic devices such as diodes, MOSFETs (metal-oxide-semiconductor field-effect transistors), and hybrid modules are produced using SiC.

SiC is the hardest material, after diamond, cubic boron nitride, and boron carbide. Due to its high abrasion resistance, SiC is used as an abrasive material to grind steel, cast iron, tungsten carbide, aluminum and nonferrous metal, and polymeric material. Its hard, brittle, and abrasive grains tend to break down under pressure making SiC grains sharper, cut faster, and also produce finer scratch patterns on most surfaces. SiC is also used in the form of abrasive paper, disks, or wheels. Grains of SiC can be bonded together by sintering to form very

hard ceramics that are widely used in applications requiring high performance, such as car brakes, bulletproof jackets, sealing rings, shaft sleeves, high-temperature nozzles, kiln furniture, automotive particulate filter, and corrosion-resistant devices.

Unfortunately, SiC only occurs in nature as an extremely rare mineral. Therefore SiC must be produced synthetically and is usually produced by the Acheson process, named after its inventor, Edward G. Acheson. Low-cost silica sand and finely ground petroleum coke are mixed and heated in an electric furnace to an elevated temperature for about 24–48 h. The SiO_2–coke reaction occurs in the range 1400°C–2700°C resulting in polycrystalline SiC of variable purity [22–24]. Generally, the accepted mechanism of carbothermal reduction of SiO_2 consists of three stages that often occur simultaneously, as described by the following equations:

$$C(s) + SiO_2(s) \rightarrow SiO\,(g) + CO\,(g) \tag{9.4.1}$$

$$SiO\,(g) + 2C\,(s) \rightarrow SiC\,(s) + CO\,(g) \tag{9.4.2}$$

$$CO_2(g) + C\,(s) \rightarrow 2CO\,(g) \tag{9.4.3}$$

In the first stage, silicon monoxide (SiO) and carbon monoxide (CO) are produced by the solid–solid reaction due to the direct contact between carbon and SiO_2 particles in the original mixtures. In the second stage, the synthesized SiO reacts with carbon and CO to produce SiC. In the third stage, CO_2 reacts with carbon according to Boudouard equation to produce CO, which reacts with SiO in stage 2 to produce SiC.

In the overall process, the first stage is considered the limiting step which is kinetically slow below 1750°C. In the second stage, once significant amounts of SiO and CO gases are produced, the reactions for SiC production progresses with little difficulty [25,26].

Depending on temperature reaction, two main crystalline phases are possible: α-SiC, having a hexagonal or rhombohedral crystal structure, is the stable form at an elevated temperature higher than 1700°C; and β-SiC, having a cubic zinc-blend structure, is formed at a temperature below 1700°C. SiC occurs in several forms: as "nonfibrous," as "polycrystalline fibers," or as one of more than 250 different single-crystal modifications (or polytypes) of "whiskers" [27,28]. The Acheson process produces coarse SiC grains that require milling and purification processes for commercial application. Obviously, the smaller the required size of the SiC powder, the higher the energy of milling.

Recently, much interest has been focused on ultrafine nanometric or submicronic SiC powder, which, due to its small size, give high-performance products and composites compared to coarse size powder. A further advantage of these ultrafine materials is their ability to be hot-formed because of their fine microstructure [29–32]. Unfortunately, the manufacturing of nanosized powders by milling of Acheson SiC products is a highly energy-intensive process [33]. A great variety of methods such as sol–gel, microwave, SHS, laser, and plasma have been tested and patented for the synthesis of fine SiC powders, although most of them do not seem commercially viable for various economic and technical issues such as low production rate, difficulties of scaling up, etc. [34–36].

Among the mentioned methods, thermal plasma is a robust technique suitable for massive production of nanosized particles using various precursors. Plasma processing methods published in the literature may differ in the type of plasma torch [arc or radio frequency (RF)], applied plasma gases, reactor design, and feedstock material, but the ruling mechanism is the same: the thermal plasma evaporates the precursors regardless of their types and reactions occur in the gas phase. In fact, Salinger injected liquid precursors such as methyltrichlorosilane and methylchlorodisilanes into a RF plasma torch of 50 kW to synthetize submicronic SiC in beta crystalline phase [37]. Ramachandran and Reddy synthesized SiC using a thermal plasma processing technique from SiO_2 as the solid feed and CH_4 as the gaseous reducing agent. Generally, spherical particulate matter of no greater than 500 nm and nanorods of about 20–30 nm in diameter are produced [38]. Freda et al. synthesized SiC powder by injecting solid precursors, pyrolysis char and silica sand, to a RF plasma torch reactor at pilot scale [39]. This activity was carried out under a research project called TyGRe (Tire Gasification Residues) that was funded by the European Community's Seventh Framework Programme (FP7/2007-2013 call FP7-ENV-2008-1) [40].

Interesting novelties of this research project is the production of submicronic SiC, framed in a circular economy approach, where waste tires are recycled as the carbon source for the production of the ceramic material. Today, the depletion of fossil source, the huge amount of carbon-based produced waste, focus on the environment and climate changes, are driving the scientific community to investigate unconventional carbon sources. In the following section, scientific works concerning SiC production from alternatives carbon sources are reviewed.

9.4.3 Production of silicon carbide from alternative carbon sources

Climate changes and problems related to the availability of fossil sources have pushed researchers to identify sustainable alternatives for the production of fuels, chemicals, and materials, with the aim to mitigate the effects of the production chains on the environment, society, and economy. The circular economy and sustainable resource management have been considered as strategic aspects within the European Commission's European Green Deal. The efficient and sustainable management of waste is a key strategy for shifting toward a society characterized by a low-carbon, greener, and circular economy. Therefore waste production should be minimized and, where waste cannot be avoided, it must be considered as a resource in order to recover its economic value and avoid or minimize its impact on the environment and on climate change. With this in mind, the Circular Economy Action Plan provides for the introduction of laws and rules for waste collection, waste recycling, and production of "sustainable products," aiming to support the circular design of products by giving priority to reduce and reuse materials before recycling them. For instance, packaging in EU markets is expected to be totally reusable or recyclable by 2030. Similar actions will be adopted to minimize plastics waste by the utilization of biodegradable and bio-based plastics.

In recent decades, the utilization of waste or biomass-derived residues as resources have received growing attention as they may be considered as valuable carbon sources for the production of fuels (e.g., synthetic oils, gasoline- or diesel-cut hydrocarbons); chemicals (e.g., methanol); and new products. The anaerobic digestion of the organic fraction of municipal solid waste to produce biomethane is an example of strategy to convert a waste stream into new valuable streams. Other examples include the production of hydrogen or methanol from plasmix waste (mixed plastic unsuitable for mechanical recycling) via gasification and the production of char and oils from the pyrolysis of tires. The mentioned examples are commercial strategies for the conversion of waste into new products. Nevertheless, the sustainability of a waste-to-goods process is strongly related to the value of the final product compared to the market alternatives. Therefore the production of high-added value from waste speeds up the transition toward a low-waste economy.

The production of SiC from waste may be considered one attractive solution. As mentioned before, SiC is currently mainly

produced by the Acheson process by using sand and coke as precursors. Carbon-containing waste and biowaste may be considered as alternative sources to fossil fuels. Nevertheless, few studies have been reported on the waste-to-SiC process; some of them are briefly reported in this chapter.

Biomass or agriculture wastes may be considered as a good sources of raw materials for SiC production since they naturally contain both SiO_2 and carbon that may react, under high-temperature pyrolysis conditions (>1200°C), to form SiC, as discussed in the review by Chiew and Cheong [41]. During the pyrolysis of biomass, four competing phenomena occur: (1) phase change of silica toward cristobalite, (2) formation of SiC fibers, (3) formation of SiC particles, and (4) graphitization of carbon. Reaction conditions should be finely tuned in order to control the kinetics of these processes. For instance, short residence time at 1200°C–1400°C favors the formation of SiC fibers, while rapid heating at 1300°C–1500°C promotes the formation of particles. Furthermore, the product quality may be controlled by focusing on other aspects, such as inert gas flowrates inside the reactor. In fact, the synthesis chamber needs to be purged continuously to remove the CO formed that may inhibit the contact between SiO_2 and C [42]. Usually, argon, hydrogen, nitrogen, or vacuum conditions may be adopted to drive away the CO from the reactor [41]. Due to the presence of inorganics in the biomass, which may reduce the purity of the final product, biomass may be pretreated with acids and subjected to various purification techniques [41]. However, carbon residues from biomass treatments (e.g., gasification) have been used as C-source for SiC synthesis.

In 2007, Galvagno et al. reported the synthesis of beta SiC powders from biomass gasification residues [43]. In particular, char produced from gasification of biomass is usually recognized as a byproduct and its management has an effect on the economic balance of the process. In this regard, residual char from biomass gasification (also called biochar) is usually applied in the production of activated carbons or solid fuels due to its high carbon content. Due to its low cost, biochar may then be used as a carbon source to replace coal in chemical reactions such as SiC synthesis. Galvagno and coworkers studied the synthesis of beta SiC by starting from a mixture prepared by mechanical mixing of silica and char (SiO_2/C weight ratio of 1.514) and by performing the synthesis in a tube furnace kept at 1550°C with residence times in the range 1–2.5 h. Biochar, obtained from gasification of poplar at 850°C, had a carbon content of about 76% by weight, thus justifying its utilization as carbon source.

The obtained powder was characterized by X-ray diffraction, Fourier-transform infrared (FT−IR) spectroscopy, thermal gravimetric analysis, and transmission electron microscopy. The authors found that residence time had an effect on both conversion and selectivity toward beta SiC. The maximum SiC yield was achieved with a residence time of 90 min. Under these conditions, a product purity of 80% was obtained. Purity may be increased by increasing the residence time but with a negative effect on the yield. X-ray diffraction (XRD) revealed that alpha-phase SiC is the main impurity of the obtained powder. The presence of amorphous silica was also observed. On the contrary, TGA analysis indicated the absence of residual carbon for residence time longer than 90 min. For shorter residence time, residual carbon as low as 1.3% was measured.

The obtained material appears as a very thin spherical-shaped SiC powder of nanometric size in the range 30−100 nm. The authors also found that, for long residence time, SiC fibers were also formed, probably due to the gas-phase reaction of SiO with CO. The authors claimed that the homogeneity of the starting mixture is an important requirement for the synthesis, in order to have an intimate solid−solid surface interaction.

In 2011, Károly et al. published a study on the continuous synthesis of SiC nanoparticles by a RF thermal plasma technology starting from commercial silica powder and various types of carbon source such as graphite, biochar, carbon black, and soot derived from tire pyrolysis [44]. The utilization of a tire-derived carbon source is of particular interest from an environmental point of view, due to the large number of ELTs annually produced and that should be properly valorized. The authors performed the SiC synthesis in a RF plasma reactor consisting of an induction plasma torch (maximum power of 30 kW at 3−5 MHz) installed on the top of the reactor connected to a filter system, a vacuum pump, and a powder feeding unit. Plasma gas was a mixture of Ar and He. After production, the residual carbon was burned off at 610°C and the residual silica removed by HF washing. The authors found that the size of the obtained SiC was around 100 nm regardless of the type of carbon source used, but with a nonspherical shape with size in the range 20−120 nm. By characterization with XRD, the authors found that carbon, metallic silicon, and amorphous phases (i.e., silica and carbon) were detected as the main impurities. In particular, amorphous silica may have been formed by a rapid oxidation of SiO in low-temperature regions of reactor. The purity of the feedstocks is an important aspect to take into account. In fact, it was found that the metallic zinc of tire pyrolitic soot was also found in the final

product. Similarly, the thermal profile inside the reactor plays a crucial role in alpha/beta phase distribution. Károly et al. found that beta-phase concentration is 20%–40% higher than alpha-phase, regardless of the carbon source. The presence of both phases may be related to the fact that the precipitated particles had different trajectories (i.e., a different thermal history), leading to the formation of an alpha/beta mixed phase. In fact, beta-phase is stable at temperatures lower than 1500°C, while alpha-phase is stable at higher temperatures. The authors also found that the conversion level was in the range 60%–73% regardless of grain size and surface specific area of the precursor particles, suggesting that, with a RF thermal plasma reactor, the reaction takes place in the gas phase after vaporization of the injected precursors.

In 2014, Rajarao et al. used char derived from pyrolysis at 700°C of electronic waste compact discs (CDs) as the carbon source [45]. The obtained carbon exhibited a high surface area (about 330 $m^2\ g^{-1}$) due to high porosity. SiC synthesis was performed by preparing a pellet of char and SiO_2 powder and subjecting it to thermal treatment in a tubular furnace at 1550°C for one hour in argon atmosphere.

The obtained SiC powder was gray green in color with spherical nanoparticles with a diameter of 40–90 nm as may be observed from the scanning electron microscope (SEM) images shown in Fig. 9.4.1.

In 2017, Maroufi et al. reported an experimental study of the synthesis of a mesoporous SiC nanofiber/particle composite starting from a binary mixture of two problematic waste streams, such as electronic waste (e-waste) glass as Si-source and ELT rubber as C-source, by means of carbothermal reduction [46]. In particular, waste computer monitors and TV screens were used as the glass

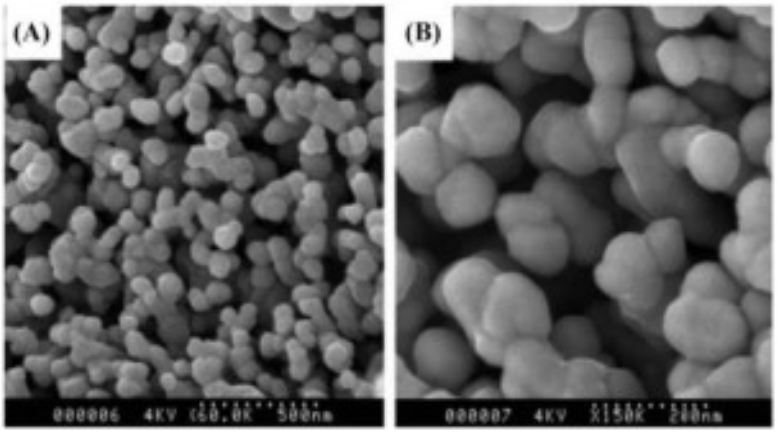


Figure 9.4.1 Low magnification (A) and high magnification (B) scanning electron microscopy (SEM) of SiC synthesized from compact disc (CD)-derived char [45]. Reproduced with the permission of Elsevier, License number: 4855771411267.

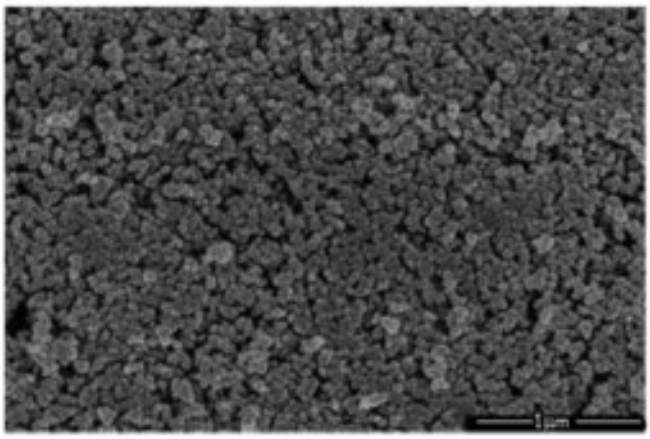


Figure 9.4.2 FE-SEM image of carbon derived waste tires via pyrolysis at 1550°C, for 10 min, under argon [46]. Reproduced with the permission of Elsevier, License number: 4855780204409.

source. The derived chunks were pulverized using a ring mill. Carbon black produced by pyrolysis at 1550°C of waste tire rubber shreds was used as the carbon source. The obtained carbon exhibits a surface area of 92.1 $m^2\ g^{-1}$ due to nanospherical particles with a size of about 30–40 nm as can be seen in Fig. 9.4.2. The tire-derived carbon consists primarily of carbon (83.8 wt.%) and a significant amount of hydrogen (7.13 wt.%), oxygen (6.8%wt), and sulfur (2 wt.%). Sulfur is used during the vulcanization treatment of tire polymers (e.g., poly-isoprene, styrene-butadiene, poly-butadiene). The obtained carbon powder also contains inorganic compounds (i.e., ash) consisting of ZnO (40.8 wt.%), SiO_2 (27 wt.%), CaO (8.4 wt.%), SO_3 (7.6 wt.%), and Al_2O_3 (3.1 wt.%) and smaller amounts of iron, magnesium, sodium, and potassium oxides.

To perform SiC synthesis, the authors prepared a paste by mixing a stoichiometric mixture of glass- and ELT-derived powders with ethyl glycol. The paste was pressed in cylindrical pellets (20 mm diameter, 3–4 mm thickness) by using a uniaxial hydraulic press operating at 100 MPa and 100°C. The resulting pellets were then treated at 1550°C under argon purge for 150 min to perform SiC synthesis.

The product obtained after heat treatment appeared as a greenish gray powder (see Fig. 9.4.3) that is typical of SiC powder. Fig. 9.4.4 shows the FE–SEM images of the obtained product revealing the presence of both surface smoothed nanofibers (5 microns in length and 10–150 nm in diameter) and nanoparticles (size 30–40 nm).

The morphology of the product is believed to depend on the reaction mechanism. In particular, gas-phase reaction between SiO and CO should promote the formation of nanofibers. In contrast, nanoparticles should be preferentially formed by reaction between

Figure 9.4.3 Image of SiC powder obtained by thermal reduction of e-waste- and ELT-derived powders [46]. Reproduced with the permission of Elsevier, License number: 4855780204409.

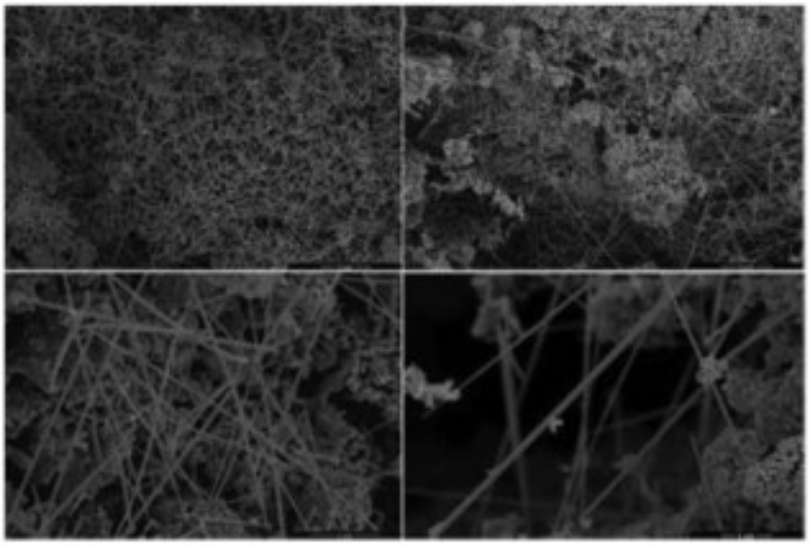


Figure 9.4.4 FE-SEM images of the SiC produced at 1550°C after 150 min [46]. Reproduced with the permission of Elsevier, License number: 4855780204409.

gas-phase SiO and carbon nanoparticles; therefore the partial pressure of SiO intermediate and the availability of surface area of carbon precursors may play an important role in SiC formation [47].

Although few studies have focused on a waste-to-SiC process, the growing market of SiC and the new scenarios on waste management will push researchers to focus more efforts on this field and also within the European project. For instance, the European Union's Seventh Framework Programme (FP7/2007-2013) founded a project (discussed above and below), named TyGRe, focused on the production of SiC from waste by using an RF plasma-torch reactor with a technological readiness level (TRL) of 5.

9.4.4 The TyGRe project

TyGRe (high-added value materials from waste **Ty**re **G**asification **Re**sidues) was a collaborative project of nine European partners: ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development), ETRA (European Tyre Recycling Association), IMEC (Hungarian Academy of Sciences), LIQTECH (Danish SiC end user), TUBITAK (The Scientific and Technological Research Council of Turkey), RWTH (Aachen University), FEBE ECOLOGIC (ENEA spin-off), ELASTRADE (granulate manufacturer), and SICAV (activated carbon manufacturer). The research and development were focused on waste tire recycling by thermal processes mainly devoted to the production of submicronic SiC. Fig. 9.4.5 shows the process scheme of TyGRe project.

In the TyGRe process, granulated waste tires were pyrolyzed in a pilot-scale rotary kiln at about 800°C to produce char and raw gas. The granulated tire mass rate was about 20 kg per hour and the char production was about 8 kg per hour. The produced char was mixed with commercial silica sand with a purity level of 99.5%, and was fed to a ball mill where it was ground to micrometric size. The ground mixture was sieved by a vibrofilter. Particles having diameter higher than 50 micron were rejected. The finer sieved mixture was fed to a 2 MHz RF plasma torch reactor where the SiC synthesis occurred. Argon gas was used to generate the plasma. The off-gas from the plasma torch reactor, composed of Ar and CO, was injected

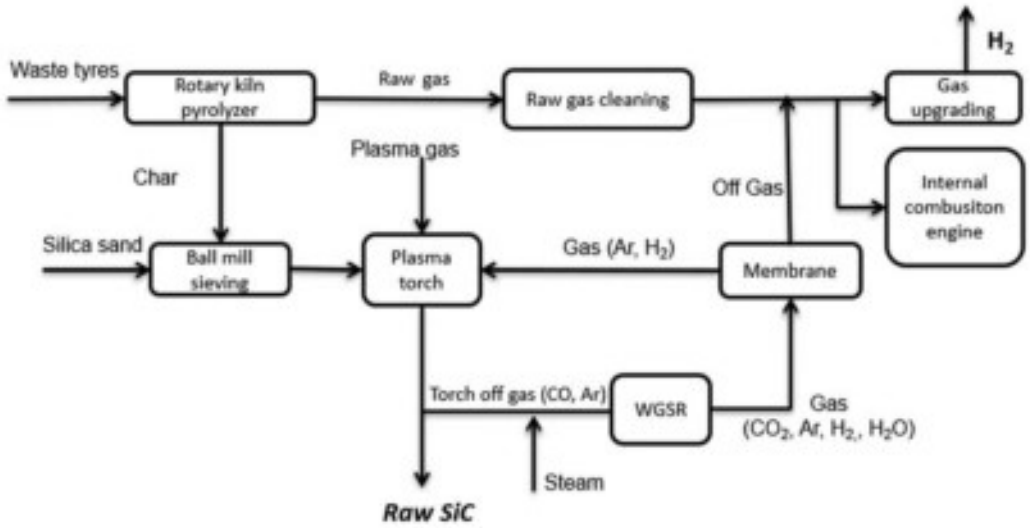


Figure 9.4.5 Process scheme of TyGRe project.

with steam and fed to a water gas-shift reactor where the CO was shifted by steam to H_2 and CO_2. The shifted gas crossed a membrane module that recovered Ar and H_2 that were recycled to the plasma torch reactor. The raw gas from the pyrolyzer crossed a cleaning unit where particulate, tar, and water were removed. The syngas was mixed with the membrane off-gas and crossed a gas-upgrading unit composed of methane steam reforming and water gas-shift units with the goal to produce hydrogen-rich gas. Otherwise, it could feed an internal combustion engine for power production (40 kW_e). The technological infrastructure was installed and run at the ENEA-Trisaia Research Centre (Italy), as shown in Fig. 9.4.6.

The heart of the technological infrastructure is the plasma torch reactor for the synthesis of submicronic SiC. The other modules of the infrastructure are based on well-established technologies; therefore the main efforts were devoted to the optimization and fine tuning of the plasma torch reactor for successful SiC synthesis.

The main differences that can be attributed to the TyGRe process compared to the conventional Acheson process include the fact that the production of SiC by TyGRe is continuous and occurs in tenths of seconds in contrast to the Acheson process where the production is batch and occurs in some days and the size of the particles produced by TyGRe is submicronic whereas coarse particles are produced by Acheson. Milling of coarse particle is energy and time consuming; moreover the SiC is polluted by the material used for the milling. Finally, the SiC from the TyGRe process has a higher added value (size and purity), which compensates for the higher energy consumption of the plasma torch reactor compared to furnace Acheson.

Plasma torch plant. The feeding system of the precursor mixture powder consists of a hopper and a screw, equipped with a vibration system that avoids cohesive and adhesive behavior of the mixture. A carrier gas (Ar) purges the feeding system. The mixture axially gets into the plasma torch, in the middle of the plasma flame, by a vertical probe. The plasma torch was provided by the plasma microsystem. It is a RF (2 MHz) induction torch mounted on the top of the reactor. RF plasma provides the largest volume and lowest velocity of the plasma gases (and as a consequence the longest residence time for the injected precursor materials) at a given power level as compared to any other type of plasma (e.g., arc, microwave). Argon/Helium were used as plasma gas. Helium increases the energy of the plasma [48]. The stainless-steel wall reactor is indirectly cooled by water that flows in a shell to avoid

Figure 9.4.6 TyGRe plant buildup in ENEA-Trisaia: (A) rotary kiln pyrolyzer; (B) raw gas cleaning; (C) mixture grinding, sieving, and feeding system to plasma torch reactor; (D) internal combustion engine; (E) gas upgrading; (F) membrane module; (G) particular of plasma torch; and (H) plasma torch reactor.

damages by the high plasma temperature. The cooled wall of the reactor hinders the SiC grain growth with production of submicronic grains. Downstream of the reactor a collecting tank, an electrofilter, and a suction fan are installed. With the goal of increasing the yield of the process, an isostatic graphite tube was installed under the plasma torch to confine the plasma flame. Isostatic graphite withstands the high temperatures of the plasma, high thermal shock at startup, and thermal dilatation [49].

Method and Results. After having ignited the torch and having set operative parameters such as the plasma gas flow rate, carrier gas rate of the mixture, and power of the torch, the mixture was fed to the plasma torch reactor. An image of the ignited plasma torch during a test is shown in Fig. 9.4.6G. After the running of the test the reactor was disassembled and the product powder was collected. It was composed of unreacted carbon and silica and SiC. Carbon was oxidized to CO_2 by air in a muffle at 700°C, according to Eq. 9.4.5:

$$C + SiO_2 + SiC + O_2 = CO_2(g)\uparrow + SiO_2 + SiC \tag{9.4.5}$$

The SiO_2 was leached by an excess of hydrogen fluoride solution, as in Eq. 9.4.6:

$$SiO_2 + SiC + 6HF = H_2SiF_6(g)\uparrow + SiC + 2H_2O \tag{9.4.6}$$

After drying, the SiC was weighed and the yield was calculated. A fine tuning of the process variables and the isostatic graphite tube provided an interesting process yield. In particular, yields above 70% were obtained with a mixture mass rate of 0.6 kg per hour, having a C/Si ratio equal to 1.3; a torch power of 65 kW, with 150 l(N) per minute of plasma gas (90 l(N) per minute Ar, 60 l(N) per minute He), and 70 l(N) per minute of carrier gas Ar. Here l(N) refers to liters at 293.15 K and 1 atm. From XRD analysis of the purified powder of SiC, clear signals can also be attributed both to the α-phase as well as to the β-phase. The dynamic light scattering (DLS) analyses have shown the production of submicronic powder with a Gaussian-like distribution with an average size in the range 300–400 nm. The SEM image confirms the size of the particles measured by dynamic light-scattering analysis. As for the morphology, the powder appears, at SEM image, as formed by small spheroidal particles and larger nonspheroidal ones. From a deep XRD analysis, some contaminants in the SiC powders were detected. The most common were quartz, corundum, graphite, metallic silicon, and silicates. Their amount ranged between 1–3 wt.%, when the yield was above 70% [39].

The TyGRe project received the Oscar Masi prize, awarded by the Italian Association Industrial Research (AIRI), as the best project for the circular economy in the category public research organizations and universities. A presentation of the project was shown at the conference promoted by DG ENVIRONMENT "What makes a successful ecotechnological European project?," held in Brussels on 20 March 2017. Three scientific papers regarding the SiC production via TyGRe process, TyGRe SiC characterization, and applications have been published [39,50,51]. Two Italian patents concerning the purification method of precursors and SiC production have been filed [49–52].

9.4.5 SiC from end-of-life tire pyrolysis streams: a simulation study

Three simulation studies by thermodynamic calculation were carried out to analyze the SiC synthesis, from silica sand as silicon source and, as carbon source, three different pyrolysis streams: char, pyrolysis oil, and pyrolysis gas. The char was simulated as elemental carbon with an ash content of 10 wt.%, as reported in the literature [53]. The pyrolysis oil was simulated by the hydrocarbon decane, with a metal content of 0.1 wt.% [54]. The pyrolysis gas was a mixture of methane (20 vol.%), hydrogen (20 vol.%), $CO-CO_2$ (5 vol.%), and C_2-C_4 (55 vol.%) at about 500°C. The main carbon sources for the SiC synthesis were methane and C_2-C_4 hydrocarbons. The relative composition is strongly influenced by the experimental condition; higher pyrolysis temperature helps the C_2-C_4 cracking toward simpler molecule of CH_4. Therefore the pyrolysis gas was simulated by propane [54]. Silica sand was simulated by SiO_2 at 99.5 wt.%, with 0.5 wt.% of Al_2O_3, similar to the silica used in the experimental tests of Freda et al. [39]. The thermodynamic calculation of the chemical equilibrium occurred minimizing the Gibbs energy of the system. The compressibility and fugacity coefficients for vapor and liquid phases and the enthalpy were calculated by the Peng–Robinson equation of state. This approach provides reliable data for potential products and their concentrations when high temperature and long enough residence time are considered. Kinetic limitations could switch the thermodynamic results from the experimental. The removal efficiency of the impurities of both carbon source and silicon source was set equal to 99%. This value is a realistic value coming from the laboratory experience of the authors.

9.4.5.1 SiC from char

For the synthesis of SiC from char and silica sand, a stream that respected the molar ratio of C and SiO_2 of the following reaction (9.4.7) was used in the calculation of the Gibbs energy:

$$3C + SiO_2 = 2CO + SiC \quad (9.4.7)$$

For the minimization of the Gibbs energy C, SiO_2, CO, and SiC were considered. From Fig. 9.4.7, it can be seen that the SiC synthesis starts at about 1400°C, and that the maximum conversion of reactants to SiC (52%) was observed at 2600°C. At higher temperatures a decreasing trend is observed with the raw produced powder of SiC polluted with unreacted char, SiO_2, and other impurities. Therefore after the chemical synthesis, char and SiO_2 must be removed to recover the SiC. Char is usually burned at about 600°C by air for about 60 min and SiO_2 leached using concentrated hydrogen fluoride [44]. On the basis of experimental results, a removal efficiency of 99% of the unreacted char, SiO_2, and impurities was considered. Under this hypothesis, the SiC content of purified powder is equal to 97.5% at 2600°C. Purity less than 90% can be observed at temperature synthesis lower than 1900°C and higher than 3350°C (Fig. 9.4.8).

From an operative and environmental point of view the use of hydrogen fluoride is very complex and detrimental and its use should be kept to a minimum. A second sensitivity analysis was carried out increasing the molar ratio between char and SiO_2 at isothermal condition synthesis of 2600°C with the goal to convert most of the SiO_2. At the temperature of 2600°C, the conversion of the SiO_2 shows an increasing asymptotic trend with the increasing C/SiO_2 molar ratio, but the purity of the produced SiC shows that with C/SiO_2 ratios of higher than 6

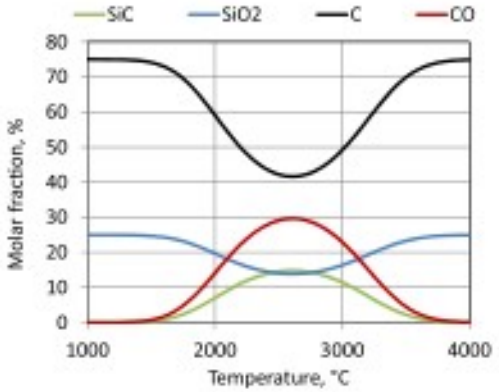


Figure 9.4.7 Molar distribution versus temperature (carbon source: pyrolysis char).

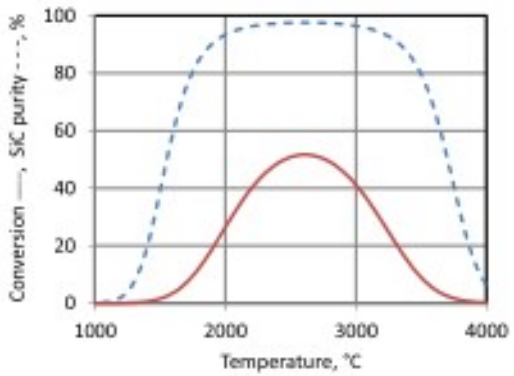


Figure 9.4.8 Conversion to SiC and SiC purity versus temperature (carbon source: pyrolysis char).

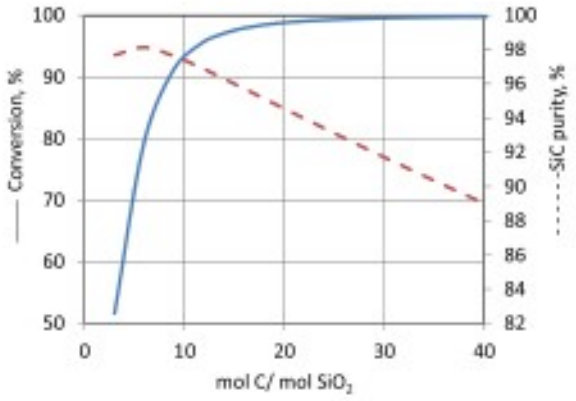


Figure 9.4.9 Conversion to SiC and SiC purity versus mol C/ SiO2 at 2600°C (carbon source: pyrolysis char).

a decreasing trend is seen (Fig. 9.4.9). In a production process the C/SiO_2 ratio should be tuned to find a compromise between the yield, the specific energy duty, and purity of the SiC.

9.4.5.2 SiC from pyrolysis oil

A stream of decane (that simulated pyrolysis oil) and silica sand was used in the Gibbs energy calculation, with a molar ratio that respects the stoichiometry coefficients of the reactants of the following reaction:

$$C_{10}H_{22} + 7SiO_2 = 7SiC + 3CO + 11H_2O \qquad (9.4.8)$$

For the minimization of the Gibbs energy the reactants and the products of the reaction (9.4.8) were considered. Fig. 9.4.10 shows that SiC synthesis occurs in a range of temperature between 950 and 3300°C. The conversion of the reactants, pyrolysis oil, and SiO_2 is quantitative, above 3300°C. From a comparison with the previous case, where char was the carbon

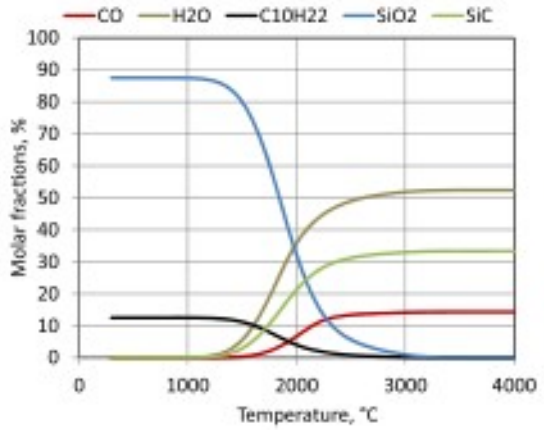


Figure 9.4.10 Molar distribution versus temperature (carbon source: pyrolysis oil).

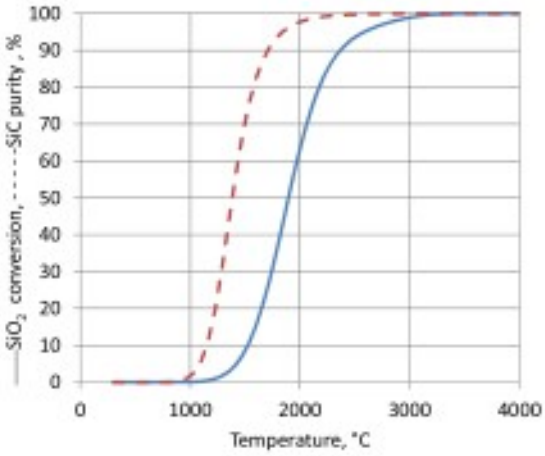


Figure 9.4.11 SiO_2 conversion, SiC purity versus temperature (carbon source: pyrolysis oil).

source, at similar stoichiometric condition, the maximum conversion to SiC (52%) was observed at 2600°C and the purity of the SiC powder was 97.5%. In the case of pyrolysis oil at 2600°C, the conversion of SiO_2 to SiC is 95% and the purity of the SiC is 99.8% (Figs. 9.4.10 and 9.4.11).

From this thermodynamic calculation, the pyrolysis oil as the carbon source seems to be advantageous compared to char, both for higher conversion to SiC, and for the higher purity of the synthesized SiC. A drawback of the process from pyrolysis oil could be the feeding system. In fact, pyrolysis oil from waste tires is a viscous liquid composed of organic compounds C_5–C_{20} or higher, with different proportions of aromatic and aliphatic compounds depending, besides the process conditions, on tire composition [55–57]. Its viscosity could create

problems in the feeding that could include carbon deposit and oil sticking (and it affects the oil flow through pipes, the atomization, and the performance and wear of the pump) [58]. Therefore a careful design of the oil feeding system should be taken into account.

9.4.5.3 SiC from pyrolysis gas

A stream of pure propane was fed with silica sand was considered in the Gibbs energy calculation, respecting the molar ratio of the stoichiometric coefficients of the reactants of the following reactions:

$$3C_3H_8 + 7SiO_2 = 7SiC + 2CO + 12H_2O \qquad (9.4.9)$$

As in the previous case, the reactants and the products of the reaction (9.4.9) were considered for the minimization of the Gibbs energy. The SiC synthesis from propane and SiO_2 occurs between about 1650°C and 3800°C. The synthesis of SiC from propane is thermodynamically less favored compared to pyrolysis oil. Compared to the synthesis from char, higher reactants conversion can be observed at temperature higher than 3000°C. Generally, the synthesis of SiC from pyrolysis gas provides a SiC with very high purity 99.99% when a temperature above 3800°C is approached (Figs. 9.4.12 and 9.4.13). Above this temperature the conversion of reactants to SiC is quantitative and the environmental impacting the HF leaching process is minimized because the condensable reaction products are composed of SiC and water and not reactive silica impurities.

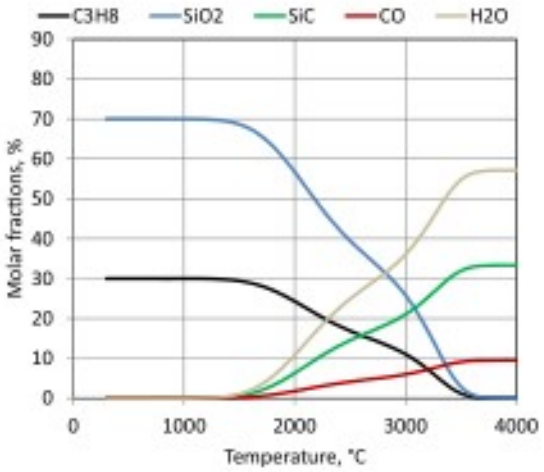


Figure 9.4.12 Molar distribution versus temperature (carbon source: pyrolysis gas, C_3H_8).

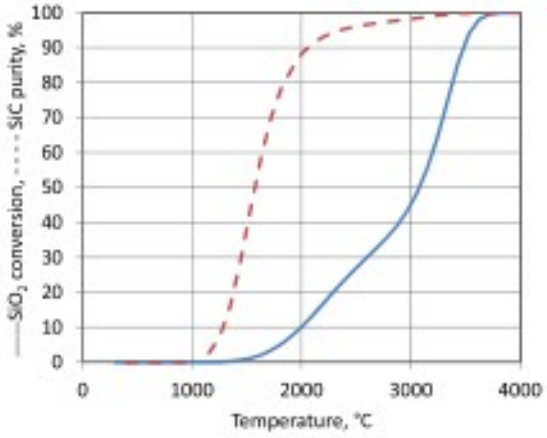


Figure 9.4.13 SiO_2 conversion, SiC purity versus temperature (carbon source: pyrolysis gas, C_3H_8).

9.4.6 Conclusion

The fate of end-of-life tires is a serious and still open environmental issue. Tires are difficult to recycle because of the cross-linked polymeric structure of their main constituent: natural or synthetic rubber. Pyrolysis of end-of-life tires degrades the chemical structure of the rubber giving three output streams: char, pyrolysis oil, and gas. They are potentially three carbon sources available for production of secondary goods that could open new paths in the recycling of waste tires by thermal treatments.

In the European project TyGRe, ELT is pyrolyzed to produce char that is fed with silica sand into a pilot-scale RF plasma torch reactor to produce ultrafine SiC. SiC is a performing material for mechanical applications as well as for use in high-power, high-voltage, and high-temperature electronic components. Under the TyGRe project, submicronic powder of SiC is produced that shows both the alpha and beta crystalline phases. The powder is contaminated by mineral impurities (1– 3 wt.%), linked with the nature of the feedstock. The process yield is about 70%. With the goal to investigate the potential of the other pyrolysis streams, oil, and gas as carbon source for SiC production, a preliminary thermodynamic analysis was carried out minimizing the Gibbs energy. Compared to char, pyrolysis oil has a much lower ash content (0.1 vs. 10 wt.%) that produces a purer SiC. Moreover, at the investigated composition of the reactants stream, the quantitative conversion was observed at 3300°C. Ultrapure SiC was produced from pyrolysis gas, but in this case, the quantitative conversion to SiC was observed at 3800°C. This preliminary thermodynamic investigation could

address the recycle of pyrolysis oil and gas from waste tires, toward high-purity SiC production. SiC purity is a stringent requirement in advanced electronic applications. However, some technical issues should be taken into account including the fact that pyrolysis oil is a viscous liquid and a tailored injection system should be designed; the fouling of the plasma torch should be prevented when hydrocarbon precursors are used; and lastly, the hydrocarbon content and type, of both oil and gas, are related to the experimental conditions of the pyrolysis.

References

[1] ETRMA. Annual Report 2017 accessed on 28/01/2020 at https://www.etrma.org/wp-content/uploads/2019/09/20170905-etrma-annual-report-2016-17-final.pdf.

[2] A. Rowhani, T.J. Rainey, Scrap tyre management pathways and their use as a fuel—a review, Energies 9 (2016) 888. Available from: https://doi.org/10.3390/en9110888.

[3] E.C. Rada, M. Ragazzi, R. dal Maschio, M. Ischia, V.N. Panaitescu, Energy recovery from tyres waste through thermal option energy recovery from tyres waste through thermal option. U.P.B. Sci. Bull., Ser. D. 74 (4) (2012).

[4] "2017 U.S. Scrap Tire Management Summary" (PDF). U.S. Tire Manufacturers Association. 18 July 2018.

[5] V.L. Shulman, Wastebook, Ch. 26 Tyre Recycling, Elsevier, 2017.

[6] D. Lo Presti, Recycled tyre rubber modified bitumens for road asphalt mixtures: a literature review, Constr. Build. Mater. 49 (2013) 863–881.

[7] A. Evans, R. Evans. The composition of a tyre: typical components. Published by The waste & Resources Action Programme. The Old Academy, 21 Horse Fair, Banbury, Oxon OX16 0AH.

[8] M.R. Islam, M.N. Islam, N.N. Mustafi, M.A. Rahim, H. Haniu, Thermal recycling of solid tire wastes for alternative liquid fuel: the first commercial step in Bangladesh, Procedia Eng. 56 (2013) 573–582.

[9] M.S. Karmacharya, V.K. Gupta, V.K. Jha, Preparation of activated carbon from waste tire rubber for the active removal of Cr(VI) and Mn(II) ions from aqueous solution, Trans. Ind. Ceram. Soc. 75 (4) (2016) 1–8.

[10] N. Cardona, F. Campuzano, M. Betancur, L. Jaramillo, J.D. Martinez, Possibilities of carbon black recovery from waste tyre pyrolysis to be used as additive in rubber goods—a review, IOP Conf. Series: Mater. Sci. Eng. 437 (2018) 012012.

[11] http://newenergy.hu/en/ accessed on 04/12/2019.

[12] F.A. López, T.A. Centeno, O. Rodríguez, F.J. Alguacil, Preparation and characterization of activated carbon from the char produced in the thermolysis of granulated scrap tyres, J. Air & Waste Manag. Assoc. 63 (5) (2013) 534–544.

[13] http://bhagirathindia.com/ accessed on 04/12/2019.

[14] N. Probst, M. Loeffler, Pyrolysis Carbon Black, an opportunity for the rubber market. Presented at the Fall 180th Technical Meeting of the Rubber Division of the American Chemical Society, Inc. Cleveland, Ohio October 11-13, 2011. ISSN: 1547-1977.

[15] Dunau Carbon report. Activated Carbon and its Applications. Accessed on 04/12/2019. https://www.donau-carbon.com/getattachment/76f78828-2139-496f-9b80-6b6b9bdc6acc/aktivkohle.aspx.

[16] G.L. Harris, Properties of Silicon Carbide, INSPEC, London, 1995.

[17] S. Somiya, Y. Inomata, Silicon Carbide Ceramics—1: Fundamental and Solid Reaction, Elsevier Science Publishers LTD, Essex, 2012.
[18] S.E. Saddow, A. Agarwal, Advances in Silicon Carbide Processing and Applications, Artech House Inc, MA, 2004.
[19] Saint-Gobain Silicon Carbide, Silicon Carbide Production Process n.d., [Online] Available: https://www.sic.saint-gobain.com/about-us/silicon-carbide-production-process [Accessed Aug. 30, 2019].
[20] C.R. Eddy Jr, D K, Silicon carbide as a platform for power electronics, Science 324 (5933) (2009) 1398–1400.
[21] European Commision. (2017). Communication from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions. Brussels.
[22] E.G. Acheson, J. Frank, Instit. 136 (1893) 279.
[23] P.J. Guichelaar, Carbide, Nitride and Boride Materials Synthesis and Processing, Chapman Hall, London, 1997, p. 324.
[24] Y.L. Chiew, K.Y. Cheong, A review on the synthesis of SiC from plant-based biomasses, Mater. Sci. Eng. B 176 (13) (2011) 951–964.
[25] K. Li, J. Wei, H. Li, C. Wang, G. Jiao, J. Univ. Sci. Technol. Beijing 15 (2008) 484.
[26] M. Dehghanzadeh, A. Ataie,S. Heshmati-Manesh. Synthesis of nanosize silicon carbide powder by carbothermal reduction of SiO_2. 2nd International Conference on Ultrafine Grained & Nanostructured Materials (UFGNSM) International Journal of Modern Physics: Conference Series 5 (2012) 263–269.
[27] R. Cheung, Silicon Carbide Microelectromechanical Systems for Harsh Environments, Imperial College Press, 2006, p. 3. ISBN 978-1-86094-624-0.
[28] E.A. Belenkov, E.N. Agalyamova, V.A. Greshnikov, Classification and structure of silicon carbide phases, Phys. Solid. State 54 (2) (2012) 433–440.
[29] G. Magnani, S. Galvagno, G. Sico, S. Portofino, C. Freda, E. Burresi, Sintering and mechanical properties of β-SiC powder obtained from waste tires, J. Adv. Ceram. 5 (2016) 40–46.
[30] V. Yong, H.T. Hahn, Monodisperse SiC/vinyl ester nanocomposites: dispersant formulation, synthesis, and characterization, J. Mater. Res. 24 (2009) 1553–1558.
[31] Z. Guo, T.Y. Kim, K. Lei, T. Pereira, J.G. Sugar, H.T. Hahn, Strengthening and thermal stabilization of polyurethane nanocomposites with silicon carbide nanoparticles by a surface-initiated-polymerization approach, Compos. Sci. Technol. 68 (2008) 164–170.
[32] P. Tatarko, S. Lojanova, J. Dusza, P. Šajgalík, Characterization of rare-earth doped Si3N4/SiC micro/nano-compositesProcess, Appl. Ceram. 4 (2010) 25–32.
[33] A.H. Rashed. (2002). Properties and Characteristics of Silicon Carbide. Decatur, 76234 TX.
[34] A. Najafi, F. Golestani-Fard, H.R. Rezaie, N. Ehsani, Synthesis and characterization ofsilicon carbide nanopowder by solgel processing, Iran. J. Mater. Sci. & Eng. 8 (2) (2011) 41–47.
[35] E. Borsella, S. Botti, M.C. Cesile, S. Martelli, R. Alexandrescu, Nanoscale SiC and Al-O-(N,C) ceramic powders by laser synthesis from gaseous precursors, Nanostructured Mater. 6 (1995) 341–344.
[36] T. Ebadzadeh, E. Marzban-Rad, Microwave hybrid synthesis of silicon carbide nanopowders, Mater. Charact. 60 (2009) 69–72.
[37] R.M. Salinger, Preparation of silicon carbide from methilchlorosilane in a plasma torch, Ind. Eng. Chem. Prod. Res. Dev. 11 (1972) 230–231.
[38] M. Ramachandran, R.G. Reddy, Thermal plasma synthesis of SiC, Adv. Manuf. 1 (2013) 50–61.

[39] C. Freda, G. Cornacchia, A. Donatelli, M. Corrado, M. Martino, A. De Girolamo Del Mauro, et al., A novel thermal plasma based technology for sub-micronic silicon carbide production at pilot scale, Ceramica 65 (2019) 92–98.
[40] http://www.tygre.eu/cms/ accessed on line, 27 April 2020.
[41] Y.L. Chiew, K.Y. Cheong, A review on the synthesis of SiC from plant-based biomass, Mater. Sci. Eng. B 176 (2011) 951–964.
[42] L. Sun, K. Gong, Silicon-based materials from rice husks and their applications, Ind. Eng. Chem. Res. 40 (2001) 5861–5877.
[43] S. Galvagno, S. Portofino, G. Casciaro, S. Casu, L. d'Aquino, M. Martino, et al., Synthesis of beta silicon carbide powders from biomass gasification residues, J. Mater. Sci. 42 (2007) 6878–6886.
[44] Z. Károli, I. Mohai, S.Z. Klébert, A. Keszler, I.E. Sajó, J. Szépvölgyi, Synthesis of SiC powder by RF plasma technique, Powder Technol. 214 (2011) 300–305.
[45] R. Rajarano, R. Ferreira, S.H.F. Sadi, R. Khanna, V. Sahajwalla, Synthesis of silicon carbide nanoparticles by using electronic waste as a carbon source, Mater. Lett. 120 (2014) 65–68.
[46] S. Maroufi, M. Mayyas, V. Sahajwalla, Waste materials conversion into mesoporous silicon carbide nanoceramics: nanofibre/particle mixture, J. Clean. Prod. 157 (2017) 213–221.
[47] Z. Ryu, J. Zheng, M. Wang, B. Zhang, Preparation and characterization of silicon carbide fibers from activated carbon fibers, Carbon 40 (2002) 715–720.
[48] J. Jonkers, M. van de Sande, A. Sola, A. Gamero, J. van der Mullen, Plasma Sources Sci. Technol. 12 (2003) 30.
[49] G. Cornacchia, C. Freda, S. Galvagno, S. Portofino, A. Donatelli, M. Martino, et al., "Apparato per il confinamento fisico di una torcia al plasma finalizzato all'incremento di resa in sintesi di materiali ceramici," Patent Appl. 102015000018115 (2015).
[50] G. Magnani, S. Galvagno, G. Sico, S. Portofino, C. Freda, E. Burresi, Sintering and mechanical properties of ß-SiC powder obtained from waste tires, J. Adv. Ceram. vol. 5 (1) (2016) 40–46.
[51] A. De Girolamo Del Mauro, G. Nenna, R. Miscioscia, C. Freda, S. Portofino, S. Galvagno, et al., Nonvolatile RRAM cells from polymeric composites embedding recycled SiC powders, Langmuir 30 (2014) 12421–12428.
[52] S. Galvagno, S. Portofino, C. Freda, G. Magnani, A. Donatelli, M. Morgana, et al. Metodo di Purificazione da Metalli per la Preparazione di Composti Ceramici ad Elevata Purezza. Patent Appl. RM2013A000277 (2013).
[53] I. de Marco Rodriguez, M.F. Laresgoiti, M.A. Cabrero, A. Torres, M.J. Chomón, B. Caballero, Pyrolysis of scrap tyres, Fuel Process. Technol. 72 (2001) 9–22.
[54] J.D. Martinez, et al., Waste tyre pyrolysis – a review, Renew. Sustain. Energy Rev. 23 (2013) 179–213.
[55] I. Rodriguez, M.F. Laresgoiti, M.A. Cabrero, A. Torres, M.J. Chomòn, B. Caballero, Pyrolysis of scrap tires, Fuel Process. Technol. 72 (2001) 9–22.
[56] J.F. Gonzalez, J.M. Encinar, J.L. Canito, J.J. Rodriguez, Pyrolysis of automobile tyre waste. Influence of operating variables and kinetics study, J. Anal. Appl. Pyrolysis 58–59 (2001) 667–683.
[57] R. Murillo, E. Aylòn, M.V. Navarro, M.S. Callén, A. Aranda, A.M. Mastral, The application of thermal processes to valorise waste tyre, Fuel Process. Technol. 87 (2006) 143–147.
[58] S. Murugan, M.C. Ramaswamy, G. Nagarajan, Performance, emission and combustion studies of a DI diesel engine using distilled tires pyrolysis oil diesel blends, Fuel Process. Technol. 89 (2008) 152–159.

10

Surface-modified materials

Alexander Paasche and Frank Lindner
Evonik Operations GmbH, Smart Materials - High Performance Polymers, Marl, Germany

10.1 Introduction

The concept of surface modification can be an economic way to improve properties of recycled rubber. A simple prerequisite of this concept is the existence of a surface that can be modified, which naturally puts the focus more on crumb rubber and rubber powders and less on reclaimed rubbers that are desulfurized as a bulk material. Some advantages can result from the fact that only a few percentages of the recycled material need to be treated: the surface or interface area. This imposes some potential benefits over bulk treatment methods:

- The material properties of the vulcanized rubber polymer are mostly conserved in the rubber particles, and not deteriorated. This is an advantage over harsh bulk treatment methods that inevitably lead to some degree of degradation of the rubber polymer chains.
- Surface treatment typically consumes less energy or material compared to processes that require treatment of the whole bulk of the rubber material by intensive mixing.
- Compared with bulk treatment methods, like desulfurization processes, surface treatment can start with small investments in machinery and equipment. Whenever it is possible to decide between the equipment costs of an extruder-based desulfurization process plant and a simple mixing plant setup for applying surface treatment chemicals to crumb rubber, the investment decision might be in favor of the latter one.

In summary, there are good reasons to consider surface treatment for many applications of recycled rubber. Surface treatment has passed its time of being an academic approach and is today applied in different fields of recycled rubber industry, like molded products from rubber powders, rubber-modified asphalt, or use in virgin rubber compounds.

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00010-7
© 2021 Elsevier Inc. All rights reserved.

10.2 Why modify?

Crumb rubber and rubber powders make up a significant part of the material recovery share of end-of-life tires. Marketwise, there is a notable difference between the Western countries, where ground tire rubbers (GTR) dominate compared to devulcanized rubber, and Asian regions, where desulfurization is still the major valorization route for material recovery. Nevertheless, ground rubber materials have shown growth rates over the last years that exceed that of the general rubber industry average, especially in Asia [1,2]. It should also be noted that value creation by material utilization of end-of-life tires is often higher, compared to burning, since the price in thermal recovery is only related to its caloric value. In material use, the value creation can be related to the competing virgin materials, which might be substituted by the secondary raw material. A partial or total replacement of virgin material demands for a processing characteristic, performance, or at least a price/benefit ratio that makes it possible to qualify the rubber powders for the respective applications. Whereas the price issue can be influenced by political measures like incentives or green public procurement, the performance and processing issue can only be solved by technical optimization and innovation. For this reason, the surface modification can be very helpful to improve this part of the total equation.

In general, there are three factors that determine processing and performance of ground rubbers:

1. Source of rubber material. The composition of the rubber compounds varies by their intended use (e.g., having higher natural rubber (NR) content in truck and bus tires, or more synthetic rubber content in passenger car tires). Hence, the choice of the recycled rubber source has an obvious impact on its properties.
2. Particle size. Smaller particle sizes result in larger rubber surface area, which influences its properties in performance, but also in processing. Larger surfaces will accelerate migration and swelling processes, as well as give more contact area with embedding matrix materials (or other rubber particles). Hence, for most applications finer ground materials will have superior properties, but also raise the material costs since the finest particle sizes like 200 mesh typically require cryogenic milling. Cryogenic processed materials typically exceed prices of ambient ground rubber powders by a factor of two to five.
3. Surface properties. The native surface properties of ground rubber particles depend on the grinding method. Ambient-ground

and water-jetted rubber typically possess high irregular surface areas, whereas cryogenic processed materials typically show more fractured and edge-flat surface morphology with lower surface area per particle. Therefore the total surface area is not only determined by the average particle size but also differs among the grinding methods. Thus slightly different processing characteristics can be expected for different materials, even when using the same mesh size.

Whenever crumb rubber is applied, the surface of the particles has a strong impact on the performance of the whole material. In general, tire rubber is a highly engineered material with regards to performance and endurance. It has a development history and learning curve of more than a full century. However, in most cases the interfacial area between the particles, or the particle and the embedding matrix, plays the decisive role in the material's mode of failure. First, even unmodified GTR can have a positive impact on the tear resistance of virgin rubber compounds to some extent. On the microscopic level, this is attributed to the crack propagation mechanism that can be trapped by filler particles and that leads to crack deflection as illustrated in Fig. 10.1. At higher percentages of GTR load, the significant reduced share of matrix material leads to a final reduction of tear strength, as well as abrasion resistance.

The surface shape is also suspected to influence the crack resistance, since more "cloudy" or "popcorn" like surface morphologies will have smoother hardness gradients between the matrix material and the ground rubber particle compared to the flat-edge shaped particles. On the other hand, flat-edge shaped structures might be more suited for an efficient crack deflection mechanism [3]. In any way, most mechanical properties like tensile strength, elongation of break, or compression set will be reduced when blending GTR with virgin rubber

Figure 10.1 Crack propagation mechanism of unbound filler particle (left-hand side) and strongly bound particle (right-hand side).

compounds or thermoplastics [4]. This is a significant barrier for the practical adoption of recycled rubber in most cases.

Moreover, the rubber particle surface properties determine the processability of the recycled rubber material. Many applications, like virgin rubber blends or rubber-modified asphalt, suffer from challenges like higher stickiness or viscosity caused by the incorporation of recycled rubber materials. Furthermore, blends of recyled rubber with virgin rubber compounds have the tendency to vulcanize too early (scorch) what is caused by migration processes between the recycled rubber (e.g., accelerators) and the matrix material (e.g., sulfur) [5].

In order to reduce the challenges associated with the use or incorporation of recycled rubber powders, the two main goals of surface modification are:

1. Solve processing problems
2. Counterbalance the loss of physical properties

In theory, there are many types of surface modifications as visible from scientific literature reviews [4]. The intended modification of rubber particle surfaces can be done by various methods, including physical, chemical, or even biological treatments. The following part of the chapter will give some practical examples, without claiming to be a complete overview of all possibilities.

10.3 Physical modification

In the broader sense, the physical treatment methods start at the grinding process. As stated above, the choice of grinding method influences the surface morphology of the rubber particles. The different shades of applied shear and impact forces above and below the glass transition temperature of rubber lead to more irregular or flat-shaped rubber particles with respectively higher or lower specific surface [6].

Therefore it can make sense to evaluate different rubber materials first, before starting to modify the surface. Nevertheless, in many cases the choice of recycled rubber material is fixed or limited for good reasons, like availability and price, which impose the need for further modification in order to change the properties in a favorable direction.

10.3.1 Free-flowing agents

A very common and simple practice of modification is the use of free-flowing agents, especially for finer rubber powders of higher mesh sizes. Rubber powders can become sticky after

the grinding process, which causes problems in further packaging or processing due to formation of unwanted rubber agglomerates. By adding small amounts of nonsticky powdered materials, this can be easily solved. A categorization as a physical treatment makes sense, since no reaction is intended between the free-flowing agent and the rubber particles. Suited materials are silica, calcium carbonate, or other commonly used free-flowing agents. They are typically added in small amounts of less than 2% by rubber powder weight.

10.3.2 Swelling

In applications where swelling of rubber particles plays a role, a modification can be done by preswelling of the rubber particles with hydrocarbons. A common use case is the dry mixing in rubber-modified asphalt, where the mechanical swelling of the rubber particles must be considered in the pavement step. If the swelling process is still in action during pavement, this might lead to unsatisfying results in the road performance and lifetime. To avoid this, a GTR type can be used, which reaches an equilibrium state very fast (e.g., using materials from truck and bus tires or materials of smaller particle sizes) [7]. Fig. 10.2 illustrates the influence of particle size, rubber source, and temperature on the swelling time in bitumen. A more labor-intense way is to preswell the recycled rubber material with some parts of bitumen that yields a modified rubber material that is already in an equilibrium state with regards to the swelling process. In most cases this is not necessary, since the practical workflow in road pavement gives enough time between asphalt mixing and paving to reach the swelling equilibrium.

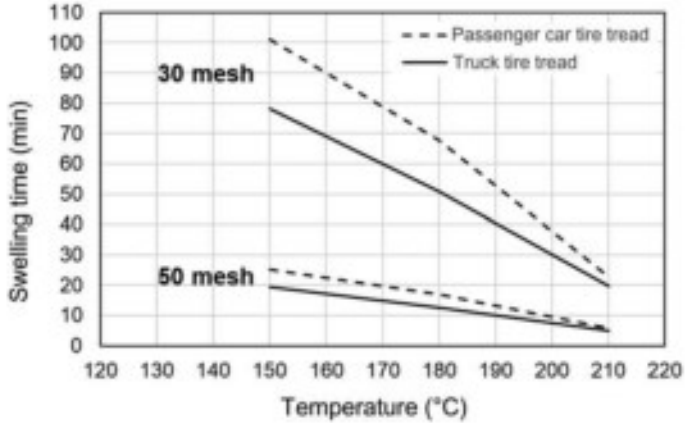


Figure 10.2 Estimated equilibrium swelling times for crumb rubber of different particle sizes in bitumen (100 pen). Data refers to the study of Artamendi et al., Diffusion kinetics of bitumen into waste tyre rubber, in: Journal of the Association of Asphalt Paving Technologists: From the Proceedings of the Technical Sessions, vol. 75 (2006).

Moreover, the swelling phenomenon can be practically used to support surface coating. For example, oils or solvents can be used to transport chemicals on or into the surface of the rubber particles, which would be a combination of chemical and physical treatment processes. Since recycled rubber powders can possess remarkable oil-swelling capacities of up to 200%, it is practically possible to apply some small amounts of oil, without losing the free-flowing properties of the rubber powder. Application of rubber powders as binders for oil spills makes extensive use of this property.

10.4 Chemical modification

Modification of rubber particles by chemical methods are characterized by a reaction between surface and/or the embedding matrix material. From a chemical point of view, the reactive groups of rubbers are alkene groups (C=C double bonds), which can be functionalized or cross-linked. Since recycled rubbers are already vulcanized, the sulfur bonds that cross-link the rubber polymer backbones can also be a target of interest for local desulfurization reactions. The most commonly applied classes of surface modifiers are discussed in the following.

10.4.1 Polyurethanes

The most widely used chemistry in combination with recycled rubber is polyurethane (PU), which is used for coloring, binding, or moisture sealing of ground rubbers. The success of this material class is attributed to its simple and versatile use. One- or two-component systems can be easily mixed with ground rubbers and enable manufacturing of colored coatings, molded goods, or flooring applications with recycled rubber. Nevertheless, the mode of action is more a coating or embedding of rubber powders than a chemical reaction on the particle's surface. Therefore it is not covered here in more detail.

10.4.2 *trans*-Polyoctenamer

Beside PU, a commercially proven example of surface modification is the application of *trans*-polyoctenamer (TOR). It is a good example to discuss here in detail, since it illustrates all chemical and physical aspects of surface modification and is used in a broad range of recycled rubber applications. Moreover, it improves processing of ground rubbers as well as

Table 10.1 Specification and properties of *trans*-polyoctenamer (tradename: VESTENAMER 8012, Evonik) [17,18].

Property		Method (norm)	Unit	Value
Molecular weight	M_w	GPC (acc. DIN 55672-1)	g/mol	140.000
Glass transition temperature	T_g	DMA (ISO 6721-5)	°C	−67
Crystallinity @23°C		DSC (ISO 11357)	%	~30
Melting point (second heating)	T_m	DSC (ISO 11357)	°C	54–56
Thermal decomposition		TGA (ISO 11357)	°C	>400
Double bonds cis/trans ratio		IR (SOP 0188)	%	20/80
Mooney viscosity @100°C	ML (1 + 4)	DIN 53523, ASTM D 1646	MU	<10
MVR (190°C, 2.16 kg load)		ISO 1133	cm^3/10 min	20

performance in application. TOR provides an unusual set of properties (Table 10.1) like having a partially macrocyclic polymer structure [8], high crystallinity [9,10], a low melting point and glass transition temperature [11,12], high thermal stability [13], as well as the ability to be vulcanized like common rubber polymers [14]. This unique combination of properties makes it a valuable tool in rubber product manufacturing [15,16] and surface modification of ground rubbers.

In general, TOR forms dispersed phases in rubber polymers, as shown by differential scanning calorimetry (DSC) measurements and microscopic analysis [19]. The fine-dispersed TOR phases provide a wetting effect, resulting in lower shear forces, and hence easier mixing and processing of the rubber compound. In binary rubber blends, addition of TOR forms a third phase at the interphase. This intermediate layer compatibilitizes the rubber domains by reducing the interfacial tension between the two rubber components. Furthermore, the recombination of domains, the so-called coalescence, is inhibited by the TOR layer. This finally results in better dispersed blends and mechanical properties, even for practical immiscible combinations like EPDM/NBR [20].

The ability to compatibilitize rubbers is a good precondition for applications of recycled rubber powders. GTR typically comprise a wide spectrum of rubber polymer types and compositions, depending on their source and sorting. For example, passenger car tires dominate in synthetic rubber polymer content, whereas truck tire treads typically have more NR content. Bladders and innerliners are mostly made from butyl or halobutyl rubbers, due to their superior gas permeation properties.

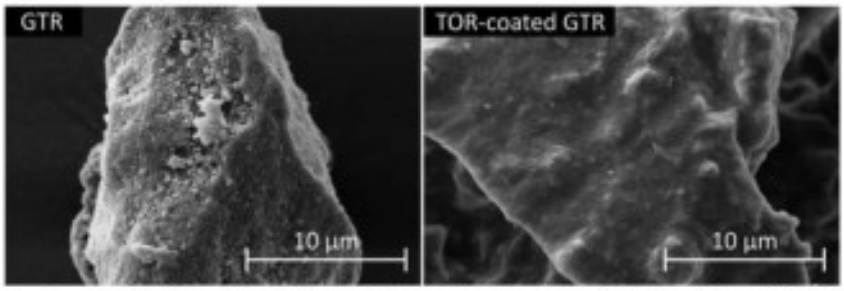


Figure 10.3 SEM pictures of GTR particle (left-hand side) and coating layer of TOR (right-hand side). *GTR,* Ground tire rubber; *TOR, trans*-polyoctenamer; *SEM,* scanning electron microscope.

Adding TOR to recycled rubber crumbs or powders results in a similar wetting effect like in virgin rubber compounds. The difference is the "domain" sizes, which are limited by the sizes of the already vulcanized recycled rubber particles. At temperatures above the melting point, TOR forms a surface layer on top of the particles. Fig. 10.3 shows an uncoated GTR particle of mesh size 200, which comprises a flat-shaped, but rough surface structure. Compared to that, a TOR-coated particle is covered by a smooth surface. This visually confirms the wetting effect as well as the good compatibility and affinity to the recycled rubber particle surface.

An even more detailed insight is revealed by transmission electron microscopy. Samples that are prepared by thin-film cuts allow a view inside of a recycled rubber particle. Fig. 10.4 shows the cross-section of a TOR-coated GTR particle, where the different zones of the GTR particle, TOR layer, and sample matrix can be identified. The TOR coating layer thickness can be estimated around 3–5 μm. Whereas the outer boundary of the surface layer is clearly visible, the inside of the particle shows a blurred transition from the TOR layer to the inside of the GTR particle. This indicates a diffusion and interpenetration of TOR into the surface of the GTR particle. This is in line with expectations from the solubility point of view—TOR shares similar chemical characteristics like common rubber polymers, and hence shows good compatibility as expressed by their solubility parameters. Moreover, the concept of interpenetrating layers has already been described by Wenig et al. for blends of TOR with thermoplastics [21,22].

The evidence for a good surface coating of GTR by TOR explains the well-described benefits in processing. TOR "masks" the GTR surface and thus prevents difficulties like higher stickiness and viscosity. It can also be assumed that the TOR layer

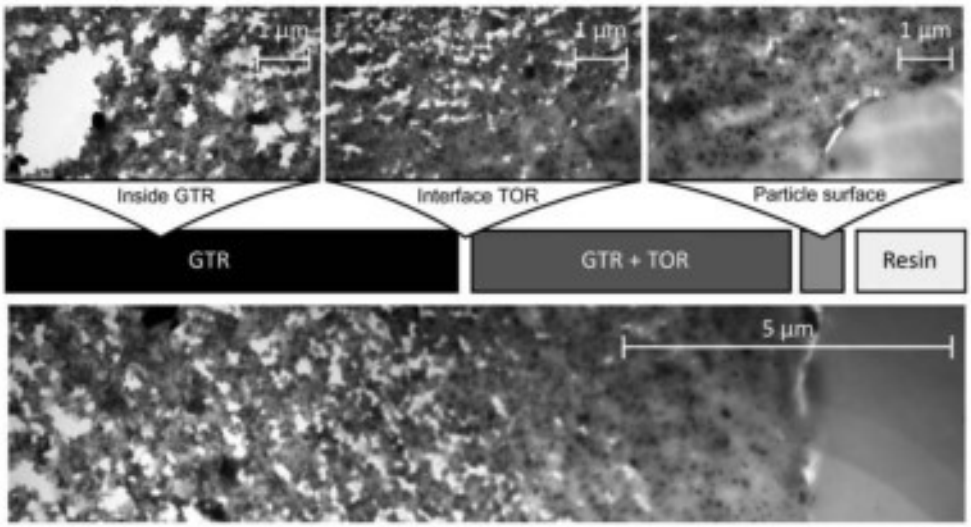


Figure 10.4 Transmission electron microscopy (TEM) pictures of a thin-film cut of TOR-coated GTR particle. *GTR*, Ground tire rubber; *TOR*, *trans*-polyoctenamer.

influences diffusion kinetics, when it comes to migration processes between GTR and the embedding matrix. Reports about reduced emissions of GTR by TOR in asphalt applications give some indications for that assumption [23].

The performance improvements observed can also be explained by the TOR-coating layer. Since TOR is chemically spoken unsaturated, and can be cross-linked like rubber, it offers a reactive surface toward the outside of the particle for compatibilization and/or cross-linking. Furthermore, it can cross-link inside the GTR particle along the interpenetrating layer. FTIR studies on the surface of TOR-coated GTR in bitumen application have shown that TOR undergoes chemical reaction at processing [24]. Since all curing chemical additives and accelerators are already present in the GTR particle (and furthermore undergo migration processes) this can be expected. Improved performance by adding additional sulfur has been reported [25,26].

From the gained insights by electron microscopic analysis, as well as the literature review shown above, a mode of action for surface modification of GTR by TOR can be concluded as depicted in Fig. 10.5.

10.4.2.1 TOR coating process

For a proper function of the "TOR effects," a good coating of the rubber particles is an important prerequisite. There are

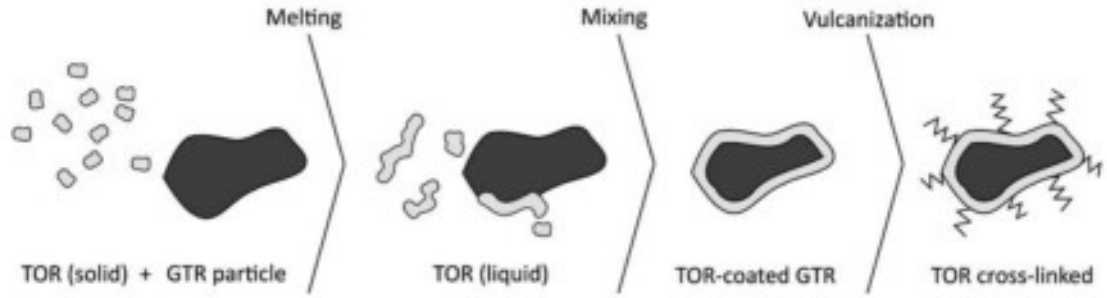


Figure 10.5 Mode of action for surface modification of GTR by TOR. *GTR*, Ground tire rubber; *TOR*, *trans*-polyoctenamer.

Table 10.2 Solubility of TOR in different oils at 100°C.

	Naphthenic black oil	TDAE process oil	Paraffinic process oil	White oil
	Nytex 4700	Vivatec 500	Sunpar 2280	Infrasolv LC1
10 wt.% TOR	Yes	Yes	Yes	Yes
20 wt.% TOR	Yes	Yes	Yes	Yes
30 wt.% TOR	Yes	Partially	No	Yes

Note: *TOR*, trans-polyoctenamer.

different ways how to achieve this, depending on the available mixing equipment.

If an internal mixer is available, which is often the case in rubber compounding facilities, TOR can simply be added together with GTR to get the desired result [27]. In laboratory procedures, a preheating of TOR can improve results and lower the mixing time. The samples shown in Figs. 10.3 and 10.4 were prepared with a mixing time of 7 min, without addition of oil.

If an internal mixer is not available, powder blenders can also be used. This offers a less capital-intensive mixing option. Since this equipment provides less intensive mixing compared to internal or Banbury-type mixers, the coating process of the particles can be facilitated by employing an oil solution of TOR. A common formulation is 20 wt.% of TOR dissolved at elevated temperatures (100°C–120°C) in a suitable oil, like paraffinic oil. Rubber process oils like TDAE work as well. Different solubilities of TOR have been observed in various oil types as listed in Table 10.2.

A further option is extruding equipment, which can be used for continuous mixing of GTR with TOR. If curing chemicals are

added, recycled rubber compounds can be produced that are ready for press- or injection-molding processes. Whenever such equipment is available, this can be an efficient process for large-scale production of rubber mats from recycled rubber powders.

Finally, high-speed mixing equipment, like that used in the PVC industry for dry blends, offer a good compromise and versatile option for coating of GTR by TOR. Compared to the capital-intensive equipment like extruders or internal mixers, such blending equipment is highly flexible and scalable. Batch volumes (and mixing equipment costs) can range between small sizes of 10 kg up to the metric ton scale, depending on the size of the mixer. It is possible to make oil-less coatings of TOR on the rubber powders, even without applying external heat. In this process option, the rubber powder is heated by the shear forces of the rotating mixing blades at high speed. Adding thermoplastic TOR pellets will directly grind and melt them in the presence of GTR and finally result in a coated ground rubber. The hot blend can then be purged and chilled under rotation together with an anticaking agent. This procedure yields a free-flowing TOR-coated ground rubber, ready to apply for rubberized asphalt or other applications.

10.4.2.2 TOR as a binder system for molded goods

As stated above, the dominating binder system for molded products from GTR is PU, which is easy to process and needs no elevated vulcanization temperatures for production of molded goods. TOR is an alternative binder system option to make new molded products from GTR, but it needs vulcanization temperatures in press-curing, comparable to production of virgin rubber products. Although the energy consumption might be higher than in PU processing, TOR can be an attractive option due to the good mechanical properties of the vulcanizates and their superior weathering resistance [28]. Moreover, excellent abrasion resistance and dynamic properties are reported. Considering the low dosage needed for TOR binding, it can also economically compete by taking the total costs of formulation and processing into account. The minimum amount of TOR in formulation is 3–4.5 parts per hundred parts (phr) of GTR. A standard formulation for GTR compound with TOR binder as well as the range of the respective physical properties for 20–40 mesh size GTR is shown in Table 10.3.

It can also be assumed that the chemical resistance of TOR-bound GTR articles is superior in many points. Compared to PU, it shares characteristics of polyolefinic materials and has a

Table 10.3 Standard recipe for molded good from GTR with TOR (left-hand side) and properties of the vulcanizate (right-hand side) [18].

Material	Phr	Properties	Unit	Value
GTR (20–40 mesh, PCR tire)	100	Press curing	min	20
TOR/oil	3/12			
ZnO[a]	0.1	Hardness	Shore A	64–74
Stearic acid	0.5	Tensile strength	MPa	4.5–8.5
Sulfur	0.8	Elongation at break	%	150–300
CBS[b]	0.8	Modulus 100%	MPa	2.0–3.0
TMTD[c]	0.2	Rebound resilience	%	50–60

Note: GTR, Ground tire rubber; *TOR*, *trans*-polyoctenamer.
[a]Zinc oxide.
[b]Primary vulcanization accelerator, N-cyclohexyl-2-benzothiazole.
[c]Ultraaccelerator, Tetramethylthiuram disulfide.

nonbranched chemical structure. This is desirable for products that undergo chemical stress, like animal bedding mats. This product is continuously exposed to excrements, and hence must withstand an acid environment. Therefore TOR improves price the performance ratio of such products by enhancing their lifetime and durability.

Recyclability becomes more and more important in the long-term transformation of our society, which is heading toward an economy that is more circular. Regarding this aspect there are some further general advantages of using TOR compared to other binder systems. Since TOR is a rubber-material itself, "rubber stays rubber" and does not become a composite product. This could simplify a further recycling step of GTR products and might help to give tires not only a second life, but even a third life: in rubber products or upcycling to other applications like rubber-modified bitumen and asphalt. Nevertheless, studies are needed to show the practical feasibility of such a third life concept.

10.4.2.3 TOR-coated GTR in virgin rubber compounds

The cost of GTR can go down to one order of magnitude lower than virgin rubber materials, depending on grinding method and size. This makes it an attractive raw material—not only from the ecological, but also from the economic point of view. On the other hand, serious processing and performance problems arise when production scrap or GTR materials are

introduced into virgin rubber compounds. The reason for this is due to migration processes between GTR and the rubber matrix as well as insufficient incorporation and bonding of the embedded GTR particles. The problems typically scale with the percentage of recycled rubber compounded into the virgin formulations [4]. Hence, its applicability is strongly limited, especially in safety critical applications like tires. In typical passenger car or truck tire compounds, the GTR content will barely exceed 10% or even 5%, whereas recycled rubber sources of higher quality and purity (e.g., treads from tire retreading processes) will be preferred. It should be noted that the situation might differ for special tire types such as earthmover or off-road tires.

Technologies that enable the use of production scrap or GTR materials are key to extending the use of these recycled materials. TOR can narrow, or even close, many technical gaps, which are often prohibitive factors for using GTR in virgin rubber compounds. This has been demonstrated by trials with some test styrene-butadiene rubber and NR compounds that were filled by high loads of 20 and 40 phr GTR. The reviewed formulations [28] are summarized in Table 10.4.

A typical challenge is the viscosity increase of the green compound that arises when GTR is added in larger amounts. The most common method in the rubber industry to measure viscosity is the rotation viscometer (Mooney viscometer), which essentially measures the torque of a standardized rotor (e.g., designated as "ML") that turns inside of a rubber specimen at a defined temperature (e.g., 100°C). Preheating time (e.g., one min) and duration of the measurement (e.g., 4 min) are noted in the unit, which is for example designated as ML(1+4) 100°C. The use of TOR-coated GTR shows improvements over untreated GTR as summarized in Fig. 10.6. This is a result of the TOR/oil solution coating, which reduces compound viscosity very close to the level of the reference compound. Further data reveals improved tensile strength where TOR improves the results by around 1 MPa. Another important property is the compression set, which can be measured by applying a specified load or force for a given time (e.g., 22 h) at elevated temperatures (e.g., 70°C) to a rubber specimen of defined size. The permanent set after release of the load or force is measured and compared to the initial size of the sample. The compression set is most commonly expressed as the percentage of the initial size, which means that low values are desirable. Polyoctenamer shows an impressive effect on the compression set, which illustrates the cross-linking function of TOR between GTR and virgin

Table 10.4 Test formulations of SBR and NR including GTR.

Materials	SBR	SBR–GTR		SBR–GTR–TOR		NR	NR–GTR		NR–GTR–TOR	
SBR 1500	100	100	100	100	100	–	–	–	–	–
NR	–	–	–	–	–	100	100	100	100	100
Carbon black N33	60	60	60	60	60	60	60	60	60	60
GTR	–	20	40	–	–	–	20	40	–	–
GTR coated (TOR)	–	–	–	20 (0.6)	40 (1.2)	–	–	–	20 (0.6)	40 (1.2)
Oil, aromatic	10	10	10	10	10	10	10	10	10	10
Antiaging package	5	5	5	5	5	5	5	5	5	5
ZnO[a]	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS[b]	1	1	1	1	1	1	1	1	1	1
CTP[c]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Note: *GTR*, Ground tire rubber; *SBR*, styrene-butadiene rubber; *NR*, natural rubber, *TOR*, trans-polyoctenamer.
[a]Zinc oxide.
[b]Primary vulcanization accelerator, N-cyclohexyl-2-benzothiazole.
[c]Vulcanization retarder (scorch control), N-cyclohexylthio-phthalimide.

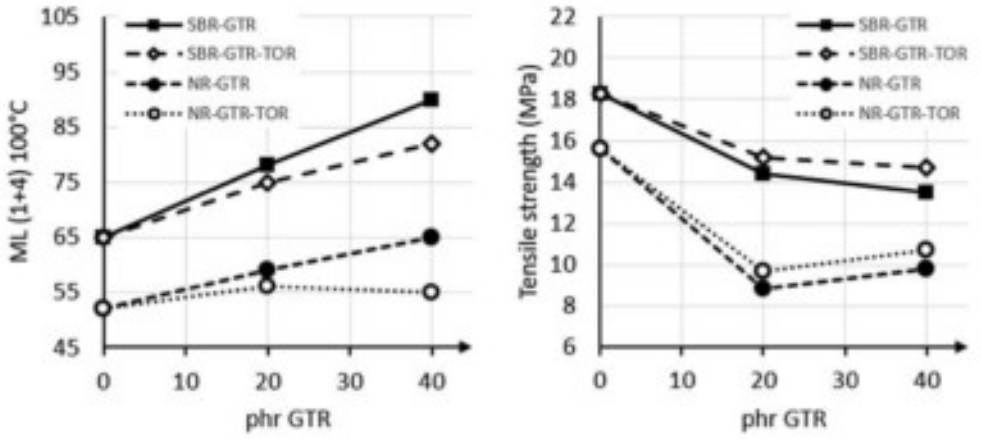


Figure 10.6 Influence of TOR coating on Mooney viscosity (left-hand side) and tensile strength (right-hand side). *TOR, trans*-polyoctenamer.

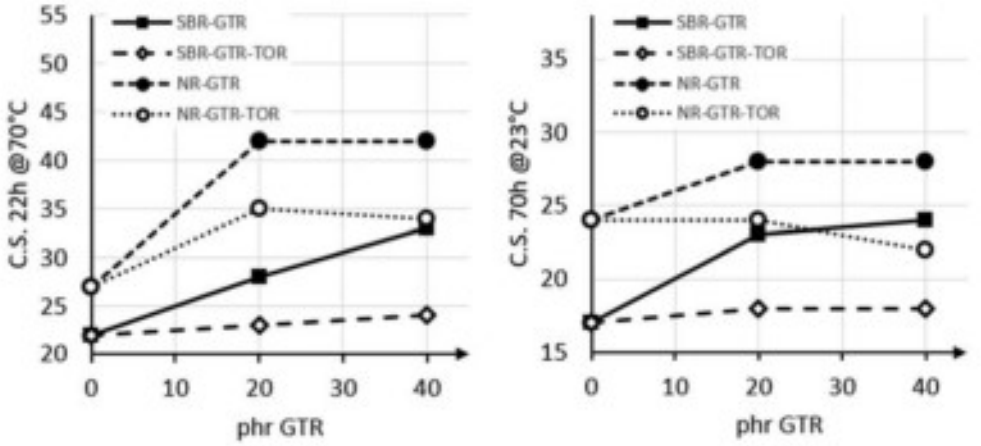


Figure 10.7 Influence of TOR coating on compression set (C.S.) in percent. Two different time/temperature combinations have been applied: 22 h of load at elevated temperatures of 70°C (left-hand side) and 70 h of load at room temperature of 23°C (right-hand side). *TOR, trans*-polyoctenamer.

polymer matrix quite well. As seen from the data in Fig. 10.7, the loss in compression set by GTR incorporation can be completely prevented by applying the TOR coating. This offers a great advantage for applications in seals, gaskets, or dampers, where compression set is an important property.

10.4.2.4 Rubber modification of bitumen and asphalt

TOR has a track record of more than 25 years as a processing additive in the bitumen and asphalt industry. In general, the

recycled rubber acts as a potent polymer modifier that improves binder properties of bitumen and hence the performance of the modified asphalt [29]. The environmental benefits of using recycled rubber is an additional argument from the perspective of sustainability and circular economy discussions [30–33].

Although the benefits of rubber in road construction have been known for a long time, it is faced with practical problems in processing like stickiness, storage problems, or emissions. Moreover, lack of knowledge about best practices in working with rubber has been a hurdle that has inhibited wider adoption of rubber modification in the asphalt industry in the past. For example, swelling times [7] and working temperatures [34,35] are critical issues to address of in rubber modification.

The situation has changed today as rubber modification moves toward more acceptance and has entered even into national strategies [36]. Surface modification by TOR empowers this market development process, since it helps to overcome the critical challenges in the practical application of rubber in road construction. The benefits of reduced stickiness, improved rutting resistance, and reduced cracks have been confirmed by many researchers all over the world [24,25,37–48]. A key challenge in the so-called "wet process," which describes the premixing of rubber and bitumen, is the settling of rubber in bitumen. This phenomenon is due to density differences between the rubber particles and the bitumen and leads to accumulation of the rubber on the bottom of the bitumen storage tanks. This is a very undesirable effect in the asphalt industry. TOR-modified crumb rubber helps to improve storage stability and pumpability of the rubberized bitumen mix, which is a valuable improvement over this initial drawback [24,49]. A further critical issue is the high processing temperatures in bitumen and asphalt mixing, which might lead to the emission of volatile compounds or decomposition of rubber material components. Positive effects of TOR on thermal stability of the rubber-modified materials have also been reported recently [23,45].

From the road construction perspective, rubber is a temperature-sensitive raw material, which means that working at lower temperature is favorable in terms of emissions. On the other hand, low temperatures lead to higher viscosities of the bitumen or asphalt mix, which can become a problem with regards to the quality of the paved area when bitumen is processed at too low temperatures. During paving, the TOR effect brings significant benefits, since it reduces the compaction resistance of rubber-modified asphalt [48]. This opens a wider temperature window for processing and therefore gives more process safety. The influence of TOR on lower compaction

resistance is shown in Fig. 10.8. The effect can also be explained by the coating mode of action (Fig. 10.5), since the swollen and sticky GTR surface is coated by TOR, which reduces the effective stickiness of the rubber particles. This is also valued for unloading of trucks, where asphalt residues on the machinery often makes tedious cleaning efforts necessary. Besides the easier processing, TOR also has a positive impact on the performance of asphalt pavements, as stated above. One important example is the improved rutting resistance. As visible from the Hamburg tests in Fig. 10.9, rutting depth is reduced using TOR

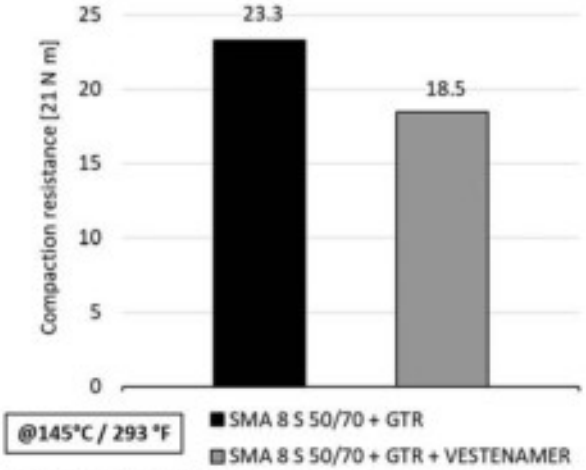


Figure 10.8 Compaction resistance reduction of rubber-modified asphalt by TOR for the example of a SMA with standard bitumen type 50/70. *TOR*, *trans*-polyoctenamer; *SMA*, stone mastix asphalt.

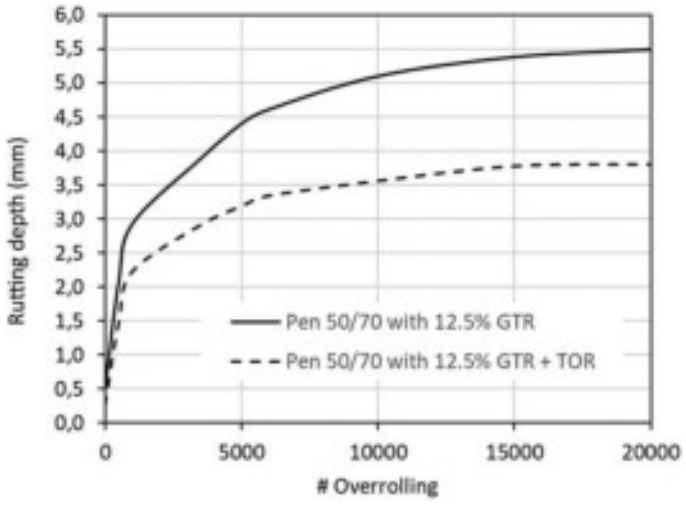


Figure 10.9 Rutting depth results by Hamburg tests of rubber-modified asphalt by GTR and GTR/TOR. *GTR*, Ground tire rubber; *TOR*, *trans*-polyoctenamer.

Figure 10.10 Successful long-term monitoring of rubber-modified asphalt projects in Germany: Rubber-modified industrial area after 11 years of heavy logistic traffic load (left-hand side), and rubber-modified city road, built with 50% recycled asphalt in top layer, after 8 years of traffic (right-hand side).

compared to rubberized asphalt mixture without TOR. In this laboratory test method, a test wheel rolls over the prepared asphalt sample several thousand times to simulate heavy traffic at elevated temperatures.

Together with the other benefits, like improved long-term aging, GTR and TOR can therefore significantly extend the lifetime of pavements. Long-term experiences by well-documented paving projects (e.g., laying for more than 11 years now) prove the laboratory results by showing a road surface in perfect state, without any rutting or cracks as shown in Fig. 10.10.

In asphalt applications, the use of reclaimed asphalt pavement (RAP) is further leverage toward more sustainability in road construction. The use of rubber modification is a perfect fit to improve the aged binders in reclaimed asphalt. A recent urban road construction project from 2012 in the city of Paderborn, Germany demonstrated that the use of 50% RAP in the top layer is possible without compromising standards and performance expectations of modern road construction.

This exhaustive overview of the example of TOR hopefully illustrates the wide spectrum of challenges that can be addressed or even solved by surface modification of recycled rubber. Finally, the need for modification will be determined by the application. Taking care about the key challenges and individual aspects of each application might give some additional guidance on how to modify and which material to choose.

10.4.3 Silanes

With the introduction of silica reinforcement more than 20 years ago, silica fillers have become an essential part of many modern tire compositions. This success is mainly attributed to the fact that silica reinforcement can partially overcome the development target conflict of reducing rolling resistance and increasing wet grip in tires at the same time. Therefore silica content in GTR has increased over time and can be considered as an additional lever for surface modifications. Noteworthy, this is predominantly the case for passenger car tire treads, and less for truck and bus tires, since silica use is more prevalent in synthetic rubber compositions. A recent study showed that the silica content in commercially GTR from passenger cars in Europe ranges from 20 to 42 phr with a mean value around 23 phr [50]. Therefore it makes up a significant portion of today's recycled rubber materials. In classical rubber compounding, silica reinforcement is done by a silica–silane system, where the silane plays the role of a coupling agent to chemically bind the silica surface to the rubber matrix by "silanization" of the filler. This concept can be employed for a second silanization of GTR as well. Beneficial effects on mechanical properties, like tensile strength, have been described for recycled rubber compounds [50,51], and also for rubber plastic composites [52]. Practically, this has been achieved by adding the commonly applied silane coupling agent TESPT in the range of 2–10 phr. It should be noted at that point that silane dosage is typically linked to the amount of silica surface and content in the formulation. Therefore individual optimization studies make sense, since the silica content (and type) will vary depending on the recycled rubber source employed. Finally, it can be expected that the general trend for silica reinforcement will continue and that this type of surface modification might gain more importance in the future.

10.4.4 Other chemicals

Beside the materials mentioned above, there are also many other chemicals described for surface modification or grafting of ground rubbers, especially in the academic literature. If other matrix materials than rubber are used, the surface modification should be adopted to the chemical and physical characteristics of the nonrubber component. For example, in thermoplastic materials like polyolefins (PP, PE, etc.), sulfur-based crosslinking concepts are of limited use, since the polyolefin component is

not really compatible or able to react with sulfur. In these cases, other surface modification concepts are more promising. The technical challenge of getting a good adhesion or bonding between a rubber and a plastic part is closely related to this. Therefore already developed solutions might give inspiration about how to improve properties of recycled rubber plastic composites. Three good examples are peroxides [53], maleic anhydrides [54,55], or trichloroisocyanuric acid [56,57]. All of them are well-established materials in the plastics (or other) industries. For their use with recycled rubber plastic composites, beneficial effects have been described as well. However, it should be noted that many of these chemical concepts can be difficult to handle due to their high reactivity. Easy and safe handling is an important factor to consider, since smaller recycling facilities or processors are often not used to handle hazardous, explosive, or corrosive materials. This can become a hurdle for implementation and should be considered right from the beginning.

10.5 Biological treatment

Rubber, especially from tires, is a long-lasting material that withstands weathering and degradation for a very long time. It has been intentionally designed for that purpose. Although this implies an intrinsic stability against biological degradation, there are possibilities of devulcanization mediated by specific microorganisms. This principle can be used for surface modification since biological species like *Thiobacillus ferrooxidans*, *Gordonia desulfuricans*, or *Sphingomonas* sp. are able to cleave sulfur bonds on the surface of GTR. Some of these species were even isolated from wastewater of tire factories [58].

For the biological process, water-based inoculum solutions, which might contain formulation aids like surfactants, are applied to ground rubber for several days. Since the microbial solutions are water-based by their nature, the treatment only affects the surface of the rubber particle that will be devulcanized in a very selective way. Since the process temperature is low and the treatment is very gentle, the rubber polymer is not deteriorated and well conserved in its properties. This is a clear advantage over other thermal, mechanical, or chemical devulcanization processes. Furthermore, it is considered as ecofriendly due to its biological nature.

Initial scientific work on this concept has already been started in the 1990s, as well as commercialization attempts [59]. Nevertheless, this process seems to have some intrinsic

drawbacks regarding industrial upscaling, throughput, and capacity. This is due to the long incubation time in direct comparison to other processes that have short mixing or processing times. On the other hand, the high cleavage selectivity and gentle processing method has the potential to deliver a recycled material of superior quality, as indicated by many compounding studies [58]. Therefore it can be expected that biologically modified GTR will be a value-driven specialty product in the price range above cryogenic milled GTR, but with higher performance and good processability. Recently, new commercialization attempts have become viable that will hopefully liberate the biological treatment from its academic niche and prove its commercial viability.

10.6 Economic considerations

In summary, surface modification can be a valuable tool to extend the range of applicability for recycled rubber powders. Whereas the intrinsic material properties of the recycled material cannot be changed and must be accepted as they are, the surface interactions between rubber particles can be altered and engineered in many ways as shown above. By doing this, developers can partially bridge performance gaps to enable or increase the use of recycled rubber in demanding applications. Moreover, surface modification can reduce processing problems, which are often a side effect of the recycled rubber material. Therefore developers can only be encouraged to consider surface modification whenever a first evaluation trial fails to reach the desired material or processing specifications.

Although sustainability aspects are good reasons to use recycled rubber powders, the most sustainable drivers are economic aspects, namely: cost savings. Surface modifications can untap cost saving potentials whenever they push the maximum of recycled material content to higher values. By focusing on the key properties that are important for the respective application (e.g., compression set for gaskets, abrasion resistance for conveyer belts, dynamic properties for dampers, etc.), surface modification should target on maintaining exactly those properties, whereas the loss in properties that are of minor importance might be acceptable. A surface modification makes economic sense when the additional cost saving overcompensates the added costs. Fig. 10.11 gives a simplified example for the "economic playground" where surface modification makes sense, depending on the recycled rubber content of a product.

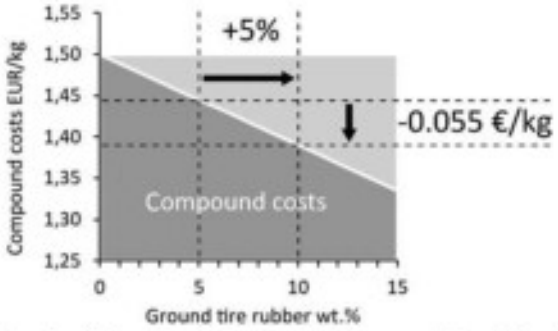


Figure 10.11 Simplified example calculation for additional savings imposed by raising the GTR content from 5% to 10% and assuming a GTR price of 0.40 €/kg. *GTR*, Ground tire rubber.

This simplified calculation example assumes initial compound costs of 1.50 €/kg and a price of 0.40 €/kg for an ambient GTR material. We assume the scenario that the acceptable technical limit (e.g., by viscosity, tensile strength, dynamical properties, flex fatigue, abrasion resistance, etc.) of using the unmodified GTR is 5%. The example illustrates that replacing an additional 5% of the virgin rubber compound would create an added value of 0.055 €/kg cost saving (4.1%) with regards to the total compound costs. This would translate to acceptable surface modification costs of up to 55 € cents/kg of GTR for the assumed technical goal of replacing 10% instead of 5% of virgin rubber. Many modification methods will be far below that economic limit, depending on dosage and processing method. Thus it can be concluded that there is a significant value creation potential by such developments. It should be noted here that more exact economic calculations take material density differences into account [60]. Nevertheless, since bulk density of ground rubbers are very close to that of most rubber compounds, the simplified calculation delivers good estimates. Finally, the success in this example will depend on the performance improvements by the surface modification that has to push the technical boundary from 5% to 10% of virgin rubber replacement. Of course, the economic lever scales with the increase of recycled rubber content and can be much higher (or lower) for other cases.

It should also be noted that surface modification can be a chance for recyclers to differentiate their products in the market. For example, in rubber-modified asphalt, the market seems to move into the direction of recycled rubber products, which are specifically designed according to the needs of the asphalt

producers. Recycled rubber additives that are easy to dose and surface modified (e.g., by TOR) can overcome market entry barriers more successfully since they can be more easily implemented into the production process (e.g., by automated conveying systems) and optimized for better performance of the road pavement. This nicely illustrates how small modification measures can create significant more value downstream, and thus extend the range and volume of recycled rubber in promising applications—a success model that we will hopefully see more often in the future for many recycled rubber applications.

References

[1] N. Thomopoulos, Global market for global market for the tire and rubber remediation and recycling industry, BCC Res. Mark. Rep. (2018).
[2] X. Qi, Waste rubber comprehensive utilization into a critical period for transformation and upgrading, China Chem. Rep. (2019) 9–11.
[3] S. Hoyer, L. Kroll, D. Sykutera, Technology comparison for the production of fine rubber powder from end of life tyres, in: Sustainable Manufacturing - Hand in Hand to Sustainability on Globe: Proceedings of the 17th Global Conference on Sustainable Manufacturing, vol. 43 (January) (2020) 193–200.
[4] S. Ramarad, M. Khalid, C.T. Ratnam, A.L. Chuah, W. Rashmi, Waste tire rubber in polymer blends: a review on the evolution, properties and future, Prog. Mater. Sci. 72 (2015) 100–140.
[5] S. Li, J. Lamminmäki, K. Hanhi, Effect of ground rubber powder and devulcanizates on the properties of natural rubber compounds, J. Appl. Polym. Sci. 97 (1) (2005) 208–217.
[6] M. Sienkiewicz, J. Kucinska-Lipka, H. Janik, A. Balas, Progress in used tyres management in the European Union: a review, Waste Manag. 32 (10) (2012) 1742–1751.
[7] I. Artamendi et al., Diffusion kinetics of bitumen into waste tyre rubber, in: Journal of the Association of Asphalt Paving Technologists: From the Proceedings of the Technical Sessions, vol. 75 (2006).
[8] T. Usami, Y. Gotoh, S. Takayama, Determination of the ring concentration in polyoctenamer, Eur. Polym. J. 21 (10) (1985) 885–889.
[9] I.W. Bassi, G. Fagherazzi, The triclinic structure of trans-polyoctenamer, Eur. Polym. J. 4 (1) (1968) 123–132.
[10] W. Wenig, H.-W. Fiedel, J. Petermann, The microstructure of trans-polyoctenamer, Colloid Polym. Sci. 266 (3) (1988) 227–234.
[11] N. Calderon, M.C. Morris, Melting temperature of trans-polyoctenamer, J. Polym. Sci. Part. -2 Polym. Phys. 5 (6) (1967) 1283–1292.
[12] W.A. Schneider, M.F. Müller, Crystallinity and thermal behaviour of trans-poly (1-octenylene), Macromol. Chem. Phys. 189 (12) (1988) 2823–2837.
[13] P.P. Chattaraj, A.K. Kalidaha, R. Mukhopadhyay, D.K. Tripathy, High-temperature and ageing properties of trans-polyoctenylene-filled natural rubber vulcanizates and their correlation with network changes, Angew. Makromol. Chem. 235 (1) (1996) 81–93.
[14] P.P. Chattaraj, R. Mukhopadhyay, D.K. Tripathy, Effect of high crystalline trans-polyoctenylene (TOR) on different cure systems of NR compounds, J. Elastomers Plast. 26 (1) (1994) 74–92.

[15] A. Draxler, Die Stellung der Polyoctenamere unter den technisch genutzten Kautschuken, Kautsch. Gummi Kunststoffe 36 (12) (1983) 1037–1043.
[16] K. Diedrich, VESTENAMER ein ungewöhnlicher Kautschuk mit vielfältigen Möglichkeiten, Kautsch. Gummi Kunststoffe (1989).
[17] A. Paasche, F. Lindner, P. Hannen, M. Gensheimer, A. Kant, Pushing boundaries! - VESTENAMER® in Recycling Rubber Applications, in: International Elastomer Conference 2019, 196th Technical Meeting - Fall 2019, Rubber Division of the American Chemical Society (ACS), Cleveland, OH (2019).
[18] A. Paasche, F. Lindner, P. Hannen, M. Gensheimer, A. Kant, Surface modification of ground rubber with trans-polyoctenamer, Rubber Plast. News (2020) 14–19.
[19] H.-M. Issel, Thermodynamische und rheologische Steuerung der Materialeigenschaften von Elastomersystemen durch trans-Poly(octenylen), Universität Hannover (1993).
[20] J. Lohmar, Elektronenmikroskopische Untersuchungen zur Phasenmorphologie von Kautschukverschnitten Mit Poly-trans-octenylen, Kautsch. Gummi Kunststoffe 39 (11) (1986) 1065–1070.
[21] W. Wenig, Lokale mischbarkeit von isotaktischem polypropylen (iPP) und trans-polyoctenylen (TOR) in grenzschichten von iPP/TOR-blends, Angew. Makromol. Chem. 200 (1) (1992) 109–123.
[22] W. Wenig, M. Brose, A. Wasiak, Dynamic mechanical analysis of the interpenetration of polypropylene and trans-polyoctenylene in isotactic polypropylene-trans-polyoctenylene, J. Mater. Sci. Lett. 11 (22) (1992) 1525–1526.
[23] M. Liang, S. Ren, W. Fan, H. Wang, W. Cui, P. Zhao, Characterization of fume composition and rheological properties of asphalt with crumb rubber activated by microwave and TOR, Constr. Build. Mater. 154 (2017) 310–322.
[24] H. Liu, Z. Chen, W. Wang, H. Wang, P. Hao, Investigation of the rheological modification mechanism of crumb rubber modified asphalt (CRMA) containing TOR additive, Constr. Build. Mater. 67 (2014) 225–233.
[25] R.K. Padhan, A.A. Gupta, R.P. Badoni, A.K. Bhatnagar, Improved performance of a reactive polymer-based bituminous mixes—effect of cross-linking agent, Road Mater. Pavement Des. 16 (2) (2015) 300–315.
[26] R.K. Padhan, A. Sreeram, A. Gupta, Evaluation of trans-polyoctenamer and cross-linking agents on the performance of waste polystyrene modified asphalt, Road Mater. Pavement Des. 21 (4) (2018) 1170–1182.
[27] K. Diedrich, B. Burns, Possibilities of ground tire recycling with trans-polyoctenamer, Gummi Fasern Kunststoffe 53 (3) (2000) 178–183.
[28] K. Diedrich, B. Burns, Possibilities of ground tire recycling with trans-polyoctenamer, in: 156th meeting of the Rubber Division, American Chemical Society (ACS), USA, Orlando, Florida (1999).
[29] D. Lo Presti, Recycled tyre rubber modified bitumens for road asphalt mixtures: a literature review, Constr. Build. Mater. 49 (2013) 863–881.
[30] I. Bakas, B.J. Kjær, A. Schmidt, N.H. Kløverpris, R. Vogt, J. Giegrich, Ökobilanzieller Vergleich zweier Verwertungsalternativen für Altreifen: Stoffliche Verwertung und Mitverbrennung im Zementofen, Copenhagen Resource Institute, FORCE Technology, IFEU - Institut für Energie- und Umweltforschung Heidelberg GmbH. LCA (2009).
[31] T. Wang, F. Xiao, X. Zhu, B. Huang, J. Wang, S. Amirkhanian, Energy consumption and environmental impact of rubberized asphalt pavement, J. Clean. Prod. 180 (2018) 139–158.

[32] R. Feraldi, S. Cashman, M. Huff, L. Raahauge, Comparative LCA of treatment options for US scrap tires: material recycling and tire-derived fuel combustion, Int. J. Life Cycle Assess. 18 (3) (2013) 613–625.
[33] S. Miliutenko, A. Björklund, A. Carlsson, Opportunities for environmentally improved asphalt recycling: the example of Sweden, J. Clean. Prod. 43 (2013) 156–165.
[34] D. Fornai, V. Persici, C. Lupi, Occupational health risk assessment for the workers exposed to rubberized asphalt fumes, in presented at the Rubberized Asphalt Rubber 2015 Conference (2015) 4–7.
[35] D.S. Fornai, C. Mazzotta, F. Bermejo, L. Saiz, A new era for rubber asphalt concretes for the green public procurement in road construction, Eur. Union Road Fed. (2016).
[36] M. Genever, K. O'Farrell, P. Randell, J. Rebbechi, National market development strategy for used tyres 2017–2022, Tyre Stewardship Australia (2017).
[37] K. Diedrich, B. Burns, Pavements from asphalts modified with ground tire rubber (GTR), Elastomery 4 (1) (2000) 9–14.
[38] G. Yadollahi, H. Sabbagh Mollahosseini, Improving the performance of crumb rubber bitumen by means of poly phosphoric acid (PPA) and vestenamer additives, Constr. Build. Mater. 25 (7) (2011) 3108–3116.
[39] K.E. Min, H.M. Jeong, Characterization of air-blown asphalt/trans-polyoctenamer rubber blends, J. Ind. Eng. Chem. 19 (2) (2013) 645–649.
[40] B. Li, J. Shen, Z. Xie, Influence of trans-polyoctenamer on rheological properties of rubberised asphalt binders after short term aging procedures, Mater. Res. Innov. 18 (5) (2014) S5-39–S5-41.
[41] Z. Xie, J. Shen, Effect of cross-linking agent on the properties of asphalt rubber, Constr. Build. Mater. 67 (2014) 234–238.
[42] H.Y. Katman, M.R. Ibrahim, M.R. Karim, N. Salim Mashaan, S. Koting, Evaluation of permanent deformation of unmodified and rubber-reinforced SMA asphalt mixtures using dynamic creep test, Adv. Mater. Sci. Eng. 2015 (2015) 1–11.
[43] K.L.N. Ng Puga, R.C. Williams, Low temperature performance of laboratory produced asphalt rubber (AR) mixes containing polyoctenamer, Constr. Build. Mater. 112 (2016) 1046–1053.
[44] R.K. Padhan, A.A. Gupta, C.S. Mohanta, R.P. Badoni, A.K. Bhatnagar, Performance improvement of a crumb rubber modified bitumen using polyoctenamer and cross linking agent, Road Mater. Pavement Des. 18 (4) (2017) 999–1006.
[45] M. Liang, X. Xin, W. Fan, S. Ren, J. Shi, H. Luo, Thermo-stability and aging performance of modified asphalt with crumb rubber activated by microwave and TOR, Mater. Des. 127 (2017) 84–96.
[46] P. Xiao, J. Zheng, A. Kang, L. Sun, Y. Wang, Aging characteristics of rubber modified asphalts in different environmental factors combinations, Appl. Sci. 7 (8) (2017) 806.
[47] H.Y. Katman, M.R. Ibrahim, S. Norhisham, N. Ismail, N.A. Rahman, Creep-recovery behaviour of crumb rubber modified bitumen (CRMB) containing trans-polyoctenamer, Int. J. Eng. Res. Technol. 11 (12) (2018) 2073–2088.
[48] D. Gogolin, Die Performance stimmt, Asph. Bitum. 6 (2019) 30–35.
[49] V. González, F.J. Martínez-Boza, F.J. Navarro, C. Gallegos, A. Pérez-Lepe, A. Páez, Thermomechanical properties of bitumen modified with crumb tire rubber and polymeric additives, Fuel Process. Technol. 91 (9) (2010) 1033–1039.

[50] J. van Hoek, G. Heideman, J. Noordermeer, W. Dierkes, A. Blume, Implications of the use of silica as active filler in passenger car tire compounds on their recycling options, Materials 12 (5) (2019) 725.
[51] M. Hernández Santana, M. Huete, P. Lameda, J. Araujo, R. Verdejo, M.A. López-Manchado, Design of a new generation of sustainable SBR compounds with good trade-off between mechanical properties and self-healing ability, Eur. Polym. J. 106 (2018) 273–283.
[52] Y. Zhou, M. Fan, Recycled tyre rubber-thermoplastic composites through interface optimisation, RSC Adv. 7 (47) (2017) 29263–29270.
[53] A. Shanmugharaj, J.K. Kim, S.H. Ryu, Modification of rubber powder with peroxide and properties of polypropylene/rubber composites, J. Appl. Polym. Sci. 104 (4) (2007) 2237–2243.
[54] A.K. Naskar, S.K. De, A.K. Bhowmick, Thermoplastic elastomeric composition based on maleic anhydride–grafted ground rubber tire, J. Appl. Polym. Sci. 84 (2) (2002) 370–378.
[55] A. Amash, A. Giese, R. Schuster, Interphase grafting of reclaimed rubber powder, Kautsch. Gummi Kunststoffe 55 (5) (2002) 218.
[56] A.K. Naskar, A.K. Bhowmick, S. De, Melt-processable rubber: chlorinated waste tire rubber–filled polyvinyl chloride, J. Appl. Polym. Sci. 84 (3) (2002) 622–631.
[57] X. Colom, M. Marín-Genescà, K. Formela, J. Cañavate, Chapter 2 - Surface treatment of rubber waste, Rubber Recycling: Challenges and Developments, The Royal Society of Chemistry, 2019, pp. 24–55.
[58] V. Tatangelo, et al., Microbial desulfurization of ground tire rubber (GTR): characterization of microbial communities and rheological and mechanical properties of GTR and natural rubber composites (GTR/NR), Polym. Degrad. Stab. 160 (2019) 102–109.
[59] W. Klingensmith, K. Baranwal, Best Practices in Scrap Tires & Rubber Recycling, Recycling Technology Assistance Partnership, Clean Washington Center, 1998.
[60] J.S. Dick, Rubber Technology: Compounding and Testing For Performance, Carl Hanser Verlag GmbH Co KG, 2014.

11

Molding industrial products from tire ground rubber

Fabrizio Quadrini, Denise Bellisario and Loredana Santo
Department of Industrial Engineering, University of Rome "Tor Vergata" Via del Politecnico 1, Rome, Italy

11.1 Introduction

Tire production is a molding manufacturing process with its own specific features. From a technical point of view, most manufacturing processes for tires may be classified as "compression molding" because of the use of a thermosetting semisolid precursor, which is shaped and hardened by the combined action of temperature and pressure. In analogy with traditional compression molding techniques, the mold is heated and the manufactured tire can be extracted, after curing, from the hot mold. In fact, heating produces material softening, and pressure allows its flow up to the full filling of the cavity mold. Temperature also activates rubber polymerization, which is often referred to as "vulcanization." Mold filling has to be performed before the rubber reaches its gel point over which material flow is stopped. As the polymerization kinetic immediately starts with heating, the correct combination of pressure, mold temperature, and processing times is necessary to avoid incomplete filling, nonhomogeneous hardening, overflow, or poor agglomeration. All these aspects are well-known in the compression molding manufacturing of thermosetting precursors. The main differences in tire use are in the structure of the mold and how the pressure is applied. In fact, only one metallic semimold is present with the negative shape of the tire tread. The mold is closed by using a bladder, which is inflated by pressurized hot steam.

Compression molded parts are typically considered difficult to recycle because of the polymerization reaction, which can occur only one time. After manufacturing, the rubber of the tire cannot flow. Heating would produce only material softening and, at high temperatures, degradation by molecular cracking or, in the presence of oxygen, oxidation and burning. From a technological

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00026-0
© 2021 Elsevier Inc. All rights reserved.

point of view, this represents a strong limitation on the possibility of obtaining a primary recycling process. "Primary" refers to the fact that recycled materials should be reprocessed with the same technologies of virgin raw materials. The perception of the impossibility of repeating the compression molding process on recycled rubber suggests that only secondary recycling strategies are possible for tires. Nevertheless, this is just a perception. In fact, it is evident that the material cannot be taken back to its original uncured state, but a partial reactivity can be recovered. Devulcanization, the breaking up of sulfur bonds by chemical, thermophysical, or biological means, improves reprocessing of recycled tire rubber [1]. Moreover, compression molding of ground tire rubber (GTR) is also possible without any addition of virgin raw materials or additives to produce parts of industrial interest. Properties of recycled parts are expected to be lower than parts made of virgin rubber, but that is typical for all the plastic recycling processes, also for thermoplastics. Despite perceptions, the concept of primary recycling is applicable to tire rubber. In analogy with thermoplastics, an optimal amount of GTR rubber could be also mixed with virgin rubber to produce new tires thus closing the cycle.

11.2 Scientific state of the art

Rubber is mainly produced for the manufacturing of tires. That is a positive fact in terms of recyclability as most end-of-life rubber has similar properties and was processed in a similar way. Moreover, most of the rubber mixtures are designed and optimized to be compression molded with many consequences in terms of additives and precursor shape. It would be reasonable to assume that molding is a valid option also for recycling but, for now, that is less than a theoretical possibility. In analogy with other compression-molded thermosets, GTR is managed as inert filler or organic fuel.

The scientific research has an increasing interest on tire recycling, but efforts seem to be limited. As a reference, digital scientific databases can be used where most of scientific contributions have been stored in the last 30 years. As shown in Table 11.1, "tire recycling" is a keyword for 2200 studies in top class journals or referenced international conferences (Scopus Source). This is a reasonably high number but not comparable to many other topics. For a fast comparison, "graphene" is a topic that is indexed in about 16,500 studies in the same digital database only for 2019. Going into detail of the search, many studies refer to "energy" (20% but only 5% also to "energy recovery") and waste management (15%). In

Table 11.1 Scientific papers published on tire recycling in the last 30 years[a].

Keywords	Number of papers	%
Tire recycling	2235	
+Energy	446	20.0
(+Energy recovery)	106	4.7
+Concrete	378	16.9
+Waste management	332	14.9
+Composite	271	12.1
+Pyrolysis	246	11.0
+Asphalt	241	10.8
+Combustion/burning	142	6.4
+Molding	52	2.3
(+Direct molding)	11	0.5
+Devulcanization	11	0.5

[a]Scopus source.

technological terms, the most commonly studied routes for tire recycling are "concrete" (17%), "composite" (12%), "pyrolysis" (11%), and "asphalt" (11%). These data confirm that researchers are also considering end-of-life tires (ELTs) as a source of inert fillers or energy, in analogy with all the other thermosets. Concretes, composites, and asphalts are all mixtures of inorganic or organic matrices with GTR and possibly other fillers and additives. They represent about 40% of overall scientific contributions. It is interesting that "molding" is indexed only in 2.3% of studies, even though it is known that composites need a molding process.

The analysis of scientific databases by using keywords is not a precise instrument of investigation because of possible use of synonymous or weak links with real research activity. Nevertheless, the perception that molding is not considered a key strategy for GTR recycling is also confirmed for researchers. Moreover, the scientific research effort is to use the excellent elastic properties of the recycled rubber granules to provide controlled compliance to products for antivibrating or dumping application. In order to give an overview of the scientific debate in this field, the contributions on "tire recycling" and "molding" in the last 20 years can be considered as follows:

1. *Composites.* The simplest solution to recycling GTR is mixing it with a thermoplastic or virgin thermosetting binder. In the case of thermoplastics, the final composite mixture can be processed with typical matrix processing technologies, from

extrusion to injection molding and thermoforming. In this case, the limitation is given by the maximum allowable amount of GTR, as the shaping and forming of the part depends only on the thermoplastic matrix. In order to simplify the mixing stage and to reduce the viscosity of the mixture, mainly liquid thermosetting resins and high-fluidity thermoplastic polymers are used. A typical drawback is the color of the part, which is always black, and also the unpleasant smell at least during production. In the case of thermoplastic matrices, there are the further advantages of high productivity and theoretical recyclability of final products, but equipment is more complex and investment costs are higher.

In 2001, Song et Hwang proposed an interesting combination of natural and synthetic materials to produce composites by compression molding [2]. Wood fibers and GTR were mixed with diphenylmethane diisocyanate resin, which was applied as a binder. The researchers preferred using a thermosetting matrix probably to simplify prototyping activities in the laboratory. Nevertheless, compression molding has the big advantage of reducing the amount of binder at very low levels. In fact, part shaping occurs by the direct squeezing action of the closing mold. Mixtures with very high viscosity may be easily molded and a small amount of resin matrix can be spread through the entire mold cavity. Therefore researchers were able to compression mold samples with a matrix content ranging from 5 to 20 wt.% and ratios between wood fibers and GTR from 25:75 to 100:0. Results showed that GTR improved composite impact strength, but reduced bending strength, bending modulus, tensile strength, Young's modulus, and internal bonding strength. In terms of material design, the choice of combining wood fiber and GTR may be questionable because of their very different behavior, one being rigid and brittle and the other soft and ductile. Nevertheless, the world of composites opens up the possibility to mix together several different fillers to obtain unexpected properties. Moreover, the use of GTR suggests designing composite materials with a strong environmental attribute by mixing with natural materials to produce biocomposites or other recycled fillers and matrices. For example, in 2009, Panigrahi et al. developed rubber and agricultural fiber-based biocomposite for industrial application [3]. In this case, a thermoplastic matrix is selected (linear low-density polyethylene, LLDPE), and the compression molding process is confirmed to manufacture thermoplastic composites with flax and GTR. From an industrial point of view, the choice of a compression molding process in the presence of a thermoplastic matrix is not optimal as part

extraction is possible only after mold cooling. As a consequence, processing times strongly increase as well as energy consumption. If a thermoplastic matrix is selected, the big potential of the processing technologies of this family of polymers should be used, from extrusion to injection molding and foaming. Also in 2009, Xin et al. evaluated microcellular injection molding of composites with polypropylene (PP) and GTR [4]. They used a chemical blowing agent and observed that both the GRT and the blowing agent content had huge effects on the cell morphology and tensile properties of composite foams. A similar study was repeated by Zang et al. in 2011 when the influence of various compatibilizers on the PP matrix was investigated [5]. It was seen that the addition of maleic anhydride-grafted styrene-ethylene- butylene-styrene (SEBS-g-MA) increased the shear viscosity of the composites as well as the void fraction and cell density whereas the average cell sizes decreased. Moreover, SEBS-g-MA enhanced the elongation properties and acted as an effective compatibilizer in the composite system.

Polyolefin such as PP or PE is the preferred matrix for thermoplastic matrix composites filled with GTR, thanks to their low price, optimal processability, and availability as recycled. Using recycled thermoplastics is a way to exalt the green design of the final industrial products such as ecological roofing tiles [6]. In 2012, Montagna and Santana produced composites by incorporating GTR waste scrap into a thermoplastic matrix made of postconsumer polypropylene or polystyrene (PS) [7]. Composites were processed by injection molding. Generally, the presence and concentration of GTR led to a reduction in the mechanical properties when compared with the unfilled matrix. The authors also discussed that this decrease was due to weak filler/matrix interactions [8]. In fact, very often a compatibilizing step is mandatory to achieve sufficient mechanical performance. In 2012, Mészáros et al. proposed the use of electron beam irradiation to improve mechanical performance of injection molded composites [9]. These composites were prepared from recycled and virgin low-density polyethylene (LDPE), GTR, and ethylene vinyl acetate (EVA) copolymer. The fresh LDPE served for reduction of the melt viscosity and EVA was used to improve the so-called "elastomeric properties." Defining these composites as "elastomers" is questionable as the observed extended ductility occurs in the plastic range whereas true elastomers exhibit high ductility in the elastic reversible range. Semicrystalline thermoplastics always show high plasticity, which is reduced and not improved by adding

elastomeric particles such as GTR. The use of electron beam irradiation improves material performance because of additional cross-linking but the process complexity is too high and the composite recyclability is partially lost.

Because of the hybrid nature of the GTR-filled thermoplastic composite, the idea of mixing polymers to obtain an optimal matrix is often applied in scientific studies, such as PP/PS [8] or LDPE/EVA [9]. Results are often not convincing and also add issues related to the complexity of the mixing phase. However, in this optic, Cazan et al. proposed in 2013 the addition of small amounts of wood waste (sawdust) to optimize rubber–HDPE–PET–wood composites by compression molding at temperatures of 240°C–260°C [10]. In conventional molding operations, high-density polyethylene (HDPE) and poly-ether-terephthalate (PET) are generally processed under different conditions because of the high difference in their melting temperature. In the proposed temperature range only HDPE is fully melted whereas PET is in a viscous semi-solid state. Compression molding technology gives the possibility to take big advantages by these different material behaviors. In further studies, PET functionalization was also assessed with polyethylene glycol (PEG 400, 1%) and sodium dodecyl sulphate (SDS 1%) [11]. Results proved that the interface properties were enhanced, and the authors found that the best mechanical properties were recorded with a molding time of 30 min at which a tensile strength of 1.56 MPa was measured. However, that is a very long molding time for thermoplastic processing. In the last development, they also found that small amounts of CaO nanoparticles can work as moisture trackers [12].

Possible combinations of polymer bases, fillers, and compatibilizers are numerous. In 2015, Lima et al. studied blends based on PP, GTR, and other rubber materials such as ethylene-propylene rubber (EPR) [13] and ethylene propylene diene monomer rubber [14]. In particular, the incorporation of EPR had a positive effect on the composite mechanical performance, which was attributed to the toughness enhancement of the PP matrix and to the establishment of shell-core morphology between the rubber phases. Nevertheless, using high-value raw materials as additives is a questionable choice for industrial purposes. For this reason, recent contributions stress the importance of ecological products by the mixing of waste materials from different recycling streams. In 2017, Luo et al. studied composites for the construction industry by combining GTR, after alkali activation, and waste wood flour, treated

with a compatibilizer, in a matrix of recycled PP or PE [15]. Coarse GTR particles were used and good results were found with low filling contents (about 5 wt.%). Higher values of filling content (about 20%) have been considered by Haworth et al. in their study about the use of composite beam structures made of recycled HDPE and GTR for acoustic energy absorption [16]. They produced test specimens by injection moulding and large-scale beam samples by compression molding using an ad hoc method. This method allowed to vary the through-thickness elastomer content as a means of obtaining composition gradients. Thermal analysis revealed a significant increase in the level of crystallinity of the HDPE by increasing the rubber content in the blend. This is evidence of an interaction between GTR filler and matrix. As a result, the graded structures produced large improvements in acoustic absorption properties in the frequency range of 2–6 kHz.

In 2018, Moghaddamzadeh and Rodrigue also added also big amounts (up to 50 wt.%) of recycled tire fibers to the typical mixture of GTR and LLDPE, with and without SEBS-g-MA as a compatibilizer [17]. Samples were manufactured by compounding and injection molding. The results show that the compatibilized compounds have lower RTF length and GTR particle size, but better distribution of rubber particles in the LLDPE matrix. The best mechanical properties were obtained at the highest fiber content (50%) and extruder screw speed (250 r/min) combined with the lowest temperature profile in both extrusion and injection molding when the compatibilizer was added [18]. The authors also observed that the incorporation of SEBS-g-MA produces an increase of the liquid mixture elasticity and viscosity due to better interfacial coupling [19]. This coupling mechanism is fundamental for increasing the amount of GTR content. The same technological steps of extrusion compounding and following injection molding have been used by Wang et al. who arrived at a GTR content of 90 wt. % in a recycled PE composite, usually referred to as "elastomeric" [20]. Two copolymers (Engage 8180 and Vestenamer 8012) were added as compatibilizers for comparison. The authors discuss how the addition of a copolymer improves the elongation at break, but Engage 8180 shows better compatibilization effect than Vestenamer 8012.

In the most recent studies about the molding processes of GTR composites, there is an interesting selection of all the previous findings. In 2019, Shivamurthy et al. proposed the insertion of GTR in a thermosetting matrix to improve the sliding wear resistance of epoxies [21]. Shaker et al. for the first time proposed

the well-known combination of GTR and LDPE for rotational molding with filling contents up to 50 wt.% [22]. In 2020, Soleimani et al. evaluated the use of cross-linking by dicumyl peroxide for the GTR/PE composite mixture [23]. Composites with tensile strength, ultimate elongation, and impact resistance of 11.5 MPa, 140%, 244 MJ/m^2, respectively, have been obtained under optimized conditions.

2. *Molding devulcanized rubber.* Several studies on GTR devulcanization are available by using all the possible technical and scientific approaches, from thermomechanical processing to bacteria [1]. In these studies, the mechanical performance of devulcanized products are evaluated and may be used for comparison but recent technological studies about devulcanized rubber molding are absent. Compression molding is the key technology for devulcanized rubber, which can also be mixed with virgin rubber in traditional processes. In 2002, Fukumori et al. already stated that test truck tire containing 10 wt.% of devulcanized rubber in the tread might exhibit wear behavior of the tread almost equal to that for the standard type with the new rubber compound [24]. They also observed that deodorization during the recycling process is possible by their continuous devulcanization method. In fact, from the point of view of on-site industrial use and for final products, deodoration is a fundamental objective. In 2003, Maridass and Gupta discussed the mixture of devulcanized rubber with 30 phr natural rubber (NR) to give satisfactory vulcanizates properties [25]. However, higher contents of recycled devulcanized rubber may also be used. Recently, Aoudia et al. used devulcanized GTR in an epoxy matrix with the result of better mechanical performance of molded products in comparison with samples with untreated GTR [26]. This may be evidence of the effectiveness of the devulcanization process, but it does not yet demonstrate the feasibility for industrial use of the improved epoxy mixture. In 2019, van Hoek et al. assessed the effect of silica as active filler in passenger car tire compounds on their recycling options [27]. In a step-wise approach they showed that the presence of silica influences both devulcanization and revulcanization. In particular, the tensile strength of the revulcanizate of 13 MPa can be reached in the best processing conditions.
3. *Other molding operations.* In recent years, minimal effort has been given to integrating GTR recycling with new technological solutions such as rotational molding [22]. In this case, the application to additive manufacturing is surely the most

interesting solution. In 2017, Domingues et al. evaluated the use of a composite made of recycled PP with 60 wt.% GTR to produce big parts such as urban furniture [28]. In 2019, Quetzeri-Santiago et al. explored inkjet printing of liquid latex and micronized rubber powder from ELTs with loadings up to 10 wt.% [29]. Multilayer objects were created from pure liquid latex and characterized. The results show that the maximum elongation length reduces from 750% to 430% because of the rubber particles but good printability is generally observed.

4. *Direct molding*. From a conceptual point of view, the nominal primary recycling of GTR is compression molding without any additive or binder. In fact, compression molding is the process used to manufacture tires, and is applied to particles cut from the same tire to make new rubber parts. In 2002, Morin et al. proposed a novel method to recycle scrap tires, namely high-pressure high-temperature sintering [30]. They found that it is possible to recycle vulcanized rubber powders made from waste rubber (namely scrap tires) through only the application of heat and pressure. The authors showed that this process is applicable to powders of every cross-linked elastomer, including silicone rubber, sulfur cured NR, styrene–butadiene rubber (SBR), peroxide cured butadiene rubber (BR), and fluoroelastomers. In particular, "sintered" samples of SBR showed over 9.5 MPa of tensile strength and 275% elongation. From a technological point of view, the term "sintering" is acceptable because of the presence of powder agglomeration under the combined action of temperature and pressure. Nevertheless, from the perspective of material science, sintering is a process where agglomeration is made due to solid state diffusion, which is a very weak mechanism for cured rubber particles. In the case of GTR, powder agglomeration is produced by the combined effect of residual reactivity of the tire rubber, particle surface reactivation by mechanical grinding, and approaching material degradation. For this reason, the term "direct molding" can be preferred to mean a compression molding process without the addition of any binder or virgin rubber [31]. Moreover, it can be applied to GTR with different particle size, from powders to granules, and also to other thermosets as well as polyurethanes [32] and rigid composites such as fiberglass [33].

Direct molding can provide complex shapes to GTR parts and secondary processing is possible in order to improve aesthetics and functions [34]. In 2012, Lucignano et al. used medium-size GTR particles (1.2 mm on average), obtained by mechanical grinding, to mold square plates with a length of

150 mm and a weight of 400 g [35]. By changing the molding pressure, different plate thicknesses were obtained (about 20 mm) as well as different densities and mechanical performance. In particular, they observed that the molding pressure can be changed to tailor final properties and aesthetics of products, but a maximum value was measured over which plate density and strength remained almost unaltered. In the same year, Guglielmotti et al. deepened the effect of different powder mixtures on the final performance of the direct molded parts [36]. Starting from three different size distributions of the rubber powder, other binary and ternary blends were prepared, for a total of 15 different powder distributions, which were compression molded at 26 bar and 250°C to produce 300 x 300 x15 mm^3 plates. It was found that the rubber powder distribution strongly affects the mechanical performance of GTR direct molded plates.

In 2013, Quadrini et al. discussed direct molding of different size distributions of GTR particles and buffings, which were used to produce rubber sheets with the size of 200 x 200 x 5 mm^3 at the temperature of 160°C and the pressure of 3 MPa in aluminum molds [37]. Rubber densities over 1 g/cm^3 were reached for all the samples with ultimate tensile strength and maximum elongation up to 1 MPa and 80%, respectively. Recently, in 2019, for the first time direct molding of large-size tiles (1 m^2) with thickness up to 50 mm without cracks or other damages have been carried out [38]. Mechanical tests have shown that tiles have similar or higher performance than tiles produced by means of conventional processes (i.e., using polyurethane binders). Moreover, the new technology was able to save up to 50% of production costs related to electric energy and raw materials.

11.3 New findings in direct molding of ground tire rubber

Direct molding of GTR is a particular compression molding process because it is not optimized for the curing process, as for virgin rubber, but for the incipient degradation of the spent material. In fact, direct molding is carried out at higher values of pressure and temperature than virgin rubber. Thanks to grinding, broken links are produced on the external particle surface of GTR. Moreover, the particle surface is partially exfoliated with the effect of much more possible new links during remolding. The surface aspect strongly depends on the adopted grinding process as well as the GTR size distribution. In the molding technology,

the pressure is important to guarantee the contact among the rubber particles, and the heat is necessary to increase the rubber temperature. Rubber flow is minimal and not sufficient for mold filling. At high temperatures the molecular mobility increases, and new links on the surface of the rubber particles can be originated from broken links and mainly from degradation. In fact, processing conditions are able to produce strong degradation phenomena in the rubber, and these phenomena start from the external particle surface. At high temperatures, molecular mobility is so enhanced that polymer cracking is possible but the formation of new links is possible as well. By calibrating the optimal conditions of pressure, temperature, and time, it is possible to make use of the advantage of particle agglomeration with limited material degradation. The high pressure helps in making more stable the material and partially preserving from degradation, thus favoring reagglomeration. However, the effect of degradation is never negligible as visible from the molded part surface in contact with the heated mold walls. The molded surface is always flat and smooth, and tends to replicate small geometrical details from the mold. Coarse particles are shaped as well due to the plasticization during molding. From an industrial point of view, this effect is not negative as it allows producing rubber products with surfaces smoother than conventional molding of GTR with polyurethane binder.

If residual reactivity is present in the GTR, repolymerization is much more effective. For this reason, it is possible to calibrate product performance by selecting the tires (e.g., from trucks or cars) or parts of the tires (e.g., from treads or side walls). The potential of direct molding of GTR is shown in Fig. 11.1. Very big and thick parts may be molded as well as small hollow parts and interlocking geometries. Granules and powders are efficiently molded and gradient structures are possible if needed. For example, large granules on the surface increase wear resistance and fine powder in the core improves strength and stiffness. Surfaces can be sculptured and very small details can be obtained if fine powder is used in the top surface.

The main phases of the direct molding process are rubber grinding (depending on the tire recycling technology); weighting; mold filling; compression molding (where pressure and temperature are applied contemporarily); demolding (i.e., slow pressure release to avoid cracks and defects); and extraction. Unlike conventional recycling process, direct molding does not require a mixing stage with binders before the molding phase. The process needs a compression molding machine that is conceptually similar to molding machines used for virgin rubber. Hydraulic presses are

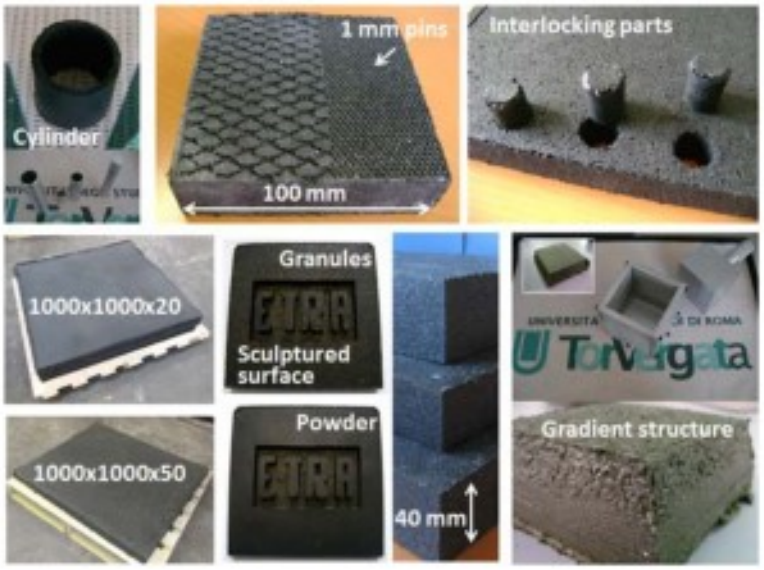


Figure 11.1 Direct molded products made from ground tire rubber (GTR), granules, and powders.

equipped with heated plates or molds, and are designed to hold the pressure for long times. Unfortunately, molding machines of virgin rubber are very expensive for small products, and their performance are lower than needed as rubber vulcanization requires lower temperatures and pressures than GTR direct molding. In order to reduce costs, old hydraulic presses from sheet forming can be modified. By increasing molding pressure and temperature, mechanical performance of direct molded products is expected to increase as well as the energy consumption. Therefore an optimal compromise is necessary between investment costs, operative costs, and product value.

After weighting, GTR powders or granules are poured in the mold and spread in all the points of the cavity. The thickness of the nonagglomerated rubber is much higher than the final thickness of the molded product because of the voids among particles, and this aspect has to be considered for mold design. In the holding stage, rubber granules are compressed and the total thickness of the part under agglomeration is reduced. After agglomeration, the pressure is released and the product minimally increases its thickness. Subsequently, after cooling, the thickness reduces again because of thermal contraction. With simple trial-and-error procedures, it is possible to evaluate the amount of rubber necessary to reach a precise density in the final molded and cold product as a function of the GTR size distribution.

Scientific and technical information on direct molding of GTR, both in laboratory and industrial scale, is available in published papers [31–38]. Many aspects have been studied, from the effect of the process variables and the GTR size distribution to final product performance and energy consumption. Studies have been made on tiles of different sizes and thicknesses, and secondary working has also been evaluated such as coating and cutting. However, the scientific assessment of this manufacturing technology is not closed yet, and many other points have to be deepened. In the following, some new research findings are reported to take a further step toward the full understanding of the mechanisms at the basis of GTR direct molding.

11.3.1 Effect of the rubber typology

In tire remanufacturing, the worn tread is removed by machining in the form of small chips (called "buffing"). The rubber compounds used for the tread are different from the side walls, and generally with higher performance and purity. Small tiles in the size 200 x 200 x5 mm^3 have been produced by using five different commercial GTR particles, three typologies of granulate, and two of buffing. Making a comparison among size distributions of granulate and buffing is complex because of their different shapes. In fact, granules do not exhibit a principal size whereas chips are long with a small section. Moreover, the external surface of the chip is flat with minimal exfoliation. In the experimentation, three different size distributions were used for granulate: small (0–0.5 mm), medium (0.5–2.0 mm), and large (2.0–3.5 mm). But two distributions were selected for buffing: small (0–0.8 mm) and large (0.8–3.0 mm).

Direct molding was carried out at 180°C for 15 min with a pressure of about 30 bar. In Fig. 11.2, two molded plates are shown after cutting for sample extraction. In particular, one sample with 5 x 5 mm^2 size was cut for dynamic mechanical analysis (DMA) and one for tensile testing.

Density was measured on the full tile. The data are reported in Table 11.2 together with the values extracted from tensile tests. Density is higher in the case of granulate than buffing, and for each category it increases by reducing the particle size. Generally, by increasing the density, the recycled rubber strength and elongation at break should increase as well. Instead, in the case of buffing, higher mechanical properties are measured with lower densities despite the poor surface exfoliation. This occurrence is rare and can be correlated to different residual reactivity of the recycled rubber.

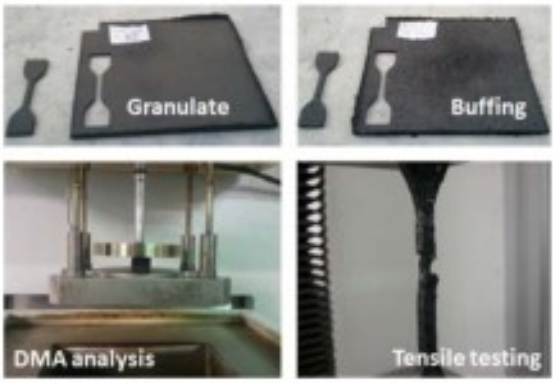


Figure 11.2 Tiles from ground tire rubber (GTR) granulate and buffing, and testing conditions.

Table 11.2 Density and ultimate tensile data from direct molded GTR samples with different rubber typology.

GTR typology	Density, g/cm^3	Tensile strength, MPa	Elongation at break, %
Small-size granulate (0–0.5 mm)	1,012	1.17	32.8
Medium-size granulate (0.5–2.0 mm)	0.519	1.09	32.0
Large-size granulate (2.0–3.5 mm)	0.639	1.08	23.1
Small-size Buffing (0–0.8 mm)	1,058	1.06	81.2
Large-size Buffing (0.8–3.0 mm)	1,115	1.05	85.0

Tensile testing is the best way to evaluate performance of agglomerated materials. In this kind of material, mechanical and functional properties mainly depend on the interface between joined particles rather than on the particle bulk. Tensile tests apply the worst loading condition as they tend to separate particles; therefore they are able to provide a correct evaluation of the molding process effectiveness. In traditional materials, process conditions that increase tensile strength generally reduce elongation at break, instead reducing strength leads to increasing elongation. In fact, if material behavior depends on its molecular or atomic mobility, strength and elongation are inversely dependent. In molded GTR, this mobility mechanism works only within particles and not with interfaces. For this reason, different from conventional materials, process conditions, which improve particle joining, will lead to increase both in tensile strength and elongation at break. This fact is

also generally confirmed by the data in Table 11.2, where the maximum strength is reported for the large-size buffing together with the highest elongation at break. The strength is 10% higher than the best result for granulates. Elongation is up to 160% more. For buffing, the effect of the density on mechanical properties is absent whereas it is evident for granulates where the highest properties are measured for GTR powders. These results show that material selection plays a fundamental role in the definition of direct molded GTR products. Sorting materials in tire recycling is expensive and most grinding technologies are optimized for high production rates. Nevertheless, in such conditions, strong benefits are found for product properties if this cost is paid. In fact, the effects of material selection may be much higher than the effect of an optimized grain size distribution, still tire recyclers do not have often this kind of perception.

If the bulk properties of molded GTR have to be measured, a compression configuration can be used. In fact, compression closes material cracks and makes samples stable. The effect of interfaces is important as well but less than under traction, and sample rupture is rare. Results from DMA tests are shown in Fig. 11.3 in terms of storage modulus E' and loss factor tgδ for all the molded samples. Isotherms tests were carried out at 30°C and increasing frequencies (1, 5, 10, 25, and 33 Hz). Each GTR sample is characterized by a line in the E'/tgδ diagram. Nevertheless, anomalies in comparison with traditional bulk materials are visible due to the agglomerated nature. Generally, by increasing oscillating frequency, E' increases and tgδ reduces. Instead for GTR, they increase both and higher loss factor values are associated with higher storage moduli. The data in Fig. 11.3 show that all the rubber samples behave in a similar

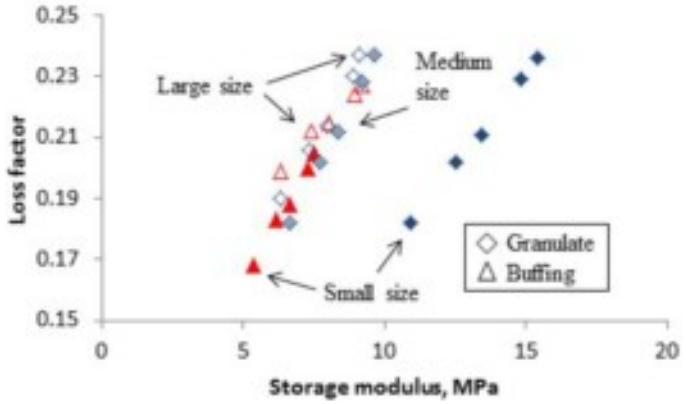


Figure 11.3 Dynamic mechanical analysis (DMA) results from direct molded ground tire rubber (GTR) samples with different rubber typology.

way despite the difference in size and type of grain. This evidence confirms that, under compression, the effect of optimal particle joining is less important than bulk properties. In fact, the highest properties are found in the sample with the highest density (granulate with small grain size).

Analyzing overall tensile and DMA data, the role of the rubber typology emerges, but it can be useless for applications where material strength is not needed. For wear and durability, good particle joining is very important. For damping and stiffness, the density is more important. However, in typical recycling processes where tires are not selected and fully ground, the effect of the density is the only one and all the properties increase by reducing porosity.

11.3.2 Effect of the grinding technology

From an industrial point of view, it is difficult to sort tires before recycling or recovering materials from different parts of the same tire. It is easy to acquire powders or granules made with different recycling technologies. Direct molding of GTR does not use any devulcanizing process or additive, and powder reactivation before molding is only achieved by the grinding technology in terms of size distribution and particle exfoliation. Therefore the selection of the grinding technology can play a role. Tests have been made to quantify this effect. GTR powders have been taken from the market with the same nominal size range (nominally 0.0–0.8 mm). Direct molding of 200 x 200 x 5 mm^3 plates was carried out at 200°C for 10 min at the holding pressure of 35 bar. For the experimentation, four different supplies of GTR powders were considered: one from high-pressure water jet, one from mechanical grinding by a shredder, and two from mechanical grinding by a mill. All the supplies were provided by different enterprises. For mechanical grinding, there are many available solutions. In all the cases, rubber particle separation is obtained by forcing the rubber to flow by shear. This shearing effect may be provided by knives or cutters (in shredders) or by forcing the rubber through small holes (in mills). In mills, the presence of steel fibers in the comminution process is not negligible.

The molded samples are shown in Fig. 11.4 before and after sample extraction. In this case, four dogbone-shaped specimens were cut from each plate along its edges. In Table 11.3, the results of testing are shown in terms of density and ultimate tensile data.

Figure 11.4 Plates from direct molding of ground tire rubber (GTR) from different tire recycling technologies, before and after sample extraction and testing.

Table 11.3 Density and ultimate tensile data from direct molded GTR samples from different tire recycling technologies.

Recycling technology	Density, g/cm^3	Tensile strength, MPa	Standard deviation, MPa	Elongation at break, %	Standard deviation, %
Water jet	1.13	1.10	0.06	48.37	4.48
Shredder	1.12	1.21	0.07	51.10	2.80
Mill – I	1.16	1.76	0.48	110.16	28.21
Mill – II	1.15	1.04	0.24	36.00	9.17

By increasing the tensile strength, the elongation at break also increases, according to the data in Table 11.2. In this case, the correlation is much higher as shown in Fig. 11.5, which confirms the strong effect of the agglomeration mechanism independent of the recycling technology. Nevertheless, the trend of mechanical data with density is not visible. This simultaneous occurrence of the strong correlation of ultimate data between them but not with the density highlights the role of the proper GTR powder selection apart from nominal grain size. It is under discussion if this discrepancy may depend on the recycling technology.

The best performance was measured for the GTR by a mill (namely Mill – I) with an average elongation at break of about 110% and maximum values over 130%. However, also the lowest performance was measured on a GTR made by a mill (Mill – II).

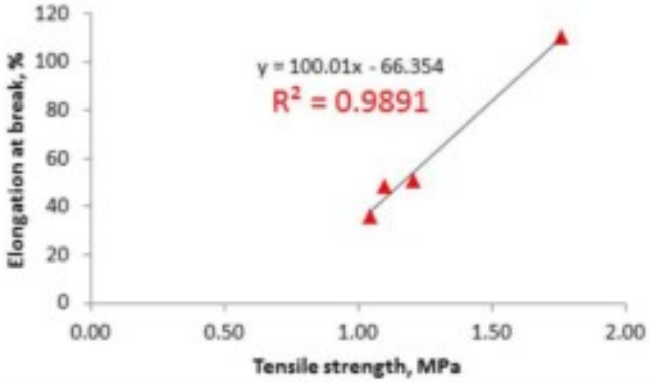


Figure 11.5 Correlation between ultimate tensile data of ground tire rubber (GTR) direct molded samples with different tire recycling technologies.

Between these two limit ends, a difference of about 70% is observed for the strength and up to 200% for the elongation. Further analysis has shown that poor performance of Mill – II depends on material contamination, mainly from textile fibers. In the middle, but closer to the lowest case, there is the performance of the samples by water jet and shredding. Good properties of the first sample by a mill (Mill – I) are dependent on the achieved high-density value, and the observed purity of the supply. Results from the shredded GTR are in line by considering the lower density whereas GTR by water jet seems to be less effective in direct molding. As the different densities may depend on the grain size distribution, the comparison between shredded and water-jet processed GTR is particularly significant. The tensile strength is only 10% higher in the mechanically ground sample whereas the elongation is comparable. As a general consideration, the recycling technology can play an important role in the definition of direct molded part performance, but its contribution is easily covered by other effects such as contamination and size distribution. Therefore the concept of maximizing the density remains valid if a sufficient level of purity is achieved in the GTR.

11.4 Conclusion

Primary recycling of ELTs is possible as compression molding of GTR is feasible without any virgin material or additive. Using GTR pretreatments or small amounts of other raw materials would improve the final performance of recycled products but this is optional. Good mechanical performance is achieved

for many industrial uses. Small products are produced with very good geometrical details though very large products should be preferred to take advantage of their higher added value. In fact, investment costs are not low because of the need of expensive equipment. Nevertheless, operative costs are lower in comparison with traditional recycling technology that uses GTR with polyurethane binders. Therefore if a good production rate is achieved, the economic benefit of GTR direct molding can make the difference. Other advantages are the unique surface aspect, which is smooth and easy to sculpt. Molded parts can be coated and machined by water jet. Disadvantages are related to the process difficulty of technology transfer in small enterprises that should use this kind of technology and to the difficulty of the process setup. In fact, part properties depend on GTR reactivation and size distribution and preliminary tests are necessary to set up an optimized process. It is also possible that changes in the supplied GTR would result in unexpected poor performance of molded products. Moreover, in analogy with other products from GTR, the unpleasant smell and the black color pose strong limitations for the market, and secondary processing by coating is necessary to overcome these disadvantages.

The industrial potential of this recycling technology has been assessed. Direct molding of GTR had immediately shown its advantages in terms of material properties at lab scale, and further research has shown the feasibility of technological transfer in industry. Large products have been prototyped and tested and the energy consumption has been measured. Technical results show that a lower cost is achieved thanks to the new process in comparison with traditional technologies, if about 50% of energy and raw materials are considered. Unfortunately, the current prototype of the molding machine is not yet optimized in terms of controlling and automation, therefore cycle times are still too large.

From a material point of view, many aspects can be used to tailor performance from grain-size distribution, to rubber type selection, purity, and recycling technology. Nevertheless, this kind of approach is time and cost expensive and material sorting means lower GTR production rate and the need for separating recycling routes. Moreover, minimal performance is achieved for any GTR supply, and poor performance may be partially covered by molding large and thick products. On the other hand, in a few cases when very high properties are required, it is possible to select the best suppliers or add subsieving or cleaning processes.

References

[1] E. Markl, M. Lackner, Devulcanization technologies for recycling of tire-derived rubber: A review, Materials 13 (5) (2020) 1246. art. no.

[2] X.M. Song, J.-Y. Hwang, Mechanical properties of composites made with wood fiber and recycled tire rubber, For. Prod. J. 51 (5) (2001) 45–51.

[3] S. Panigrahi, J. Fung, S. Panigrahi, Development of rubber and agricultural fiber based biocomposite for industrial application, SAE Int. J. Commer. Veh. 1 (1) (2009) 284–292.

[4] Z.X. Xin, Z.X. Zhang, K. Pal, D.J. Kang, S.H. Lee, J.K. Kim, Effects of waste ground rubber tire powder (WGRT) and chemical blowing agent content on the cell morphology and physicomechanical properties of injection-molded polypropylene/WGRT foams, J. Vinyl Addit. Techn 15 (4) (2009) 275–280.

[5] Z.-X. Zhang, J.-L. Fan, K. Pal, J.K. Kim, Z.-X. Xin, Influence of compatibilizers and processing temperature on microcellular injection-molded polypropylene/(waste tire powder), composites, J. Vinyl Addit. Techn. 17 (4) (2011) 254–259.

[6] R. Gaggino, M.J. Positieri, P. Irico, J. Kreiker, R. Arguello, M.P. Sánchez Amono, Ecological roofing tiles made with rubber and plastic wastes, Adv. Mat. Res. 844 (2014) 458–461.

[7] L.S. Montagna, R.M.C. Santana, Influence of rubber particle size on properties of recycled thermoplastics containing rubber tyre waste, Plast. Rubber Compos. 41 (6) (2012) 256–262.

[8] L.S. Montagna, L.S. Bento, M.R. Da Silva Silveira, R.M.C. Santana, Evaluation of the effect of the incorporation of rubber tire waste particles on the properties of PP, HIPS and PP/HIPS matrices, Polimeros 23 (2) (2013) 169–174.

[9] L. Mészáros, M. Fejos, T. Bárány, Mechanical properties of recycled LDPE/EVA/ground tyre rubber blends: effects of EVA content and postirradiation, J. Appl. Polym. Sci. 125 (1) (2012) 512–519.

[10] C. Cazan, D. Perniu, M. Cosnita, A. Duta, Polymeric wastes from automotives as second raw materials for large scale products, Environ. Eng. Manag. J. 12 (8) (2013) 1649–1655.

[11] C. Cazan, M. Cosnita, A. Duta, Effect of PET functionalization in composites of rubber–PET–HDPE type, Arab. J. Chem. 10 (3) (2017) 300–312.

[12] M. Cosnita, C. Cazan, A. Duta, The influence of inorganic additive on the water stability and mechanical properties of recycled rubber, polyethylene terephthalate, high density polyethylene and wood composites, J. Clean. Prod. 165 (2017) 630–636.

[13] P.S. Lima, J.M. Oliveira, V.A.E Costa, Partial replacement of EPR by GTR in highly flowable PP/EPR blends: effects on morphology and mechanical properties, J. Appl. Polym. Sci. 132 (22) (2015) 42011. art. no.

[14] P. Lima, S.P. Magalhães Da Silva, J. Oliveira, V. Costa, Rheological properties of ground tyre rubber based thermoplastic elastomeric blends, Polym. Test. 45 (4439) (2015) 58–67. art. no.

[15] J. Luo, Q. Li, H. Shang, S. Gao, C. Zhang, S. Sun, Mechanical and damping properties of wood plastic composite modified by ground waste rubber tire, Prog. Rubber Plast. Re 33 (3) (2017) 127–138.

[16] B. Haworth, D. Chadwick, L. Chen, Y.J. Ang, Thermoplastic composite beam structures from mixtures of recycled HDPE and rubber crumb for acoustic energy absorption, J. Thermoplast. Compos. 31 (1) (2018) 119–142.

[17] S. Moghaddamzadeh, D. Rodrigue, The effect of polyester recycled tire fibers mixed with ground tire rubber on polyethylene composites. Part I: morphological analysis, Prog. Rubber Plast. Re. 34 (4) (2018) 200–220.
[18] S. Moghaddamzadeh, D. Rodrigue, The effect of polyester recycled tire fibers mixed with ground tire rubber on polyethylene composites. Part II: physico-mechanical analysis, Prog. Rubber Plast. Re. 34 (3) (2018) 128–142.
[19] S. Moghaddamzadeh, D. Rodrigue, Rheological characterization of polyethylene/polyester recycled tire fibers/ground tire rubber composites, J. Appl. Polym. Sci. 135 (34) (2018) 46563. art. no.
[20] Y.-H. Wang, Y.-K. Chen, D. Rodrigue, Production of thermoplastic elastomers based on recycled pe and ground tire rubber: Morphology, mechanical properties and effect of compatibilizer addition, Int. Polym. Proc. 33 (4) (2018) 525–534.
[21] B. Shivamurthy, D. Doreswamy, J. Nishanth, H.C. Shiva Prasad, Physical and tribo-mechanical properties of waste rubber tyre/epoxy composites, Mater. Res. Express 6 (9) (2019) 095321. art. no.
[22] R. Shaker, D. Rodrigue, Rotomolding of thermoplastic elastomers based on low-density polyethylene and recycled natural rubber, Appl. Sci. 9 (24) (2019) 5430. art. no.
[23] M. Soleimani, D. Cree, L. Olson, L.G. Tabil, S. Panigrahi, Fabrication of nonextruded recycled rubber–polyethylene composites, J. Appl. Polym. Sci. (2020) 49067. art. no.
[24] K. Fukumori, M. Matsushita, H. Okamoto, N. Sato, Y. Suzuki, K. Takeuchi, Recycling technology of tire rubber, JSAE Rev. 23 (2) (2002) 259–264.
[25] B. Maridass, B.R. Gupta, Recycling of waste tire rubber powder, KGK-Kau. Gummi. Kunst. 56 (5) (2003) 232–236.
[26] K. Aoudia, S. Azem, N. Aït Hocine, M. Gratton, V. Pettarin, S. Seghar, Recycling of waste tire rubber: microwave devulcanization and incorporation in a thermoset resin, Waste Manage. 60 (2017) 471–481.
[27] J.W. van Hoek, G. Heideman, J.W.M. Noordermeer, W.K. Dierkes, A. Blume, Implications of the use of silica as active filler in passenger car tire compounds on their recycling options, Materials 12 (5) (2019) 725. art. no.
[28] J. Domingues, T. Marques, A. Mateus, P. Carreira, C. Malça, An additive manufacturing solution to produce big green parts from tires and recycled plastics, Procedia Manuf. 12 (2017) 242–248.
[29] M.A. Quetzeri-Santiago, C.L. Hedegaard, J.R. Castrejón-Pita, Additive manufacturing with liquid latex and recycled end-of-life rubber, 3D Print. Addit. Manuf. 6 (3) (2019) 149–157.
[30] J.E. Morin, D.E. Williams, R.J. Farris, A novel method to recycle scrap tires: high-pressure high-temperature sintering, Rubber Chem. Technol. 75 (5) (2002) 955–968.
[31] A. Guglielmotti, C. Lucignano, F. Quadrini, Production of rubber pads by tyre recycling, Int. J. Mater. Eng. Innov. 1 (1) (2009) 91–106.
[32] F. Quadrini, D. Bellisario, L. Santo, Recycling of thermoset polyurethane foams, Polym. Eng. Sci. 53 (7) (2013) 1357–1363.
[33] F. Quadrini, D. Bellisario, L. Santo, Molding articles made of 100% recycled fiberglass, J. Compos. Mater. 50 (21) (2016) 2959–2969.
[34] C. Lucignano, F. Quadrini, New technological solutions for recycling spent tire rubber, Int. J. Manuf. Mater. Mech. Eng. 2 (1) (2012) 1–10.
[35] C. Lucignano, A. Guglielmotti, F. Quadrini, Compression moulding of rubber powder from exhausted tyres, Polym.-Plast. Technol. 51 (4) (2012) 340–344.

[36] A. Gugliemotti, C. Lucignano, F. Quadrini, Production of rubber parts by tyre recycling without using virgin materials, Plast. Rubber Compos. 41 (1) (2012) 40–46.
[37] F. Quadrini, D. Bellisario, L. Santo, I. Hren, Direct moulding of rubber granules and powders from tyre recycling, Appl. Mech. Mater. 371 (2013) 315–319.
[38] F. Quadrini, L. Santo, E. Musacchi, A sustainable molding process for new rubber products from tire recycling, Prog. Rubber Plast. Re 35 (1) (2019) 41–55.

PART

IV

Key markets for recycling materials, products, and applications

This page intentionally left blank

12

Environmental impact of tires used in marine construction

K.J. Collins

Ocean and Earth Science, University of Southampton, Southampton, United Kingdom

12.1 Introduction

The longevity, resistance, and shape of tires have been exploited for many marine construction applications [1–3]: breakwaters (onshore and offshore), retaining walls in harbors and estuaries, and artificial reefs for fishery enhancement. Underwater, tires are protected from ultraviolet degradation and are in a neutral, stable chemical environment, which may limit leaching. Two extensive artificial reef bibliographies [4,5] list some 60 tire breakwater papers and over 200 references to tire reefs, and describe tire reefs from North America, the Caribbean, Europe, the Middle East, Asia/Pacific, and Australia.

Prohibition of landfilling of whole tires since July 2003 by the EU Landfill directive and landfilling of shredded tires by July 2006 by the EU Landfill Directive [6] has accelerated the drive to recycle and reuse end-of-life tires.

One of the barriers to utilization of tires is a widespread impression that they are inherently toxic [7]. There have been many studies related to road runoff and leaching studies of tire wear particles, which have demonstrated potential toxicity to freshwater and marine organisms, most recently comprehensively reviewed in Ref. [8]. However, as discussed below, there are many orders of magnitude difference between the leachate concentrations from whole tires compared to that from finely divided tire particles.

The negative view of tires arises from much publicized massive tire dump fires that are very visible, producing huge plumes of choking black smoke and very difficult to extinguish [9]. Best, Brookes [10] describe the impact of a large fire in April 1978 in a quarry used as a dump for 15,000 tons of used tires and unknown amounts of chemical wastes. Attempts to extinguish

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00017-X
© 2021 Elsevier Inc. All rights reserved.

the fire with water produced a large volume of oily leachate containing 200 different chemicals, including alkenes, alkanes, aromatic hydrocarbons and their derivatives, terpenes, phenolic compounds, ketones, alcohols, ethers, esters, benzothiazoles, pyridines, anilines, amines, amides, quinolines, and sulfur compounds. Tire-ash leaching studies [11] showed the heavy metal concentrations were dominated by zinc with lesser quantities, in descending order of lead, copper, chromium, and cadmium. Pearce [12], discussing the changes in UK legislation intended to improve tire disposal, compared concerns over the problems caused by tire mounds and fires with the opening of the UK's country's first commercial tire incinerator to generate electricity for the national grid. There is, however, a great difference between the uncontrolled, variable temperature combustion of tires in a dump fire compare to the consistent high temperatures of combustion during power generation and similarly as a fuel in cement production.

12.2 Marine applications for whole tires

Whole tires are a familiar sight on boats, barges, docks, and wharfs as fenders for mooring, preventing damage both to vessel and shore structures. The tires offer good durability for these tasks because of their load deflection, energy absorption, and toughness. Fig. 12.1 shows whole tires in use as a bedding layer for house boats moored in the Thames estuary, protecting the hull when the tide ebbs and the boat settles on the seabed. A seawall using tires in Taiwan is shown in Fig. 12.2.

12.2.1 Tire artificial reefs

Tires are a particularly popular choice for artificial reef construction because they are readily available at low cost, simple to assemble into units, easy to handle manually or with mobile equipment, durable, and they have a large surface area-to-volume ratio providing a more useful habitat than other materials (Fig. 12.3). The author has collaborated with many artificial reef groups worldwide through the international Conference on Artificial Reef and Related Habitats series, first organized in 1974 in Texas, United States with aims to improve the exchange of information among people interested in artificial reefs and focus international attention on their potential in fishery management [13]. European collaboration was initiated through the European Artificial Reef Research Network [14,15].

Figure 12.1 House boat base on the River Thames.

12.2.1.1 Tire artificial reefs in the United States

Tires are relatively buoyant in seawater, and initial attempts to construct tire reefs in the United States were poorly engineered and quickly washed ashore by storms [16,17]. This led to restrictions or banning in some states such as California and Washington [18]. Of the 14 coastal states surveyed in an assessment of Atlantic reef activities [19], 12 had documented records of reef development and 9 had government-sponsored reef programs. There were 273 permitted reef sites along the entire coast with 26 of these still waiting for deployment of reef structures. Florida and North Carolina were the most active reef-building states, accounting for 65% of the total Atlantic sites. Stone et al. [20] reported 40 artificial reefs on the US east coast that used approximately 700,000 tires and subsequently this

Figure 12.2 Taiwan coastal protection using tires.

Figure 12.3 Tire reef prior to deployment in the Black Sea.

had increased to 73 on the Atlantic seaboard [21]. Addressing the instability of early US tire reefs, the concept of "rubber rocks" was developed for New Jersey fishing reefs [22,23]. These were made by compressing a stack of tires and filling the central void with concrete. These were very successful [24,25]. Heavy metal (Cd, Cr, Cu, Mn, Ni, Pb, Zn) analyses of mussels growing on New Jersey tire reefs compared to those from control natural reefs showed no significant differences [26].

12.2.1.2 Tire artificial reefs Malaysia

Artificial reefs built from tires are particularly popular in the southwest Pacific around the Philippines and Malaysia. In Malaysia more than 50 reefs have been created using about 1.5 million tires [27]. Saharuddin et al. [28] described how artificial reefs have been established in Malaysian fisheries waters since 1975 using various materials such as discarded tires, derelict and confiscated fishing vessel, reinforced concrete, polyvinyl chloride, fiberglass reinforce concrete, fiberglass, ceramic, combination of several materials (reef balls) as well as abandoned oil platforms. They are used as a possible tool for fisheries management in maximizing resource enhancement, resource conservation, habitat rehabilitation and mitigation as well as one of the steps to alleviate the problem of depleting fish resources in the coastal waters. This was carried out by four main departments: the Department of Fisheries Malaysia, Fisheries Development Authority Board of Malaysia, Marine Park Department, and the Malaysian Maritime Enforcement Agency. One of the chief issues was that the concept and purpose of establishing reefs was not clearly defined by these agencies from the beginning and has caused an unsustainable way of managing the reefs, rather than the inherent environmental compatibility of the waste materials employed, including tires. These issues were explored further in Refs. [29,30].

12.2.1.3 Tire artificial reefs in Hong Kong

Hong Kong's fisheries are heavily exploited. In the 1960s, the Hong Kong Government promoted trawling technology to the local fishing industry and the local waters have been bottom-trawled ever since. After 30 years, the seabed was reduced to a muddy flat. The degraded marine habitat provided little shelter for fish to rest against the constant ocean current and the local fishery deteriorated drastically. As one of the measures to restore local fisheries, the Hong Kong Government provided HK$100 million to finance a 5-year artificial reef program to

enhance fisheries resources and promote biodiversity in Hong Kong's marine environment [31]. Between July and September 1998 some 200 tire reef units were deployed at eight sites in Hoi Ha Wan and Yan Chau Tong Marine Parks. Each tire unit consisted of 42 tires strapped together to form a pyramidal-shaped structure, nearly 3 m high and 20 m^3 in volume. Tires were chosen because they would be lighter than concrete and not sink into the soft seabed sediments as had occurred with several concrete reefs off on the west coast of Taiwan. The Hong Kong tire reefs were also designed to serve as antitrawling devices because by law trawling was not allowed within marine parks. For over 16 years tire reefs had survived the seawater environment, trawling, dynamite fishing and none had sunk into the muddy seabed [32].

12.2.1.4 Tire artificial reefs Australia

Australia has built at least 30 tire reefs [33]. The creation of an artificial reef off Busselton, Western Australia, involved the dumping of some 34,000 tires about 8 nautical miles from Busselton off Quindalip in 20 m of water [34]. The reef was made for recreational line fishermen and sport divers; professional fishermen and spear fishing is banned. It was expected that the reef would increase the catches of recreational fishermen and provide extra opportunities for recreational diving, thus increasing tourism to the region. Bennet [35] reported that 1997 Quindalup tire reef has worked well and that there was confidence in future reefs, financed in part from recreational fishing licenses, reinvesting the money raised ($520,000) into better recreational facilities.

12.2.1.5 Tire artificial reefs Israel

A small tire reef in the Red Sea off Eilat, Israel has been successfully colonized by corals (Fig. 12.4). One of the concerns with using tire as a reef building material in tropical waters is that the tires will flex during storms and shed their coral epifauna [36]. Heavy metal (Cd, Cr, Cu, Mn, Ni, Pb, Zn) analyses of algae, hydroids, sponges and ascidians growing on a tire reef and steel barge as control in the Mediterranean off Haifa, Israel tire reefs, showed no significant differences [26].

12.2.1.6 Poole Bay artificial reef

The UK availability scrap tires that could be used as fuel in a power station, was investigated [37]. Information related to current arisings of waste tires was already available and it was

Figure 12.4 Red Sea tire reef with corals, off Eilat, Israel.

known that for more than 50 years tires have been scrapped and disposed of in progressively increasing numbers. Humberside was found to have the highest concentration of tire stockpiles in the UK [37,38]. The Humberside coast, northeast UK is rapidly eroding at rates of up to 5 m per year [39] with an Integrated Coastal Zone Management Plan specifically encouraging "rollback" as the main response to erosion as the least cost option. Addressing both issues, in 1993, concrete-filled compressed scrap tire bales "rubber rocks" were proposed for use in building offshore breakwaters off Holderness, Humberside. If accepted, this could have been a self-financing coastal defense scheme using the tire disposal fees to pay for the preparation and deployment of the rubber rocks, a first in the UK. Sadly this was never implemented and ironically at the time, there was the likelihood of using subsidized waste tires from Germany rather than reducing the local stockpiles because the former would have been cheaper.

So far, millions of tires used in marine artificial reefs around the world have been colonized by marine organisms without apparent ill effects. However, until detailed environmental compatibility studies had been carried out, the UK or any other European country would not sanction their use in the sea.

The majority of papers concerning tire artificial reefs concentrate on fish populations and catches. However, when considering their potential environmental impact in the marine environment, the growth of organisms on the tire surface may be more revealing than the mobile fauna, as their exposure to any chemical release is greater. Colonization by a range of flora and fauna has been described by many authors such as Gordon [40–47].

Zinc oxide is nearly 2% by weight of the average tire (i.e., ~150,000 mgZn/tire) [48]. It is employed in tires as a vulcanization activator at concentrations of 1%–2% by weight. Zinc forms chelates with a number of sulfur-containing accelerators during the vulcanization process, such that the majority of zinc in tire treads is excess ZnO and a variety of Zn-accelerator complexes [49]. Turner and Rice [50] studying the release of zinc added tire wear particles filed from the treads of end-of-life vehicle tires to seawater to seawater. In laboratory studies this leachate produced reduction in the efficiency of photochemical energy conversion of the green alga *U. lactuca*.

Abernathy et al. [51] reported that tires placed in a tank of flowing water were nonlethal to trout so long as the flow rate was greater than 1.4 L/min per 600 L of water volume and that tires collected from an artificial reef in Lake Erie were less toxic than scrap tires that were never exposed to an aquatic environment. An investigation of contaminated sediments in San Francisco Bay [52] found several benzthiazoles, assumed to be derived from the use of antioxidants in the manufacture of rubber tires. The investigations confirm that two of these compounds, benzthiazole and 2-(4-morpholinyl)-benzthiazole, occur in street runoff, and that they can result from the weathering of a commercially used antioxidant in rubber manufacture. These compounds were proposed as potential indicators of the contribution of street runoff to the contaminants in sediments of urban coastal areas. Kumata et al. [53] similarly proposed 2-(4-morpholinyl)benzothiazole as an indicator of tire-wear particles and road dust in the urban environment.

A preliminary study [1] noted the release of zinc and polycyclic aromatic compounds including benzothiazoles from tires in laboratory seawater leaching studies. A marine environmental evaluation procedure was developed for cement-stabilized coal ash in which, after a series of laboratory trials (physical, chemical, and biological), an experimental structure was deployed in Poole Bay, off the central south coast of England [54,55]. Repeating this protocol in July 1998, tire modules and concrete control modules were deployed alongside the existing cement stabilized coal-ash reef study site in 12 m of water. Five hundred scrap tires were formed into three types of modules: (1) concrete-filled single

Figure 12.5 Poole Bay artificial reef units: tire pyramids and concrete filled rubber rocks.

tires; (2) stacks of 6/7 car tires forming a cylinder filled with concrete ("rubber rocks" c.f. Figley [23]); and (3) open lattice structures (tetrahedra) using either 4 or 13 tires held together by stainless steel bolts and with the basal tires filled with concrete (Fig. 12.5). Concrete blocks ($20 \times 20 \times 40$ cm) were used as the control. The reef was arranged (in the same way as the earlier coal ash reef) as eight separate units, each 5 m across by 1 m high replicating each of the three tire structures and the concrete controls [56].

Initial recruitment of fouling organisms occurred rapidly after reef deployment. Within 3 weeks, seven species of drift algae, including brown (*Laminaria* sp.) and red algae (*Brongniartella byssoides* and *Chondria dasyphylla*) were attached and growing. By winter, 5 months after deployment, both concrete and tire units were hydroid dominated with some bryozoans, ascidians, barnacles, and worms. One year later a thick cover of algae was present on all upper surfaces (Fig. 12.6). Erect bryozoans were the dominant group on vertical surfaces of concrete and tetrahedral units and encrusting bryozoans on vertical surfaces of rubber rock units. There were no significant differences ($P > .05$) between concrete and tire substratum except for encrusting bryozoans (attributed to habitat configuration). Throughout 3 years after reef deployment, tire and concrete module surfaces were dominated by hydroids,

Figure 12.6 Poole Bay tire artificial reef tetrahedral module 1 year after deployment.

bryozoa, and red algae, responsible for more than 70% of the total cover. The percentage contribution to total cover varied between module surfaces and time of year. Hydroids and bryozoa were dominant in spring, accounting for around half the total cover. As the year progressed red algae and bryozoa dominated. Through each summer red algae became dominant on horizontal surfaces and bryozoa was the major contributor to total cover on vertical surfaces. Cluster analysis and multidimensional scaling ordination revealed that surfaces are grouped primarily according to surface orientation. Less extensive organisms, including barnacles, sponges, and ascidians, appeared to account for a greater percentage of total cover on vertical surfaces than for horizontal surfaces on the same module. Cluster analysis showed that there was little difference in the benthic community structure between the rubber rock modules and the concrete control units [57,58]. Twenty years later this experimental tire reef is still flourishing (Fig. 12.7).

Metal (Zn, Cu, Pb, and Cd) concentrations within four individual epibiotic species (Hydroida: *Halecium* sp.; Bryozoa: *Bugula fabellata*; Ascidia: *Styela clava*, and *Ascidiella aspersa*) sampled after 11 months showed that that significant tire/concrete substrate differences in metal content were restricted to *Halecium* sp. Collins et al. [58]. The monitoring work continued [59,60] to investigate if there were further changes in the relative uptake of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn) between epibiota on tires and concrete. The results did not show any significant trends in metal concentrations over time in any taxonomic groups sampled on either the concrete or tire reef substrata.

Figure 12.7 Poole Bay tire artificial reef "rubber rock" module 20 years after deployment.

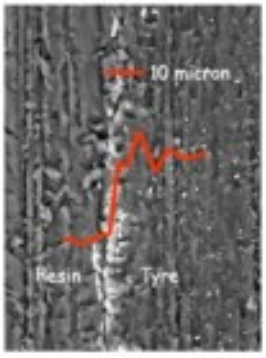


Figure 12.8 Scanning electron microscope section of a tire immersed in seawater for 10 years and embedded in resin. The red graph line represents the concentration profile from resin (no zinc) to the zinc concentration within the tire.

Laboratory studies [1] suggested that leaching occurs from the outer surface of the rubber, a few microns deep, and rates of release will decrease with exposure time. Fig. 12.8 shows a scanning electron microscope section with zinc concentration profile through a tire surface after 10 years in the sea. The leaching of the zinc extends only a few microns into tire suggesting an estimated total release of 10 mg zinc per whole car

tire [1]. This is supported by the modeling of release of zinc from tires bales at Pevensey described below.

Results to date showed no evidence for significant uptake by reef organisms of tire compounds. Interestingly, the author's attempts to monitor the concentrations of benzothiazoles, a key organic tracer for tires, in control natural reef organisms compared to those on the tire reefs, were thwarted by the background level in coastal seawater presumably derived from road run-off [56].

12.2.2 Coastal protection with tires

Whole tires have been employed in a very simple fashion to protect the coastline as shown in Figs. 12.9 and 12.10. The extensive civil engineering applications of tires have been described in Ref. [61]. Tire bales can and have been used extensively for the core of concrete structures especially in the United States. Another application is to use them as fill material within conventional coastal defense structures such as rock groynes, revetments, and beaches [3]. This latter application makes use of the energy absorption capabilities of the bales in withstanding wave energy through the overlying rock armor.

Tire bales consist of approximately 100 tires compressed by a downstroke baler and held in compression by plastic strapping or

Figure 12.9 Seawall footings protection Copperas Bay in the Stour Estuary, Suffolk/Essex boundary.

Figure 12.10 Coastal cliff protection Copperas Bay in the Stour Estuary, Suffolk//Essex boundary.

galvanized wire (Fig. 12.11). The equipment may be mobile, which is of great cost benefit potentially avoiding the costly transportation of loose tires to a processing center. Production, engineering properties and wider applications of tire bales in marine, freshwater, and terrestrial are described in detail in Ref. [3]. Since 2005, WRAP (the Waste and Resource Action Program) has been helping to develop and create reuse opportunities for used tires. To support these aims they have produced a Quality Protocol for tire-derived rubber products with the Environment Agency. Outside of the protocol, WRAP commissioned the BSI (British Standards Institute) to develop a specification for tire bales used in construction in collaboration with the tire reprocessing industry. This specification, BSI PAS 108 [62], has helped to put used tires on a similar footing to other geotechnical materials.

12.2.2.1 Pevensey trial

Pevensey Beach is a 9 km shingle embankment that protects 50 km^2 of the low-lying Pevensey Levels, 35 km^2 of which is a Site of Special Scientific Interest. A major beach replenishment took place during the summer of 2002. However, littoral drift through Pevensey Bay results in a net loss to the frontage of 20,000 m^3/year. This amount has to be replenished annually to

Figure 12.11 Tire baler, note door open on left, closed during compression by the hydraulic ram and steel binding wires at base of tire bale ready to be wrapped around the compressed bale.

maintain the level of defense. This would normally require the import of large amounts of natural shingle to build up the beach to the required level. Shingle is dredged from the seabed in vast amounts for beach renourishment schemes in the UK. Any reduction in dredging is welcome as it preserves the offshore shingle resource for the future [3].

A pilot trial was carried out in which 350 tire bales were buried in the landward side of the beach in November 2002, generating shingle that could be used on the seaward beach slope and crest. The bales were used, placed in a block 14 bales long, 5 bales wide, and 5 bales high. A geogrid (Tensar SS20) (4 m wide) was placed on the shingle below the bales and wrapped round them as they were placed, so that the entire block was enclosed within it. Early construction is shown in Fig. 12.12. The geogrid is a reinforcing geosynthetic fabric that held the bales together, but has open mesh spaces in a grid pattern large enough to allow shingle to migrate into the bales. The first eight rows had shingle placed into the voids between the tires that were then washed over with water to assist shingle ingress. The beach profile has been maintained ensuring that the tire bales were never exposed (Fig. 12.13).

Figure 12.12 Excavation of Pevensey shingle beach ready to receive a block of tire bales.

In order to monitor the water quality for any changes produced by the tires, sampling wells were placed through the tire bales. Reference wells were placed on the far side of a concrete culvert through the beach for a local river assuming that any effects from the tire bales will not pass through this channel. The author with his research students routinely monitored the well-water levels and metal concentrations for 5 years post deployment of the bales in November 2002 [63–68]. Sampling at Pevensey was constrained to when spring high tides were higher than 3.3 m, thus ensuring the tires bales were submerged. Water collection took place 3 h after high tide allowing for the lag time of the tidal prism to pervade through the beach embankment [63].

The highest dissolved zinc concentrations in seawater from within the tires bales are shown in Fig. 12.14. As this interstitial water drained from the bales this water mixed with the much large tidal prism within the shingle beach diluting it by orders of magnitude before it returned to the sea.

Figure 12.13 Cross-sectional diagram of Pevensey beach showing the placement of the block of bales behind the maximum beach recession line, indicated by arrow.

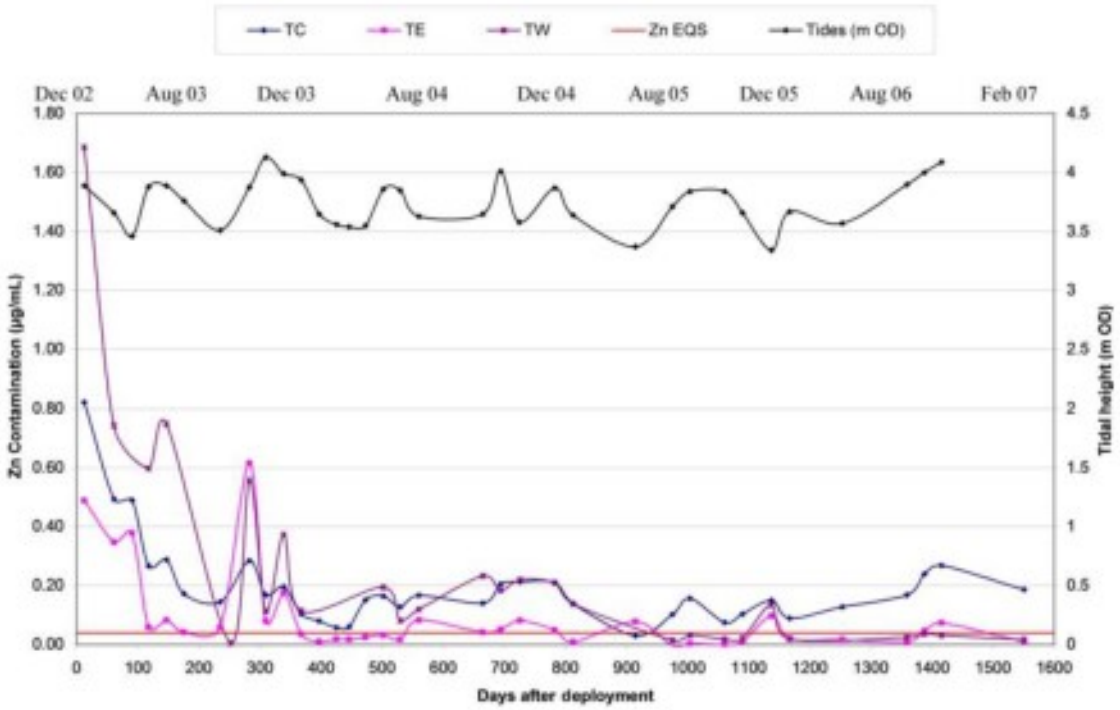


Figure 12.14 The highest zinc contamination measured within three tire bale wells, displayed with the corresponding tide for that sampling date.

From the well water level it was possible to determine to what extent the bales were exposed to water on every tide. Leaching was modeled in 5 cm layers through the entire tire bale block and the amount leached estimated based on the number of times that layer had been wetted previously. Thus assuming, for example, 1% of potentially leachable material is lost per wetting a lookup table could be created. The amount of leachable material lost with each wetting is a major uncertainty in the numerical model and the lookup table makes it easy to vary this amount and test different iterations of the numerical model that assume different losses of material with each wetting. It was assumed that a wetted layer of tires would leach an amount of material proportional to the potential leachable amount left in it after previous wettings. The same formula is applied to all of the tire layers and the model takes the sum of the zinc release from all the layers as the total zinc release for any particular tide. These figures where then compared to monitored figures at Pevensey Bay by considering each modeled release as a percentage of the initial release recorded at Pevensey Bay. A similar procedure can be applied to comparing the numerical model with a small-scale laboratory physical model. The latter showed a strong linear relationship between cumulative zinc concentration and number of wettings ($r^2 = 0.99$) inferring a 1% loss in leachable material with each wetting. Longer-term monitoring over 4 years found that a 1.5% loss with each wetting gave the best fit. After 5 years of monitoring the best-fit model (Fig. 12.15) suggested that this rate of loss of leachable zinc has reduced to 1% per wetting [68]. Modeling of dissolved zinc levels in the interstitial water [63] suggested that the total amount of Zn leached over the year post

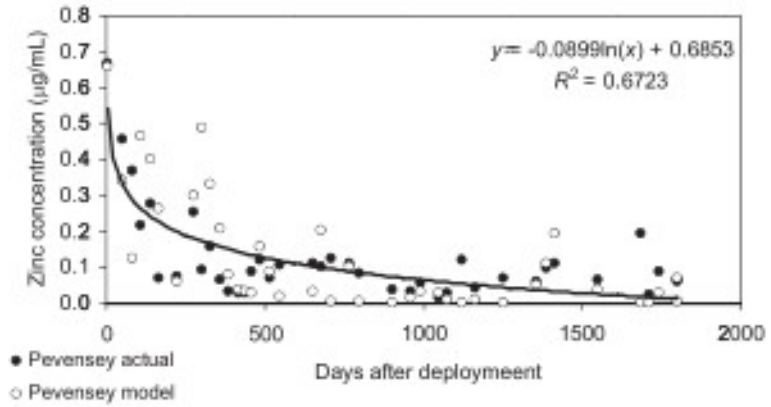


Figure 12.15 Comparison of measured tire well dissolved zinc concentrations with best fit model after 5 years of monitoring.

deployment equated to an average of $0.04 \pm 0.005\,\mu g/mL$ equal to the annual average EC Environmental Quality Standards for marine and estuarine waters. This total annual amount of zinc leached subsequently reduced year by year confirmed by the above monitoring and modeling.

12.3 Microplastics

Concern over the environmental impact of waste plastics in the natural environment have accelerated in recent years and in the past decade has focused on smaller size ranges, such as microplastics [69]. Most authors refer to tire wear particles as microplastics due to its (semi)-synthetically produced polymer structure, solid state, insolubility, and particle size included in the size range $1-1000\,\mu m$ [70].

There have been many studies of the environmental impact of road run-off that contain a variety of materials including tire wear particles: from UK motorways [71,72], Hamburg [73], Paris [74], quantifying metals [75], formulating an integrated budget for contaminants [76], and impact on freshwater sediments [77]. Baensch-Baltruschat et al. [8] recently published a comprehensive review of tire and road wear particles (TRWP), their generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment. They suggest that due to their relative high density TRWP can be expected to play a minor part in the marine environment compared to other polymers of lighter specific weight. However, these particles will already have leached much of their metal and organic compound content into rainwater run-off and freshwater streams before entering the sea as noted with benzothialozole described above.

The fine particles in road run-off potentially could release their entire content of heavy metals and organic compounds because of their high surface area-to-volume ratio. As discussed above a whole automobile tire is likely to leach 10 mg zinc [1] compared to its typical total zinc content of 150,000 mg [48]. This has been confirmed by the intensive 5-year monitoring of the Pevensey trial. The numerous colonization studies of tire artificial reefs around the world including the long-term study of the Poole Bay artificial reef indicate the potential of tires as a marine construction material.

Modern society accepts and is heavily dependent on vehicle tires and appears to accept the leachates from their wear entering our fresh and seawater environments while marine construction with waste tires is often met with concern. We still need a wide

range of recycling options for used tires. It would be unfortunate to block those applications, such as artificial reefs, which utilize the unique properties of tires that have taken over a century to develop.

References

[1] K.J. Collins, A.C. Jensen, S. Albert, A review of waste tyre utilisation in the marine environment, Chem. Ecol. 10 (3-4) (1995) 205–216.

[2] J.D. Simm, M.J. Wallis, C. Elliot, K.J. Collins, R. Atkins, Sustainable re-use of materials in coastal and river engineering, Eng. Sustainability, Proc. Inst. Civ. Eng. ES3 (04) (2004) 131.

[3] J.D. Simm, M.J. Wallis, K.J. Collins, Sustainable Re-use of Tyre in Port, Coastal and River Engineering, Guidance for Planning, Implementation and Maintenance, HR Wallingford, 2005, p. 226.

[4] G. Stanton, D. Wilber, A. Murray, Annotated Bibliography of Artificial Reef Research and Management, Florida Sea Grant College, 1985.

[5] T.L. Berger, Artificial Reef Bibliography: A Reference Guide, Artificial Reef Development Center, NW, Washington, DC, 1993.

[6] European Commission, The Landfill Directive1999/31/EC, 1999. https://ec.europa.eu/environment/waste/landfill_index.htm. (Accessed 15 June 2020).

[7] K. Collins, A. Jensen, P. Smith, The science and politics of using stabilised waste materials in the marine environment, in: R.K. Dhir, T.D. Dyer, K.A. Paine (Eds.), Sustainable Construction: Use of Incinerator Ash, Thomas Telford, London, 2000, pp. 392–404.

[8] B. Baensch-Baltruschat, B. Kocher, F. Stock, G. Reifferscheid, Tyre and road wear particles (TRWP)—a review of generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment, Sci. Total. Environ. 733 (2020) 137823.

[9] J. Warren, Mammoth dump catches fire in northern San Joaquin Valley, 1999. https://www.latimes.com/archives/la-xpm-1999-sep-23-mn-13314-story.html. (Accessed 14 June 2020).

[10] G.A. Best, B.I. Brookes, Water pollution resulting from a fire at a tyre dump, Environ. Pollut. (Ser. B) 2 (1) (1981) 59–67.

[11] A.A. Adeyi, P.O. Oladoye, Assessment of heavy metals in simulated leachates and the ashes of end-of-life tyres, Int. J. Environ. Waste Manag. 25 (4) (2020) 474–486.

[12] F. Pearce, Scrap tyres: a burning issue, N. Sci. 140 (1900) (1993) 13–14.

[13] S.A. Bortone, CARAH (International Conference on Artificial Reefs and Related AquaticHabitats): an historical perspective of accomplishments, J. Appl. Ichthyol. 31 (Suppl. 3) (2015) 3–14.

[14] A.C. Jensen, European artificial reef research, in: Proceedings of the First EARRN Conference, March 1996, Ancona, Italy, Southampton Oceanography Centre, 1997.

[15] A.C. Jensen, K.J. Collins, A.P.M. Lockwood, Artificial Reefs in European Seas, Kluwer Academic Publishers, The Netherlands, 2000.

[16] D.M. Morley, R.L. Sherman, L.K.B. Jordan, K.W. Banks, T.P. Quinn, R.E. Spieler, Environmental enhancement gone awry: characterization of an artificial reef constructed from waste vehicle tires, Environ. Probl. Coast. Reg. VII C. A. Brebbia 99 (2008) 73–87.

[17] R.L. Sherman, R.E. Spieler, Tires: unstable materials for artificial reef construction, in C.A. Brebbia (Ed.), Environmental Problems in Coastal Regions VI: Including Oil Spill Studies, vol. 88. WIT Press, 2006, p. 215.

[18] R.B. Stone, National Artificial Reef Plan, NOAA, US Deptartment of Commerce., Washington, DC, 1985.
[19] J. McGurrin, An assessment of Atlantic artificial reef development, Fisheries 14 (4) (1989) 19–25.
[20] R.B. Stone, L. Coston, D. Hoss, F. Cross, Experiments on some possible effects of tire reefs on pinfish and black sea bass, Mar. Fish. Rev. 37 (1975) 18–20.
[21] J. McGurrin, A Profile of Atlantic Artificial Reef Development, Atlantic States Marine Fisheries Commission, 1988.
[22] D.O. Myatt, E.N. Myatt, W.K. Figley, New Jersey tire reef stability study, Bull. Mar. Sci. 44 (2) (1989) 807–817.
[23] W. Figley, Tire Reef Construction Manual, New Jersey Department of Environmental Protection and Energy, Division of Fish, Game and Wildlife, Marine Fisheries Aministration, Port Republic, NJ, 1991.
[24] F. Steimle, W. Figley, 1994 Epifauna on Tire Units from the Garden State North and Garden State South Artifical Reefs off Long Beach Island, New Jersey, US Department of Commerce, NOAA, National Marine Fisheries Service, Northeast Region, Woods Hole, MA, 1996.
[25] F.W. Steimle, W. Figley, The importance of artificial reef epifauna to Black Sea Bass diets in the Middle Atlantic Bight, North. Am. J. Fish. Manag. 16 (1996) 433–439.
[26] K.J. Collins, W. Figley, E. Spanier, Bioaccumulation studies of tyre artificial reef biota, in: Third International Ocean Pollution Symposium, Harbor Branch Oceanographic Institution, Florida, 7–11 April 1997, 1997.
[27] R. Zakaria, Ecosystem boost with tyre reefs, N. Straits Times (1993) 25.
[28] A.H. Saharuddin, A. Ali, M.H. Lokman, W. Salihin, IEEE, Recent Development and Management of Artificial Reefs (ARs) in Malaysia. Oceans, 2012—Yeosu, 2012.
[29] A. Ali, N.I. Tajudin, R. Hazizi, Research and development on the design and construction of artificial reefs in Malaysia (1975–2017), in: S.A. Bortone (Ed.) Marine Artificial Reef Research and Development: Integrating Fisheries Management Objectives, vol. 86, 2018, pp. 289–313.
[30] J.M. Rani, E. Olson, G. Patenaude, Re-exploring the application of artificial reefs for community-based fishery management in Malaysia, in: S.A. Bortone (Ed.) Marine Artificial Reef Research and Development: Integrating Fisheries Management Objectives, vol. 86, 2018, pp. 235–249.
[31] K.D.P. Wilson, D.C. Cook, Artificial reef development: a marine protected area approach, in: Hird international Conference on the Marine Biology of the South China Sea, Hong Kong, Hong Kong University Press, 1996.
[32] M&P Consulting Engineers (HK) Ltd., 9.6.20. Tyre Artificial Reefs for Marine Conservation, 2020. https://www.maoandpartners.com/tyre-artifical-reefs/.
[33] S. Kerr, Artificial Reefs in Australia: Their Construction, Location and Function, Bureau of Rural Resources, Canberra, 1992.
[34] C. Young, Instant reefs, FINS 21 (2) (1988) 12–17.
[35] R. Bennet, Artificial reef excites fishers, 2013 (Accessed 15 June 2020). https://www.busseltonmail.com.au/story/1454384/artificial-reef-excites-fishers/
[36] E.D. Gomez, A.C. Alcala, L.C. Alcala, Growth of some corals in an artificial reef off dumaguete, central visayas, Philippines, Kalikasan Philippine J. Biol. 11 (1) (1982) 148–157.
[37] P.J. Scott, Study of Location of Major UK Tyre Deposits, AEA Environment and Energy, Harwell, 1993.

[38] A.B. Hird, P.J. Griffiths, R.A. Smith, Tyre Waste Resoucre Management: A Mass Balance Approach, Viridis, TRL Ltd., Crowthorne, 2002, p. 78.
[39] DTA, The Rollback Caravan Holiday Home Park. From the Eroding East Yorkshire Coastline, The East Riding of Yorkshire Council, Nottingham, 2003, p. 96.
[40] M.R. Gordon, A study of the Palm Beach county artificial reef with emphasis on biological succession on tire units, Florida Sea Grant Report, St. Petersburg, FL, June 10–11, 1972.
[41] R.T. Tsuda, H.T. Kami, Algal succession on artificial reefs in a marine lagoon environment in Guam, J. Phycol. 9 (1973) 260–264.
[42] D.J. Alfieri, "Organismal development on an artificial substrate, July 1, (1972)–June 6, (1974), Estuar. Coast. Mar. Sci. 3 (4) (1975) 465–472.
[43] A.C. Alcala, L.C. Alcala, E.D. Gomez, M.E. Cowan, Growth of certain corals, molluscs and fish in artificial reefs in the Philippines. The reef and man, in: Proceedings of the Fourth International Coral Reef Symposium, 1981.
[44] E. Gomez, Growth of some corals in an artificial reef off Dumaguete, Central Visayas, Philippines, Kalikasan Philippine J. Biol. 11 (1) (1982) 148–157.
[45] E.D. Prince, O.E. Maughan, P. Brouha, Summary and update of the Smith Mountain Lake artificial reef project, in: F.M. D'Itri (Ed.), Artificial Reefs—Marine and Freshwater Applications, Lewis Publishers, Inc., Michigan, 1986.
[46] D.I. Vyshkvartsev, E.B. Lebedev, Experimental reef of used tires in Novgorodskaya bight of Pos'et Bay (Japan Sea), in: L.A. Dushkina (Ed.), Artificial Reefs for Fisheries, USSR, VNIRO, Moskva, 1990.
[47] H.A. Reimers, K. Branden, Algal colonisation of a tyre reef—influence of placement date, Bull. Mar. Sci. 55 (1994) 460–469.
[48] S.M. Ogilvie, Opportunities and Barriers to Scrap Tyre Recycling, AEA Technology, National Environmental Technology Centre (NETCN), Culham, Abingdon, Oxon, UK, 1995.
[49] P. Fauser, J.C. Tjell, H. Mosbaek, K. Pilegaard, Quantification of tire-tread particles using extractable organic zinc as a tracer, Rubber Chem. Technol. 72 (1999) 969–977.
[50] A. Turner, L. Rice, Toxicity of tire wear particle leachate to the marine macroalga, Ulva lactuca, Environ. Pollut. 158 (12) (2010) 3650–3654.
[51] S.G. Abernathy, B.P. Montemayor, J.W. Penders, The Aquatic Toxicity of Scrap Automobile Tires, Aquatic Toxicology Section, Standards Development Branch, Ontario Ministry of Environment and Energy, Toronto, 1996.
[52] R.B. Spies, B.D. Andresen, D.W. Rice, Benzothiazoles in estuarine sediments as indicators of street runoff, Nature 327 (6124) (1987) 697–699.
[53] H. Kumata, H. Takada, N. Ogura, 2-(4-morpholinyl)benzothiazole as an indicator of tire-wear particles and road dust in the urban environment, Mol. Markers Environ. Geochem. ACS 671 (1997) 291–305.
[54] K.J. Collins, A.C. Jensen, A.P.M. Lockwood, A.W.H. Turnpenny, Evaluation of stabilized coal-fired power station waste for artificial reef construction, Bull. Mar. Sci. 55 (2/3) (1994) 1251–1262.
[55] A.C. Jensen, K.J. Collins, A.P.M. Lockwood, J.J. Mallinson, W.H. Turnpenny, Colonization and fishery potential of a coal-ash artificial reef, Poole Bay, United Kingdom, Bull. Mar. Sci. 55 (2/3) (1994) 1263–1276.
[56] K.J. Collins, A.C. Jensen, J.J. Mallinson, S.M. Mudge, V. Roenelle, A. Russell, et al., Environmental impact assessment of a scrap tyre reef, in: 7th International Conference on Artificial Reefs and related Aquatic Habitats (7CARAH), San Remo, Italy 7–11 October 1999, SIBM, Genoa, Italy, 1999.

[57] K.J. Collins, A.C. Jensen, J.J. Mallinson, S.M. Mudge, A. Russel, I.P. Smith, Scrap tyres for marine construction: environmental impact, in: R.K. Dhir, M.C. Limbachiyya, K.A. Paine (Eds.), Recycling and Reuse of Used Tyres, Thomas Telford, London, 2001, pp. 149–162.
[58] K.J. Collins, A.C. Jensen, J.J. Mallinson, V. Roenelle, I.P. Smith, Environmental impact assessment of a scrap tyre artificial reef, ICES J. Mar. Sci. 59 (2002) S243–S249.
[59] K.J. Collins, A.C. Jensen, J.J. Mallinson, S.M. Mudge, A. Russell, I.P. Smith, Scrap tyres for marine construction: environmental impact, in: R.K. Dhir, M.C. Limbachiya, K.A. Paine (Eds.), Recycling and Reuse of Used Tyres Symposium, Thomas Telford, Dundee, Scotland, 2001, pp. 149–162.
[60] M. Taihlo, Heavy Metal Bioaccumulation in Scrap Tyre Artificial Reef Biota, University of Southampton, 2004.
[61] V.L. Shulman, Tyre Recycling After 2000: Status and Options, European Tyre Recycling Association, Paris, 2000.
[62] BSI, PAS 108: Specification for Production of Tyre Bales For Use in Construction, British Standards Institution, London, 2007, p. 57.
[63] D.J. Howell, Environmental Impact Assessment of Tyres in Coastal Defence (M. Sc. dissertation), Southampton, 2003.
[64] N. Fisher, Environmental Assessment of Post Consumer Tyres in Coastal Defence At Pevensey Bay, BSc Oceanography, Southampton, Sussex, UK, 2004.
[65] G. Allen, The Environmental Impacts of Tires in Coastal Defence, BSc Oceanography, Southampton, 2004.
[66] M. Fox, Environmental Impact Assessment of Used Tyres As Coastal Defenses—Pevensey Bay, BSc Oceanography, Southampton, Sussex, 2006.
[67] A. Orbell, An Environmental Impact Assessment of Used Tyres in Coastal Defence at Pevensey Bay, Monitoring and Modelling Leachate Release BSc Oceanography, Southampton, Sussex, UK, 2007.
[68] A. Sinclair, An Investigation Into the Leaching of Zinc From Tyres in a Marine Environment, BSc Oceanography, Southampton, 2008.
[69] D. Sedlak, Three Lessons for the Microplastics Voyage, Environ. Sci. Technol. 51 (14) (2017) 7747–7748.
[70] N.B. Hartmann, T. Hüffer, R.C. Thompson, M. Hassellöv, A. Verschoor, A.E. Daugaard, et al., Are we speaking the same language? recommendations for a definition and categorization framework for plastic debris, Environ. Sci. Technol. 53 (3) (2019) 1039–1047.
[71] C. Bickmore, S. Dutton, Water polltion in motorway runoff, Environ. Pollut. 310 (1981) 106–116.
[72] L. Maltby, A.B.A. Boxall, D.M. Forrow, P. Calow, C.I. Betton, The effects of motorway runoff on fresh-water ecosystems. 2. Identifying major toxicants, Environ. Toxicol. Chem. 14 (6) (1995) 1093–1101.
[73] W. Danneker, M. Au, H. Stechmann, Substance load in rainwater runoff from different streets in Hamburg, Sci. Total. Environ. 93 (1990) 385–392.
[74] M.C. Gromaire-Mertz, S. Garnaud, A. Gonzalez, G. Chebbo, Characterisation of urban runoff pollution in Paris, Water Sci. Technol. 39 (2) (1999) 1–8.
[75] R.S. Hamilton, D.M. Revitt, R.S. Warren, M.J. Duggan, Metal mass balance studies within a small highway dominated catchment, Sci. Total. Environ. 59 (1987) 365–368.
[76] C.N. Hewitt, M.B. Rashed, An integrated budget for selected pollutants for a major rural highway, Sci. Total. Environ. 93 (1990) 375–384.
[77] A.B.A. Boxall, L. Maltby, Characterization and toxicity of sediment contaminated with road runoff, Water Res. 29 (9) (1995) 2043–2050.

13

Civil engineering applications

13.1

Surface modification of crumb rubber by cold plasma for performance enhancement of rubberized asphalt

Serji Amirkhanian[1], Feipeng Xiao[2] and Jin Li[2]

[1]Department of Civil, Environmental and Construction Engineering, The University of Alabama, Tuscaloosa, AL, United States [2]Key Laboratory of Road and Traffic Engineering of Ministry of Education, Tongji University, Shanghai, P.R. China

13.1.1 Introduction

The recycling of solid waste in engineering construction projects has been increasing for many years around the world [1–5]. One of these environmentally friendly methods of recycling is the utilization of crumb rubber (CR)-modified asphalt or rubberized asphalt that has been developed and studied in road engineering field for decades [6–9]. Asphalt binder is a viscoelastic material, while CR is known to possess excellent elastic bulk properties. Therefore the rubberized asphalt is expected to obtain greater elastic recovery performance at high temperatures and stronger resistance to thermal brittle cracking at low temperatures. However, the weak compatibility of CR particles with asphalt matrix causes, in some cases, severe phase separation in rubberized asphalt when mixed at an elevated temperature, namely loss of homogeneity within the composite material [10].

This storage instability issue certainly causes many issues and difficulties in its application. Some practical methods, such as using fine CR particles, adjusting curing process, and employing compatibilizers, have been used in improving the storage stability of rubberized asphalt to some extent. However, they might bring adverse effects to the binder performance in

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00015-6
© 2021 Elsevier Inc. All rights reserved.

some cases [11,12]. From another point of view, it was further found that the interactions between the CR particles and asphalt matrix primarily occurred on the surface of CR particles. Accordingly, a low-cost, high-efficiency, and time-saving surface treatment technology for CR particles is suggested as another potential method for enhancing the storage stability and other properties of the matrix.

Many surface treatment technologies have been studied including chemical and physical treatments. Chemical treatment can generally introduce the expected functional groups and obtain better effect. For example, Kocevski et al. performed surface treatment on CR particles by grafting acrylic acid [13]. The results showed the bonding between CR particles and asphalt matrix was strengthened, which could be attributed to the increasing of surface area and the formation of anhydride. Chen et al. adopted motor oil and zinc stearate to activate the surface of CR particles [14]. This novel treatment was found to improve the workability, failure temperature, and elasticity of rubberized asphalt, due to the improved asphalt–CR adhesion. However, the chemical treatments are generally complicated, time-consuming, and possibly, in some cases, hazardous. Therefore physical treatment has gained popularity in recent years, the primary principle of which included enhancing surface affinity, surface roughness, and so on. In recent years, the technologies utilized in this area included ultraviolet radiation, ultrasonic cleaning, ozone treatment as well as plasma treatment [15–18].

Among these methods, the plasma surface treatment has its own advantages, such as simple operation, energy conservation, and no pollution entering into the environment. Plasma was also known as the fourth state of matter except for solid, gas, and liquid. As shown in Fig. 13.1.1, it is composed of charged particles (electrons and ions) and neutral particles. Applying for surface treatment, plasma has shown that it can improve the surface properties (e. g., surface wettability, surface free energy, and surface roughness) of polymers without altering the bulk properties [19–23]. Several studies and research projects have been conducted in this area. For example, Liao et al. used low-temperature microwave plasma to modify the rubber surface [24]. They discovered the water contact angle of rubber surface decreased from 90 to nearly 30 degrees and the amount of carboxyl and carbonyl greatly increased. As a result, the adhesion of treated rubber to steel became stronger. Moreover, both Lee and Romero– Sanchez proposed the atmospheric pressure plasma torch as a surface treatment for vulcanized styrene–butadiene R2 (SBR2) rubber compound [25,26]. It was

reported that though the SBR2 rubber surface was significantly modified, its adhesion to polyurethane adhesive was only slightly enhanced according to results of T-peel test.

Ortiz–Magan et al. further assessed the effect of low-pressure oxidizing (oxygen and air) and nonoxidizing (nitrogen and argon) gas plasma on synthetic vulcanized styrene–butadiene R1 (SBR1) rubber [27]. The results of this study showed that the acceptable adhesion value of plasma-treated SBR1 rubber could generally be obtained for all plasmas, according to the T-peel test results. Meanwhile, the reduction of water contact angle and the creation of polar functional groups were observed for all plasmas. However, the oxidizing plasmas might produce the ablation of the rubber surface, thus leading to the degradation of mechanical performance.

Cheng and the coworkers also conducted a set of studies on surface modification of crumb waste tire rubber (WTR) by cold plasma and the application of WTR particles on oil-well cement [21,22,28]. After plasma treatment, they found the contact angle remarkably dropped from 122 to 34 degrees, and the oxygen atomic percent soared from 8.11% to 24.83% in the WTR surface. Consequently, the tensile strength of cement modified by plasma increased by 11.03% and the flexural strength increased by 9.65%. However, the authors pointed out that the timeless effect or aging behavior of plasma treatment should not be ignored. Meanwhile, they reported the treatment power and time set as 100 W and 150 s, respectively, were optimal.

In summary, the plasma treatment has been proven in effectively modifying the surface of rubber materials (including the molded rubber and rubber particles) and generally enhancing its adhesion to the matrix (e. g., asphalt binder). However, the application of plasma-treated CR particles in modifying asphalt binder has not been studied in great detail. This work, described in this chapter, is thus aimed to introduce cold plasma, generated in the laboratory setting, to improve the surface affinity or activity of CR particles and to further enhancing the engineering performance of rubberized asphalt. Furthermore, it is noted that the plasma processing parameters, such as discharge power, treatment time, and gas pressure, can be varied to investigate the possible optimal condition. Moreover, the size and content of CR particles generally plays an important role in its interaction with the asphalt matrix. Therefore to achieve the tailored performance enhancement, the main body of this chapter is composed of the following three parts:

1. Investigation on surface characteristics of plasma-treated CR particles with varying discharge power and processing time,

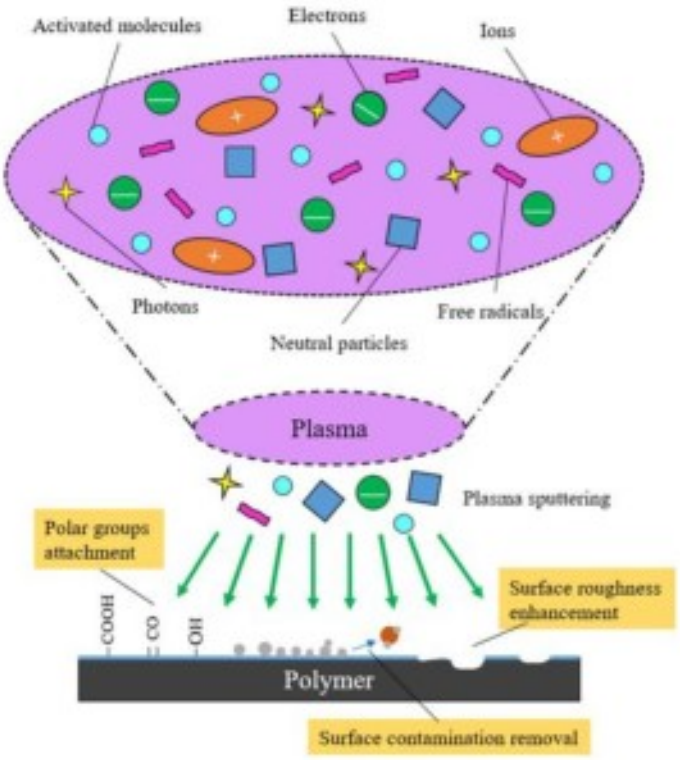


Figure 13.1.1 Composition and primary modification mechanisms of plasma.

including surface lipophilicity, surface hydrophilicity, surface chemistry, and surface morphology.

2. Evaluation of engineering performance of rubberized asphalt with varying CR size, content, and base asphalt source, in terms of rotational viscosity, high-temperature rutting resistance, low-temperature cracking resistance, moderate-temperature fatigue resistance, and storage stability.
3. Discussion on the possible mechanisms behind the performance enhancement of plasma-treated rubberized asphalt, by means of gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR) analysis.

13.1.2 Materials and methods

13.1.2.1 Cold plasma surface treatment

A commercial plasma machine (OPS–OMEGA–DT03) was employed in this study, which was mainly composed of a reaction chamber, a vacuum system, a flow control system, and a

power system. For the cold plasma treatment, its efficiency and uniformity mainly depends on discharge power and processing time. Generally, high discharge power is more likely to bring depolymerization and etching effect, while low discharge power is prone to cause polymerization. On the other hand, the practical processing time ranges from a few seconds to several minutes, depending on the material to be processed. For the rubber materials, the recommended processing time was 3–7 min according to the limited studies. Accordingly, these two parameters were varied in this study to determine the optimal processing parameters. The schematic diagram of the applied cold plasma treatment is shown in Fig. 13.1.2, and the specific processing parameters are presented in Table 13.1.1.

First, 20 g of CR particles were spread evenly on an 18 × 18 cm glass plate. Then, the CR particles were put into the reactor chamber. The vacuum degree was set at 150 sccm by using a roots pump and the dry air was injected into the chamber at a flow rate of 50 sccm afterward. Once the pressure stabilized, the process started under the selected power until the preset exposure duration ran out. Finally, with the pressure in the reaction chamber returning to atmospheric pressure, the plasma-treated CR particles were taken out and used for further testing.

13.1.2.2 Preparation of rubberized asphalt

In this study, the CR particles used for surface modification and preparation of rubberized asphalt were obtained from the ambient mechanical shredding of scrap tires. The −30 mesh (0.6 mm), −40 mesh (0.42 mm), and −80 mesh (0.177 mm) CR particles were used and the CR contents included 10%, 15%, and 20% by weight of base asphalt. Two PG 64-22 base asphalt binders from different crude oil sources were used for preparing rubberized asphalt, referred to as S and E. The basic properties of base asphalts are presented in Table 13.1.2.

To produce the rubberized asphalt, about 400 g base asphalt was first weighed and preheated in a cylindrical metal container at 177°C. Then the given size and content of CR particles were added into the base asphalt and blended at 177°C (1000 rpm) for 60 min.

13.1.2.3 Testing methods

13.1.2.3.1 Surface characterization of crumb rubber

In this study, a video contact angle meter (CAM200) was employed to evaluate the surface hydrophilicity of CR particles.

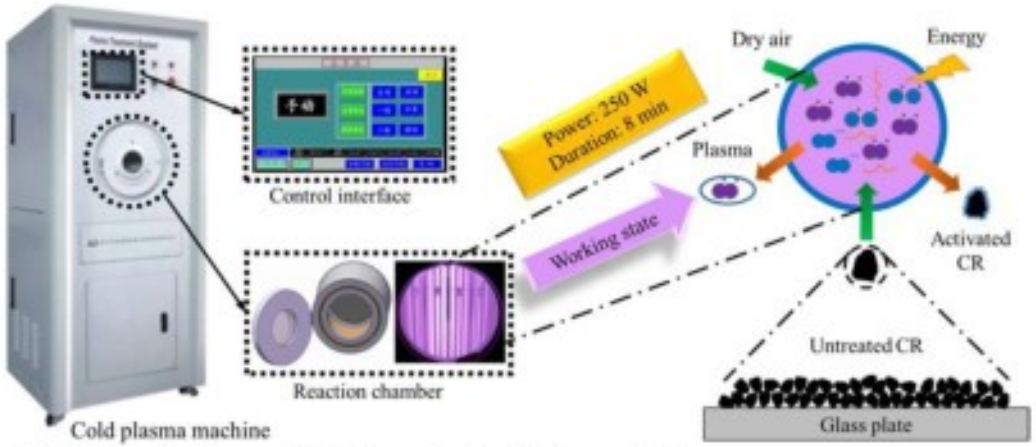


Figure 13.1.2 Schematic diagram of cold plasma treatment. *CR*, crumb rubber.

Table 13.1.1 Processing parameters of cold plasma treatment.

Parameter	Value
Discharge power	250, 150, 50 W
Processing time	8, 5, 2 min
Operation vacuum degree	150 sccm (25 Pa)
Working gas	Dry air
Gas flow rate	50 sccm
Frequency of RF power	13.56 MHz

To facilitate the measurement of water contact angle, the CR particles were pressed into a tablet prior to the test. A drop of distilled water was first dropped onto the surface of tablet CR sample. Then an image was captured when the water droplet stabilized. The angle between the solid–liquid interface and the tangent line of the gas–liquid interface was the contact angle. For each tablet CR sample, three parallel tests were performed.

The developed oil-wetting test was applied to investigate the surface lipophilicity of CR particles. In this test, the fresh cooking oil was applied, which contained a great amount of unsaturated fatty acids, similar to the light oil components of asphalt matrix. Like the water contact angle test, a drop of cooking oil was first dropped onto the surface of the CR tablet. However, as the cooking oil could immerse into the CR tablet, the "oil contact angle" was inapplicable. Hence, the cooking oil-wetting test

Table 13.1.2 Basic properties of the base asphalts.

Aging status	Property	Binder S	Binder E	Specifications
Unaged binder	Rotational viscosity at 135°C, Pa · s	0.522	0.513	AASHTO T 316
	$G^*/\sin\delta$ at 64°C, kPa	1.461	1.412	AASHTO T 315
	Failure temperature, °C	66.8	66.4	AASHTO T 315
RTFO aged residue	$G^*/\sin\delta$ at 64°C, kPa	3.021	2.981	AASHTO T 315
	Failure temperature, °C	67.0	66.2	AASHTO T 315
RTFO + PAV aged residue	$G^*\sin\delta$ at 25°C, kPa	3659	3970	AASHTO T 315
	Stiffness at −12°C, MPa	244.5	229.0	AASHTO T 313
	m-value at −12°C	0.303	0.322	AASHTO T 313

PAV, pressure aging vessel; *RTFO*, rolling thin film oven.

was developed and an index of "oil-wetting time" was introduced in this work. This index was defined as the duration from the cooling oil droplet just encountering the CR tablet to the droplet completely immersing into the CR tablet. Similarly, all tests were repeated three times for each CR sample.

X-ray photoelectron spectroscopy (XPS) was used for the quantitative surface chemical analysis of CR particles. Both the atomic composition and chemical bond changes of CR particle surface before and after cold plasma treatment were measured in this study. The measurements were carried out on CR particles by a commercial XPS spectrometer (ESCALAB 250Xi), which used monochromatic AI K_α (1486.6 eV) X-ray source and was equipped with an electron energy analyzer. The peak positions were based on calibration with respect to the primary XPS region, C1s peak at 284.8 eV. In addition, its software was also employed to analyze the C1s and O1s high-resolution spectra through Gaussian and Lorentzian nonlinear curve fittings and deconvolution.

In this study, the surface morphology of CR particles was observed by a Scanning Electron Microscope (SEM, Nova NanoSEM 450). To obtain high-definition images, all CR samples were sputter-coated with an Au film in vacuum condition prior to imaging. The SEM tests were operated at 3.00 kV, and the 10k× and 30k× SEM images of untreated and plasma-treated CR particle surface were taken.

13.1.2.3.2 Performance evaluation of rubberized asphalt

Rotational viscosity of rubberized asphalt was measured by a Brookfield rotational viscometer at 135°C in accordance with

AASHTO T 316. In this test, a sample of 10 g and a #27 spindle were used. High temperature rheological properties of unaged and rolling thin-film oven (RTFO)-aged rubberized asphalts were tested by a dynamic shear rheometer (DSR) based on AASHTO T 315 and AASHTO M 320, respectively. A 25-mm plate was used in these DSR tests and the working gap between two parallel plates was set as 2 mm. Moreover, a bending beam rheometer (BBR) was used to determine the low-temperature cracking resistance and PG low-temperature grade of rubberized asphalt. The rubberized asphalt in this test had been long-term aged by pressure aging vessel (PAV) in accordance with AASHTO R 28, and the three test temperatures used were −6°C, −12°C, and −18°C.

The rutting resistance of rubberized asphalt was evaluated by multistress creep and recovery (MSCR) test in accordance with AASHTO T 350, which was run on the RTFO-aged residues. In the MSCR test, the 25-mm parallel plate geometry was used with a 2-mm working gap, considering the reasonable gap-to-maximum CR particle size ratio for repeatability. The rubberized asphalt was tested at two altered temperatures (64°C and 76°C) and two stress levels (0.1 and 3.2 kPa). The creep lasted for 1 s at a static loading, followed by a 9 s recovery. In total, 10 creep and recovery cycles were applied at each stress level. The result of strain response was used to determine the following response parameters: percent recoverable strain (R) and nonrecoverable creep compliance (J_{nr}) as well as the percent difference between nonrecoverable creep compliance at two stress levels ($J_{nr,diff}$).

According to AASHTO TP 101-12, the linear amplitude sweep (LAS) test was used to evaluate the fatigue resistance of rubberized asphalts by applying cyclic load with increasing amplitude. It was conducted on DSR with a 2-mm working gap and an 8-mm diameter plate at 25°C. Meanwhile, each sample had been further aged using RTFO and PAV to simulate the long-term aging of asphalt pavement. Based on the viscous-elastic continuum damage (VECD) theory, the test results [i. e., the fatigue life (N_f)] could be calculated as Eq. (13.1.1). The failure of asphalt binder was defined as 35% decrease in its initial modulus.

$$N_f = A_{35}\left(\gamma_{\max}\right)^{-B} \tag{13.1.1}$$

where N_f was the failure life; $\gamma_{\max}$ was the maximum shear strain for the given pavement structure; and A_{35} and B were the parameters that depended on the material characteristics.

The hot (cigar) tube test was used to determine the storage stability of rubberized asphalt according to ASTM D7173. At

first, about 45 g rubberized asphalt binder was poured into an aluminum tube and conditioned in a vertical position at 163°C for 48 h. At the end of the conditioning period, the tube was moved to a refrigerator at −18°C for at least 4 h. Then, the aluminum tube with the rubberized asphalt inside was cut into three sections. Finally, the binders of the top and bottom portions were subjected to further DSR test based on AASHTO T 315. The separation index (SI) is defined as Eq. (13.1.2):

$$\mathrm{SI} = \frac{\left(G^*/\sin\delta\right)_{\max} - \left(G^*/\sin\delta\right)_{avg}}{\left(G^*/\sin\delta\right)_{avg}} \tag{13.1.2}$$

where $\left(G^*/\sin\delta\right)_{\max}$ and $\left(G^*/\sin\delta\right)_{\mathrm{avg}}$ represents the maximum and average value of rutting factor between the bottom and top portion, respectively.

The GPC test was run on each rubberized asphalt to determine its molecular size distribution (MSD). Waters 1515 High-Pressure Liquid Chromatography Pump and Waters 2414 Refractive Index (RI) detector were applied to perform the GPC tests, and tetrahydrofuran (THF) was selected as the mobile phase solvent. To prepare for the test, about 20 mg asphalt sample was first placed in a 10 mL volumetric flask and the sample was dissolved with 10 mL THF for at least 24 h. Then, this sample with a concentration of 2.0 mg/mL was filtered through a 0.45 mm Polytetrafluoroethylene (PTFE) filter and collected in a 0.5 mL centrifugal tube. During the test, the columns were kept at 35°C constantly and the mobile phase was flowing at 1.0 mL/min. Finally, 50 μL of the dissolved sample was injected into the injection module and then a combination of three columns separated the constituents of asphalt sample by molecular size. Furthermore, the analysis of GPC result was accomplished by the method shown in Fig. 13.1.3. The chromatogram profile was

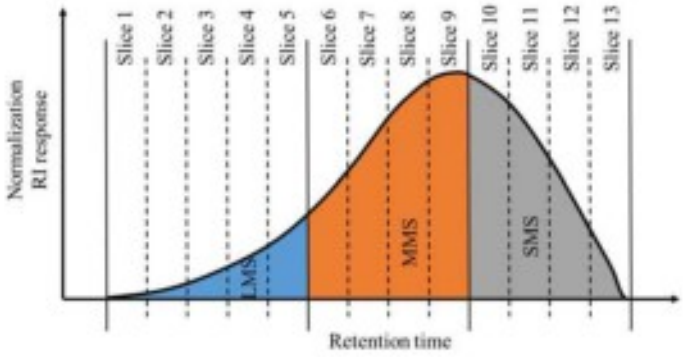


Figure 13.1.3 Analysis method of gel permeation chromatography result. *LMS*, large molecular size; *MMS*, medium molecular size; *SMS*, small molecular size.

first divided into 13 slices of equal width at first, which is the most common method used by many researchers. The large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS) were then quantified as the relative area under the curve when the retention time reached the end of slice 5, 9, and 13, respectively.

The infrared spectra of both CR particles and rubberized asphalts were collected using a Bruker TENSOR FTIR spectrometer equipped with a reflection diamond ATR accessory. Approximately 1 g asphalt sample was first placed on the surface of ATR accessory and was fixed by the steel loader making sure that the asphalt sample homogenously was contacted with the accessory. Then, the spectra of the sample were collected from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, and the peaks of functional groups of interest were further analyzed.

13.1.3 Surface characteristics of plasma-treated crumb rubber

13.1.3.1 Surface hydrophilicity

In this work, the surface hydrophilicity of CR particles was analyzed by the water contact angle, which was a common and direct indicator. The result of water contact angle measurement is shown in Fig. 13.1.4, and the typical images of the water droplet on the untreated and plasma-treated CR tablet surface are also shown in Fig. 13.1.4A inset. As seen in Fig. 13.1.4A, the water contact angle dramatically dropped from 107.7 to 4.7 degrees, with the ever-increasing treatment power and time. It indicated that the cold plasma treatment could significantly improve surface hydrophilicity of CR particles.

As discussed above, the water contact angle of plasma-treated CR particles strongly depended on discharge power and processing time. Based on the variation tendency of contact angle value under varying power and time and considering the coupling effects of these two parameters, a binary exponential function was selected to fit the 10 discrete points obtained from the tests. The fitting surface is shown in Fig. 13.1.4B and the fitting equation with an R-square of 0.8527 is listed as Eq. (13.1.3):

$$WCA = 101.19 \cdot e^{\wedge}(0.000578 \cdot p - 0.001454 \cdot t - 0.001351 \cdot pt) \quad (13.1.3)$$

where WCA represents water contact angle (degrees), p and t, respectively, represent treatment power (W) and time (min).

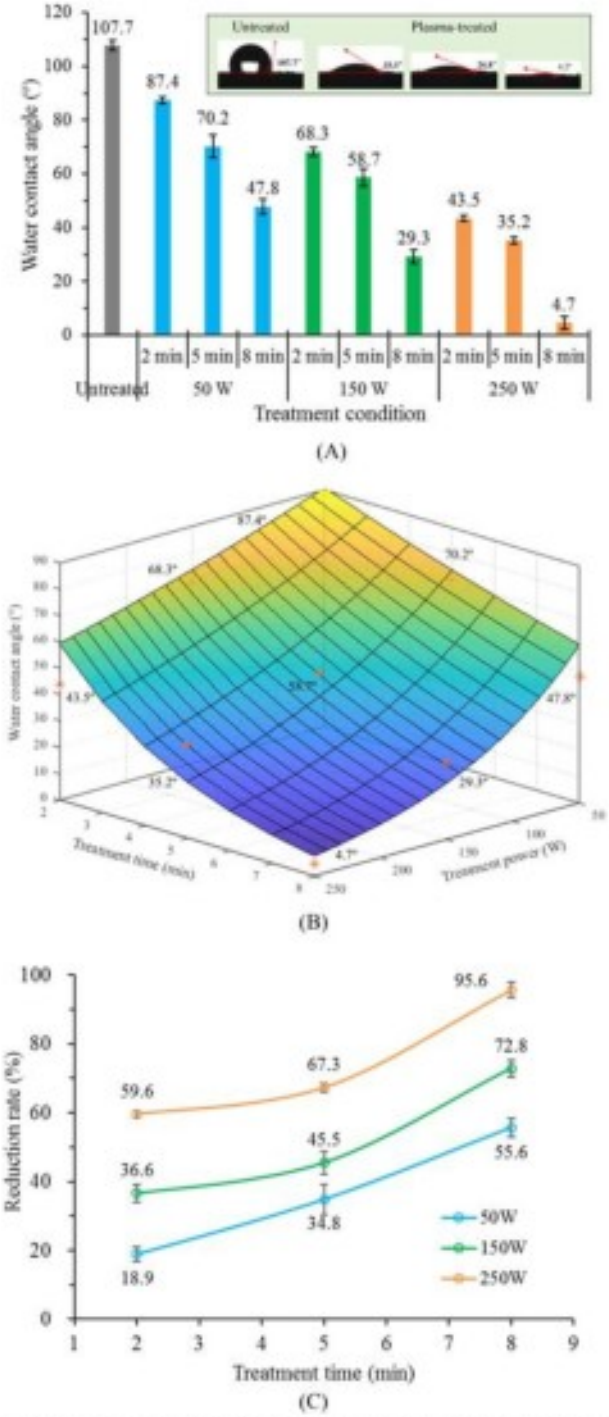


Figure 13.1.4 Surface hydrophilicity analysis of untreated and plasma-treated CR particles. (A) Water contact angle, (B) fitting surface, and (C) reduction rate of water contact angle.

In addition, as shown in Fig. 13.1.4C that the reduction rate of the water contact angle reached the maximum value of 95.6% under the treatment condition of 250 W and 8 min. Therefore in terms of surface hydrophilicity, the combination of 250 W and 8 min was the optimal processing parameter. In addition, this indicated that, by optimizing the processing parameters, the cold plasma treatment employed in this research work could lead to quite effective surface modification for CR particles.

Apparently, the enhanced surface hydrophilicity, indicated by the decrease in water contact angle, could lead to a decrease in the difference of solubility parameters and further improve the compatibility between CR particles and polar asphaltenes components. Furthermore, it was also found that the surface hydrophilicity of CR particles was strongly related to its surface chemistry, which will be further discussed in Section 13.1.3.3.

13.1.3.2 Surface lipophilicity

The result of oil-wetting tests conducted on the plasma-treated CR particles is shown in Fig. 13.1.5. The cold plasma treatment remarkably enhanced the surface lipophilicity of CR particles, with the oil-wetting time dropping from 9.08 to 2.60 s at most. With the processing power increased from 50 to 250 W, the oil-wetting time constantly decreased and might reach nearly 0 s with an even higher power. However, it was also

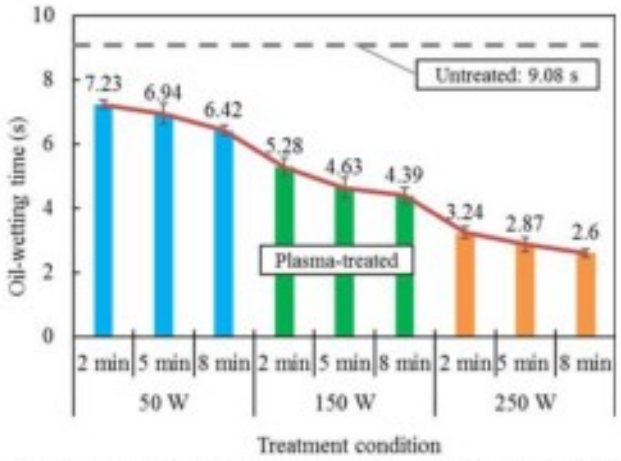


Figure 13.1.5 Surface lipophilicity analysis of untreated and plasma-treated crumb rubber particles.

observed that the oil-wetting time rapidly decreased in the first 2 min of treatment while kept steady with prolonged exposure. Therefore it could be induced that the processing power played a more important role in the improvement of surface lipophilicity than processing time.

In general, when CR particles were being immersed in asphalt matrix at an elevated temperature during the blending process, the aromatic oil diffused into CR particles. This process was attributed to their thermodynamic compatibility, and these light components were prone to aggregate at the asphalt–rubber interface. Then, the interfacial adhesion was strengthened with the light oil components acting as surfactants. Therefore the shortened cooking oil-wetting time, namely the enhanced surface lipophilicity of plasma-treated CR particles, could lead to an even greater level of swelling and interfacial adhesion.

13.1.3.3 Surface chemistry

The surface chemistry of plasma-treated CR particles was evaluated by XPS. The XPS analysis results by means of wide-spectrum scanning are shown in Fig. 13.1.6, and the surface atomic compositions of untreated and various plasma-treated CR particles are summarized in Table 13.1.3. It was noted that the XPS actually detected the zinc, oxygen, nitrogen, carbon, sulfur, and silicon as well as other elements. However, only the carbon, oxygen, and sulfur as well as their related functional groups were selected for further chemical analysis in this work, which dominated the surface atomic composition.

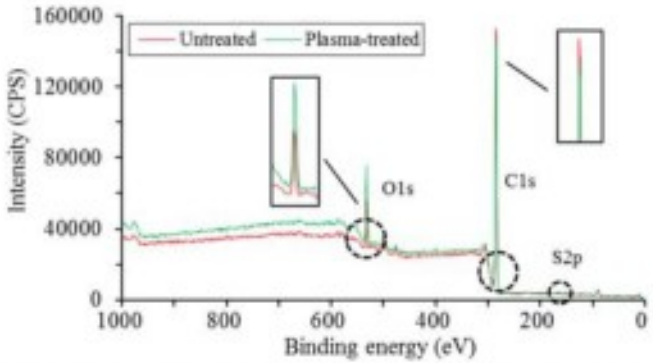


Figure 13.1.6 X-ray photoelectron spectroscopy spectrums of untreated and plasma-treated crumb rubber particles.

Table 13.1.3 Surface atomic composition of untreated and plasma-treated crumb rubber particles.

Plasma treatment condition	Atomic composition (%)			O/C ratio
	C	O	S	
Untreated	92.23	7.12	0.61	0.077
50 W, 2 min	89.35	8.94	0.56	0.100
50 W, 5 min	89.32	9.57	0.55	0.107
50 W, 8 min	88.80	10.39	0.56	0.117
150 W, 2 min	90.17	9.27	0.54	0.103
150 W, 5 min	89.58	9.86	0.53	0.110
150 W, 8 min	87.93	11.51	0.51	0.131
250 W, 2 min	89.57	9.77	0.53	0.112
250 W, 5 min	87.91	11.35	0.49	0.130
250 W, 8 min	86.32	13.15	0.43	0.152

According to the survey scan spectra, the surface of untreated CR particle was mainly composed of 92.23 at.% of carbon, 7.12 at.% of oxygen, and only 0.65 at.% of sulfur. Compared with the untreated, the carbon concentration of the plasma-treated CR particle surface evidently dropped, while the oxygen and sulfur concentrations increased. Furthermore, with the increased treatment power and time, the atomic composition of carbon started constantly declining, while the oxygen composition increased. In addition, Table 13.1.3 also shows that the O/C ratio constantly increased. Meanwhile, a relatively small variation of sulfur concentration was also observed. This might be attributed to the cleavage of S–S or S–C bonds on CR particle surface, subsequently with a breakage of vulcanized network structure and decrease in cross-linkage extent. However, the varying treatment power and time played a limited role in the sulfur concentration, with its composition reduced by 0.07 at. % at most under the power of 250 W and exposure of 8 min.

To determine the mechanism behind these changes in surface chemical composition, the C1s and O1s high-resolution spectra of the untreated and plasma-treated (250 W, 8 min) CR particles were further analyzed, as presented in Fig. 13.1.7 and Fig. 13.1.8, respectively.

As shown in Fig. 13.1.7, the concentration of C–C and/or C–H bonds decreased after plasma treatment, while the concentration of oxygen-containing groups (such as C–O, C=O/

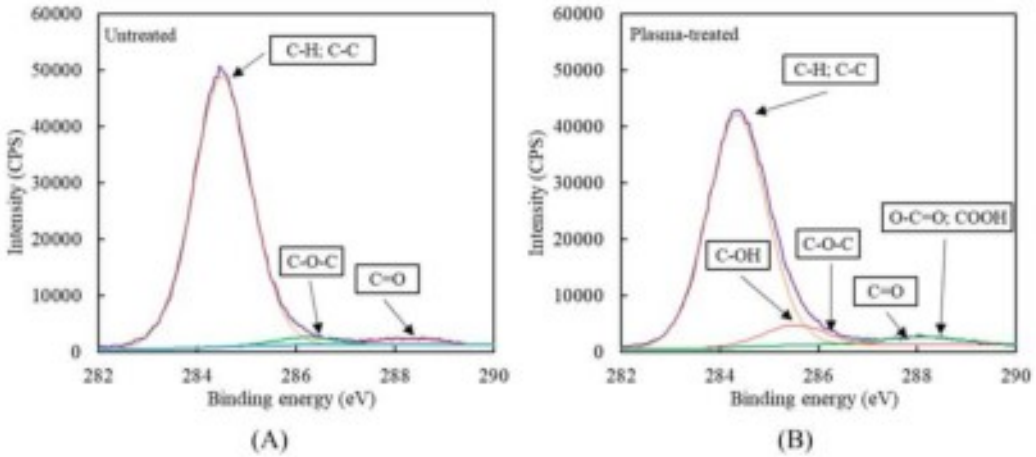


Figure 13.1.7 C1s high-resolution spectra of crumb rubber particles. (A) Untreated, (B) plasma-treated (250 W, 8 min).

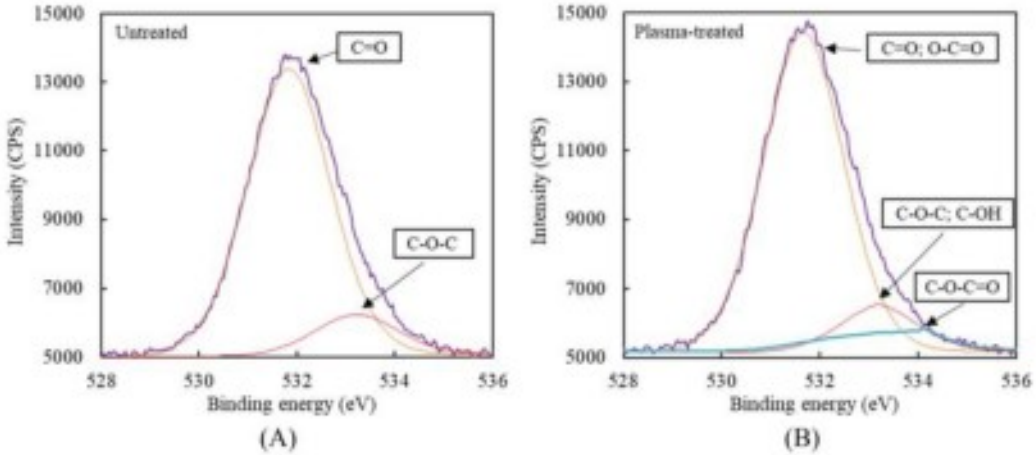


Figure 13.1.8 O1s high-resolution spectra of crumb rubber particles. (A) Untreated, (B) plasma-treated (250 W, 8 min).

O−C−C and O−C═O/COOH) strongly increased. The intensity changes of chemical bonds presented in Fig. 13.1.8 also verified the incorporation of these new polar groups, especially the hydroxyl and carboxyl. Furthermore, the incorporation of oxygen could take place when the CR particles were placing in the air plasma or shortly after the plasma treatment via reactions of the modified surface with ambient air.

Regarding the changes in surface chemical composition in Table 13.1.3, it could be induced: The high-speed plasma particles, including electrons, free radicals, and active species,

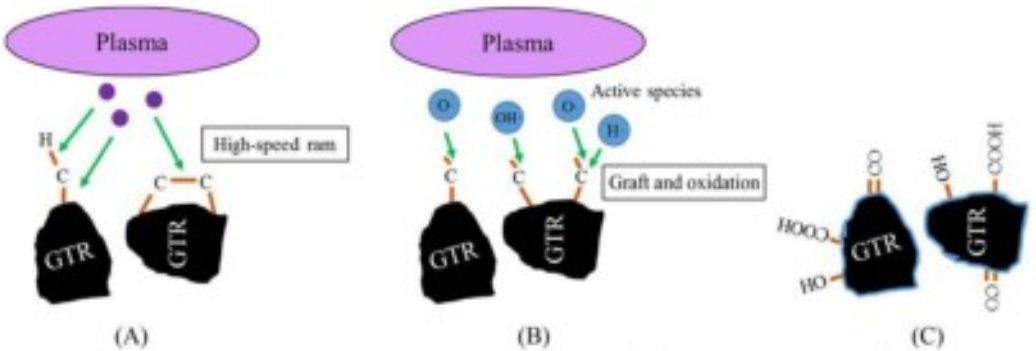


Figure 13.1.9 Mechanisms of oxygen-containing groups attachment. (A) Attack to weak bonds, (B) chains scission, and (C) oxygen-containing polar groups formation.

Table 13.1.4 Bond energy of typical chemical bonds in polymers.

Chemical bond	C–C	C–H	C–N	C–Cl	C–F	C–S	C=C	C=O
Bond energy (eV)	3.4	4.3	2.9	3.4	4.4	2.8	6.1	8.0

attacked the weak chemical bonds (e. g., C–C and C–H) at first during the processing, as shown in Fig. 13.1.9A. In general, the energy required for cold plasma treatment was less than 20 eV, which was higher than the bond energy of most chemical bonds in the polymers (less than 8 eV) presented in Table 13.1.4. Consequently, the chain scission occurred on the CR particle surface and these broken chains then reacted with the oxygen and hydrogen species, as shown in Fig. 13.1.9B. Finally, the new oxygen-containing polar groups were thus formed and detected by XPS, as shown in Fig. 13.1.9C.

13.1.3.4 Surface morphology

In addition to changing surface chemistry, the cold plasma was also expected to have a physical etching effect on CR particle surface that could alter its surface morphology. In this present work, the surface microscopic imaging was applied to reveal the surface roughness changes of plasma-treated CR particles, via a SEM with magnifications of 10k× and 30k×. The representatives of original SEM images with the scale bar inside were presented in Fig. 13.1.10 for qualitative comparison. It was noticed that a considerably rougher and porous surface was

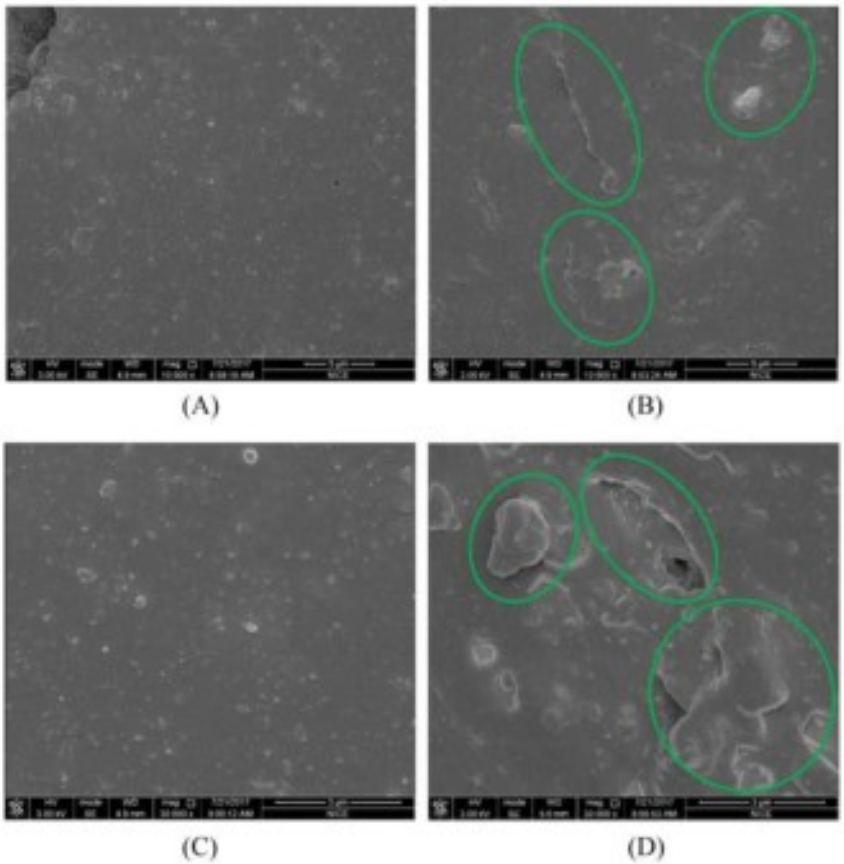


Figure 13.1.10 Original SEM images of crumb rubber particle surface. (A) Untreated (10k×), (B) plasma-treated (10k×), (C) untreated (30k×), and (D) plasma-treated (30k×).

observed after plasma treatment, with the formation of cavitation and stratification on the surface (highlighted with green circles in Fig. 13.1.10B and D). Nevertheless, it should be noted that these images were not taken from the same position of CR particle surface due to the technical limitation, but they could represent the overall condition.

To further quantitatively determine the changes in surface roughness, the original SEM images in Fig. 13.1.10 were grayscale-processed via an image processing software (Image Pro Plus 6.0) in this study. After that, the grayed SEM images for quantitative analysis were presented in Fig. 13.1.11, and there were nearly 62,000 pixels in each image. Regarding a pixel, the higher the gray level, the rougher the area. The surface roughness index of CR particles was thus defined as the sum of the

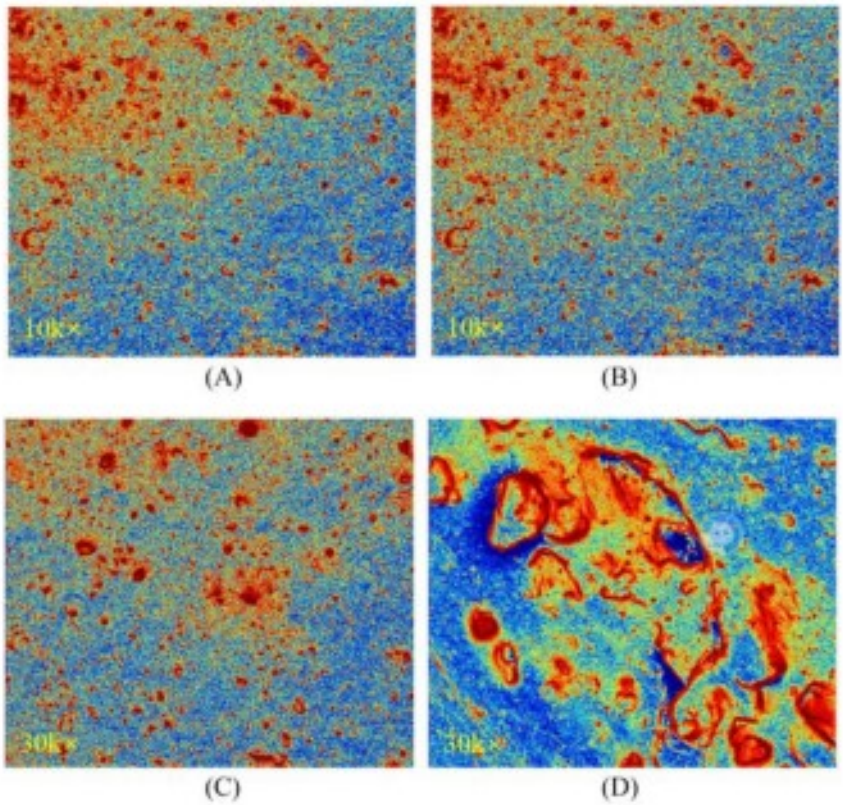


Figure 13.1.11 Grayed SEM images of CR particle surface (corresponding to Fig. 13.1.12). (A) Untreated (10k×), (B) plasma-treated (10k×), (C) untreated (30k×), and (D) plasma-treated (30k×).

grayscale value of each pixel in its grayed SEM image. According to analysis results, the surface roughness of CR particles significantly increased by 23.6% (10k× images) and 33.6% (30k× images) after plasma treatment (250 W, 8 min).

Furthermore, the above surface morphology changes induced by cold plasma treatment could provide a larger surface specific area for interaction and cause a subsequently higher rate of interaction. In addition, the relatively porous surface might format additional mechanical interlocking between CR particles and asphalt matrix, thus improving the physical interfacial adhesion.

In total, the cold plasma remarkably changed the surface lipophilicity, surface hydrophilicity, surface chemistry, and surface morphology of CR particles, which all contributed to the improvement of its surface affinity or activity. Furthermore, the

optimal processing parameters of the applied cold plasma treatment in this work were the discharge power of 250 W and the processing time of 8 min, in terms of the extent of the surface properties improvement.

13.1.4 Engineering performance of plasma-treated rubberized asphalt

13.1.4.1 Rotational viscosity

The rotational viscosity of asphalt binder was generally used to evaluate its flow characteristic and to ensure that it can be pumped and handled at the hot mixing plants as well as in providing a guide for determining the mixing and compacting

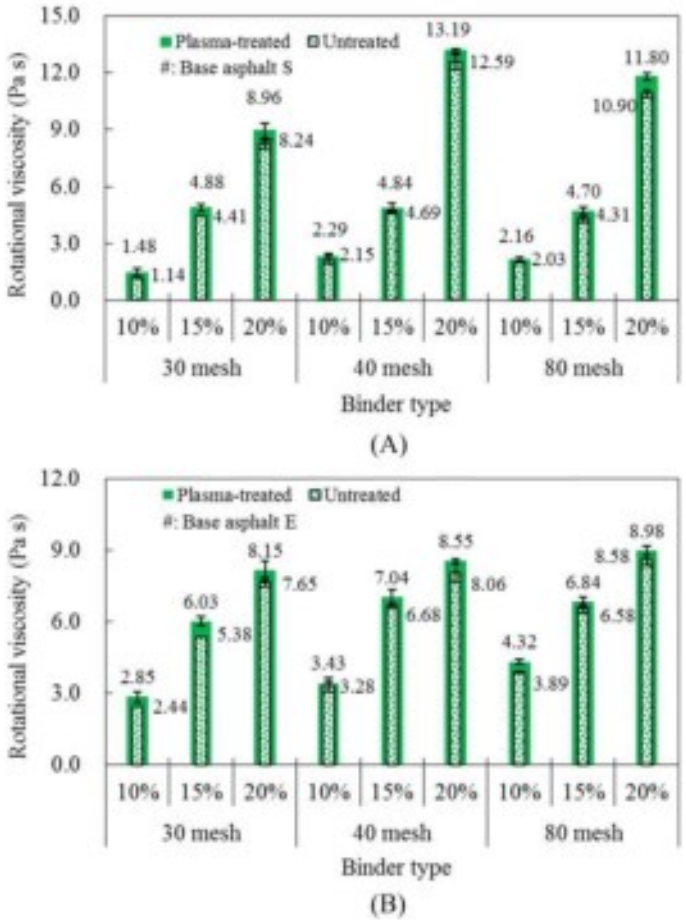


Figure 13.1.12 Rotational viscosity of rubberized binders. (A) Base asphalt S, (B) base asphalt E

temperatures of asphalt mixtures. The rotational viscosity (at 135°C) of various rubberized asphalt in this study are presented in Fig. 13.1.12. It was obvious that the rotational viscosity values of plasma-treated rubberized asphalts were slightly higher than that of the untreated. In addition, the increased dosage of plasma-treated CR particles constantly improved the viscosity as expected. However, the effect of CR size on rotational viscosity was dependent on the base asphalt source.

13.1.4.2 High-temperature rutting resistance

One of the major advantages of the MSCR test is the ability to provide a remarkable amount of information about the creep compliance, elastic recovery, and stress sensitivity, which could not be captured by the rutting factor ($G^*/\sin\delta$). In this study, the average values of J_{nr}, R, and $J_{nr,diff}$ at different temperatures

Table 13.1.5 Response parameters of base asphalt and rubberized asphalts at 64°C (base asphalt E).

Binder type	Crumb rubber size (mesh)	Crumb rubber content (%)	0.1 kPa		3.2 kPa		$J_{nr,diff}$ (%)	$J_{nr,slope}$ (%)	Grade
			J_{nr} (kPa^{-1})	R (%)	J_{nr} (kPa^{-1})	R (%)			
Base asphalt			2.0060	3.1	2.2821	0.3	13.8	8.9	S
Untreated	30	10%	0.3725	49.7	0.5698	30.4	50.3	6.4	V
		15%	0.0764	77.3	0.2810	39.4	267.8	6.6	E
		20%	0.0291	91.2	0.1534	60.8	426.5	4.0	E
	40	10%	0.5263	47.3	0.8326	24.3	58.2	9.9	V
		15%	0.2785	59.8	0.4484	36.8	75.4	5.5	E
		20%	0.1276	77.1	0.3294	48.7	158.1	6.5	E
	80	10%	0.6957	39.7	1.0660	16.9	51.9	11.9	H
		15%	0.3913	47.6	0.6334	24.2	61.9	7.8	V
		20%	0.1342	76.8	0.3998	40.7	194.3	8.6	E
Plasma-treated	30	10%	0.2681	57.3	0.4862	31.8	81.4	7.0	E
		15%	0.0698	81.1	0.1754	51.5	151.4	3.4	E
		20%	0.0001	99.9	0.0995	67.7	1106.7	3.2	E
	40	10%	0.4816	50.0	0.7935	25.6	64.8	10.1	V
		15%	0.2070	59.1	0.3685	36.7	78.0	5.2	E
		20%	0.0916	83.5	0.3170	50.6	246.0	7.3	E
	80	10%	0.6216	42.0	0.9444	19.8	53.2	10.4	V
		15%	0.3121	51.0	0.5158	27.3	65.3	6.6	V
		20%	0.1168	78.5	0.3437	44.8	197.9	7.3	E

E, extremely heavy traffic; *H*, heavy traffic; *S*, standard traffic; *V*, very heavy traffic.

Table 13.1.6 Response parameters of base asphalt and rubberized asphalts at 76°C (base asphalt E).

Binder type	Crumb rubber size (mesh)	Crumb rubber content (%)	0.1 kPa		3.2 kPa		$J_{nr,diff}$ (%)	$J_{nr,slope}$ (%)	Grade
			J_{nr} (kPa^{-1})	R (%)	J_{nr} (kPa^{-1})	R (%)			
Base asphalt			10.720	0.3	11.691	0.1	9.0	31.3	/
Untreated	30	10%	1.4981	43.3	3.2772	6.2	118.7	57.4	S
		15%	0.3805	73.3	2.1012	8.4	452.0	55.5	S
		20%	0.1854	81.3	1.0651	23.5	474.2	28.4	H
	40	10%	2.0620	42.1	4.3111	5.2	109.0	72.6	S
		15%	1.3620	48.6	3.1112	8.7	128.5	56.4	S
		20%	0.6004	65.0	1.9191	15.7	219.7	42.5	H
	80	10%	2.9490	30.3	5.2361	2.7	77.2	73.8	/
		15%	1.7080	39.5	3.6270	4.4	112.4	61.9	S
		20%	0.6405	64.7	2.2041	10.9	244.0	50.4	S
Plasma-treated	30	10%	1.2510	44.7	2.8861	7.0	130.7	52.7	S
		15%	0.2379	77.8	1.3003	15.5	446.5	34.3	H
		20%	0.0225	96.7	0.7113	30.4	3063.6	22.2	V
	40	10%	2.0410	41.4	4.2533	5.2	108.4	71.4	S
		15%	0.9066	52.6	2.4211	8.7	167.0	48.9	S
		20%	0.3947	75.6	1.8582	16.4	370.6	47.2	H
	80	10%	2.6666	31.5	4.7232	3.7	77.5	66.3	/
		15%	1.3010	45.3	3.0951	5.0	138.0	57.9	S
		20%	0.5199	68.8	1.9600	13.0	277.0	46.5	H

E, extremely heavy traffic; *H*, heavy traffic; *S*, standard traffic; *V*, very heavy traffic; */*, failure under standard traffic loading.

(64°C and 76°C) and stress levels (0.1 and 3.2 kPa) were measured to evaluate the rutting resistance of rubberized asphalts after cold plasma treatment, as presented in Tables 13.1.5 and 13.1.6. In addition, the performance grade of each binder determined by the J_{nr} value at 3.2 kPa is also presented, in accordance with AASHTO M 332.

First of all, the increase in test temperature and stress level resulted in a continuous decrease in rutting resistance of all binders, based on the variation of J_{nr} and R values presented in Tables 13.1.5 and 13.1.6. Compared to the base binder, rubberized binders showed excellent rutting performance as expected with quite higher R values and lower J_{nr} values. It is also worth mentioning that the R value of PG 64-22 base binder was nearly equal to 0 when subjected to test temperature of 64°C, indicating the binder could be seen as a purely viscous fluid without ability to resist stress at its high PG temperature.

Parameter R directly measured the percent of elastic response in total strain response, including the instantaneous and delayed elastic response. With the incremental content and size of CR particles, increase in the R value of rubberized binders could be observed at different test temperatures and stress levels. It thus indicated the most desirable resistance to permanent deformation of rubberized binders could be obtained from the largest size and the highest content of CR particles in this research work. Furthermore, the highest recovery could even reach around 100% for several binders under specific conditions, which highlights the effect of CR particles on elasticity enhancement of binder. This could be attributed to the interlocked network formed in the binder, which made the rubberized binders capable of bearing higher stress level and service temperature. Likewise, as another indicator of the resistance to permanent deformation under repeated loading, the variation of J_{nr} value regarding different test conditions and binder formulations further verified the findings above. Additionally, the performance grade determined by J_{nr} value at 3.2 kPa reported that most rubberized binders in this study could be served under extremely heavy traffic conditions at 64°C (PG 64E), while were only capable for standard traffic levels at 76°C (PG 76S). Such reduction in grade with the increase in temperature could be seen for all binders.

Furthermore, the effect of cold plasma treatment on the creep and recovery response of rubberized binder should also be highlighted. Regardless of CR size and content as well as the applied test temperature and stress level, the plasma-treated rubberized binders generally had higher R value and lower J_{nr} value than the untreated. It demonstrated the plasma treatment on CR particles consequently strengthened the resistance of rubberized binder to nonrecoverable deformation. It could be attributed to the strengthened interfacial adhesion between the base binder and plasma-treated CR particles, with the surface physical roughness and chemical affinity of CR particles significantly improved.

Though the findings above reported a considerable potential of rubberized binders in antirutting, the stress sensitivity evaluated by $J_{nr,diff}$ value was less than satisfactory according to the AASHTO specification. In this regard, the AASHTO M 322 recommends that this value should be no more than 75% to ensure the binder could deal with the unusually high temperature and unexpected heavy loading. As shown in Tables 13.1.5 and 13.1.6, the base binder was found far away from being sensitive to stress at any temperature in this respect. It was found

that the $J_{nr,diff}$ values were much higher than the threshold value of 75% for all rubberized binders at 76°C and a few at 64°C. Nevertheless, other studies have reported that the $J_{nr,diff}$ proposed in AASHTO specification actually lacked universality to evaluate the stress sensitivity of highly modified binders. Accordingly, an alternative parameter $J_{nr,slope}$ defined as the percent change of J_{nr} value with an increment in stress level was further proposed. Similar to parameter $J_{nr,diff}$, the lower value of parameter $J_{nr,slope}$, the less sensitive the binder will be to stress level. As shown in Tables 13.1.5 and 13.1.6, the $J_{nr,slope}$ value of each rubberized binder at 64°C was remarkably lower than that at 76°C. It is hypothesized that the rubberized binder is a kind of multiple-phase material composed by the binder phase and the CR particle phase. At the relatively low temperature (64°C in this study), the interfacial adhesion strength between two phases might be strong enough to transfer the loading from binder to CR particles when subjected to different stress level. However, the bonding strength would deteriorate with the increase in temperature, as the binder phase becomes softer and more flowable. Accordingly, the CR-binder bonding might fail in transferring the loading, sharply weakening the rutting resistance at high stress level. Meanwhile, the $J_{nr,slope}$ value roughly decreased with the increasing CR content and size, which was exactly contrary to the variation of $J_{nr,diff}$ value. Furthermore, the plasma-treated binders were found to be less sensitive to the varying stress and temperature than the untreated, with relatively low $J_{nr,slope}$ values. This could be attributed to the enhanced rubber-binder bonding after cold plasma treatment, which consequently brought extra bridge effect to unite the both phase and benefited the loading transfer. In addition, the difference in the J_{nr} results at two stress levels also indicated a remarkable degree of nonlinear behavior of rubberized binders in MSCR test, which would be an origin of nonlinear modification of rheological modeling described in the subsequent sections.

13.1.4.3 Low-temperature cracking resistance

This study employed BBR to measure the deformation of asphalt beam as a function of loading time, thus stiffness and m-value could be calculated at different temperatures (−6°C, −12°C, and −18°C). However, it was difficult to evaluate low temperature cracking resistance by simply comparing the value of stiffness (S) and m-value (m). Therefore the factor λ ($\lambda = m/S$), combining the above two parameters, was adopted.

The binder with higher value of λ performed better at low temperature. The results are presented in Table 13.1.7.

As shown in Table 13.1.7, the λ values of rubberized binders with 30 mesh and 40 mesh generally fell after cold plasma treatment while most binders with 80 mesh increased. It seemed that cold plasma treatment only enhanced the low-temperature cracking resistance of 80-mesh rubberized asphalts while weakened the performance of 30-mesh and 40-mesh rubberized asphalts. However, with the certain combinations of CR content and size, the cold plasma treatment could either increase or reduce the λ value at different test temperatures. In addition, it was easily found that the parameter λ had a linear positive correlation with the CR content at a low temperature. This could explain that CR could improve the toughness of asphalt. Moreover, this correlation depended on the base binder source and cold plasma treatment. As the CR content increased, the λ value of rubberized binders produced by binder E rose more sharply than binder S, and those treated binders tended to increase with a larger gradient than those untreated ones.

However, considering the various variables and their variability, whether the cold plasma treatment had a positive or negative effect on low-temperature performance of rubberized binder could not simply be determined through the λ factor. Therefore further discussion would be presented by calculated the PG low-temperature grade for each binder.

To prevent the low-temperature cracking, the creep stiffness of asphalt binder has set to have a maximum limit of 300 MPa and minimum m-value of 0.3 at 60 s of loading time in AASHTO specification. Based on the threshold values, the critical low temperatures for each rubberized asphalt under study were determined and presented in Table 13.1.8. As shown in the last column of Table 13.1.8, the cold plasma treatment could either increase or maintain the critical low temperature within low percent change. Therefore it was reasonable to conclude that the cold plasma treatment had no significant impact on the low-temperature cracking resistance of rubberized asphalt.

This finding could be explained by analyzing the anticracking mechanism of rubberized asphalt. When the environmental temperature drops, the asphalt binder loses its elasticity generally due to its high brittle point. Then, the thermal microcracks will be generated from the surface under the thermal stress and propagate to the bottom gradually. Meanwhile, the CR particle mixed in the binder is still in a high-elastic state, so it works as a barricade to prevent the microcracks from expansion. Therefore it could be concluded that the CR particles improved

Table 13.1.7 Stiffness (*S*), m-value (*m*), and λ values of rubberized asphalts.

Binder type	Crumb rubber size (mesh)	Crumb rubber content (%)	−6°C			−12°C			−18°C		
			S	m	$\lambda/10^{-3}$	S	m	$\lambda/10^{-3}$	S	m	$\lambda/10^{-3}$
Untreated S	30	10%	76	0.336	4.42	151	0.272	1.80	298	0.209	0.70
		15%	51	0.356	6.95	101	0.294	2.91	195	0.240	1.23
		20%	48	0.364	7.58	97	0.305	3.14	198	0.255	1.29
	40	10%	68	0.366	5.38	139	0.299	2.16	275	0.244	0.89
		15%	50	0.388	7.82	99	0.323	3.25	199	0.260	1.31
		20%	45	0.391	8.60	84	0.338	4.04	176	0.269	1.53
	80	10%	80	0.368	4.60	158	0.299	1.89	312	0.232	0.74
		15%	57	0.390	6.89	117	0.320	2.74	235	0.253	1.08
		20%	50	0.400	8.00	102	0.335	3.28	209	0.265	1.27
Plasma-treated S	30	10%	88	0.310	3.52	175	0.265	1.51	348	0.205	0.59
		15%	61	0.331	5.46	116	0.288	2.48	227	0.225	0.99
		20%	59	0.355	6.02	112	0.300	2.68	220	0.238	1.08
	40	10%	82	0.369	4.48	171	0.300	1.76	334	0.238	0.71
		15%	47	0.377	8.11	86	0.323	3.74	174	0.257	1.48
		20%	42	0.414	9.78	77	0.366	4.77	175	0.294	1.68
	80	10%	78	0.376	4.82	153	0.321	2.10	298	0.215	0.72
		15%	53	0.394	7.41	110	0.339	3.08	181	0.219	1.21
		20%	45	0.399	8.87	86	0.352	4.09	168	0.231	1.38
Untreated E	30	10%	89	0.354	3.99	152	0.305	2.01	331	0.231	0.70
		15%	66	0.371	5.66	146	0.295	2.02	327	0.229	0.70
		20%	49	0.392	8.08	93	0.347	3.74	213	0.251	1.18
	40	10%	66	0.395	5.97	129	0.322	2.49	320	0.243	0.76
		15%	49	0.416	8.51	112	0.336	3.00	235	0.267	1.14
		20%	42	0.419	9.99	82	0.350	4.29	195	0.284	1.46
	80	10%	74	0.395	5.35	145	0.316	2.18	344	0.234	0.68
		15%	55	0.417	7.64	122	0.332	2.72	261	0.265	1.02
		20%	44	0.423	9.71	88	0.364	4.15	226	0.285	1.26
Plasma-treated E	30	10%	105	0.359	3.42	198	0.314	1.59	447	0.221	0.49
		15%	80	0.370	4.63	169	0.295	1.75	218	0.215	0.99
		20%	35	0.397	11.47	70	0.331	4.74	164	0.260	1.59
	40	10%	72	0.387	5.38	143	0.313	2.19	346	0.241	0.70
		15%	49	0.407	8.37	109	0.335	3.07	230	0.269	1.17
		20%	45	0.418	9.27	85	0.368	4.31	225	0.276	1.23
	80	10%	66	0.405	6.10	145	0.326	2.26	293	0.260	0.89
		15%	53	0.414	7.75	118	0.338	2.86	249	0.275	1.10
		20%	42	0.436	10.37	86	0.371	4.31	223	0.290	1.30

Table 13.1.8 Critical low-temperature values of various rubberized asphalts.

Base asphalt source	Crumb rubber size (mesh)	Crumb rubber content (%)	Untreated			Plasma-treated			Percent change (%)
			S-controlled (°C)	m-controlled (°C)	Critical temp (°C)	S-controlled (°C)	m-controlled (°C)	Critical temp (°C)	
S	30	10%	−14.2	−10.2	−10.2	−15.6	−10.0	−10.0	−2.0
		15%	<−24	−11.7	−11.7	−24	−12.4	−12.4	6.0
		20%	<−24	−13.0	−13.0	<−24	−12.8	−12.8	−1.5
	40	10%	−19.5	−12.3	−12.3	−16.8	−12.3	−12.3	0.0
		15%	<−24	−14.2	−14.2	<−24	−15.2	−15.2	7.0
		20%	<−24	−15.2	−15.2	<−24	−17.9	−17.9	17.8
	80	10%	−15.1	−10.9	−10.9	−16.2	−11.1	−11.1	1.8
		15%	−23	−12.0	−12.0	<−24	−12.4	−12.4	3.3
		20%	<−24	−13.7	−13.7	<−24	−14.7	−14.7	7.3
E	30	10%	−17.3	−11.5	−11.5	−13.7	−11.8	−11.8	2.6
		15%	−17.4	−11.8	−11.8	<−24	−11.4	−11.4	−3.4
		20%	<−24	−14.4	−14.4	<−24	−14.4	−14.4	0.0
	40	10%	−18.2	−13.5	−13.5	−17	−13.3	−13.0	−3.7
		15%	−22.9	−15.2	−15.2	<−24	−15.2	−15.2	0.0
		20%	<−24	−17.0	−17.0	<−24	−17.0	−17.0	0.0
	80	10%	−17.1	−13.1	−13.1	−19.1	−14.5	−13.5	3.1
		15%	−20.9	−15.2	−15.2	−21.9	−14.8	−14.8	−2.6
		20%	<−24	−16.6	−16.6	<−24	−17.3	−17.3	4.2

The PG low temperature grade was determined by the temperature which was equal to the critical temperature subtracts 10°C (according to the time–temperature superposition).

the low-temperature performance of asphalt binder, mainly through its elastic behavior rather than surface characteristic. However, as mentioned previously, the cold plasma treatment mainly affected the surface property of CR particles, which limited its effect on the low-temperature performance of rubberized asphalt. As Table 13.1.8 suggested, the low-temperature cracking resistance was also closely related to the properties of base binder, as some studies have indicated that the CR particles could dissolve more easily in a softer binder than a harder binder.

13.1.4.4 Moderate-temperature fatigue resistance

The fatigue factor ($G^* \sin \delta$) did not consider the nonlinear viscoelastic behavior of asphalt binder, its reliability in evaluating the fatigue resistance has been questioned by many researchers. In addition, the fatigue factor does not show a significant correlation with four-point bending beam fatigue test results of asphalt mixture, so it somewhat could not be used for determining the long-term performance of asphalt pavement. Therefore a few studies have been conducted in developing an

Table 13.1.9 Values of parameter A_{35} and B.

Base asphalt source	Crumb rubber size (mesh)	Crumb rubber content (%)	Untreated		Plasma-treated	
			A_{35} ($*10^9$)	B	A_{35} ($*10^9$)	B
S	30	10%	1.107	5.5562	1.652	5.4945
		15%	2.171	5.6839	4.425	5.5855
		20%	3.228	5.6624	4.989	5.5533
	40	10%	1.003	5.5467	1.722	5.6523
		15%	1.668	5.5448	3.778	5.6799
		20%	2.831	5.4837	4.157	5.6055
	80	10%	0.885	5.6989	1.455	6.0210
		15%	1.533	5.6839	2.004	6.0258
		20%	2.495	5.6420	3.153	5.9026
E	30	10%	0.739	5.5606	1.206	5.5581
		15%	1.218	5.5267	1.337	5.5143
		20%	2.620	5.5248	3.901	5.5242
	40	10%	0.583	5.3755	0.668	5.3676
		15%	2.142	5.2862	3.280	5.2782
		20%	3.291	5.2510	4.275	5.2621
	80	10%	0.369	5.2965	0.474	5.3134
		15%	0.714	5.1923	0.775	5.1741
		20%	1.863	5.2803	1.913	5.2787

accurate, effective and time-saving binder fatigue test, which led to the introduction of the LAS test. The LAS test has been developed in order to obtain considerable amount of data in 30 min, and its fair relation to the field fatigue cracking data has been proven. The values of parameters obtained from VECD analysis are listed in Table 13.1.9 and the N_f values for all studied binders are calculated used Eq. (13.1.1). Moreover, the surfaces drawn in Fig. 13.1.13 presented the relationships between fatigue life (N_f), applied shear strain and CR size (or content), and the N_f results in a logarithmic scale.

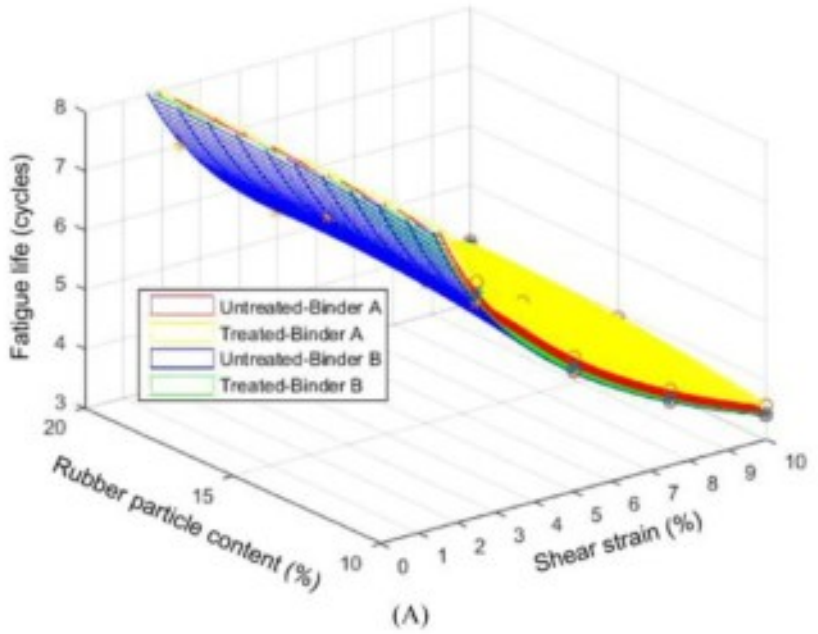
As shown in Table 13.1.9, the rubberized asphalts treated by cold plasma tended to have higher A_{35} values and lower B values compared with the untreated, which revealed greater fatigue resistance. Fig. 13.1.13 could better depict this trend, in which the treated surfaces were located above the untreated. It is also important to note that the rubberized asphalts produced by base binder S obviously performed better in fatigue resistance than those produced by base binder E, which was the result of base binder S has greater fatigue resistance than binder E.

Moreover, it could be concluded that the increasing rubber content resulted in a longer fatigue life. This finding was ascribed to that of a high content rubber (an elastic additive) could better improve the elastic behavior of modified binders, on which fatigue cracking resistance was highly depended.

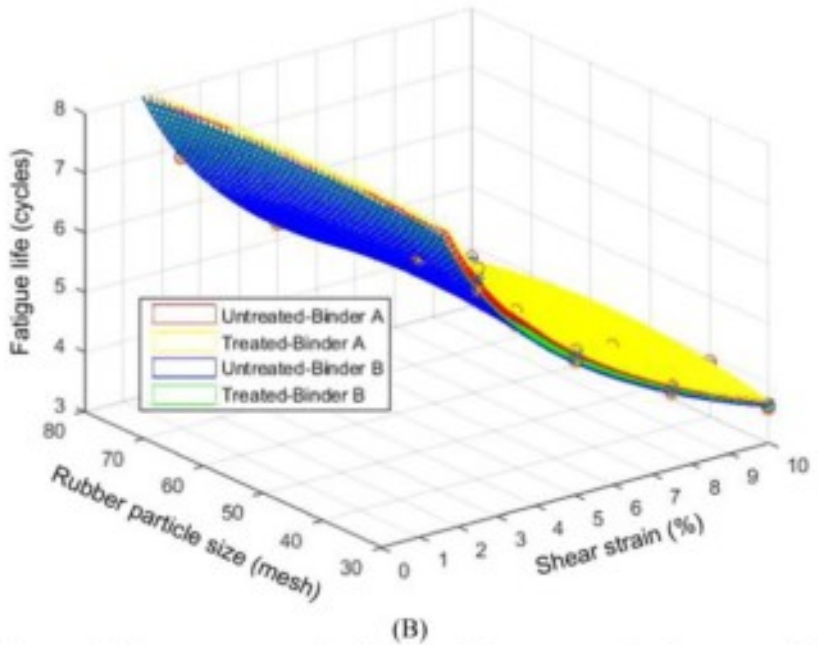
It is also seen that the antifatigue performance increased with a larger CR size. At an intermediate temperature, the rubberized binder could be seen as a combination of a viscoelastic material and elastic particles. When being applied the cyclic loading, a larger particle size was prone to perform better as a whole than several smaller particles with the same weight. This is due to the fact that the adhesive force between rubber particle and matrix was weaker than particle's internal cohesive force.

13.1.4.5 Storage stability

The storage stability has been regarded, by many produces and users, as an indicator of great importance in determining the quality of polymer modified binders, especially the rubberized asphalt. As mentioned previously, the hot tube test was employed in investigating the storage stability of rubberized asphalt after cold plasma treatment in this study. The SI calculated by Eq. (13.1.2) is shown in Fig. 13.1.14.



(A)



(B)

Figure 13.1.13 Linear amplitude sweep test results. (A) Fatigue life versus crumb rubber content, (B) fatigue life versus crumb rubber size.

According to Fig. 13.1.14, the cold plasma was found to effectively improve the storage stability of rubberized asphalt except for those with 20% CR. It indicated the enhanced compatibility between CR particles and asphalt matrix. In addition, the storage stability decreased as the CR particle size increased and the content decreased. With respect to the binders made of 20% CR particles, the high-content CR particles were prone to swell fully during the test period (at 163°C for 48 h) and form a tight semisolid continuous phase, which inhibited the migration of free asphalt to some extent. Therefore whether the CR particles treated by cold plasma or not, the 20% content rubberized asphalt binders showed similar and slight phase separation tendency. Nevertheless, it did not conflict with the compatibility enhancement effect of cold plasma treatment.

With respect to the phase behavior of liquid rubberized asphalt, it could be approximately seen as a suspension system

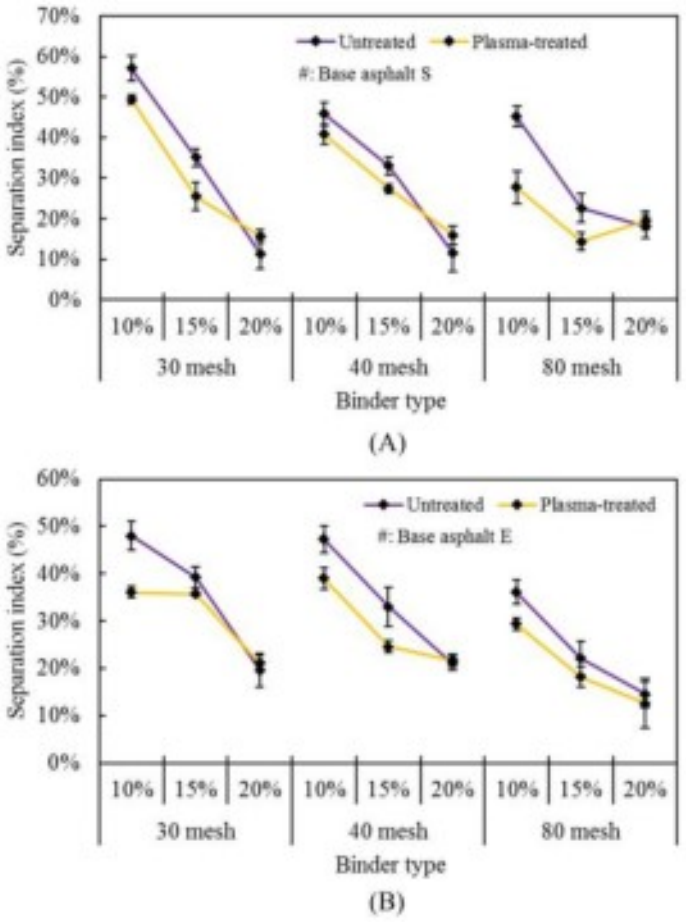


Figure 13.1.14 Separation index of rubberized binders. (A) Base asphalt S, (B) base asphalt E.

at elevated temperature during the static storage period. According to the Stokes' law, the viscous resistance (f) imposed on each CR particle in rubberized asphalt could be calculated as Eq. (13.1.4):

$$\mathrm{f} = 6\pi\eta r v \tag{13.1.4}$$

Therefore as shown in Eq. (13.1.5), the join force coming from buoyancy and friction is balanced by the gravity force of an individual CR particle.

$$\rho_1 \mathrm{g}\frac{4}{3}\pi r^3 = \rho_0 \mathrm{g}\frac{4}{3}\pi r^3 + 6\pi\eta r v \tag{13.1.5}$$

The sedimentation velocity (x) of CR particle could thus be determined when the forces reached a balance, as presented in Eq. (13.1.6):

$$\mathrm{v} = \frac{2g(\rho_1 - \rho_0)r^2}{9\eta} \tag{13.1.6}$$

In the equations above, η represents the viscosity of rubberized asphalt; r is the CR particle size; ρ_1 and ρ_0 are the density of CR particles and asphalt matrix, respectively; and g is the gravitational acceleration.

As shown in Eq. (13.1.6), the higher the viscosity, the lower the sedimentation velocity. The increased rotational viscosity reported in Fig. 13.1.12 thus also revealed the improved storage stability, namely a more compatible CR/asphalt system with a slower creaming rate. In addition, the phase separation reduced with the decreased CR particle size.

13.1.5 Mechanisms behind performance enhancement

13.1.5.1 Gel permeation chromatography analysis

To further figure out the mechanisms behind the performance enhancement of rubberized asphalt after cold plasma treatment, several chemical analyses were conducted to determine the internal changes in rubberized asphalt. Firstly, the GPC tests on base and rubberized asphalts provided both qualitative and quantitative insights as to how the fractions of binder changes during the asphalt−CR interaction and what changes in MSD further occurred after the cold plasma treatment on the CR particles. The typical chromatogram profiles of base and

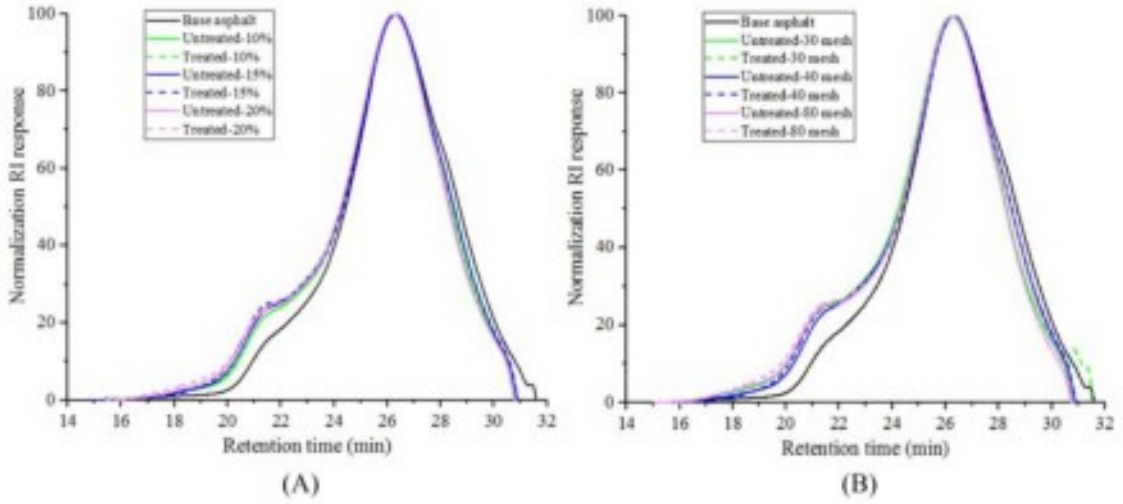


Figure 13.1.15 Representative chromatogram profiles of base and rubberized asphalt binders. (A) Varying content with a constant size of −40 mesh, (B) varying size with a constant content of 15%.

rubberized asphalts (including the untreated and plasma-treated) are presented in Fig. 13.1.15.

As shown, the profiles of base asphalt shifted to the left, which indicated a change in the MSD resulting from the addition of CR particles. This was attributed to the fact that the lower molecular weight solvents in asphalt binder diffused more readily into the CR modifier. At a constant size of CR particles, the binder with higher CR content obviously absorbed lighter components of the binder, based on the shift of profiles in Fig. 13.1.15A. As shown in Fig. 13.1.15B, the smaller CR particles also tended to interact with asphalt matrix more actively, due to the larger specific surface area. In addition, comparing the untreated binder to the plasma-treated, it could be found that the profiles slightly shifted to the left, suggesting that the cold plasma treatment further promoted the asphalt−CR interactions.

To quantitatively analyze the changes in MSD of the binder after CR modification and cold plasma treatment, the three fractions of each binder (i. e., LMS, MMS, and SMS) were calculated according to the corresponding profile, as shown in Fig. 13.1.16. With respect to the effect of cold plasma on the MSD of the binder, the rubberized asphalt generally had higher LMS values while the SMS values were lower than the base asphalt. It has been suggested that a reduction in the percentage of lighter fractions retained in the binder after removing the CR modifier. The SMS was considered to have the lowest

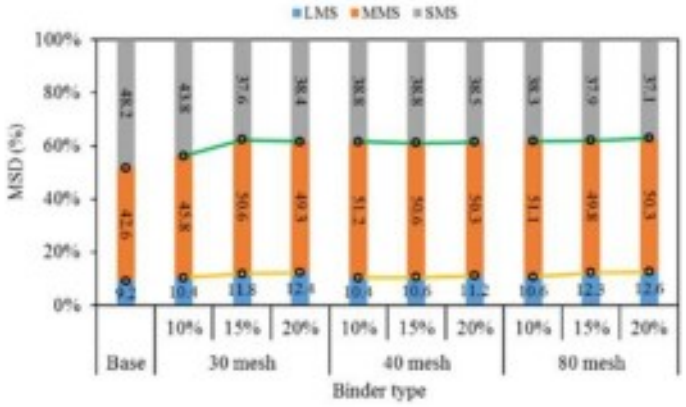


Figure 13.1.16 MSD of base and rubberized asphalt. *MSD*, molecular size distribution.

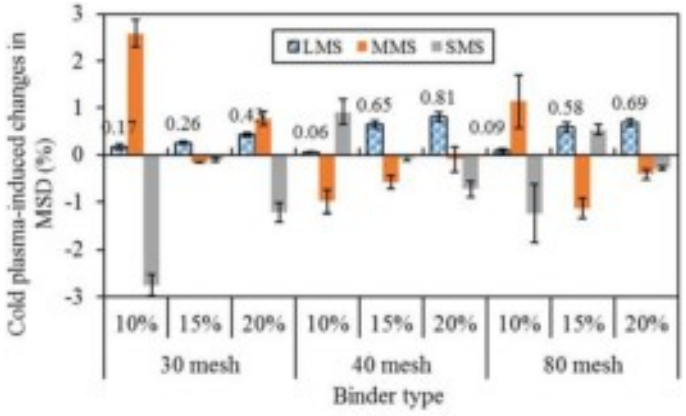


Figure 13.1.17 Cold plasma-induced changes in MSD of rubberized asphalt. *LMS*, large molecular size; *MMS*, medium molecular size; *MSD*, molecular size distribution; *SMS*, small molecular size.

molecular weight, thus rapidly diffusing into the CR particles and consequently resulting in a relative increase in LMS values. It could also be easily concluded that the LMS increased with the increased content and reduction in CR size of CR modifier. On the contrary, the SMS fraction decreased under the same condition. In addition, there was a slight correlation between changes in MMS and varying CR size and content.

Furthermore, the changes in the MSD of rubberized asphalt induced by cold plasma treatment are presented in Fig. 13.1.17. The left shift of chromatogram profiled in Fig. 13.1.15 after cold plasma treatment was reinforced by the increase in LMS in Fig. 13.1.17. The results indicated that the cold plasma treatment promoted the interactions (mainly swelling) between asphalt matrix and CR particles with the plasma-treated surface. Furthermore, the cold plasma-induced changes in LMS generally

increased with the increase in CR content and reduction in the size, while no regular tendency was found in MMS and SMS.

13.1.5.2 Fourier transform infrared spectroscopy analysis

To identify the changes in the molecular structure of an asphalt binder after CR modification and cold plasma treatment, the infrared spectra of both CR modifier and asphalt binders (including base asphalt and rubberized asphalts) were collected and are shown in Fig. 13.1.18.

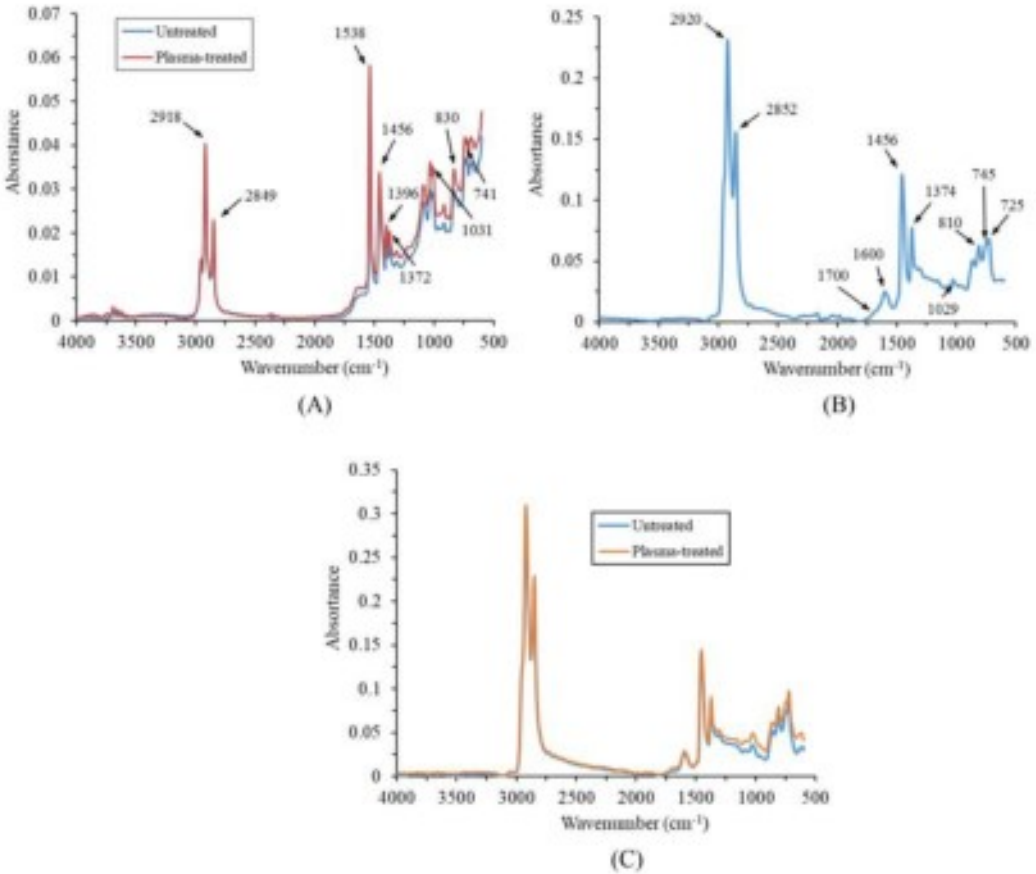


Figure 13.1.18 Fourier transform infrared spectroscopy spectra of (A) crumb rubber modifier, (B) base asphalt, and (C) rubberized asphalt binders.

Firstly, the infrared spectra of untreated and plasma-treated CR particles are shown in Fig. 13.1.18(A). The main functional groups in CR modifier were introduced in detail as follows:

2918 cm^{-1}: asymmetric C−H stretching vibrations of methylene group;

2849 cm^{-1}: symmetric C−H stretching vibrations of methylene group;

1538 cm^{-1}: C═C stretching of carbonyl group;

1456 cm^{-1}: $-CH_2-$ scissor vibration of methylene group;

1396 cm^{-1}:═C−H in-plane bending vibration;

1372 cm^{-1}: C−H deformation of methyl group;

1031 cm^{-1}: S═O stretching;

830 cm^{-1}:═C−H out-plane bending vibration;

741 cm^{-1}: C−Cl stretching of organic choline.

No change in peak position was found after cold plasma surface treatment, only the peak intensity slightly changed. This might be attributed to only physical changes occurred in the plasma-treated surface of CR particles or the changes in surface chemistry of CR could not be detected by the FTIR. Secondly, the FTIR spectra of base asphalt is shown in Fig. 13.1.18B, and its primary functional groups were explained as follows:

2920 cm^{-1}: asymmetric C−H stretching vibrations of methylene group;

2852 cm^{-1}: symmetric C−H stretching vibrations of methylene group;

1700 cm^{-1}: C═O stretching of carbonyl group;

1600 cm^{-1}: C═C stretching of carbonyl group;

1456 cm^{-1}: $-CH_2-$ scissor vibration of methylene group;

1374 cm^{-1}: C−H deformation of methyl group;

1029 cm^{-1}: S═O stretching;

810 cm^{-1}:═C−H out-of-plane deformation of vinyl group;

745 cm^{-1}: C−Cl stretching of organic choline;

725 cm^{-1}: C−C rocking vibration of alkane groups.

However, when comparing the infrared spectra of the rubberized asphalt (Fig. 13.1.18C) with base asphalt, no new peak appeared and only changes in peak intensity were observed. This finding meant no new bond emerged in the molecular structure of base asphalt after CR modification. Although CR modifier consisted of several different functional groups in the molecular chain of vulcanized rubber (e. g., SBR), most of them were also consumed when blending with asphalt binder. In addition, the cold plasma-induced changes in chemical properties of binder could also not be determined by the FTIR spectra. Therefore it was

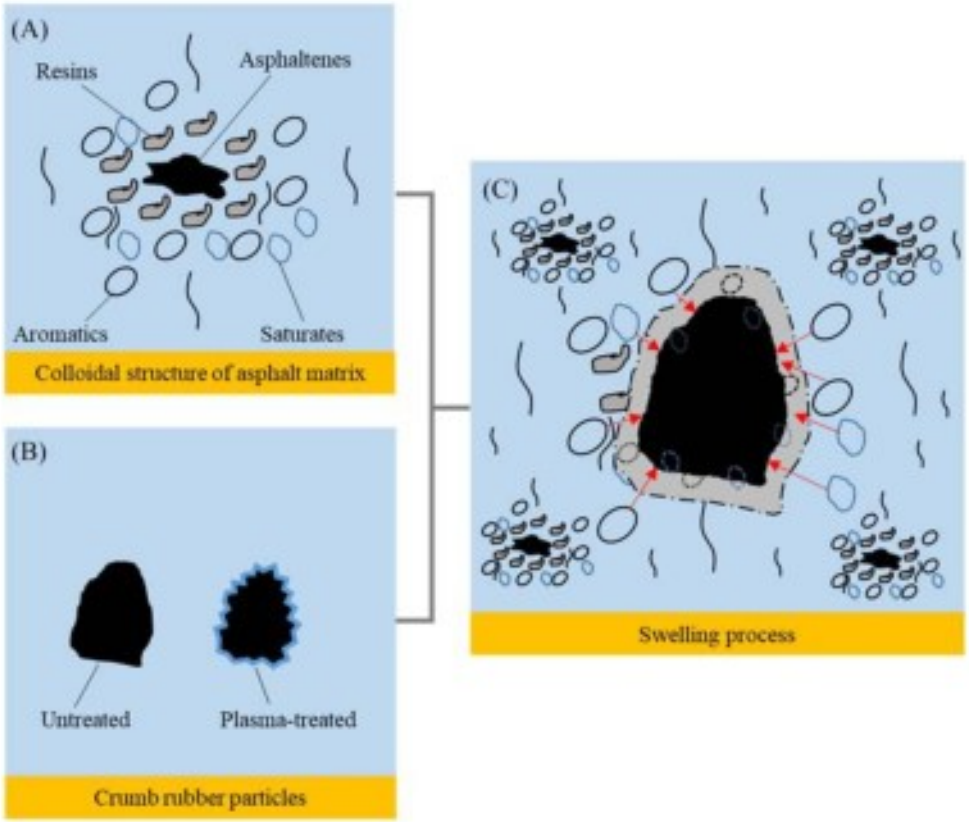


Figure 13.1.19 Swelling process between crumb rubber particles and asphalt matrix. (A) Colloidal structure of asphalt matrix, (B) crumb rubber particles, and (C) swelling process.

concluded that the FTIR test failed to detect the effect of CR modification and cold plasma treatment for the materials used in this study, though FTIR was a useful method in investigating the modification mechanism of other polymer-modified asphalt.

Finally, according to the chemical analysis and the widely recognized knowledge about the CR–asphalt interactions, the mechanism of performance improvement of rubberized asphalt after cold plasma treatment is discussed below. In the colloidal theory, the asphalt binder could be seen as a colloidal dispersion. As shown in Fig. 13.1.19A, it was composed of four fractions, namely saturates, aromatics, resins, and asphaltenes (SARA). In general, the interactions between CR and asphalt were predominated by the CR particle swelling at the interface (in Fig. 13.1.19C). Hence, the ultimate performance of

rubberized asphalt was dominated by the swelling process, which can be seen as the premise of desirable engineering performance.

Furthermore, the swelling was a diffusion-induced process, during which the CR particles absorbed saturates and aromatics of light asphalt components from asphalt matrix with its volume expanding. It started at a fast-growing stage and then leveled off to the equilibrium. As this physical interaction mainly occurred on the CR surface, the surface characteristic of CR particles was thus a vital influencing factor. Meanwhile, as reported above, the cold plasma treatment significantly improved the surface properties of CR particles, especially under the optimal processing condition. Therefore it could be concluded that:

1. The enhanced surface lipophilicity could accelerate the absorption of light oil fraction and improve the swelling extent of CR particles.
2. The improved surface hydrophilicity and incorporation of oxygen-containing polar groups could improve the adsorption capacity of CR particles to the polar asphalt components and strengthen the interaction with certain functional groups (i. e., carboxyl) in the asphalt matrix.
3. The roughened and porous surface could directly cause an increase in the interfacial contact area and interaction rate.

In total, the observed enhancement in engineering performance of plasma-treated rubberized asphalt was essentially attributed to the improved surface properties of CR particles after cold plasma treatment. In addition, regardless of the base asphalt source, CR particle size, and content, the plasma-treated rubberized asphalts performed better than the untreated.

13.1.6 Conclusions

For the first time, this study applied the cold plasma to surface modification of CR particles for performance enhancement of rubberized asphalt binders. According to the investigation on surface characteristics of CR particles and engineering performance of rubberized asphalt after cold plasma treatment as well as the discussion on the possible mechanisms behind the performance enhancement, the primary conclusions can be stated as follows:

Firstly, in terms of the surface characteristics of plasma-treated CR particles with varying discharge power and processing time:

- By optimizing the processing parameters, the employed cold plasma treatment could result in quite effective surface modification technique. The optimal processing parameters were the discharge power of 250 W and the processing time of 8 min.
- Three primary mechanisms of cold plasma surface modification on CR particles were found: (1) enhancing surface lipophilicity indicated by the decrease in oil-wetting time; (2) improving surface chemical affinity conferred by the decrease in water contact angle and incorporation of oxygen-containing polar groups; and (3) increasing the surface roughness driven by the plasma physical etching and bombardment effect.

Secondly, regarding the engineering performance of rubberized asphalt binder with varying base asphalt source, CR particle size, and content:

- Cold plasma treatment on CR particles certainly enhanced the engineering performance of rubberized asphalt, including high-temperature rutting resistance, moderate-temperature fatigue resistance, and storage stability. However, it had no obvious effect on the low-temperature performance.
- The increased content of plasma-treated CR particles from 10% to 20% constantly showed a positive effect on performance improvement of rubberized asphalt. However, the effects of CR size should be considered separately for each specific property.

Thirdly, the possible mechanisms behind the performance enhancement of rubberized asphalt after cold plasma treatment were further summarized as follows:

- The enhanced surface lipophilicity could accelerate the absorption of light oil fraction and improve the swelling extent of CR particles.
- The improved surface hydrophilicity and incorporation of oxygen-containing polar groups could improve the adsorption capacity of CR particles to the polar asphalt components and strengthening the interaction with certain functional groups (i. e., carboxyl) in asphalt matrix.
- The roughened and porous surface could directly cause an increase in the interfacial contact area and interaction rate.

Finally, it was mentioned the sources of CR material and base binder considered in this research work were limited. However, based on reliable experimental data, the primary mechanisms of cold plasma treatment on CR particles and rubberized asphalt had been investigated. Therefore similar findings could be observed with respect to the employment

of cold plasma treatment on different materials, as long as the operation was appropriately performed. For future studies, it is recommended to investigate different sources of CR particles and base asphalt with different chemical composition and vary other processing parameters of cold plasma treatment for betterment. In addition, it is important to note that this surface modification technique could be implemented in the field applications. The cost of the mass production compared to the enhancement made to the modified binder and durability of the pavements must be investigated and studied.

References

[1] J.-S. Chen, P.-Y. Chu, J.-E. Chang, H.-C. Lu, Z.-H. Wu, K.-Y. Lin, Engineering and environmental characterization of municipal solid waste bottom ash as an aggregate substitute utilized for asphalt concrete, J. Mater. Civ. Eng. 20 (2008) 432–439. Available from: https://doi.org/10.1061/(ASCE)0899-1561(2008)20:6(432).

[2] Y. Huang, R.N. Bird, O. Heidrich, A review of the use of recycled solid waste materials in asphalt pavements, Resour. Conserv. Recycl. 52 (2007) 58–73. Available from: https://doi.org/10.1016/j.resconrec.2007.02.002.

[3] J. Li, F. Xiao, L. Zhang, S.N. Amirkhanian, Life cycle assessment and life cycle cost analysis of recycled solid waste materials in highway pavement: a review, J. Clean. Prod. 233 (2019) 1182–1206. Available from: https://doi.org/10.1016/j.jclepro.2019.06.061.

[4] M.R. Mohd Hasan, J.-W. Chew, A. Jamshidi, X. Yang, M.O. Hamzah, Review of sustainability, pretreatment, and engineering considerations of asphalt modifiers from the industrial solid wastes, J. Traffic Transp. Eng. Engl. Ed. 6 (2019) 209–244. Available from: https://doi.org/10.1016/j.jtte.2018.08.001.

[5] Z. Zhao, F. Xiao, S. Amirkhanian, Recent applications of waste solid materials in pavement engineering, Waste Manage. 108 (2020) 78–105. Available from: https://doi.org/10.1016/j.wasman.2020.04.024.

[6] T. Wang, F. Xiao, S. Amirkhanian, W. Huang, M. Zheng, A review on low temperature performances of rubberized asphalt materials, Constr. Build. Mater. 145 (2017) 483–505.

[7] L.G. Picado-Santos, S.D. Capitão, J.M.C. Neves, Crumb rubber asphalt mixtures: a literature review, Constr. Build. Mater. 247 (2020) 118577. Available from: https://doi.org/10.1016/j.conbuildmat.2020.118577.

[8] T. Wang, F. Xiao, X. Zhu, B. Huang, J. Wang, S. Amirkhanian, Energy consumption and environmental impact of rubberized asphalt pavement, J. Clean. Prod. 180 (2018) 139–158. Available from: https://doi.org/10.1016/j.jclepro.2018.01.086.

[9] D.L. Presti, Recycled tyre rubber modified bitumens for road asphalt mixtures: a literature review, Constr. Build. Mater. 49 (2013) 863–881. Available from: https://doi.org/10.1016/j.conbuildmat.2013.09.007.

[10] M. Sienkiewicz, K. Borzędowska-Labuda, A. Wojtkiewicz, H. Janik, Development of methods improving storage stability of bitumen modified with ground tire rubber: a review, Fuel Process. Technol. 159 (2017) 272–279. Available from: https://doi.org/10.1016/j.fuproc.2017.01.049.

[11] L. Han, M. Zheng, C. Wang, Current status and development of terminal blend tyre rubber modified asphalt, Constr. Build. Mater. 128 (2016) 399–409. Available from: https://doi.org/10.1016/j.conbuildmat.2016.10.080.
[12] S. Wang, Recent developments in the application of chemical approaches to rubberized asphalt, Constr. Build. Mater. 131 (2017) 101–113. Available from: https://doi.org/10.1016/j.conbuildmat.2016.11.077.
[13] S. Kocevski, S. Yagneswaran, F. Xiao, V.S. Punith, D.W. Smith, S. Amirkhanian, Surface modified ground rubber tire by grafting acrylic acid for paving applications, Constr. Build. Mater. 34 (2012) 83–90. Available from: https://doi.org/10.1016/j.conbuildmat.2012.02.040.
[14] Z. Chen, J. Pei, T. Wang, S. Amirkhanian, High temperature rheological characteristics of activated crumb rubber modified asphalts, Constr. Build. Mater. 194 (2019) 122–131. Available from: https://doi.org/10.1016/j.conbuildmat.2018.10.223.
[15] O. Xu, M. Li, D. Hou, Y. Tian, Z. Wang, X. Wang, Engineering and rheological properties of asphalt binders modified with microwave preprocessed GTR, Constr. Build. Mater. 256 (2020) 119440. Available from: https://doi.org/10.1016/j.conbuildmat.2020.119440.
[16] M. Xu, J. Liu, W. Li, W. Duan, Novel method to prepare activated crumb rubber used for synthesis of activated crumb rubber modified asphalt, J. Mater. Civ. Eng. 27 (2015) 04014173. Available from: https://doi.org/10.1061/(ASCE)MT.1943-5533.0001115.
[17] J. Li, S. Yao, F. Xiao, S.N. Amirkhanian, Surface modification of ground tire rubber particles by cold plasma to improve compatibility in rubberised asphalt, Int. J. Pavement Eng. (2020) 1–12. Available from: https://doi.org/10.1080/10298436.2020.1765242.
[18] F. Xiao, S. Yao, J. Wang, J. Wei, S. Amirkhanian, Physical and chemical properties of plasma treated crumb rubbers and high temperature characteristics of their rubberised asphalt binders, Road Mater. Pavement Des. 21 (2020) 587–606. Available from: https://doi.org/10.1080/14680629.2018.1507922.
[19] O.M. Ba, P. Marmey, K. Anselme, A.C. Duncan, A. Ponche, Surface composition XPS analysis of a plasma treated polystyrene: evolution over long storage periods, Colloids Surf. B Biointerfaces 145 (2016) 1–7. Available from: https://doi.org/10.1016/j.colsurfb.2016.04.026.
[20] Z. Chang, C. Yao, H. Mu, G. Zhang, Study on the property evolution of atmospheric pressure plasma jets in helium, Plasma Sci. Technol. 16 (2014) 83–88. Available from: https://doi.org/10.1088/1009-0630/16/1/18.
[21] X. Cheng, D. Long, S. Huang, Z. Li, X. Guo, Time effectiveness of the low-temperature plasma surface modification of ground tire rubber powder, J. Adhes. Sci. Technol. 29 (2015) 1330–1340. Available from: https://doi.org/10.1080/01694243.2015.1026958.
[22] X. Cheng, S. Huang, X. Guo, W. Duan, Crumb waste tire rubber surface modification by plasma polymerization of ethanol and its application on oil-well cement, Appl. Surf. Sci. 409 (2017) 325–342. Available from: https://doi.org/10.1016/j.apsusc.2017.03.072.
[23] A. Van Deynse, P. Cools, C. Leys, N. De Geyter, R. Morent, Surface activation of polyethylene with an argon atmospheric pressure plasma jet: influence of applied power and flow rate, Appl. Surf. Sci. 328 (2015) 269–278. Available from: https://doi.org/10.1016/j.apsusc.2014.12.075.
[24] B. Liao, T. An, Y. Wang, S. Zhu, A study of rubber surface modification using microwave plasma, J. East China Norm. Univ. Sci. (2003) 40–45.

[25] M.D. Romero-Sánchez, J.M. Martín-Martínez, Surface modifications of vulcanized SBR rubber by treatment with atmospheric pressure plasma torch, Int. J. Adhes. Adhes. 26 (2006) 345–354. Available from: https://doi.org/10.1016/j.ijadhadh.2005.05.002.

[26] B. Lee, Y. Kusano, N. Kato, K. Naito, T. Horiuchi, H. Koinuma, Oxygen plasma treatment of rubber surface by the atmospheric pressure cold plasma torch, Jpn. J. Appl. Phys. 36 (1997) 2888–2891. Available from: https://doi.org/10.1143/JJAP.36.2888.

[27] A.B. Ortíz-Magán, M.M. Pastor-Blas, J.M. Martín-Martínez, Surface modifications and adhesion of vulcanized SBR rubber treated with RF plasmas of different cases, J. Adhes. 80 (2004) 613–634. Available from: https://doi.org/10.1080/00218460490477071.

[28] X. Cheng, H. Chen, S. Huang, Z. Li, X. Guo, Improvement of the properties of plasma-modified ground tire rubber-filled cement paste, J. Appl. Polym. Sci. 126 (2012) 1837–1843. Available from: https://doi.org/10.1002/app.36907.

13.2

Application of rubberized asphalt mixtures in low-temperature environments

Serji Amirkhanian[1], Feipeng Xiao[2] and Tao Wang[3]

[1]Department of Civil, Environmental and Construction Engineering, The University of Alabama, Tuscaloosa, AL, United States [2]Key Laboratory of Road and Traffic Engineering of Ministry of Education, Tongji University, Shanghai, P.R. China [3]School of Civil Engineering, Beijing Jiaotong University, Beijing, P.R. China

13.2.1 Introduction

Many parts of the world, including the EU, face cold temperatures during winter months.

For example, in the EU, the lowest daily maximums belong to Reykjavík, Iceland, which has an average temperature of approximately 7°C (44.6°F) throughout the year. Other locations such as Ufa, located near the Ural Mountains, have average lows that are nearly 4°C (7°F) lower than Reykjavík's.

In other locations around the EU, such as in southern and western parts, the weather does not get nearly as frigid as those to the north and east. For instance, southern Europe's coldest major city is Sarajevo in Bosnia and Herzegovina, followed closely by Ljubljana, Slovenia, both averaging highs of 15°C (59°F) and lows below 5°C (41°F). In addition, in many other parts of the world such as Canada, United States, and Mongolia, the temperatures fall to below zero.

One of the major distresses in asphalt pavements is low-temperature cracking usually occurring during cold and freezing weather. The thermal tensile stress in asphalt pavements exceeds its resistance strength with the decrease of temperature, leading to the occurrence of thermal cracking. Cracks in asphalt pavements affect and shorten the service life of a typical asphalt pavement. The cracking resistance performance of pavements are closely correlated with the properties of the binder and mixture [1,2]. The addition of crumb rubber to asphalt binders has been recommended for resisting and reducing the thermal cracking of asphalt pavements. Crumb rubber as a modifier of a

typical binder was used in pavements in the United States in the early 1960s [3]. At present, the use of crumb rubber produced from scrap tires to modify binder may not only enhance the properties of the binder, but also take advantage of the economical and environmental benefits of reducing disposal of scrap tires in landfills. Due to low susceptibility to temperature variances, crumb rubber has low stiffness and maintains elastically at low-temperature conditions [4,5]. Many researchers have indicated that crumb rubber-modified binders (CRMB) improved low-temperature cracking performance of asphalt pavements through improving fracture toughness [6,7] and increasing tensile strength [8].

As has been discussed in other chapters of this book, the addition of crumb rubber to asphalt may be achieved in variety of ways including by wet and dry approaches [9]. Crumb rubber modification by the wet method has proved to contribute to the improvement of low-temperature anticracking resistance of asphaltic mixes. It has been hypothesized that the swelling process of the interaction between crumb rubber and binder has a major and direct impact on the performance improvement. The absorption of light components of the binder by the crumb rubber may make the particle swell up to three to five times its original volume [10]. Many factors affect the properties of CRMB including (1) type of binder; (2) crumb rubber content; (3) crumb rubber type; (4) particle size; and (5) production parameters such as mixing time, mixing temperature, mixing type, and so on [11,12]. Several additives have been added to CRMB (e.g., Advera, LEADCAP, epoxidized soybean oil, etc.) to promote its low-temperature performance.

There are many different methods to evaluate the low-temperature properties of CRMB and its mixture. One of the earliest methods to measure the low-temperature performance of asphalt was the Fraass brittle point test which, currently, is not widely used [13]. Since traditional test methods do not accurately predict low-temperature mechanical behavior, the limiting stiffness values of the material as a way to evaluate the thermal cracking of asphalt pavements has been suggested by some researchers [14–16]. The bending beam rheometer (BBR) and/or the direct tension tester (DTT) were recommended for characterizing the low-temperature properties of an asphalt in the Superpave specifications. The low-temperature limit of an asphalt was controlled by the DTT failure strain, which was not less than 1.0% [17,18]. Although most unmodified binders may be evaluated by the stiffness

and m-value in Table 1 of AASHTO M 320, the standards did not apply well to polymer-modified binders. Therefore an alternative asphalt binder specification (Table 2 of AASHTO M 320) was developed and adopted. The alternative specification requires that the critical temperature for the thermal cracking of a modified binder be determined using both BBR and DTT tests.

For many years, there has not been a reliable direct test for measuring the susceptibility of low temperature of an asphalt mixture [13]. Many research projects have been carried out based on theoretical or empirical methods for better understanding of the thermal cracks and to select the appropriate materials to improve the fracture resistance. The thermal stress–restrained specimen test (TSRST), developed during the Strategic Highway Research Program, was widely used for determining the low temperature of asphalt mixtures [19–22]. However, the evolution of cracks over time and the impact of traffic loading were not considered in the TSRST test. The indirect tensile test (IDT) was also developed to evaluate the low-temperature cracking resistance of asphalt mixtures [23–25].

The IDT test is currently considered to be the most promising approach to predicting the low-temperature properties of an asphalt mixture [25]. Fracture mechanics, as an effective method, has been applied to study the process of cracking initiation and propagation in asphalt mixtures for many years [26]. There are many fracture test methods in hot-mix asphalt (HMA) including (1) the IDT fracture parameter [27,28]; (2) the disc–shaped compact tension test (DCT) [29,30]; and (3) the semicircular bend [31,32]. Obviously, as with most tests, there are advantages and disadvantages to all of these test procedures [29].

Each year, in many parts of the world, pavements fail due to a variety of distresses including low-temperature cracking of asphalt pavements costing taxpayers billion of dollars in repairs. The objective of this chapter is to discuss the impacts of different factors and evaluation methods utilized on the low-temperature properties of crumb rubber-modified binder and mixtures. The main topics presented here include: (1) the mechanism of crack resistance of crumb rubber-modified asphalt; (2) the key factors that affect the low-temperature properties of CRMB; (3) low-temperature evaluation tests of CRMB and mixtures and chemical modification; and (4) physical treatment methods used to improve the low-temperature properties of rubber asphalt and mixtures.

13.2.2 Mechanism of crack resistance of rubberized asphalt

13.2.2.1 Mechanism of adding crumb rubber to asphalt binder

Crumb rubber, as has been discussed in detail in other chapters, is a complex material comprised of natural rubber, synthetic rubber, carbon black, aromatics, and other materials. Carbon black is used as a reinforcement agent and the aromatics can increase the softness and workability of the rubber [33–35]. Similarly, asphalt is a colloidal substance with complex chemical components, which is generally divided into four fractions, namely, asphaltenes, aromatics, resins, and saturates [36].

Some researchers have indicated that there are two main interaction mechanisms that may explain the process of the addition of crumb rubber modifier (CRM) to the asphalt including (1) rubber particle swelling [37] and (2) degradation (devulcanization and depolymerization) [38]. Fig. 13.2.1 shows the reaction process of rubber particles and asphalt. The rubber particles usually swell up double or triple their original size by absorbing the aromatic oils of the asphalt, becoming a gel-like material under high interaction temperature [9]. It has been noted that the material exchange between the binder and rubber particle is a nonchemical reaction [9,38]. Moreover, CRM swells by the absorption of the lightweight components and aromatics of the binder and reduces the free light content in the binder [39].

Figure 13.2.1 Description of swelling of rubber and asphalt [9].

The temperature-sensitive property of CRMB drops so that the low-temperature performance of CRMB is improved. In addition, the carbon black in the rubber particle mixed with the binder causes the improvement of high-temperature properties of the asphalt [40,41]. The rubber particles interact with the binder to form a continuous or interdigitated three-dimensional space network structure. The nodes of the network structure may enhance the low-temperature relaxation ability of the asphalt and improve the low-temperature property of CRMB [42].

Several researchers have studied the dissolution of crumb rubber in binder and the effects of various parameters on the extent and rate of dissolution [43–46]. It has been confirmed that the dissolution process of crumb rubber is greatly affected by mixing time, rate, and temperature of the interaction [44]. Green et al. [47] recognized the importance of controlling the mixing time and temperature during the swelling processes. The temperature during the interaction process affects the swelling rate and swelling extent of rubber particles. While the swelling mechanism is controlled by rubber particle size and ultimately affects the performance of CRMB [47]. In addition, the time required for the particle swelling is prolonged as the particle radius squared increased [48]. Also, the acidity and aromaticity of the binder has a positive effect on the degree and rate of crumb rubber dissolution [49,50].

However, a chemical reaction may exist during this process, as was shown by Bahia et al. [51], which suggests that this reaction is calculated by the change in viscosity of the binder. The research indicated that the type of reaction not only promotes rubber particles to swell, but also changes the properties of the binder liquid phase [51]. Fig. 13.2.2 shows the rubber–binder

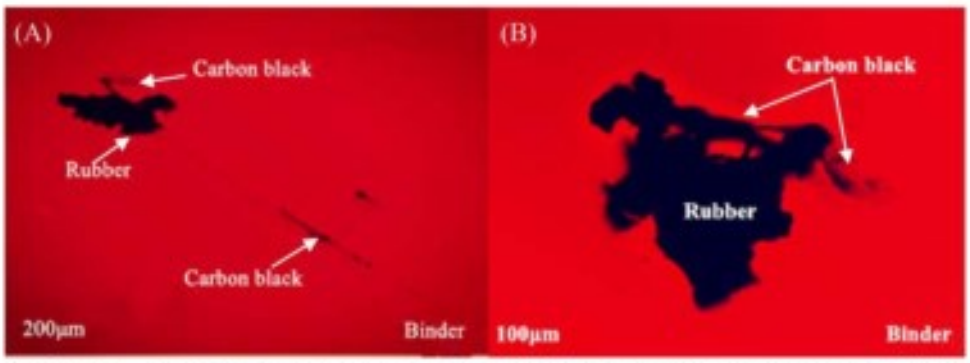


Figure 13.2.2 Rubber–binder interaction observed under the optical microscope. (A) Trace of carbon black separated from the rubber particle. (B) A large amount of carbon black around the rubber particle [52].

interaction process where the carbon black in the rubber is dissolved into the binder [52].

Some researchers have suggested that the phenomenon of partial dispersion of crumb rubber in the binder is devulcanization or depolymerization [45,46]. The hypothesis is that the chemical reaction between rubber and binder destroys the chemical bonds of the rubber and reduces its molecular weight. Some researchers observed that, under high blending rate and high temperature of extreme interaction conditions, the crumb rubber will be depolymerized/devulcanized and will dissolve the polymeric substance into the virgin binder [44–46,53]. It was concluded in two different studies that the network, formed by S–S or S–C bonds, of the rubber is destroyed because of desulfurization. This might be due to the S–S bonds or S–C bonds being less stable than C–C bonds under chemical and thermal attacks [54]. Ghavibazoo et al. concluded that rubber particles swell only at a temperature of 160°C [55], and the polymeric compounds of crumb rubber begin dissolving into the matrix binder when the interaction temperature is higher than 200°C [56].

13.2.2.2 Mechanism of low-temperature anticracking of rubberized asphalt

Low-temperature cracking is a key problem of asphalt pavements in cold areas. When the stress concentration due to low-temperature shrinkage is greater than the limited tension stress strength, low-temperature cracking will occur and thus result in a decrease in the performance of asphalt pavements. The properties of the asphalt and mixture directly affect the crack resistance of the asphalt pavement, which is sensitive to temperature variances, and becomes brittle and hard under low temperatures [1,57]. Adding crumb rubber into asphalt makes it insensitive to the temperature variance and allows it to maintain flexibility under low-temperature conditions. The results of the above research projects indicate that crumb rubber has a relatively low stiffness at low temperatures and improves the anticracking properties of modified asphalt when it is added to asphalt binder [4,5].

The lower Fraass breaking point of a typical binder indicates the better low-temperature cracking resistance of a mixture. As shown in Fig. 13.2.3, the brittle point of rubber-modified asphalt is the lowest of the different types of asphalts, indicating that CRMB has excellent low-temperature anticracking performance in cold weather.

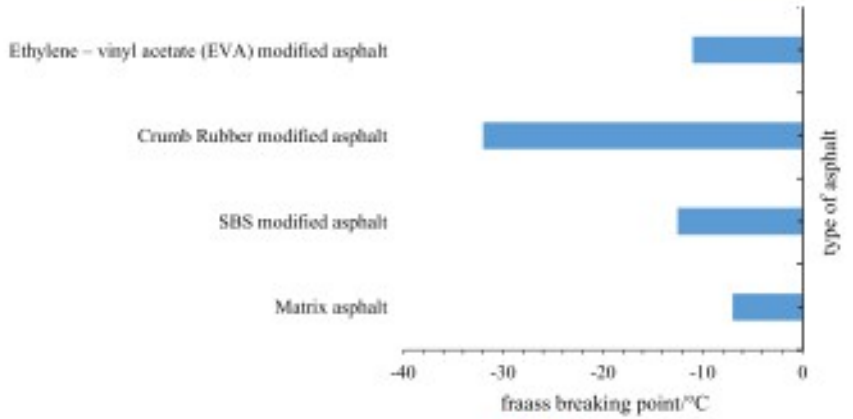


Figure 13.2.3 Fraass breaking point of different types of asphalt [58–61]. 6% (by the weight of asphalt binder) SBS-modified asphalt, 20% (by the weight of asphalt binder) crumb rubber-modified asphalt.

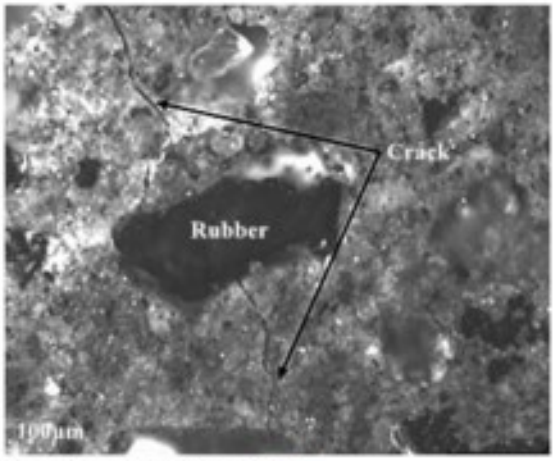


Figure 13.2.4 Cracking bridging effect of rubber particles [65].

Rubber particles, in general, possess favorable elasticity and the unswollen particles may act as stress concentration points to enhance impact strength in cold temperatures [62,63]. Microcracks could not be developed into destructive cracks due to the effect of larger crumb rubber particles; therefore the CRMB mixtures produced favorable performance at low temperatures [64]. The results of other research projects have shown that rubber particles can prevent cracks from expanding (Fig. 13.2.4) [65]. Billiter et al. [50] pointed out that the crumb rubber particles may act as an elastic filler in the binder because of their good elasticity in low-temperature conditions.

In addition, the glass transition temperatures of crumb rubber and the binder have been found to be close, and the flexibility of the binder can be enhanced by utilizing the crumb rubber [50]. Researchers also have concluded that improvements in crack resistance of the binder in the presence of CRM occur due to the crack blunting and crack pining function of the rubber particles, which improve the toughness of the asphalt [66,67].

13.2.3 Key factors influenced low-temperature performance of rubberized asphalt

13.2.3.1 Asphalt properties

13.2.3.1.1 Asphalt grade and type

It is usually assumed that the low-temperature cracking resistance of asphalt mixture is closely related to the properties of the asphalt used [68]. Table 13.2.1 summarizes the low-temperature cracking properties of CRMB. The low-temperature parameters of CRMB with various types of matrix binders are different. The properties of CRMB are greatly affected by the

Table 13.2.1 Performance grade, source, type of modifications, and average properties of binders.

	PG64-22 Neat Binder	PG64-22 +GRT	PG58-22 +GTR	PG64-22 +GRT	PG64-22 +GTR	PG64-22 +GTR
Source	Aggregate industries	–	Iranian asphalt	Detroit asphalt	Middle Eastern	Gorman
Modification	None	12% Ground tire rubber (GTR)	10% Waste tire rubber (WTR)	15% Ground tire rubber (GTR)	15% Ground tire rubber (GTR)	12% Ground tire rubber (GTR)
PG grade	PG64-28	–	–	–	–	PG88-16
Continuous grade	67.9–29.2	–	–	–	–	88.7–19.8
AASHTO T313 BBR creep stiffness (60 s) S(MPa)	263 (−18°C)	66.1 (−12°C)	157 (−18°C)	193 (−18°C)	108 (−12°C)	43.6 (−6°C)
AASHTO T313 BBR slope (60 s) m value	0.316 (−18°C) [18]	0.355 (−12°C) [69]	0.364 (−18°C) [70]	– [5]	0.325 (−12°C) [71]	0.318 (−6°C) [72]

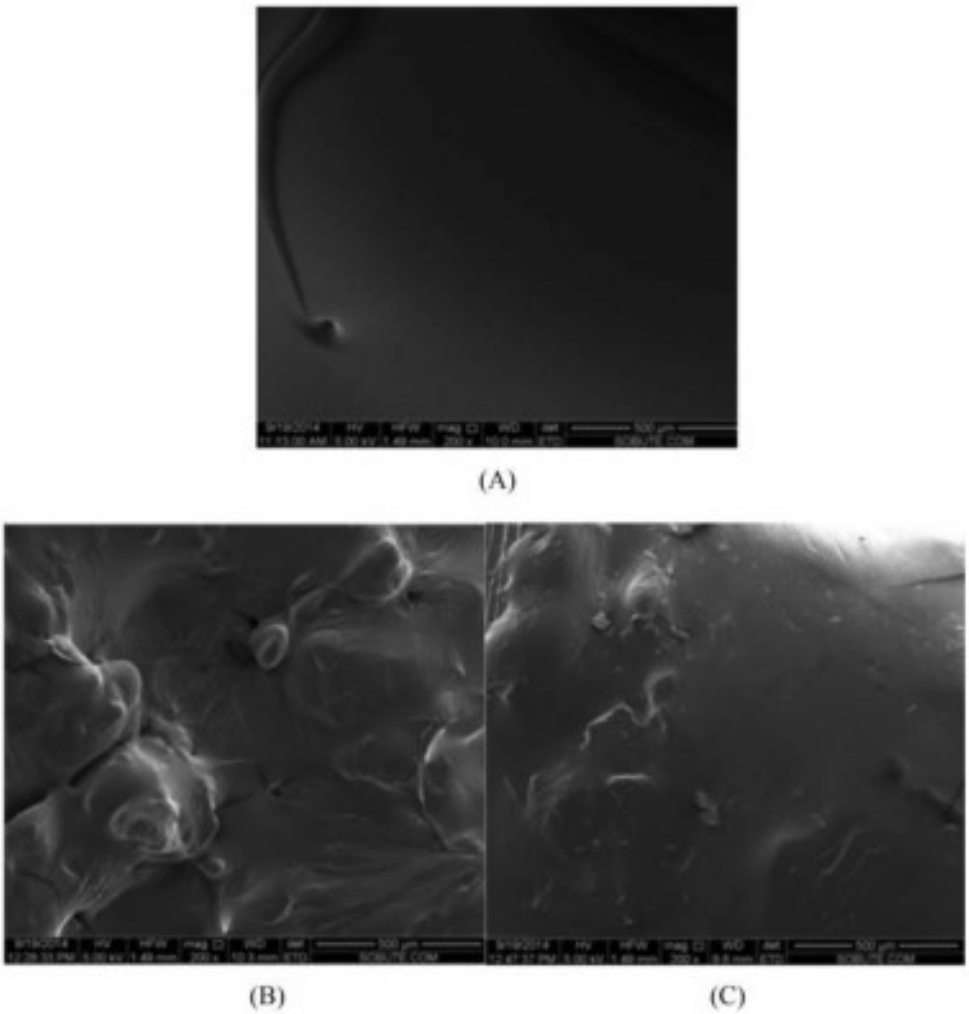
quality of matrix binder. Some researchers have indicated that crumb rubber-modified particles may dissolve more in a softer binder with a lower performance grade (PG) compared with a harder binder. They speculate that the CRM particles may more easily absorb the light components of a softer binder [37,50,73,74].

In a study completed by Tauer, it was concluded that asphalt grade, its acidity and chemical composition, played an important role in the dissolution of CRM [49]. Aliha et al. [74] pointed out that the low-temperature PG of binders has a remarkable impact on the low-temperature anticracking properties of CRMB. It was also reported that the CRM binder produced from high PG grade binders with more light components have favorable low-temperature anticracking properties [75].

Asphalt type has a remarkable effect on the low-temperature properties of CRMB. The results of several studies indicate that softer binders with higher degrees of aromaticity have a better dissolution rate to the rubber particles. Compared with a stiffer binder containing the same content as rubber modification, a softer binder shows better properties at a low temperature [76]. CRMB exhibited better low-temperature performance due to the use of softer binder with a higher percentage of lightweight fractions [33]. The effect of base binder containing asphaltenes, resin, aromatics, and saturates on the degree of crumb rubber particles swelling in CRMB was studied by Henia et al. The results of this work showed that the binder with a higher aromatic content had a higher sensitivity to temperature than a stiffer binder [77]. In addition, the binder type displayed a major effect on the fracture resistance of the mixture under low-temperature conditions [75,78]. The stiffness difference of the CRM binders manufactured form different binder types was observed and determined. However, the impact of the binder type on the stiffness of CRMB may be weakened with the increase of CRM content [51,71].

13.2.3.1.2 Asphalt morphology

The asphalt morphology with the addition of crumb rubber has been studied using many advanced means. Many advanced means include SEM, ultrasonic focusing device, and fluorescent microscope. The effect of compatibility between crumb rubber and the binder on the properties of CRMB was critical. Fig. 13.2.5 shows that the surface of base binder is smoother than that of desulfurized rubber binder and the surface of crumb rubber modified binder is rougher than that of desulfurized rubber binder The



(A)

(B) (C)

Figure 13.2.5 SEM pictures for different binders: (A) virgin binder, (B) crumb rubber-modified binder, and (C) desulfurized rubber-modified binder [79].

crumb rubber particles absorbed the lightweight component of the binder to swell and formed a gel-like film. The crumb rubber particles contact each other though the surrounding gel film. Better integration of crumb rubber into base binder, in general, has a positive effect on binder properties [79].

Fig. 13.2.6A shows that the interface of ordinary crumb rubber particle is smooth leading to a poor absorbed lightweight component of the binder. The compatibility between the binder and crumb rubber is poor as shown in Fig. 13.2.7A [80]. The CRMB

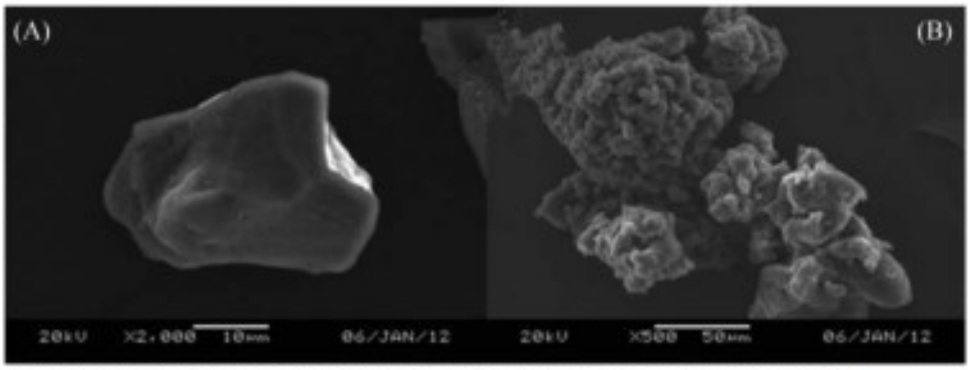


Figure 13.2.6 SEM images of (A) preactivated crumb rubber; (B) postactivated crumb rubber [80].

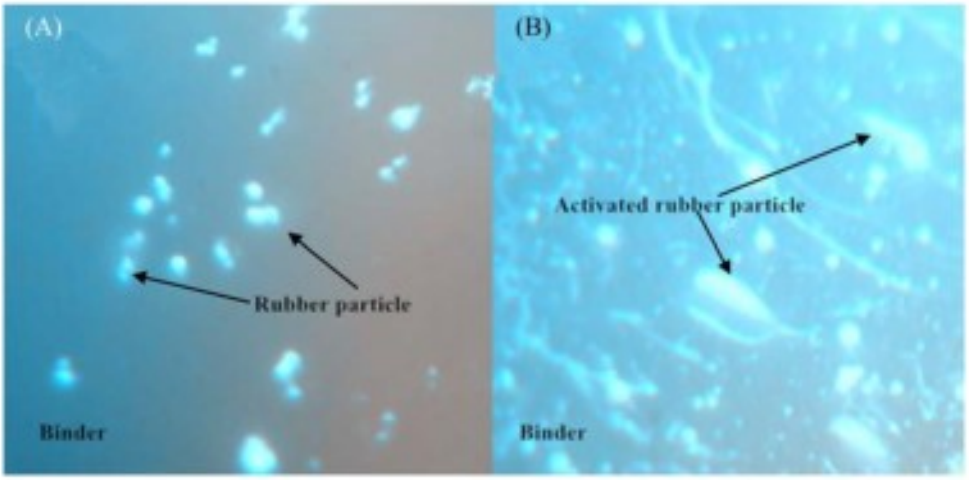


Figure 13.2.7 Fluorescence micrographs at 400 magnification of modified asphalt by (A) ordinary crumb rubber; (B) activated crumb rubber [80].

system was not very stable and prone to produce the two-phase separation from the view of thermodynamics [81]. Fig. 13.2.6B shows the crumb rubber activated by ultrasonic focusing device with a popcorn appearance. Due to ease of absorption of the light component into the binder, the activated crumb rubber greatly alleviates the free radicals [82,83]. Activated crumb rubber acting as additive and stabilizer forms the polymer reticular structure in virgin asphalt and improves the Fraass breaking point and elastic recovery of CRMB, as shown in Fig. 13.2.7B [80].

Using fluorescent microscope, Cong et al. [76] investigated the morphology of CRMB to illustrate the distribution characteristic of

the discontinuous phase and continuous phase. They found that the low-temperature properties of CRMB can be determined by the chemical component of matrix binder and the swelling of crumb rubber [76]. Morphology observation by an optical microscope found that an intertwined network consisting of linear low-density polyethylene (LLDPE) and crumb rubber is formed in the binder and the swelling of polymer in binder is further promoted by dioctyl phthalate. In addition, the dioctyl phthalate may enhance the performance of CR/LLDPE-modified binder at low temperatures [84]. It was observed by SEM that the crumb rubber surface after microwave treatment has good reactivity, permeability, and affinity at the interface with epoxidized soybean oil, which penetrates into the structure of asphalt, helping to restore and improve the parts of performance of the binder after an aging process [85].

13.2.3.2 Crumb rubber properties

Glass transition is a reversible change from viscous or rubbery state to glassy or brittle state (or vice versa). The glass transition temperature of crumb rubber is very low, leading to insensitivity to temperature variances and allowing the crumb rubber to maintain elasticity at a temperature below 0°C [86,87]. The crumb rubber may ameliorate the low-temperature properties of CRM binder when added into asphalt binder [4,5]. The low-temperature property of CRM binder is governed by the crumb rubber properties. Meanwhile, the properties of crumb rubber are related the factors such as crumb rubber compositions, content, type, particle size, production process, elasticity, mixing process, and so on.

13.2.3.2.1 Crumb rubber composition and content

Crumb rubber from scrap tires is mainly comprised of natural rubber content, synthetic rubber content, fillers, carbon black,

Table 13.2.2 Chemical compositions of different types of tires [33].

Chemical composition	Heavy truck tread rubber (%)	Passenger/light truck tread rubber (%)	Range (%)
Rubber hydrocarbon	50.2	42.9	7.3
Carbon black	33.2	32.7	1.2
Extract	11.4	17.2	5.8
Ash	5.1	4.8	0.29

acetone extractables, and antioxidants [33,34]. The chemical compositions of different types of tires are shown in Table 13.2.2 and covered in great detail in other chapters. These chemical compositions have a great impact on the low-temperature properties of CRMB. Rubber hydrocarbon, maintaining flexibility, is the main component in crumb rubber. A cross-linked structure is formed by adding the crumb rubber into base binder. The low-temperature crack resistance of the binder is enhanced by the elastic network of crumb rubber [88].

The extract mainly included acetone and chloroform [33]. The extract had a positive effect on the promotion of the component exchange between the crumb rubber and matrix asphalt. Significant compatibility and swelling are obtained by the component exchange, which increases the low-temperature performance of CRMB [80]. Carbon black plays a role in filling and reinforcing crumb rubber. It may improve the strength of crumb rubber, and may effectively improve the low-temperature properties of rubber [89]. Ash has an adverse effect on low-temperature performance of CRMB. The elastic recovery, cohesive force, and ductility of CRMB may be improved by lowering the ash content of crumb rubber [80].

There are different proportions of synthetic rubber, natural rubber, and other ingredients between passenger car tires and truck tires. Although the interaction between the rubber particles and binder is mainly based on the exchange materials without any chemical reaction [9,38], passenger car tires contain high synthetic rubber when compared with heavy truck tires, which contain more natural rubber. Therefore the interaction between rubber particles and asphalt may be affected. Ghavibazoo et al. [56] found that the viscoelastic properties of asphalt increase due to increasing the dissolution of crumb rubber from the mixture of passenger car and truck tires, while the properties of the CRM binder do not change as a result of increasing the dissolved portion of crumb rubber only from truck tires [56]. However, different from Ghavibazoo et al.'s findings, the results from Thodesen et al. show the opposite conclusion, which indicate that the modified binder produced by truck tire crumb has the highest viscosity [90]. At the same time, Cao and Bai concluded that crumb rubber produced from truck tires provides better performance at low temperature [91]. Due to the contradictory conclusions, it is recommended to conduct related research at a molecular level.

Many researchers have shown that the rubber content plays a significant role in improving the low-temperature performance of rubberized binders [76,92–95]. With the increase of crumb rubber content from 5% to 20%, softening point, elastic recovery, complex

shear modulus, and viscosity of CRMB increase noticeably. The reason for this phenomenon is due to rubber particles absorbing the light fraction oil of asphalt, resulting in enhanced rubber particle swelling reaction during mixing [92]. At the same time, the stiffness of CRM binder reduces under low-temperature condition as the crumb rubber content increases [95]. This indicates that crumb rubber may effectively improve the toughness of asphalt and greatly reduce the possibility of cracking at low temperature. This is because the crumb rubber has lower stiffness and modulus at a low temperature [95].

Taking into account the low-temperature performance, crumb rubber may effectively reduce the creep stiffness and aging index of CRM binder, which may improve the low-temperature cracking ability of the asphalt pavement [5,50,60,96]. Based on the BBR tests, the crumb rubber content from 18% to 22% had little effort on the fracture and tensile performance of CRMB [34,97]. Liu et al. [89] reported that CRM binder has the best low-temperature anticracking with 5%–20% of crumb rubber content according to the economic factor, which significantly improved the viscoelastic properties of CRM binder, showing an increased resistance to low-temperature cracking of CRMB [5,89]. In addition, Mcgennis [98] found that the rise of crumb rubber content leads to a reduction of stiffness and an increase of m-value of CRM binder. For the m-value property of CRM binder, however, Kim et al. [99] came to different conclusions which had little impact on the m-value as the crumb rubber content increased.

13.2.3.2.2 Crumb rubber type and particle size

In addition to the rubber compositions and content, some other factors may also affect the low-temperature properties of the CRM binder. For example, the low-temperature properties of CRM binder are also affected by crumb rubber type and particle size [51,71,94,100,101]. There are many types of crumb rubber types and their sources are broad, so the modified rubberized binders are also different. The types of crumb rubber include heavy truck crumb rubber, small truck crumb rubber, tread rubber-crumb rubber, agriculture tire crumb rubber, sole tire crumb rubber, hose crumb rubber, and ball crumb rubber [56,102].

Several studies have been conducted to investigate the relationship between the performance characteristics of CRM binders and crumb rubber type. Based on the results of Liu et al.'s study, the findings are shown in Fig. 13.2.8 [102].

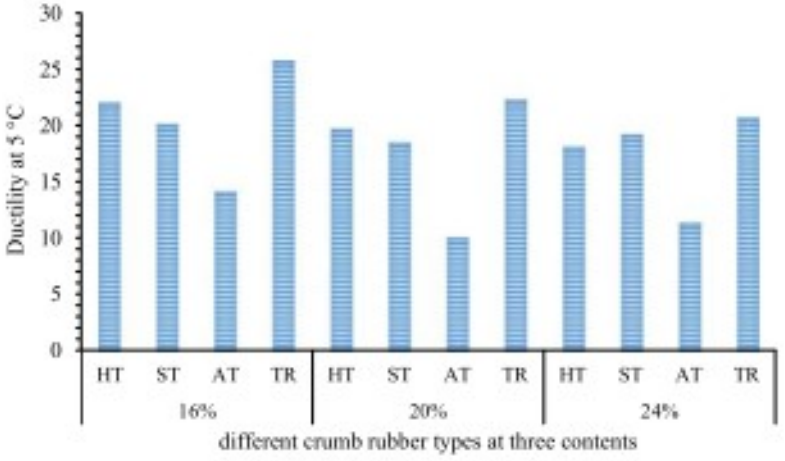


Figure 13.2.8 Performance characteristics of different CRM asphalts at three contents. *AT*, agriculture tire; *HT*, heavy truck; *ST*, small truck; *TR*, tread rubber. Revised from S. Liu, W. Cao, J. Fang, S. Shang, Variance analysis and performance evaluation of different crumb rubber modified (CRM) asphalt, Constr. Build. Mater. 23(7) (2009) 2701–2708.

Variance analysis illustrated that the content is the most important factor influencing the low-temperature property of CRMB, followed by crumb rubber type and particle size [102]. TR–crumb rubber and HT–crumb rubber have a better modified effect, while the low-temperature ductility of AT–CRM asphalt is the worst so it is not recommended to be used in cold regions [102]. However, Bahia and Davis found that the crumb rubber type has little effect on the stiffness and m-value of CRMB [51].

Crumb rubber, made by shredding scrap tire, may be classified into four groups: superfine (100–200 mesh or 150–75 μm); fine (40–80 mesh or 425–180 μm); medium size (10–30 mesh or 2 mm–600 μm); and coarse (9.5 mm and 6.3 mm) [103]. The impact of crumb rubber particle size in determining the low-temperature performance of CRM binder cannot be ignored [104]. Wang et al. pointed out that fine crumb rubber may reduce the creep stiffness of CRMB at a low temperature through testing of two different fine rubber types and same gradations [5]. CRMB showed better low-temperature properties, elasticity, and adhesion with the decreased crumb rubber particle size [84]. Another study demonstrated that adding coarser rubber into binder with an increased content of the crumb rubber and high-shear modules lessens the creep stiffness, which may result in favorable thermal cracking resistance [105]. A similar conclusion was obtained by Cao and Bai [91]. However, some researchers have obtained different results and conclusions. Sebaaly et al. and Gopal et al. report no significant impacts of crumb rubber size on the low-temperature properties of asphalts [102,104,106].

13.2.3.2.3 Crumb rubber production process

There are two main methods in producing crumb rubber: ambient and cryogenic grinding [107]. The microstructure of the crumb rubber surface is different based on the manufacturing method. The microstructure of crumb rubber particles produced through cryogenic and ambient method is shown in Fig. 13.2.9 [71]. Crumb rubber particles manufactured by ambient grinding method have a porous and rough appearance, while rubber particles produced by the cryogenic process have a smooth, cracked, angular surface structure [108]. The surface area of crumb rubber produced by the ambient grinding method is about two times higher than by the cryogenic method [105]. Larger surface area may lead to faster absorption of lightweight components in the binder, so that the crumb rubber fully swells [47].

Some studies suggest that CRMB produced by ambient crumb rubber have larger angle, higher complex modulus, and higher elasticity [71,105,109]. In general, crumb rubber processed by the ambient method provided a more excellent property than its cryogenic counterpart [76]. In addition, Lee et al. found that the stiffness value of CRM binder produced by ambient crumb rubber is lower than that with cryogenic crumb rubber. It was concluded that CRM binders containing ambient crumb rubber provide better low-temperature anticracking performance than those produced by cryogenic crumb rubber [71]. Additionally, binders with ambient CRM have the lowest temperature among the modified binders in Fig. 13.2.10. It may be that the binder with ambient CRM has better thermal cracking resistance performance than that with cryogenic CRM [110].

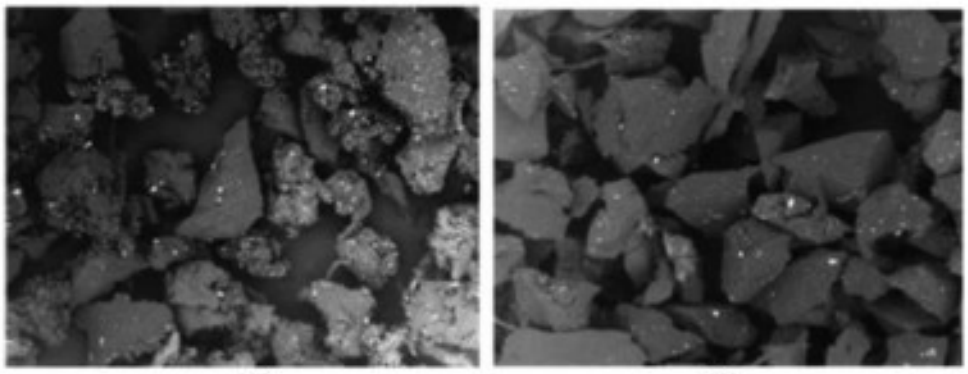


Figure 13.2.9 SEM micrographs at 120 × magnification of CRM [71]. (A) ambient CRM (40 mesh) and (B) cryogenic CRM (40 mesh).

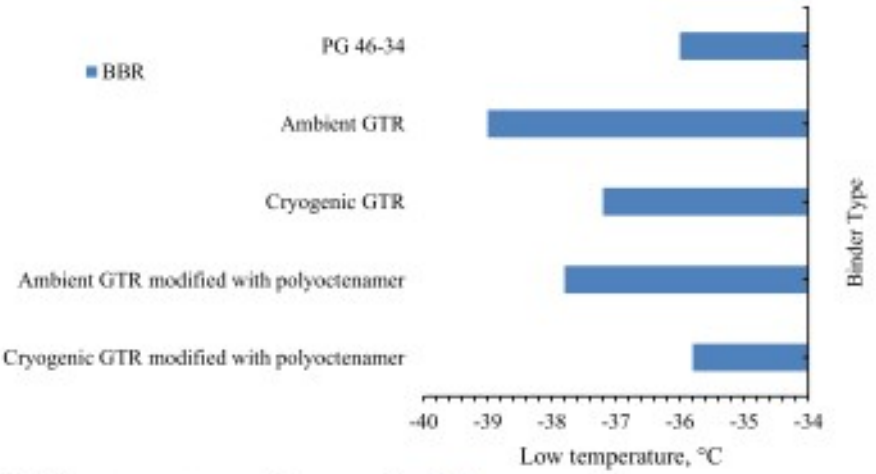


Figure 13.2.10 BBR low-temperature continuous grading [110].

13.2.3.2.4 Elasticity of rubber type

The primary nature of rubber is its high elasticity, which permits it to withstand large deformation when load is applied and instantaneously recover with removal of the load. Rubber is a kind of polymer, also known as an elastomer, and thus the molecular structure of rubber determines its elastic properties [111]. Similar to asphalt, rubber is a thermoplastic viscoelastic material and its deformation response under load is affected by two factors: rate of strain and temperature. Compared with asphalt, to a great extent, the broader scope of elastic behavior of rubber depends on the cross-linking of the long molecules. Rubber is also more ductile than asphalt at high load rates and low-temperature conditions [112]. Due to the complex cross-linking construction of rubber and the vulcanization during rubber production, crumb rubber is difficult to dissolve and reactwit h the asphalt. The solid crumb rubber particles are in contact with each other through the ambient gel membrane to form a sturdy elastic network in a typical asphalt. The low-temperature anticracking of asphalt rubber is improved through the elastic network of crumb rubber [88]. This elasticity may allow the pavement to become more flexible and improve the low-temperature anticracking ability of the pavement [113].

13.2.3.3 Mixing process

The inherent temperature susceptibility of the binder decreases with the addition of crumb rubber. The improvement

of low-temperature performance of CRM binders is generally dependent on the interaction between the binder and crumb rubber [9,45,51,74,114]. Mixing temperature, mixing time, and mixing rate are the factors that affect the swelling rate and depolymerization rate of crumb rubber [55,93,105,115,116]. Table 13.2.3 summarizes the mixing parameters used by some researchers.

Aflaki et al. [119] researched the impact of mixing conditions on the modification efficiency of the CRM. Compared with the low-shear mixing, they observed that the effect of the low-temperature performance improvement was more affected by high-shear mixing. High-shear blending effectively increased the low-temperature properties of crumb rubber-modified binder [119]. The main drawback of incorporating crumb rubber in bituminous mixes is its instability. Binder and crumb rubber may be better evenly mixed through high-shear mixing [120]. The reaction process itself is made of the change of ingredients between binder and crumb rubber [121]. The effect of the mixing time and mixing temperature on the performance of

Table 13.2.3 Mixing parameters used by some researchers.

Source	Binder PG	Mixing temperature (°C)	Mixing time (min)	Crumb rubber (%)	Creep stiffness (MPa)	m-value
Kim et al. [72]	64–22	170	30	10	194 (−12°C)	–
Xin et al. [69]	64–22	175	45	18	66.1 (−12°C)	0.3559 (−12°C)
Yadollahi et al. [70]	58–22	175	60	10	157 (−18°C)	0.364 (−18°C)
Wang et al. [5]	64–22	175	45	15	193 (−18°C)	–
Lee et al. [71]	64–22	177	30	15	108 (−12°C)	0.325 (−12°C)
Kim et al. [72]	64–22	170	30	10	167 (−12°C)	–
Amir et al. [117]	58–28	190	60	10	141 (−18°C)	0.324 (−18°C)
Xin et al. [118]	64–22	175	60	18	122 (−12°C)	0.304 (−12°C)
Ma et al. [79]	58–22	180–190	30	20	131 (−12°C)	0.352 (−12°C)

CRMB indicated that both a higher mixing temperature and a longer mixing time contributed to the improvement of low-temperature properties of rubberized asphalt [115]. The low-temperature performance of CRMB may be affected by the time and temperature used to promote the integration of components between the binder and CRM.

The effect of mixing time on the properties of CRMB is not significant when the mixing time increases from 30 to 60 min, whereas the increase of mixing temperature results in the increase in complex shear modulus, elastic recovery, and ductility [71,92,93,115,122–124]. On the other hand, some studies also showed that the reaction time has little effect on the physical properties of CRMB and a minor impact on the low-temperature performance of CRMB [93,105,108,120,125]. With the decrease of mixing temperature, the failure strain shows a clear downward trend as can be seen in Fig. 13.2.11. It is considered that the low mixing temperature has a negative impact on the low-temperature anticracking of rubber asphalt mixtures [79].

The properties of CRMB are also affected by the mixer type. The high-shear blending process does increase the low-temperature performance of CRMB [119]. A study by Abdelaziz investigated the effect of a high-shear mixer and an ordinary propeller type mixer on the low-temperature properties of CRMB [126]. The results show that the CRM binder manufactured by the high-shear mixer has slightly superior performance when compared with that manufactured by the propeller type mixer [127]. On the other hand, Celauro et al. [121] pointed out that crumb rubber-modified asphalt with a good performance may be produced by a low-shear blending as long as the proper crumb rubber and virgin binder are selected.

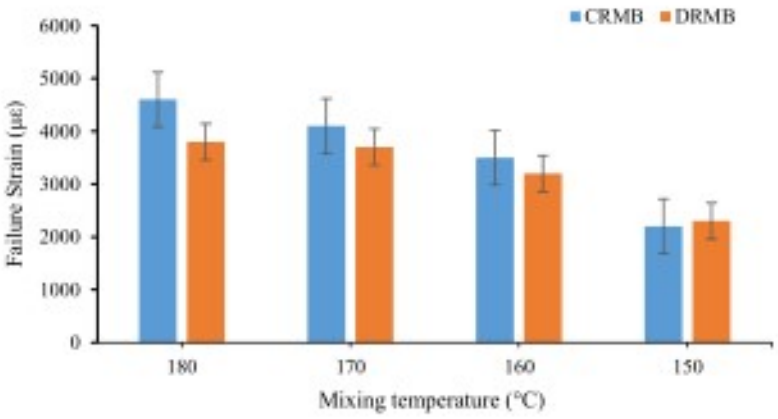


Figure 13.2.11 Low-temperature BBR test results for different rubber-modified mixtures. *DRMB*, desulfurized rubber-modified binder; *CRMB*, crumb rubber-modified binder [79].

13.2.4 Field applications

The abovementioned research projects prove that the utilization of CRM in cold environments is feasible and the performance of rubberized mixtures are better than conventional mixtures. However, in many cases the findings in the laboratory do not translate to successful projects in the field. The following is a brief summary of some of the projects complete all over the world, mostly in colder environments, showcasing that the rubberized asphalt mixtures have been successfully implemented in the field for many decades.

Ontario, Canada: In a research study, the performance of rubberized asphalt pavements in Ontario, Canada was evaluated. The temperature in most of the province is often below 0°C day and night and can drop below −30°C. Canada has approximately 900,000 km of roads, which, like many other countries, are a key element in the success of the country's economy; therefore the importance of maintaining the roads to their highest standards. One of the methods used to build quality pavements is the implementation of rubberized asphalt mixtures. Many factors affect the performance of the pavement including the environment, materials used to construct the road, and traffic. There are many distresses cause by these factors that affect the performance of the pavement including: (1) thermal cracking, (2) fatigue cracking, (3) rutting, and (4) roughness or smoothness of the road as is measured by the International Roughness Index (IRI). For the rubberized projects constructed around Canada, these factors were monitored and measured.

Several sections of pavements around the province were constructed with CRMB. In addition, several control sections, constructed with standard binder, were also observed and evaluated [128]. These control sections were placed alongside CRMB mixtures. After several years of use, the conclusions, from visual observations and laboratory testing, were as follows:

1. The CRMB mixes had better ride quality according to IRI measurements and values.
2. The CRMB mixes show fewer distresses (e.g., thermal cracking) compared to the control sections.
3. Several tests were conducted in the laboratory with the field mixtures to determine and predict the performance of the CRMB mixtures. One of the tests utilized during this research work was the thermal stress restrained specimen test (TSRST). During this test, both ends of a prepared beam of the material is fixed and the sample is subjected to a

constant drop in temperature (10°C per hour) introducing stress in the beam. The results indicated that the CRMB mixtures were able to withstand an average of approximately 10°C lower temperatures than the conventional mixtures. In addition, for the CRMB mixtures, the stress at failure was lower indicating that the CRMB mixtures are able to withstand colder temperatures better than the conventional mixes.

4. Overall, the performance of the CRMB mixtures have been better than the control sections considering all factors (e.g., environment, traffic, etc.).

Flagstaff, Arizona, United States: For many decades, the Arizona Department of Transportation (ADOT) has been using rubberized asphalt mixtures very successfully. While most people think of Arizona as a warm state, there are regions in Arizona that get very cold during winter months. For example, Flagstaff gets 53 cm (21 in.) in rain and over 2 m (82 in.) of snow each year. In addition, the 10-year average temperature (2010–19) shows that the low for October, November, December, January, February, and March were 0, −5, −8, −8, −7, and −4°C, respectively. Several kilometers of rubberized asphalt pavements have been used in the Flagstaff area for many years.

For example, in 1990, the ADOT constructed a large-scale asphalt–rubber (AR) project in Flagstaff. This project was located on a very heavily traveled Interstate 40 pavement with several thousands of cars and trucks traveling every day. The project included a relatively thin overlay with an AR mix in order to reduce the reflective cracking. AR is a mixture of 80% asphalt binder and 20% CRM. This mixture is also commonly referred to, in many parts of the world, as the asphalt rubber wet process or McDonald process.

The project was constructed over a badly cracked concrete pavement that was in need of reconstruction [129]. Overall, the ADOT reported that the AR overlay project performed very well and beyond original expectations. After 9 years of service, the overlay was still virtually crack free, with good ride (good skid resistance), with virtually no rutting and no maintenance required. The ADOT reported that the use of rubberized mixture on this project resulted in savings of about $18 million in construction cost and 4 years or less construction time. Based on the results of this project and others, the ADOT has paved several thousands of km of AR pavements, 4.2 million tons of AR mix, since 1990. Most of these projects have lasted for many more years than the conventional mixtures.

Babbitt, Minnesota, United States: Five rubberized asphalt mixtures plus two control test sections were placed in Babbitt, Minnesota, in the fall of 1993. In this study, researchers investigated the pretreated CRM rubberized asphalt mixture performance in the field. This location's cold season lasts for 3 months, from late November to late February, with an average daily high temperature below −2°C (29°F) with the coldest day of the year in mid-January, with an average low of −20°C (−3°F).

For this project, crumb rubber, obtained from processing scrap passenger tires, was pretreated with a low-viscosity petroleum-based product and then used as an aggregate replacement in asphalt mixtures [130]. Many testing procedures were used to determine the properties of the mix including: aggregate gradation, mix design, temperature susceptibility, moisture sensitivity, low-temperature behavior, and permanent deformation. Several variables in the rubberized sections were investigated, which included pretreated and untreated crumb rubber and CRM mixtures in just the wear course or throughout the 150-mm (6-in.) pavement section. Laboratory results indicated that there was little difference in the temperature susceptibility between the mix design and behind-the-paver mixtures. Although the mix design samples indicated some increase in the moisture sensitivity of the CRM mixtures, no difference was seen in the behind-the-paver materials. There was some indication that the CRM mixtures may exhibit a greater ability to dissipate thermal stresses through a better ability to strain at cold temperatures. Some slight-to-moderate improvements were seen in both moisture sensitivity and low-temperature behavior when the crumb rubber was pretreated. Falling weight deflectometer results were used to backcalculate the layer moduli for all of the test sections. The results showed no difference in any of the layer moduli; these results agreed with the laboratory resilient moduli results. After two winters, all test sections were performing equally well. Anticipated damage by snowplows to the coarser gradation used with the CRM mixtures did not occur.

New Jersey, United States: The New Jersey DOT (NJDOT) has paved a section of Route 95 with AR in order to reduce noise levels in neighboring communities. The low temperature of this part of the state sometimes reaches up to −1°C. Approximately 365 metric tons of CRM were used to produce the paving mix. NJDOT had previously conducted several laboratory tests, which showed that the rubberized mixtures are extremely durable, providing an excellent skid resistance condition, as well as good ride quality and improved visibility. In addition, they

concluded that the AR costs less when dealing with maintenance issues compared to traditional pavements. The officials concluded that the taxpayers save money since it is much cheaper to construct quiet pavements than to construct noise walls. This project was part of a $19 million New Jersey resurfacing project. Several DOT engineers believe the new pavement will extend the life of this specific roadway by at least 15 years.

Washington, United States: In another project, the Washington DOT (WSDOT) initiated years ago testing quiet pavement sections on I-5, I-405, and State Route 520 in order to reduce traffic noise. The challenge for the WSDOT engineers were designing pavements that provide durable, smooth, and safe surfaces while simultaneously reducing noise. The performance of these mixtures has been very satisfactory, even though the low temperatures for this part of the state reaches to −5°C.

Alaska, United States: There have been several rubberized projects constructed in Alaska. One of the projects, constructed in 1985, was located in Anchorage with a low average daily winter temperature of −15°C. The engineers, after 22 years of service, concluded that even though the rubberized mixture was more expensive, it had performed very well for all those years. The DOT conducted a cost analysis and determined the following cost per ton for each mixture:

- Unmodified mix: $65
- Polymer modified: $76
- Rubberized Asphalt: $106

The estimated life for each mix was 5, 8, and 20 years, respectively. The initial cost of the rubberized asphalt was estimated to be approximately 65% higher than the unmodified mixture. However, the estimated life expectancy was 300% more for the rubberized asphalt pavement compared to the standard pavement mixture. The officials also calculated the cost of a 10,000-ton mix and reported that the life-cycle cost of the unmodified mix was $340,000, $185,000, and $138,000 per year, respectively, making the rubberized asphalt mix the most cost-effective option.

Europe: In Europe, there have been many rubberized projects constructed in many countries including France, Spain, Italy, Sweden, Poland, Portugal, Austria, Germany, and many more. For instance, in France, after 10 years of rubberized asphalt experiments, porous asphalt concrete mixes were used in solving the problems of aquaplaning, water projection, noise reduction, and better visibility during night driving. After several studies, the conclusions were that porous mixtures containing rubberized asphalt resulted in durable, constant draining

properties, performing very well under heavy truck traffic (fatigue and rutting resistance) and in bad weather. In the 1990s, Colas, one of the Europe's largest construction companies, developed "noise-reducing" mixes to control traffic noise. The attenuation of noise emissions can be as great as 7 decibels.

In 2006, the Swedish Road Administration (currently Swedish Transport Administration) initiated the Rubber Development Project to evaluate the potential implementation of AR on Swedish roads. The government officials decided to use the "wet process" for the construction process. Since then, several different applications of AR have been tested and evaluated in Sweden. For example, in 2011, a different approach to AR was tested in the north of Sweden, using a dense graded asphalt mix containing softer asphalt binder due to its flexibility and aging properties. In these parts of Sweden, the main issues for pavements are not heavy traffic as much as ground movements such as frost heaving and special attention must be paid to aging properties rather than load and wear resistance. There were several reasons the Agency decided to implement these rubberized asphalt projects around the country including:

- Reducing the annual life-cycle costs, due to expected prolonged life of pavements
- Decreasing tire noise and emission of particles
- Improving traffic safety due to higher friction between wet road surface and vehicle tires

In general, officials have reported that overall experience from using rubberized asphalt mixtures has been positive so far. Test results and the visual appearance of the pavement in Storuman and Stensele indicate that the project has been successful in achieving the expectations set forth by the transport experts. The officials believe that due to the higher binder content and the higher flexibility of the AR, it is most likely that the dense-graded AR will have a much longer life than the standard dense-graded mixtures. This translates to savings to taxpayers and various agencies.

There have been unique civil engineering projects, unrelated to pavements, that have used rubberized asphalt materials for various purposes. For instance, engineers in the Netherlands demonstrated that mixtures of asphalt and aggregate may be utilized for slope protection of coastal embankments subjected to heavy wave action. Three asphalt/aggregate materials formulations were evaluated: sand–asphalt, stone–mastic, and stone–asphalt–rubber. They evaluated several properties including fatigue life, thermal cracking, and long-term creep. In addition,

various finite-element analyses on sand–asphalt lining systems were carried out to determine their structural behavior under wave loading and their resistance to low-temperature cracking and to creep deformation at high temperatures. The officials concluded that the use of stone–asphalt–rubber mix is a suitable option for construction of these manmade islands which will freeze-thaw cycles and of water action associated with the offshore arctic environment. This is an indication that, with proper testing and design program, the utilization of crumb rubber in paving or other related applications in cold climates is suitable.

13.2.5 Conclusions

Crumb rubber modification of binder has been proven to enhance the low-temperature properties of a typical asphalt binder. The factors that have effects on the low temperature of CRMB have been widely studied. In order to obtain a superior CRMB in terms of low-temperature properties, it is required to choose reasonable and accurate production variables. There are many test methods available to evaluate the low-temperature performance of CRMB and CRM asphalt mixtures, and each method has its advantages and disadvantages. Chemical modification of CRMB and physical treatment of CRMB have been studied. Based on these studies, the following conclusions can be made:

- Improvement in crack resistance of the binder involved CRM because of crack blunting and crack pining function of these rubber particles, which improved the toughness of the asphalt binder.
- The CRM binders produced from low PG grade binders with more light components possessed favorable low-temperature anticracking properties.
- The rubber content played a very significant role in improving the low-temperature performance of rubberized binders. Fine crumb rubber helped reduce the creep stiffness of CRMB mixtures.
- The low-temperature properties of CRMB were affected by mixing temperature, mixing time, and mixing rate, and the production parameters should be reasonably selected.
- The BBR test is the most frequently used method to evaluate the low-temperature properties of CRMB. The ductility test is not suitable for evaluating the low-temperature properties of rubber-modified binder.

- The low-temperature anticracking properties of CRMB can be improved by chemical modifications and physical treatment methods to some extent.
- Many field projects all over the world have demonstrated that the rubberized mixtures, in many shapes and forms, may be successfully implemented in very cold and freezing environments. In addition, in many cases the life-cycle cost of the rubberized mixtures are more cost effective than the conventional mixtures.

References

[1] S. Pirmohammad, M.R. Ayatollahi, Asphalt concrete resistance against fracture at low temperatures under different modes of loading, Cold Reg. Sci. Technol. 110 (2015) 149–159.

[2] S. Im, Y.-R. Kim, H. Ban, Rate- and temperature-dependent fracture characteristics of asphaltic paving mixtures, J. Test. Eval. 41 (2) (2013) 257–268.

[3] L.A. Scofield, The history, development, and performance of asphalt rubber at adot. Special Report. Final Report, Binders (1989) AZ-SP-8902.

[4] C. Thodesen, F. Xiao, S.N. Amirkhanian, Modeling viscosity behavior of crumb rubber modified binders, Constr. Build. Mater. 23 (9) (2009) 3053–3062.

[5] H. Wang, Z. You, J. MillS–Beale, P. Hao, Laboratory evaluation on high temperature viscosity and low temperature stiffness of asphalt binder with high percent scrap tire rubber, Constr. Build. Mater. 26 (1) (2012) 583–590.

[6] N.K. Lee, G.R. Morrisson, S.A.M. Hesp, Low temperature fracture of polyethylene-modified asphalt binders and asphalt concrete mixes, 64 (1995).

[7] A.M.S. Hesp, T. Terlouw, W.C. Vonk, Low temperature performance of SBS-modified asphalt mixes, 69 (1999).

[8] A.F. Stock, W. Arand, Low temperature cracking in polymer modified binders, J. Assoc. Asph. Paving Technol. 62 (1993) 23–53.

[9] Heitzman. State of the practice: design and construction of asphalt paving materials with crumb-rubber modifier. Final report, Asphalt Rubber, 47(2) (1992) 171–174.

[10] J. Peralta, H.M.R.D. Silva, A.V. Machado, J. Pais, P.A.A. Pereira, J.B. Sousa, Changes in rubber due to its interaction with bitumen when producing asphalt rubber, Road Mater. Pavement Des. 11 (3) (2010) 1009–1031.

[11] M.R. Ibrahim, H.Y. Katman, M.R. Karim, S. Koting, N.S. Mashaan, A review on the effect of crumb rubber addition to the rheology of crumb rubber modified bitumen, Adv. Mater. Sci. Eng. 2013 (2013) 1–8.

[12] J.W.H. Oliver, Optimising the improvements obtained by the digestion of comminuted scrap rubbers in paving asphalt, Asphalt Paving Technology: Association of Asphalt Paving Technologists-Proceedings of the Technical Sessions, 51 (1982) 169–188.

[13] S.S. Kim, Development of an Asphalt Binder Cracking Device, Final Report for Highway IDEA Project 99, 2007.

[14] W.J. Gaw, Measurement and Prediction of Asphalt Stiffnesses and Their Use in Developing Specifications to Control Low-Temperature Pavement Transverse Cracking, American Society for Testing and Materials, 1977, pp. 57–67.

[15] H.J. Fromm, W.A. Phang, Temperature-Susceptibility Control in Asphalt-Cement Specifications, Highway Research Board, 1971.
[16] P.S. Kandhal, Evalution of low-temperature pavement cracking on elk county research project, Transp. Res. Rec. 777 (1980) 39–50.
[17] A.B.O.A. Standards, Annual Book of ASTM Standards, ASTM, 1970.
[18] W.S. Mogawer, A.J. Austerman, S.-S. Kim, Effect of binder type, mastic, and aggregate type on the low-temperature characteristics of modified hot mix asphalt, J. Test. Eval. 41 (6) (2013) 20120181.
[19] D. Jung, T.S. Vinson, Low temperature cracking resistance of asphalt concrete mixtures, J. Assoc. Asph. Paving Technol. 62 (1993).
[20] N.M. Jackson, T. Vinson, Analysis of thermal fatigue distress of asphalt concrete pavements, Transp. Res. Rec. J. Transp. Res. Board 1545 (1) (1996) 43–49.
[21] H. Zubeck, T. Vinson, Prediction of low-temperature cracking of asphalt concrete mixtures with thermal stress restrained specimen test results, Transp. Res. Rec. J. Transp. Res. Board 1545 (1) (1996) 50–58.
[22] H. Zubeck, H. Zeng, T. Vinson, V. Janoo, Field validation of thermal stress restrained specimen test: six case histories, Transp. Res. Rec. J. Transp. Res. Board 1545 (1) (1996) 67–74.
[23] T.S. Vinson, V.C. Janoo, R. Haas, Summary Report on Low Temperature and Thermal Fatigue Cracking, Transportation Research Board, 1989. SHRP-A-306.
[24] W.G. Buttlar, R. Roque, N. Kim, Accurate asphalt mixture tensile strength, Materials for the New Millennium, 2014.
[25] D.W. Christensen, R.F. Bonaquist, Evaluation of indirect tensile test (IDT) procedures for low-temperature performance of hot mix asphalt, Nchrp Report, 2004.
[26] F. Moavenzadeh, Asphalt fracture, Assoc Asphalt Paving Technol Proc, 36 (1967) 51–72.
[27] Z. Zhang, R. Roque, B. Birgisson, B. Sangpetngam, Identification and verification of a suitable crack growth law, J. Assoc. Asph. Paving Technol. 70 (44) (2001) 1108–1114.
[28] B. Birgisson, R. Roque, G. Page, Performance-based fracture criterion for evaluation of moisture susceptibility in hot-mix asphalt, Transp. Res. Rec. J. Transp. Res. Board 1891 (1) (2004).
[29] M.P. Wagnoner, W.G. Buttlar, G.H. Paulino, Disk-shaped compact tension test for asphalt concrete fracture, Exp. Mech. 45 (3) (2005) 270–277.
[30] M.P. Wagoner, W.G. Buttlar, G.H. Paulino, P. Blankenship, R. Roque, W. Rongzong, et al., Laboratory testing suite for characterization of asphalt concrete mixtures obtained from field cores, Asph. Paving Technol. Assoc. Asph. Paving Technol. Proc. Tech. Sess. 75 (2006) 815–852.
[31] X. Li, M. Marasteanu, Evaluation of the low temperature fracture resistance of asphalt mixtures using the semi circular bend test, Asph. Paving Technol.: Assoc. Asph. Paving Technol. Proc. Tech. Sess. 73 (2004) 401–426.
[32] X. Li, M.O. Marasteanu, Investigation of low temperature cracking in asphalt mixtures by acoustic emission, Road Mater. Pavement Des. 7 (7) (2006) 491–512.
[33] U.S.D.O. Transportation, Crumb Rubber Modifier Workshop Notes: Design Procedures and Construction Practices, 1993, FHWA-SA-93-011.
[34] Y. Huang, R.N. Bird, O. Heidrich, A review of the use of recycled solid waste materials in asphalt pavements, Resour. Conserv. Recycl. 52 (1) (2007) 58–73.
[35] F.R. Eirich, Science and Technology of Rubber, Academic Press, 1978.

[36] M.M. Hattingh, The fractionation of asphalt, Association of Asphalt Paving Technologists Proceedings, 53, 1984, pp. 197–215.
[37] G.D. Airey, Rheological properties of styrene butadiene styrene polymer modified road bitumens, Fuel 82 (14) (2003) 1709–1719.
[38] I. Gawel, R. Stepkowski, F. Czechowski, Molecular interactions between rubber and asphalt, Ind. Eng. Chem. Res. 45 (9) (2006) 3044–3049.
[39] A. Ghavibazoo, M. Abdelrahman, Effect of crumb rubber dissolution on low-temperature performance and aging of asphalt-rubber binder, Transp. Res. Rec. J. Transp. Res. Board 2445 (-1) (2014) 47–55.
[40] E.M. Dannenberg, Bound rubber and carbon black reinforcement, Rubber Chem. Technol. 59 (3) (1986) 512–524.
[41] S.S. Choi, C.E. Son, Influence of silane coupling agent on bound rubber formation of NR/SBR blend compounds reinforced with carbon black, Polym. Bull. (2016) 1–12.
[42] B.V. Kök, M. Yilmaz, A. Geçkil, Evaluation of low-temperature and elastic properties of crumb rubber–and SBS–modified bitumen and mixtures, J. Mater. Civ. Eng. 25 (2) (2013) 257–265.
[43] B.J. Putman, S.N. Amirkhanian, Characterization of the interaction effect of crumb rubber modified binders using HP-GPC, J. Mater. Civ. Eng. 22 (2) (2010) 153–159.
[44] T.C. Billiter, J.S. Chun, R.R. Davison, C.J. Glover, J.A. Bullin, Investigation of the curing variables of asphalt-rubber binder, Pet. Sci. Technol. 15 (5–6) (2007) 445–469.
[45] L. Zanzotto, G. Kennepohl, Development of rubber and asphalt binders by depolymerization and devulcanization of scrap tires in asphalt, Transp. Res. Rec. J. Transp. Res. Board 1530 (1) (1996) 51–58.
[46] T. Billiter, R. Davison, C. Glover, J. Bullin, Production of asphalt-rubber binders by high-cure conditions, Transp. Res. Rec. 1 (1997) 50–56.
[47] E.L. Green, W.J. Tolonen, The chemical and physical properties of asphalt-rubber mixtures. Part I. Basic material behavior, Roads (1977). FHWA-AZ-HPR-14–162.
[48] D.J. Buckley, M. Berger, The swelling of polymer systems in solvents. II. Mathematics of diffusion, J. Polym. Sci. 56 (163) (1962) 175–188.
[49] J.E. Tauer, R.E. Robertson, J.E. Tauer, R.E. Robertson, Effects of carboxylic acids on the rheological properties of crumb rubber modified asphalt, Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem. 41 (4) (1996).
[50] T.C. Billiter, R.R. Davison, C.J. Glover, J.A. Bullin, Physical properties of asphalt-rubber binder, Pet. Sci. Technol. 15 (3–4) (2007) 205–236.
[51] H.U. Bahia, R. Davies, Effect of crumb rubber modifiers (CRM) on performance-related properties of asphalt binders, Asph. Paving Technol. 63 (1994) (1994) 414–449.
[52] F.J. López-Moro, M.C. Moro, F. Hernández-Olivares, B. Witoszek-Schultz, M. Alonso-Fernández, Microscopic analysis of the interaction between crumb rubber and bitumen in asphalt mixtures using the dry process, Constr. Build. Mater. 48 (2013) 691–699.
[53] R.E. Robertson, J.F. Branthaver, P.M. Harnsberger, J.C. Petersen, S.M. Dorrence, J.F. Mckay, et al., Fundamental properties of asphalts and modified asphalts, volume II: final report, new methods, Transp. Res. Rec. J. Transp. Res. Board. (2001). FHWA-RD-99–212.
[54] L. Reich, S.S. Stivala, Elements of Polymer Degradation, McGraw-Hill, NYC, 1971.

[55] M. Abdelrahman, S. Carpenter, Mechanism of interaction of asphalt cement with crumb rubber modifier, Transp. Res. Rec. 1661 (1) (1999) 106–113.
[56] A. Ghavibazoo, M. Abdelrahman, Composition analysis of crumb rubber during interaction with asphalt and effect on properties of binder, Int. J. Pavement Eng. 14 (5) (2013) 517–530.
[57] S. Im, Y.R. Kim, H. Ban, Rate- and temperature-dependent fracture characteristics of asphaltic paving mixtures, J. Test. Eval. 41 (2) (2013) 257–268.
[58] P. Kumar, S. Chandra, S. Bose, Strength characteristics of polymer modified mixes, Int. J. Pavement Eng. 7 (7) (2006) 63–71.
[59] X. Lu, U. Isacsson, J. Ekblad, Influence of polymer modification on low temperature behaviour of bituminous binders and mixtures, Mater. Struct. 36 (10) (2003) 435–441.
[60] E.M. Nejad, P. Aghajani, A. Modarres, H. Firoozifar, Investigating the properties of crumb rubber modified bitumen using classic and SHRP testing methods, Constr. Build. Mater. 26 (1) (2012) 481–489.
[61] S. Biro, B. Fazekas, Asphalt rubber versus other modified bitumens, Road Mater. Pavements Des. (2005) 1–17.
[62] J. Shen, S. Amirkhanian, S.J. Lee, B. Putman, Recycling of laboratory-prepared RAP mixtures containing crumb rubber modified binders in HMA, Transp. Res. Rec. J. Transp. Res. Board. 1962 (1) (2006) 71–78.
[63] S.J. Lee, H. Kim, S.N. Amirkhanian, K.W. Kim, Relation of mechanical properties of recycled aged CRM mixtures with binder molecular size distribution, Constr. Build. Mater. 23 (2) (2009) 997–1004.
[64] R. Dong, J. Li, S. Wang, Laboratory evaluation of pre-devulcanized crumb rubber–modified asphalt as a binder in hot-mix asphalt, J. Mater. Civ. Eng. 23 (8) (2011) 1138–1144.
[65] N. Segre, C. Ostertag, P.J.M. Monteiro, Effect of tire rubber particles on crack propagation in cement paste, Mater. Res. 9 (3) (2006) 311–320.
[66] G.R. Morrison, S.A.M. Hesp, A new look at rubber-modified asphalt binders, J. Mater. Sci. 30 (10) (1995) 2584–2590.
[67] J.C.T. Hui, G.R. Morrison, S.A.M. Hesp, Improved low-temperature fracture performance for rubber-modified asphalt binders, Transportation Research Record 1436, TRB, National Research Council, Washington, D.C., 1994, pp. 83–87.
[68] U. Isacsson, H. Zeng, Cracking of asphalt at low temperature as related to bitumen rheology, J. Mater. Sci. 33 (8) (1998) 2165–2170.
[69] X. Yu, Z. Leng, Y. Wang, S. Lin, Characterization of the effect of foaming water content on the performance of foamed crumb rubber modified asphalt, Constr. Build. Mater. 67 (2014) 279–284.
[70] G. Yadollahi, H. Sabbagh Mollahosseini, Improving the performance of crumb rubber bitumen by means of poly phosphoric acid (PPA) and Vestenamer additives, Constr. Build. Mater. 25 (7) (2011) 3108–3116.
[71] S.J. Lee, C.K. Akisetty, S.N. Amirkhanian, The effect of crumb rubber modifier (CRM) on the performance properties of rubberized binders in HMA pavements, Constr. Build. Mater. 22 (7) (2008) 1368–1376.
[72] H. Kim, K.-D. Jeong, M.S. Lee, S.-J. Lee, Performance properties of CRM binders with wax warm additives, Constr. Build. Mater. 66 (5) (2014) 356–360.
[73] L.E.M. Leite, B.G. Soares, Interaction of asphalt with ground tire rubber, Pet. Sci. Technol. 17 (17) (1999) 1071–1088.

[74] G.D. Airey, M.M. Rahman, A.C. Collop, Absorption of bitumen into crumb rubber using the basket drainage method, Int. J. Pavement Eng. 4 (2) (2003) 105–119.
[75] M.R.M. Aliha, H. Fazaeli, S. Aghajani, F. Moghadas Nejad, Effect of temperature and air void on mixed mode fracture toughness of modified asphalt mixtures, Constr. Build. Mater. 95 (2015) 545–555.
[76] P. Cong, P. Xun, M. Xing, S. Chen, Investigation of asphalt binder containing various crumb rubbers and asphalts, Constr. Build. Mater. 40 (7) (2013) 632–641.
[77] M.N. Partl, M. Ould-Henia, A.G. Dumont, Effect of base bitumen composition on asphalt rubber binder properties, International Symposium on Asphalt Pavements and Environment (ISAP), Zürich, 2008, pp. 21–30.
[78] S.-J. Lee, C.K. Akisetty, S.N. Amirkhanian, Recycling of laboratory-prepared long-term aged binders containing crumb rubber modifier, Constr. Build. Mater. 22 (9) (2008) 1906–1913.
[79] T. Ma, Y. Zhao, X. Huang, Y. Zhang, Characteristics of desulfurized rubber asphalt and mixture, KSCE J. Civ. Eng. 20 (4) (2015) 1347–1355.
[80] M. Xu, J. Liu, W. Li, W. Duan, Novel method to prepare activated crumb rubber used for synthesis of activated crumb rubber modified asphalt, J. Mater. Civ. Eng. 27 (5) (2015) 04014173.
[81] K.M. Shatanawi, S. Biro, A. Geiger, S.N. Amirkhanian, Effects of furfural activated crumb rubber on the properties of rubberized asphalt, Constr. Build. Mater. 28 (1) (2012) 96–103.
[82] A.B. Sabbagh, A.J. Lesser, Effect of particle morphology on the emulsion stability and mechanical performance of polyolefin modified asphalts, Polym. Eng. Sci. 38 (5) (1998) 707–715.
[83] F.J. Navarro, P. Partal, A.F. Martinezboza, C. Gallegos, Influence of crumb rubber concentration on the rheological behavior of a crumb rubber modified bitumen, Energy Fuels 19 (2005) 1984–1990.
[84] F. Zhang, C. Hu, The research for crumb rubber/waste plastic compound modified asphalt, J. Therm. Anal. Calorim. 124 (2) (2015) 729–741.
[85] J. Yin, S. Wang, F. Lv, Improving the short-term aging resistance of asphalt by addition of crumb rubber radiated by microwave and impregnated in epoxidized soybean oil, Constr. Build. Mater. 49 (2013) 712–719.
[86] P. Kriz, J. Stastna, L. Zanzotto, Glass transition and phase stability in asphalt binders, Road Mater. Pavement Des. 9 (Suppl. 1) (2011) 37–65.
[87] B. Brule, J.P. Planche, G. King, P. Claudy, J.M. Letoffe, Relationships between characterization of asphalt cements by differential scanning calorimetry and their physical properties, Division of Petroleum Chemistry, 37, American Chemical Society, 1990, pp. 330–337 [Preprints].
[88] H.S. Kim, S.J. Lee, S. Amirkhanian, Rheology investigation of crumb rubber modified asphalt binders, KSCE J. Civ. Eng. 14 (6) (2010) 839–843.
[89] S. Liu, W. Cao, J. Fang, S. Shang, Variance analysis and performance evaluation of different crumb rubber modified (CRM) asphalt, Constr. Build. Mater. 23 (7) (2009) 2701–2708.
[90] C. Thodesen, K. Shatanawi, S. Amirkhanian, Effect of crumb rubber characteristics on crumb rubber modified (CRM) binder viscosity, Constr. Build. Mater. 23 (1) (2009) 295–303.
[91] R. Cao, Q. Bai, Laboratory evaluation of performances of asphalt rubber and gap graded mixtures, Seventh International Conference of Chinese Transportation Professionals (ICCTP), 2008, pp. 786–798.
[92] N.S. Mashaan, A.H. Ali, M.R. Karim, M. Abdelaziz, Effect of crumb rubber concentration on the physical and rheological properties of rubberised bitumen binders, Int. J. Phys. Sci. 6 (4) (2011) 684–690.

[93] N.S. Mashaan, M.R. Karim, Investigating the rheological properties of crumb rubber modified bitumen and its correlation with temperature susceptibility, Mater. Res. 16 (1) (2013) 116–127.
[94] R. Cao, Laboratory study on process parameters of asphalt rubber and their effects on performance, J. Southeast. Univ. 38 (2) (2008) 269–273.
[95] H. Wang, Z. You, Intermediate temperature fatigue and low temperature cracking properties of rubber asphalt binder, International Conference of Chinese Transportation Professionals, 21(1), (2011) 129–137.
[96] A.M. Rodríguez-Alloza, J. Gallego, I. Pérez, A. Bonati, F. Giuliani, High and low temperature properties of crumb rubber modified binders containing warm mix asphalt additives, Constr. Build. Mater. 53 (2014) 460–466.
[97] M. Hossain, S. Swartz, E. Hoque, Fracture and tensile characteristics of asphalt-rubber concrete, J. Mater. Civ. Eng. 11 (4) (1999) 287–294.
[98] R.B. McGennis, Evaluation of Physical Properties of Fine Crumb Rubber-Modified Asphalt Binders, Transportation Research Record. 1488, Transportation Research Board, Washington, D.C., 1995, pp. 62–71.
[99] H.H. Kim, S.J. Lee, Evaluation of rubber influence on cracking resistance of crumb rubber modified binders with wax additives, Can. J. Civ. Eng. 43 (4) (2014) 326–333.
[100] Y. Yildirim, Polymer modified asphalt binders, Constr. Build. Mater. 21 (1) (2007) 66–72.
[101] F.J. Navarro, P. Partal, F. Martinez-Boza, C. Gallegos, Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens, Fuel 83 (14–15) (2004) 2041–2049.
[102] S. Liu, W. Cao, J. Fang, S. Shang, Variance analysis and performance evaluation of different crumb rubber modified (CRM) asphalt, Constr. Build. Mater. 23 (7) (2009) 2701–2708.
[103] N. Sunthonpagasit, M.R. Duffey, Scrap tires to crumb rubber: feasibility analysis for processing facilities, Resour. Conserv. Recycl. 40 (4) (2004) 281–299.
[104] V.T. Gopal, P.E. Sebaaly, J. Epps, Effect of Crumb Rubber Particle Size and Content on the Low Temperature Rheological Properties of Binders, Transportation Research Board, Washington, D.C., 2002, pp. 1–21.
[105] J. Shen, A. Serji, F.P. Xiao, B.M. Tang, Influence of surface area and size of crumb rubber on high temperature properties of crumb rubber modified binders, Constr. Build. Mater. 23 (1) (2009) 304–310.
[106] P.E. Sebaaly, V.T. Gopal, J.A. Epps, Low temperature properties of crumb rubber modified binders, Road Mater. Pavement Des. 4 (1) (2003) 29–49.
[107] B.J. Putman, Quantification of the Effects of Crumb Rubber in CRM Binders (Ph.D. thesis). Clemson University, 2005.
[108] J. Shen, S. Amirkhanian, The influence of crumb rubber modifier (CRM) microstructures on the high temperature properties of CRM binders, Int. J. Pavement Eng. 6 (4) (2005) 265–271.
[109] K.M. Shatanawi, C.C. Thodesen, S.N. Amirkhanian, Effects of crumb rubber variability on failure temperature of crumb rubber modified binders, Road Mater. Pavement Des. 9 (9) (2008) 291–309.
[110] N. Puga, K.L. Nieve, Rheology and Performance Evaluation of Polyoctenamer as Asphalt Rubber modifier in Hot Mix Asphalt, Iowa State University, 2013.
[111] A. Beaty, Latex-modified bitumen for improved resistance to brittle fracture, Highw. Transp. 39 (9) (1992) 40–41. 32-4, 36-7.
[112] L. Artamendi, G.C. Eastmond, H. Khalid, Influence of crumb rubber modifier(CRM) from tyre waste on the rheological properties of

bituminous binders, Proceedings of The 3rd International Conference on Bituminous Mixtures and Avements, Held Thessalonikl, Greece, 1, 2002, pp. 65–74.
[113] Y. Dong, Y. Tan, L. Yang, Evaluation of performance on crumb-rubber-modified asphalt mixture, J. Test. Eval. 40 (7) (2012) 20120186.
[114] G.D. Airey, T.M. Singleton, A.C. Collop, Properties of polymer modified bitumen after rubber-bitumen interaction, J. Mater. Civ. Eng. 14 (4) (2002) 344–354.
[115] K.-D. Jeong, S.-J. Lee, S.N. Amirkhanian, K.W. Kim, Interaction effects of crumb rubber modified asphalt binders, Constr. Build. Mater. 24 (5) (2010) 824–831.
[116] L.F.M. Leite, R.S. Constantino, A. Vivoni, Rheological studies of asphalt with ground tire rubber, Road Mater. Pavement Des. 2 (2) (2001) 125–139.
[117] A. Ghavibazoo, M. Abdelrahman, M. Ragab, Mechanism of crumb rubber modifier dissolution into asphalt matrix and its effect on final physical properties of crumb rubber-modified binder, Transp. Res. Rec. J. Transp. Res. Board. 2370 (-1) (2013) 92–101.
[118] X. Yu, Y. Wang, Y. Luo, Effects of types and content of warm-mix additives on CRMA, J. Mater. Civ. Eng. 25 (7) (2013) 939–945.
[119] S. Aflaki, M. Memarzadeh, Using two-way ANOVA and hypothesis test in evaluating crumb rubber modification (CRM) agitation effects on rheological properties of bitumen, Constr. Build. Mater. 25 (4) (2011) 2094–2106.
[120] F. Moreno, M.C. Rubio, M.J. Martinez-Echevarria, Analysis of digestion time and the crumb rubber percentage in dry-process crumb rubber modified hot bituminous mixes, Constr. Build. Mater. 25 (25) (2011) 2323–2334.
[121] B. Celauro, C. Celauro, D.L. Presti, A. Bevilacqua, Definition of a laboratory optimization protocol for road bitumen improved with recycled tire rubber, Constr. Build. Mater. 37 (37) (2012) 562–572.
[122] N.S. Mashaan, A.H. Ali, M.R. Karim, M. Abdelaziz, Effect of blending time and crumb rubber content on properties of crumb rubber modified asphalt binder, Int. J. Phys. Sci. 9 (2013) 2189–2193.
[123] S.J. Lee, S.N. Amirkhanian, Effects of Reaction Time on Physical and Chemical Properties of Rubber-modified Binders (Doctoral dissertation). Clemson University, 2006.
[124] F. Xiao, B.J. Putman, S.N. Amirkhanian, Laboratory investigation of dimensional changes of crumb rubber reacting with asphalt binder, in: Paper Presented at the Proceeding Asphalt Rubber 2006 Conference, Palms Spring, California, 2006, pp. 693–715.
[125] L. Fontes, P. Pereira, G. Triches, J. Pais, R. Luzia, Laboratory optimization of continuous blend asphalt rubber, Proceedings of the 3rd European Pavement & ASSET Management Conference(EPAM3), Coimbra, Portugal, 2008.
[126] M. Abdelaziz, Effect of mixing type on performance of rubberised porous asphalt, Proceedings of the Eastern Asia Society for Transportation Studies, 5, 2005, 762–771.
[127] M. Abdelaziz, Effect of mixing type on performance of rubberised porous asphalt, Proceedings of the Eastern Asia Society for Transportation Studies, 5, 762–771.
[128] M. Hegazi, Evaluation of Cold Weather Performance of Rubber Modified Asphalt Placed in Ontario (M.S. thesis). University of Waterloo, Civil Engineering Waterloo, Ontario, Canada, 2014.

[129] G.B. Way, Flagstaff I-40 asphalt rubber overlay project: nine years of success, Transp. Res. Rec. J. Transp. Res. Board 1723 (1) (2000) 45–52. Available from: https://doi.org/10.3141/1723-06. Issue published: January 1.
[130] M. Stroup-Gardiner, B. Chadbourn, D.E. Newcomb, Babbitt, Minnesota: case study of pretreated crumb rubber modified asphalt concrete, Trans. Res. Rec. J. Transp. Res. Board 1530 (1) (1996) 34–42CE Department, University of Minnesota, Minneapolis, Minn. Available from: https://doi.org/10.1177/0361198196153000105.

13.3

Application of rubberized asphalt materials: Chinese experiences

Feipeng Xiao, Qidi Zong and Xiangdao Hou

Key Laboratory of Road and Traffic Engineering of Ministry of Education, Tongji University, Shanghai, P.R. China

13.3.1 Introduction

With the rapid development of the Chinese economy, the number of vehicles has increased. As a consequence, the amount of waste tires has shown a sharp increase. It is estimated that by the end of 2020, the output of waste tires in China will reach 20 million tons, and could cause a serious environmental problem [1]. Therefore it is important to find an economical and environmentally friendly way to dispose of waste tires.

Rubberized asphalt had been around since the 1950s [2]. Many countries in the world have carried out extensive research and paving tests on rubber-modified asphalt (called rubber asphalt in this chapter). In the 1960s, the United States started to use rubber powder-modified asphalt for pavements [3]. The US government has always strongly supported the recycling of scrap rubber. California, Arizona, and other states use rubber asphalt for paving, and have developed a mature rubber asphalt design. In addition, Russia, Japan, Canada, France, and South Africa have also used waste crumb rubber-modified asphalt (CRMA) to build heavy duty pavements. Rubberized asphalt technology was introduced into China in the 1980s [4]. Over the past twenty years, with the promotion of environmental protection issues and a great investment in solid waste, rubberized asphalt technology has developed rapidly in China [5].

Researchers in China have achieved significant success in rubberized asphalt materials. At present, the main production methods of waste rubber powder in China include room-temperature pulverization, low-temperature pulverization, and wet or solution pulverization [6]. The differences among them relate to the particle size and shape of crumb rubber powder. There are two main preparation methods to produce rubberized asphalt: a dry process

and a wet process [7]. The dry process of rubber asphalt mixture involves adding rubber particles to a mixture in the form of aggregate, but its pavement performance is not as good as the wet process. The wet method involves mixing waste rubber powder with the base asphalt at a high temperature with continuous blending over time. The wet process produces two types of rubber-modified asphalts: asphalt rubber (AR, or wet process-high viscosity) and the terminal blend (TB, or wet process no-agitation) [8]. Li et al. found that the addition of rubber powder can significantly reduce the rut depth at a high temperature and improve the low-temperature performance, as well as provide excellent aging resistance [9–14]. However, the increased viscosity due to crumb rubber increases the mixing and compaction temperatures of asphalt mixture [12]. In general, CRMA mixture has advantages over the base asphalt mixture [15,16].

Recently, Chinese researchers and engineers have developed some unique techniques for rubber powder, rubberized asphalt, and rubberized mixture production [17–22]. These technologies are discussed in the following sections.

The objective of this chapter is to investigate the unique Chinese experiences in rubberized asphalt application and includes the following aspects: production of rubber powder; properties of rubberized asphalt; properties of rubberized asphalt mixture; production and construction of rubberized asphalt mixture; applications in asphalt pavement such as thin overlays, waterproof materials, bridge deck and tunnel paving, and chip seal; and environmental and economic evaluations of rubberized asphalt pavements. The overall structure of this chapter is shown in Fig. 13.3.1.

13.3.2 Rubberized asphalt

13.3.2.1 Influence of rubber powder

Chinese researchers found that the performance of modified asphalt could be improved by activating the rubber powder. After a surface pretreatment, the volume expanded greatly, and the performance of high-temperature and low-temperature of rubberized asphalt was improved [23,24]. The surface activated included using bulk polymerization of acrylic acid. This modified the surface of crumb rubber, which increased the viscosity and failure temperature of rubberized asphalt [25]. Furthermore, after the surface treatment by hydrogen peroxide, the oxidized surface of rubber powder significantly improves the bonding

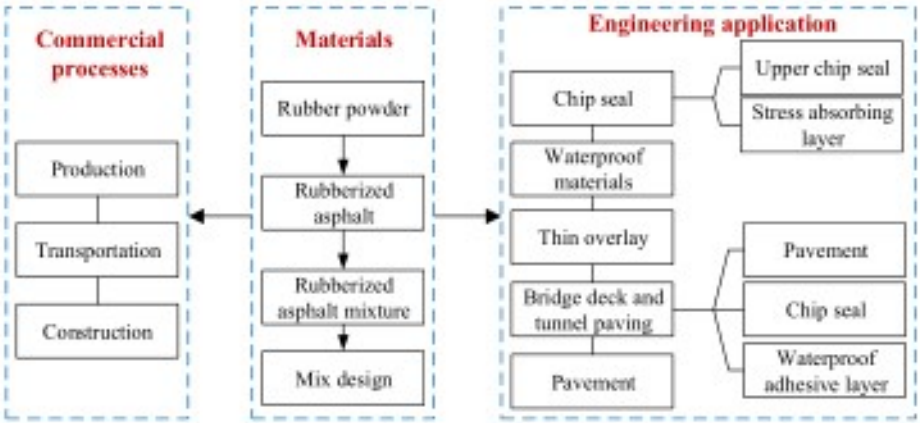


Figure 13.3.1 Structure of the article.

strength between the rubber particles and the asphalt [26]. In addition, Xiao et al. studied the physical and chemical properties of the powders using a plasma process [27] that greatly improved the surface composition and roughness of the rubber powder and increased the resistance to deformation.

Production processes of rubber powder can be divided into ambient and cryogenic crumb rubbers (CR) [28]. Shen et al. found that viscosity of ambient CRMA was between 1.2 and 1.6 times as much as for the cryogenic CRMA [28]. Furthermore, Li et al. showed that the high-temperature performance of cryogenic CRMA was better than for the ambient CRMA [9]. In addition, Wang et al. compared the truck tire powder and passenger car tire powder and found that the CRMA with truck tire powder showed better performance [29]. The reasons were that truck tire contained a higher percentage of styrene-butadiene rubber (SBR) and the natural rubber in truck tires was about 70%, higher than in passenger car tires; natural rubber modified asphalt more effectively than did synthetic rubber [30].

With respect to the influence of rubber particle size, Shen et al. concluded that binders with finer particle produce lower viscosity [28,31] and reducing the fineness of rubber powder enhances its compatibility with asphalt to some extent [32].

Increasing the dosage of rubber powder could improve the rutting resisting at high temperatures and markedly increase the softening point of binder, the viscosity, and the penetration [9,10,28,33,34]. Furthermore, when the dosage of rubber powder was less than 20%, the rubber powder had the most significant effect on asphalt modification [35]. For TB asphalt, the binder with a higher rubber dosage had lower penetration [36].

13.3.2.2 Influence of base asphalt

The impacts of binder source and grade on viscosity of rubberized asphalt have also been studied. For example, Shen et al. concluded that the surface area of rubber particle had little influence on its viscosity regardless of binder type [28]. However, the increase of viscosity increased the mixing and compacting temperatures of asphalt mixture [10]. In addition, it was found that the rubber powder had greater effect on high-temperature performance, ductility, and elastic recovery of low-grade asphalt than on high-grade asphalt [10,37]. Moreover, Ye et al. showed that the light component of asphalt had a significant influence on the performance of the rubberized asphalt [35,38].

13.3.3 Rubberized asphalt mixture

13.3.3.1 Descriptions of materials

13.3.3.1.1 Preparation of rubberized asphalt

The properties of the rubberized asphalt was related to the type of rubber powder, rubber dosage, asphalt grade, mixing duration, mixing temperature, and mixing speed.

Liu et al. indicated that asphalt grade had a slight influence on the number of functional groups in the reaction process, but was mainly dependent on the reaction temperature and duration [38]. With the increases of mixing temperature and duration, the volume expansion rate of rubber powder increased at first and then decreased slightly [39]. It is widely accepted that the mixing duration should be controlled to ensure that the rubber particles and asphalt are fully miscible. In addition, mixing temperatures should not be too high to avoid the asphalt aging [34,38,40–42]. Li found that only when the mixing temperature was higher than 160°C and reaction duration was greater than 1.5 h did chemical degradation of the rubber particles occur [43]. Wang et al. showed that when the mixing temperature was within the range of 170°C~200°C, elastic recovery was significantly affected by the temperature. In addition, when the mixing duration was within 45 min~4 h, the elastic recovery was the most sensitive to the reaction time [44].

As shown in Table 13.3.1, the recommended factors were No. 90 of base asphalt, 40~60 mesh of particle size, 20% dosage, mixing temperature of 190°C, and 1 h mixing duration. In addition, Sheng et al. recommended conditions for 20% rubber content, as 7000 RPM, mixing temperature of 170°C, blending

Table 13.3.1 Main factors of rubberized asphalt preparation.

Researchers	Asphalt	Particle size (mesh)	Rubber dosage	Temperature (°C)	Mixing time (min)	Attention
Lv et al. [40]	No.90	40	20%	190	60	Stirring speed: 2000r/min
Guo et al. [34]	No.90	60	20%	190	60	Suitable to Hebei district
Yang et al. [41]	No.90	40 ~ 60	≥ 20%	180 ~ 190	60 ~ 90	Seasonal freezing areas and heavy traffic conditions
Li et al. [25]	No.90	60	20%	≤ 195	≤ 90	Stirring speed: 2000r/min
He et al. [45]	No.70	40	20% ~ 25%	180 ~ 190	30 ~ 60	
Li et al. [46]	No.90	40	18.5%	190	45	

Notes: No. 90 and No. 70 mean the penetration values of binders.

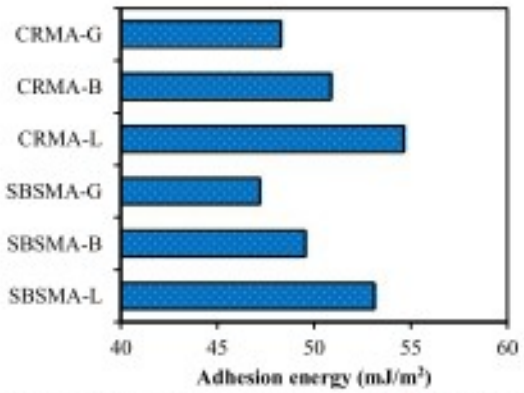


Figure 13.3.2 Adhesion energy values between binders and aggregate [48]. *CRMA*, crumb rubber modified asphalt; *SBSMA*, SBS modified asphalt; *G* = granite; *B* = basalt; *L* = limestone.

duration of 60 min, and development duration of 45 min for desulfurization [47].

13.3.3.1.2 Aggregate performance

The adhesion process and spalling process between asphalt and aggregate were exothermic and spontaneous [48]. As a consequence, aggregate property had a significant influence on the moisture sensitivity.

Aggregate type had a significant impact on adhesion. It can be seen in Fig. 13.3.2 that the mixture prepared using limestone showed the best adhesion performance, followed by basalt and

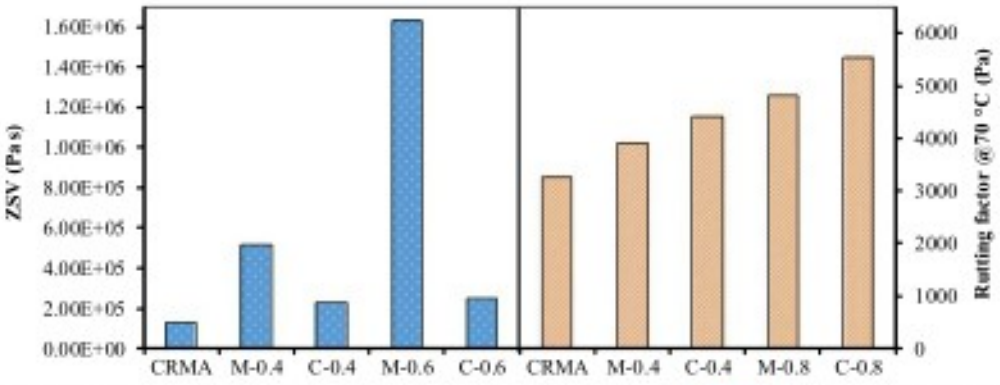


Figure 13.3.3 The ZSV and rutting factors of CRMA mastic with different fillers [50,51]. ZSV, zero shear viscosity; M, mineral powder CRMA mastic; C, cement CRMA mastic, 0.4 means filler-to-binder ratios (F/B) = 0.4.

granite. In addition, the CRMA showed better adhesion performance than SBSMA. Wang et al. showed that the rubberized mixture produced by limestone had the best resistance to moisture with the maximum tensile strength ratio [48]. In addition, the content of clay also affected the moisture resistance of CRMA. Xie confirmed that the influence of clay on moisture sensitivity could be ignored when the content was less than 1% [49]. However, when the clay content exceeded 2%, serious moisture damage of rubberized mixture was observed.

The proper addition of filler not only filled the gap but also formed a mastic with binder. As shown in Fig. 13.3.3, adding the cement or mineral filler improved the high-temperature performance of CRMA. The results of zero shear viscosity (ZSV) showed that the mineral powder was more effective than cement [50]. However, the Chen et al. results showed just the opposite. [51]. Thus further study is necessary. Yu believed that, when the filler/binder (F/B) was around 1.2, its high-temperature performance could be guaranteed without affecting the construction of mixture [50]. Meanwhile, the change of filler content did not affect the viscoelasticity of rubber asphalt mortar [52,53]. In addition, adding filler (including slake lime and cement) could effectively improve the moisture resistance of rubberized asphalt mixture [54].

13.3.3.2 Aggregate gradation

13.3.3.2.1 Gradation for crumb rubber-modified asphalt mixture

The gradation had an obvious effect on the volumetric design of CRMA [55–57]. Presently, there are three gradations

typically used in the surface course for crumb rubberized asphalt mixture, namely, AR–AC, AR–SMA, and RAC. AR–AC refers to the CRMA mixture with gap gradation. It is also called gap-graded asphalt rubber (GGAR) and was first developed in Arizona, United States [58]. Its design principle was to use coarse aggregate to form the skeleton, with fine aggregate and asphalt binder filling in the skeleton, so that the designed asphalt mixture is very dense and thus its porosity is small, with a high-temperature resistance to permanent deformation [58].

AR–SMA refers to the CRMA mixture with stone mastic asphalt. As shown in Fig. 13.3.4, AR–AC mixture and AR–SMA mixture have similar Marshall stability values with conventional SMA mixture. AR–SMA has the best rutting resistance, followed by conventional SMA, and then AR–AC. In addition, AR–SMA has better aging resistance and high-temperature stability than AR–AC [53,59]. AR–AC has greater fatigue resistance than conventional SMA [58]. Unlike AR–AC and AR–SMA, RAC (rubberized asphalt concrete) is usually used for overlay or stress absorbing layer; its nominal particle size is small and no filler is required [60]. In addition, its target void is lower, so it has higher fatigue resistance, crack resistance, and antiaging properties compared to other asphalt mixtures [60–62].

Ling believed that it was necessary to reduce the proportion of fine aggregates and fillers so as to increase the voids in mineral aggregate (VMA) and to ensure space for rubber particles, and improving high-temperature resistance of rubber–asphalt mixture [53]. Huang et al. indicated that rubberized asphalt mixture with less mineral powder and fine aggregate had greater moisture resistance [56]. Chen et al. indicated that the rubberized asphalt mixture with gap gradation and coarser

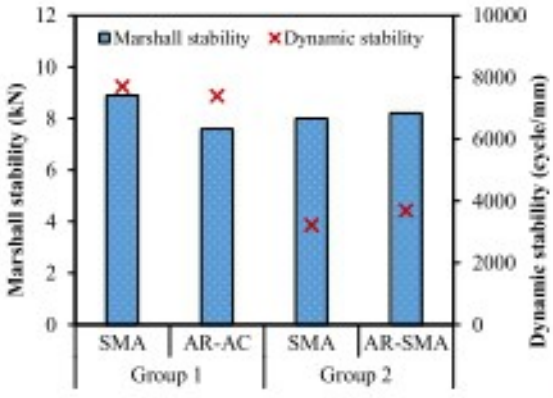


Figure 13.3.4 Marshall stability and dynamic stability results of three types of mixtures [53,58].

gradation performed well [55]. In conclusion, the SMA and GGAR gradations were more suitable for the CRMA mixture compared to dense gradation.

13.3.3.2.2 Gradation optimization

Chinese researchers optimized the SMA for CRMA mixtures by comparing nine gradations according to Chinese specification, and the optimal gradation was confirmed by You et al. [52]. Liu et al. designed the recommended AR–AC–13 based on the volumetric properties [58]. Fig. 13.3.5 shows the recommended gradations.

In addition, stone asphalt concrete (SAC) was a kind of gap-graded rubberized mixture developed by Chinese researchers [60]. The results showed that when gradation of SAC–13 was applied to rubberized mixtures, the content of coarse aggregate was slightly lower than that of common asphalt mixtures. Huang also proposed the recommended gradation range of AR–SAC–13 [63]; see Table 13.3.2.

With respect to the pore structure of RAC, experiments were conducted for aggregate less than 12%, in the range of 2.36 ~ 4.75 mm, [60]. To achieve the best pore structure, Wu

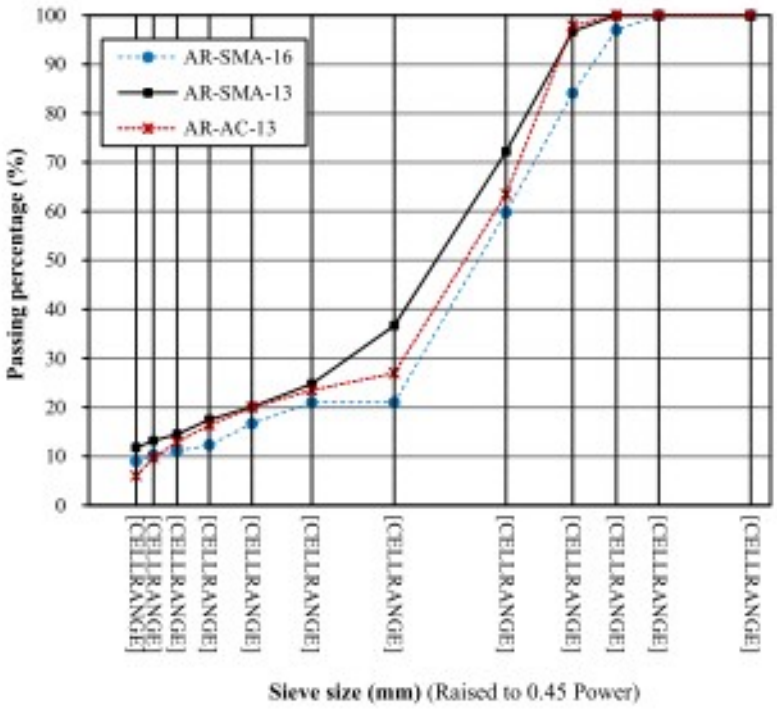


Figure 13.3.5 Recommended gradations of AR–SMA and AR–AC [52,58,62].

Table 13.3.2 Recommended gradation range of AR–SAC–13.

Recommended ranges of AR–SAC–13			
Sieve size (mm)	>9.5	4.75~9.5	4.75~2.36
Mass fraction (%)	30~45	20~40	<10

Table 13.3.3 Optimum asphalt–aggregate ratios of typical rubberized asphalt mixture.

Grading type	Optimum asphalt–aggregate ratio (%)	Cite
AR–AC–13	7.5	[58]
AR–AC–13	8.3	[64]
AR–AC–16	6.1	[15]
AR–SMA–10	7.6	[55]
AR–SMA–13	6.2	[53]
AR–SMA–16	6.5	[62]
RAC–G-10	8.5~9.5	[60]

AR ~ asphalt rubber; AC ~ asphalt content; SMA ~ stone matric asphalt; RAC ~ rubberized asphalt concrete.

et al. found that the dosage of rubber powder ranging from 7% to 7.5% was the most appropriate for RAC–13 produced by dry process [61].

13.3.3.3 Optimum asphalt content

Determining the optimal asphalt content was an important part of the mix design based on volumetric properties. The high-temperature stability of rubberized asphalt mixture was significantly affected by the asphalt–aggregate ratio, related to optimal asphalt content. The optimum asphalt content increased with the increased thickness of asphalt binder on aggregate surface [55]. As shown in Table 13.3.3, the optimum asphalt–aggregate ratio of rubberized asphalt mixture was obtained based on volumetric design. This ratio of AR–SMA–13 was about 1%~2% lower than that of AR–AC–13 [64]. AR–AC had a higher air void than the traditional SMA. As a consequence, its optimum asphalt content was generally higher than for SMA [58]. In addition, there was a good linear relationship between asphalt–aggregate ratio and air void of rubberized mixture [60,65]. It was found that an increased ratio of 0.5%

resulted in a void decrease of 1.1% and this ratio decreased significantly when a warm-mixture technology was used [60,65].

13.3.3.4 Properties of rubberized mixture

Similar to traditional asphalt mixture, the properties of rubberized mixture include high-temperature performance, low-temperature performance, fatigue performance, and moisture resistance. Fig. 13.3.6 compares the engineering properties (nondimensionalized) of the CRMA mixture to those properties of an AC mixture.

Li found that conventional asphalt mixture had the best bearing capability followed by gap-grading CRMA mixture and continuous grading CRMA mixture based on the results from a discrete element method [66]. In addition, the CRMA mixture had higher resistances for rutting and cracking compared to the common asphalt mixture [15,16].

The factors that influenced the high-temperature properties were compaction temperature, rubber powder content, air void, passing percentage of 2.36 mm, and asphalt content [53,65,67]. It was found that a 3% rubber, rubberized asphalt mixture prepared by the dry process had the best high-temperature performance [68]. In addition, the plant-produced rubberized asphalt (PRA) mixture exhibited a greater rutting resistance than a SBS-modified asphalt mixture and a field-produced rubberized asphalt (FPA) mixture [69].

In addition, CRMA mixture exhibited low-temperature anticracking property [15,67]. The fatigue life of rubberized asphalt mixture was generally longer than for SBS-modified asphalt

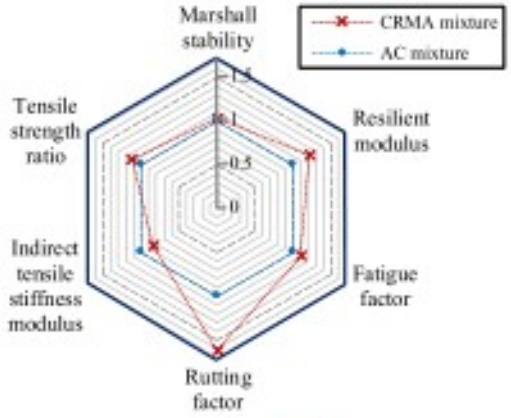


Figure 13.3.6 Properties of CRMA mixture and AC mixture [15,16].

mixtures and base asphalt mixtures [69]. Huang et al. used a four-point bending test to evaluate the fatigue performance of TB-modified asphalt mixture, and found that the smaller the air void, the longer the fatigue life [70]. TB−AC−13 mixture had a shorter fatigue life than that of the SBS−AC−13, but its self-healing ability was much higher [70].

Furthermore, with the addition of rubber particles in the dry process, the tensile strength of the mixture was reduced to some extent [71]. The larger the size of rubber particles, the greater the influence of rubber particles on the tensile strength of the mixture [72]. Feng investigated the moisture resistance of CRMA mixture under the condition of salt-freezing cycles, and the results showed that the freezing temperature, the concentration of snowmelt salt, and freeze-thaw cycles had a great influence on the tensile strength and Marshall modulus of the mixture [73].

13.3.4 Production and construction processes

13.3.4.1 Production process

13.3.4.1.1 Production of rubber powder

At present, the most common methods of producing waste rubber powder in China involve room-temperature pulverization, low-temperature pulverization, and wet or solution pulverization, as shown in Fig. 13.3.7.

Room-temperature pulverization generally referred to the mechanical shear force action that crushed rubber at 50°C or at a higher temperature. The rubber powder produced by room-temperature pulverization has an uneven surface [6]. The

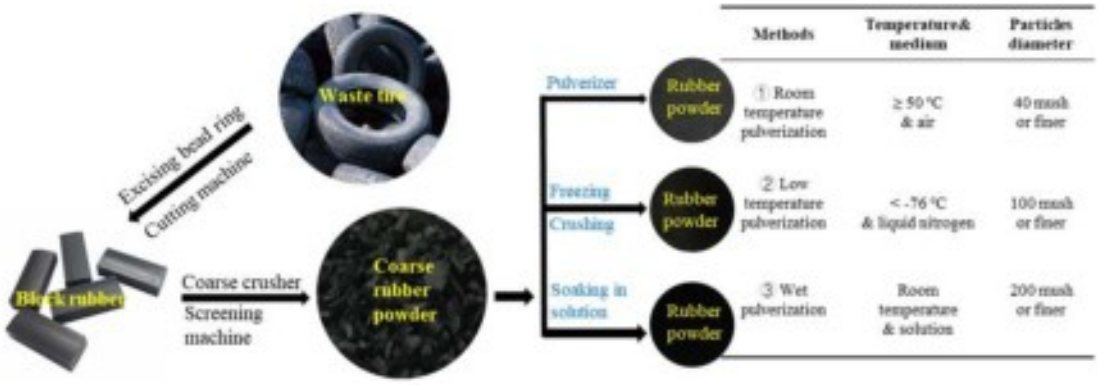


Figure 13.3.7 Common methods of producing rubber powder in China.

earliest production adopted in China was the roller crushing method, producing particle greater than 40 mesh. The method of continuous pulverization at normal temperature uses a rotary disk crusher for coarse and fine crushing. This method produces fine rubber powder with a mesh finer than 40 mesh [6]. Extruder pulverization is another method of producing rubber powder. Extruders are divided into single-screw and double-screw extruders [74,75]. The rubber powder produced has a particle size of less than 40 mesh.

In addition, other methods are used to produce crumb rubber; these include high-pressure water gun method; blasting method; ozone method; and a normal temperature immersion mixed crushing method [76].

Chinese researchers have also created production equipment for rubber powder. These include a smelting auxiliary machine to produce rubber matrix; Chen et al. a technology to effectively control the double spiral conveyor and, boost weighing accuracy of the smelting auxiliary machine, and improve the mixing efficiency (by Chen et al.) [77]; a waste tire free-shear breaking and hydraulic system to reduce electric power consumption (by Qiu) [78].

Low-temperature pulverization is an effective method to crush rubber (typically using liquid nitrogen). The rubber powder produced by this method had a small particle size (usually less than 100 mesh), smooth surface, and low degree of thermal oxidation but with a high production cost. Liang established a cryogenic pulverizing system by using a heat separator and a vortex mill, which was more effective than mechanical grinding [79]. Another cryogenic grinding system uses a jet-vortex mill. [80]. In addition, air-cooling and water-cooling technologies have been used to produce the rubber powder [76].

Wet or solution comminution was another method of producing rubber powder using a solvent or a solution. The surface state of rubber powder produced by this method was similar to that from the room-temperature method, but the particle size was smaller than 200 mesh. The method was first developed by the British plastics association, but has limited application in China [81].

13.3.4.1.2 Production of rubberized asphalt

The wet method involved mixing crumb rubber with base asphalt at high temperatures. The wet process produced two modified asphalts known as asphalt rubber (AR) and TB binders [8].

The ASTM D8 includes an authoritative definition of AR, which contains coarser rubber particles (less than 30 mesh) and a relatively high rubber concentration (minimum 15% by weight of virgin asphalt). The rubberized asphalt concrete application guide issued by the California Department of Transportation confirms that the viscosity of AR should be higher than 1500 cP at 177°C [8].

Different from AR, TB technology relies mainly on the desulphurization or depolymerization of rubber in hot asphalt and the full precipitation of rubber in the blend to obtain a uniform and stable modified binder. It is more like a polymer-modified binder because it does not require a special paddle. As shown in Fig. 13.3.8, the appearance of TB is uniform and smooth without obvious discrete particles, while the AR binder has a rough and granular surface [8]. The main differences between AR and TB lies in their storage stability and viscosity. Furthermore, TB does not require special agitating equipment and has better low-temperature performance than does AR [82].

The production processes of AR and TB is shown in Fig. 13.3.9. TBs are usually processed by adding 40 mesh or finer CRM to modify the base binder to ensure that the ground rubber particles decompose rapidly or disperse through normal circulation in the tank rather than being stirred by special paddles. The typical procedure to produce TB binder is as follows. The base binder is first heated to nearly 200°C, then rubber powder is added at 3000–8000 RPM for 40–60 min [83]. The typical swelling process of rubberized binder is replaced by the depolymerization or desulphurization of rubber in the base asphalt [84].

Asphalt type		
Rubber content	≥15%	5 ~20%
Viscosity	High viscosity	Low viscosity
Application	Chip seal、interlayer and hot mix asphalt mixture	Hot mix overlay or chip seal

Figure 13.3.8 Comparisons of asphalt rubber and terminal blend [82].

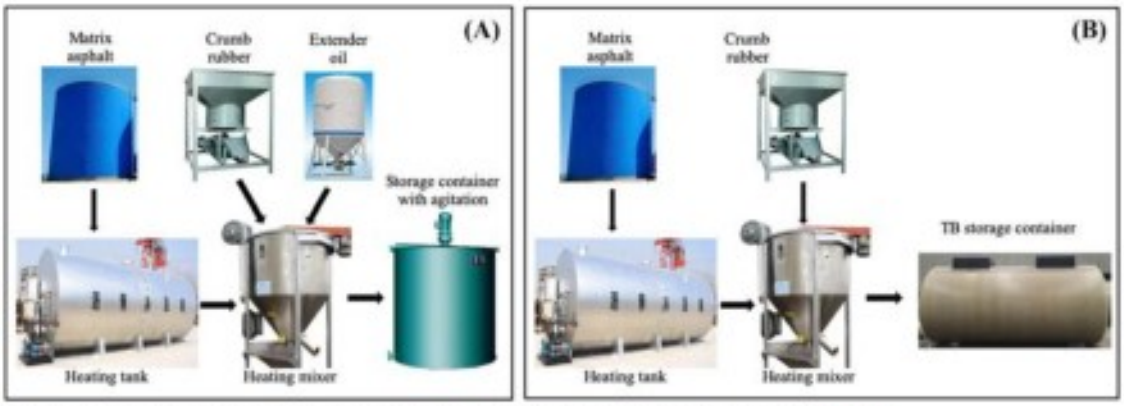


Figure 13.3.9 Production of rubberized asphalt: (A) Asphalt Rubber; (B) Terminal Blend [83].

In addition, recently Chinese researchers have investigated high-temperature pyrolytic rubber-modified asphalt. In this process, desulfurization and pyrolysis of swelling rubber powder takes place. The three-dimensional cross-linking network structure is changed due to the fracture of c−c, c−s, and s−s bonds. The rubber particle size is decreased, and the light components of asphalt, rubber oil, and carbon black are released. As a consequence, the performance of the modified asphalt is improved [85]. Dong et al. found that asphalt binder exhibited much better low-temperature performance at 250°C with stirring for 1 h, compared to the sample prepared at 230°C with stirring for 2 h [85].

Recently, a new production process of rubberized asphalt was developed by Ni et al., which is divided into preblending and masterbatch processes [82]. Kuang et al. used the extraction oil of furfural to predegrade the waste rubber powder, and then added the predegradation product to asphalt for modification [86]. The results showed that the predegradation process could improve the low-temperature ductility and high-temperature storage stability.

In the field, rubberized asphalt production equipment is mainly comprised of base asphalt heating unit, premix unit, reaction unit, and a controlling system [87]. The base asphalt heating unit is required to rapidly heat asphalt to over 190°C. Therefore the choice of the heat exchanger is very important. Wang specially designed a rubberized asphalt heat exchanger. [88] and Wu and Wang designed a new heating equipment for producing rubberized asphalt [89,90].

The premix unit is comprised of a conveying and premixing system to treat rubber powder and asphalt. Yang designed a

new feeding machine that could precisely manage the amount of rubber powder [91]. Chinese manufacturers have adopted the continuous rubber asphalt production equipment [87]. Wang found that a three-blade inclined paddle agitator was the most suitable for rubber-modified asphalt [92]. The design of blade angle, agitator size, stirring speed, and stirring power is important in determining the mixing efficiency [93,94].

13.3.4.1.3 Production of rubberized asphalt mixture

Rubberized mixtures can be produced by wet and dry processes. The wet process is widely used. The dry process involves adding rubber particles into the mixture directly and can consume more crumb rubber than the wet process [95]. The main differences between the wet and the dry process are shown in Table 13.3.4. It was shown that the addition of rubber powder in mixtures by the dry or wet process could improve the resistance to permanent deformation and low-temperature cracking [96–98].

Zhang found that the addition of rubber particles could reduce the Marshall modulus of the mixture [17]. In addition, the mixture with small particle size had a higher Marshall stability and a lower flow value. In addition, the SMA mixture produced by the dry and wet processes had similar relaxation modulus [99]. The VMA and air voids of rubberized asphalt mixture produced by the dry process were higher than those produced by the wet process [100]. CRMA from the dry process processed similar roughness with that from the wet process after short-term aging [101]. However, as shown in Fig. 13.3.10, the mixture from the wet process has a lower rutting depth than that from the dry process [99].

In addition, Cao creatively combined the wet process and dry process to produce rubber-modified asphalt [102,103]. The results indicated that the mixture produced by this method performed well and consumed more crumb rubber compared to the single process.

Table 13.3.4 Differences between dry process and wet process [7].

	Dry process	Wet process
Rubber particle size	≥1 mm	<1 mm
Dosage	1% to 5% (mass of aggregate)	5% to 20% (mass of asphalt)
Modification effect	Little	Obvious
Special equipment	No	For producing binder

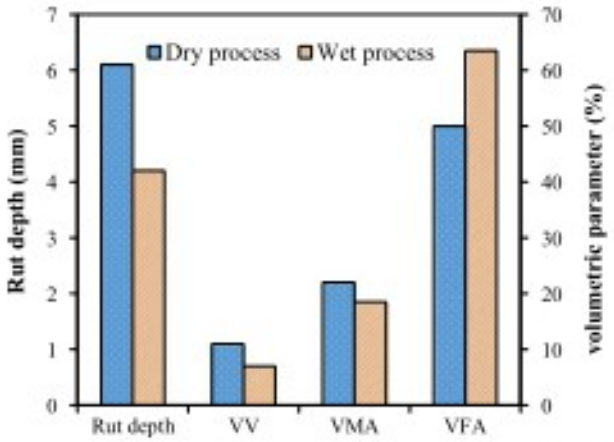


Figure 13.3.10 The performance of mixtures produced by dry and wet processes [99,100]. VV, total air voids content; VMA, voids of mineral aggregate; VFA, voids filled with asphalt.

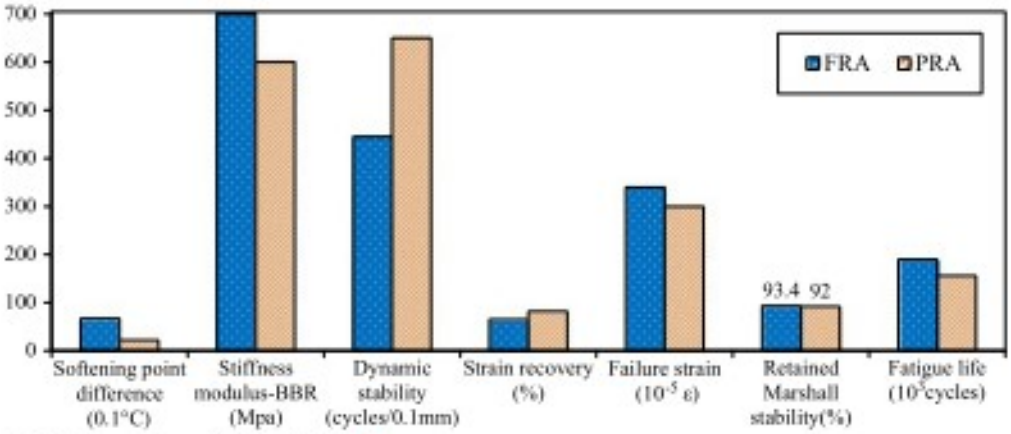


Figure 13.3.11 Properties of FPA and PRA [69].

13.3.4.2 Transportation and storage technologies

Plant-produced rubber asphalt (PRA) and field-produced rubber asphalt (FRA) are typically used to produce the rubberized mixture. However, the storage stability of these two products is generally different.

It can be seen in Fig. 13.3.11 that the storage stability of PRA is much better than that of field-produced asphalt. Furthermore, the PRA binder showed better resistance to permanent deformation and fatigue resistance. FRA mixtures showed better resistance to low-temperature cracking and moisture susceptibility. FRA and PRA mixtures both had long fatigue lives [69].

It was found that when the reaction temperature was 180°C ~ 190°C, the storage stability of rubberized was at its best [104]. And the smaller the particle size, the better the storage stability [105]. Huang et al. and Wang indicated that the quality of rubberzied asphalt showed strong time dependence and temperature dependence [104,106]. Practice proved that when the viscosity was between 1.5 and 4 Pa · s at 177°C, it could achieve high construction operability and high-temperature stability [106].

There are chemical methods to improve storage stability. The addition of the stabilizer, furfural extraction oil, can enhance the interface adhesion between asphalt and rubber, thus improving storage stability [107]. According to the current literature, conjugated diene polymers, polyphosphoric acid, hydrozilylation catalysts, fluid catalytic cracking slurry, and sulfur-based cross-linking agents have proved to effectively alleviate the phase-separation tendency [8]. Reducing the storage temperature is also an economical and simple method. Activation or desulfurization of crumb rubber can improve the compatibility between asphalt and rubber, thereby reducing the separation potential [25,108].

Wang designed a new storage unit of equipment by adding a vertical spiral agitator and a traverse filtering net [109]. Zhang designed a special horizontal agitator for storage equipment [110]. The heating storage device had been redesigned to improve the storage stability of CRMA [111,112].

13.3.4.3 Construction of rubberized mixture

The CRMA mixture required a higher compaction temperature than the common mixture. In the range of 160°C–180°C, the VV, VMA, and VFA values of CRMA mixture were not sensitive to temperature. However, when the temperature was below 160°C, the VMA rose rapidly, VFA fell rapidly, and the air void increased linearly [77,113]. It was thus necessary to enhance the compaction temperature to improve the properties of CRMA mixture.

In addition, the compaction methods have a notable influence on the compaction degree. The gyratory compaction showed a slight refinement and was close to the actual construction situation [114]. The more the compaction effort, the denser the mixture. However, compaction could also crush aggregate, and thus changed the gradation characteristics of the original mixture and ultimately affected the performance. You et al. indicated that 50 gyrations were appropriate for AR–SMA mixtures [52]. Yu determined the optimum laboratory compaction procedure by comparing four procedures (i.e., superpave gyratory compaction,

vibratory compaction, large-scale Marshall compaction, and vibratory compaction plus large-scale Marshall compaction). Vibratory compaction combined with large-scale Marshall compaction was considered the best compaction method in terms of air void ratio [95].

When the compaction temperature was 190°C, the rubber powder dosage had an obvious influence on the compaction process [113]. With respect to the dry process mixture, when the rubber content exceeded 8%, the air void of mixture generally was over 6%. For the actual pavement with a compaction of 98% degree, the void content might reach 8%, which meant that the mixture was easy affected by moisture. Hence, the recommended rubber dosage should be about 5.5% [95].

In addition, the application of warm-mix asphalt (WMA) technology decreased the viscosity of the CRMA and improved the workability of the mixtures [115]. The WMA additive played a significant role at low temperatures and had slight effect on workability at high temperatures [115,116]. When the temperature dropped to 145°C and lower, the WMA additive showed obvious improved workability [115,117].

The performance of rubberized asphalt mixture based on surfactant additive was significantly affected by the asphalt–aggregate ratio. As shown in Fig. 13.3.12, the AR–SMA mixture containing

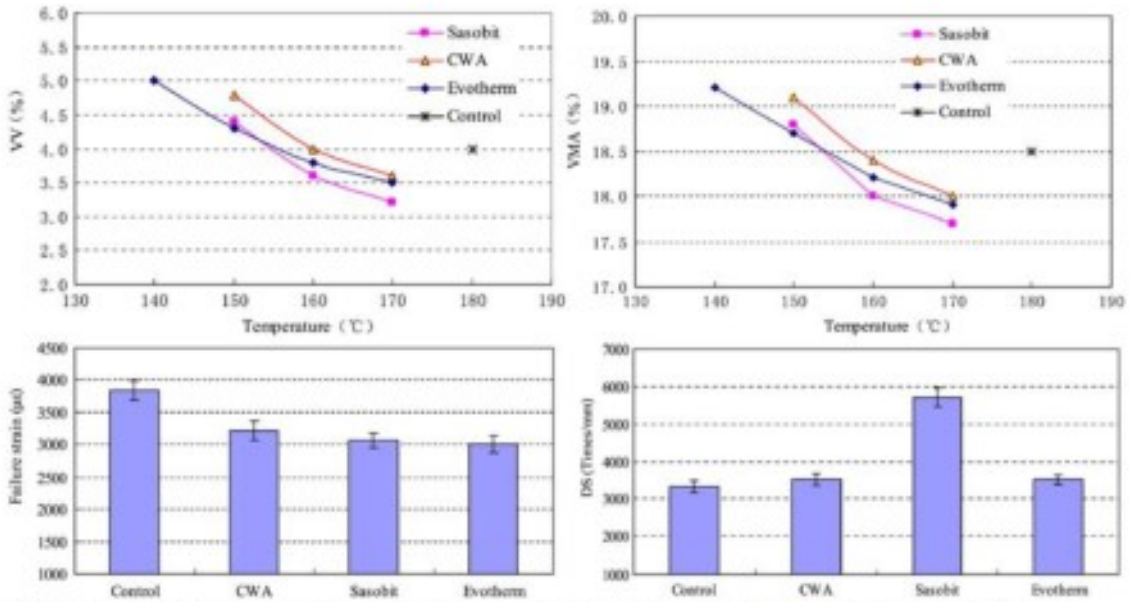


Figure 13.3.12 Properties of CRMA mixtures with Sasobit, Evotherm, and CWA [118]. (A) Void values, (B) VMA values, (C) failure strains, and (D) DS values.

Sasobit (warm-mix additive type) presented the best rutting resistance among all mixtures [118]. Fan suggested that the compaction temperature of AR–SMA should be between 140 and 150°C [65].

13.3.5 Typical application of rubberized asphalt mixtures

13.3.5.1 Standard development of rubberized asphalt mixtures in China

The research studies of rubberized asphalt and mixture in China were started in the 1980s. After over 30 years, some provinces, cities, and industry departments issued technical regulations and guidelines on design and construction. For example, Beijing city published "The technical guide for design and construction of waste tire powder asphalt and mixture" in 2006; Jiangsu province published "The technical regulations for rubber asphalt pavement" in 2005; and Tianjin issued "The technical regulations for rubber powder-modified asphalt pavement of waste tire" in 2006.

In 2001, the Ministry of Transport (MOT) of the People's Republic of China carried out the "Technical research on the use of waste rubber powder in road construction." In 2006, the "Technical exchange meeting on the application of rubber asphalt in pavement engineering" was published in Hainan. In 2008, the MOT compiled and published the "Technical guide for design and construction of rubber asphalt and mixture," and provided a base specification for the construction of rubberized asphalt and mixture in China. After further research study and investigation, the specification of rubberized asphalt mixture was further updated. In 2015, the MOT released the "Technical specification for rubber asphalt pavement" (draft for comments). As of 2020, the final draft was still being finalized.

13.3.5.2 Typical rubberized asphalt mixture types in pavement

13.3.5.2.1 Typical overlay application in highway pavement

Typical CRMA pavements widely used in China are listed in Table 13.3.5. During the CRMA construction, some main factors such as compaction, smoothness, friction coefficient, and texture depth were considered. The requirements of CRMA pavement were the same as other modified asphalt pavements as

Table 13.3.5 Typical crumb rubber-modified asphalt pavement projects in China.

Site and cite	Type	Road structure	Road performance			
			Compactness (%)	Friction coefficient (BPN)	Texture depth (mm)	Flatness (mm)
Gansu [119]	ORT	ARAC13 (5 cm) + asphalt concrete road	97	–	–	–
Zhejiang [120]	ORT	ARAC13 (4 cm) + old road	>98	53BPN	0.7	2.1
Chongqing [121]	ORT	ARAC13 (4 cm) + old road	90	–	–	–
Hebei [122]	NR	ARAC13 (4 cm) + ARAC20 (6 cm) + ATB30 (8 cm) + ARAC13 (4 cm) + cement stabilized macadam	ARAC13: 99.5; ARAC20: 100	0.86	0.67	0.54
		ARAC13 (4 cm) + ARAC20 (6 cm) + ATB30 (12 cm) + cement stabilized macadam		0.88	0.66	0.41
Northern regions [123]	ORT	CRMA concrete (specially designed grading) + old road	98.8	0.78	0.71	–
Beijing [46]	NR	ARAC13 (4 cm) + ARAC16 (6 cm) + lime-fly ash stabilized aggregate	–	48.7	1.07	–

NR, New road; *ORT*, Old road transformation.

per specifications of China (JTJ−059−95). On the basis of different projects, the results indicated that the CRMA generally performed well in various conditions in China.

In addition, Li et al. replaced the original AC−20 mixture in the middle layer by CR−modified AC−20, and the upper layer was an SMA mixture [124]. It was found that the dynamic stability was 10,000 cycles/mm, far more than the value from AC−20 mixture. In addition, the AR−SMA was also applied to high modulus pavements. Zhao found that when AR−SMA was applied in lower layer of the AR−porous European mix, no rutting depths were found after a three-year heavy traffic loading, however, the conventional mixture showed obvious permanent deformation [125].

In addition, Guo applied the close-proximity trailer method to analyze the noise spectrum of rubberized pavement and concluded that the CRMA pavement was helpful in noise reduction

[126]. Zhang designed low-noise asphalt pavement (LNAP) [127]. According to the results of the on-board sound intensity test, the LNAP mixture had a higher absorption coefficient than the open grade friction course (OGFC) mixture [128,129].

13.3.5.2.2 Technologies for improving pavement performance

Chinese researchers also applied different technologies to improve the properties of the rubberized asphalt pavement, such as warm-mix technique, hot in-place recycling (HIR) technology, and involvements of SBR latex or sand antifracture (SAF).

The warm-mix technology was commonly used in the paving of rubberized pavement. Application of double-layer rubberized pavement with warm-mix technology in Hebei province proved to be feasible in old cement concrete pavement [130]. The pavement conducted in Yunnan province indicated that the warm-mix technology was feasible in making a new highway pavement [131]. In addition, some researchers successfully combined the HIR and the rubberized mixture for sustainable development in Guizhou province [132].

Additionally, SBR latex combined with rubber powder was also applied in the pavement to improve the moisture sensitivity, rutting resistance, and noise reduction [133]. In addition, Geng developed a newly stabilized rubber-modified asphalt pavement with the addition of SAF, exhibited excellent high-temperature performance, fatigue resistance, and reflective cracking resistance in Xinjiang province [134,135].

13.3.5.3 Rubberized asphalt thin overlay

13.3.5.3.1 Typical application in China

The rubberized asphalt thin overlay (meaning the rubberized asphalt mixture added on the original pavement surface with a thickness less than 30 mm) has been used for pavement repair in recent years. It can also be used as a new antisliding surface layer [18].

Some typical thin overlay mixtures such as AR–AC, AR–SMA, AR–OGFC, and RAC have been used in China. As shown in Table 13.3.6, the thicker overlay used in Guangdong province was confirmed to effectively resist rainy and wet weather. In Table 13.3.6, the AR–SMA–5 and AR–SMA–10 show greater smoothness and lower water permeability coefficient compared to other mixtures [137].

Table 13.3.6 Thin overlay projects in China.

Site and Cite	Gradation	Thickness (mm)	Compactness (%)	TD (mm)	FC (BPN)	Water permeability coefficient (ml/min)	Flatness (mm)
Guangdong [136]	AR–AC–10	40	–	0.89	70	57	2.4
Guangdong [137]	AR–AC–13	40	>93	1.1	–	<120	–
[138]	AR–SMA–5	–	–	077	58	13	0.75
Hebei [139]	AR–SMA–10	20	99.7	0.79	59	12	0.7
Hebei [140]	TBRA–SMA–10	30	94.7	0.77	58	13	0.75
Jiangsu [18]	AR–OGFC–13	25	–	–	–	>1000	–

FC, friction coefficient; *TD*, texture depth.

To achieve the goal of energy conservation, low-carbon TBRA–SMA was successfully developed [138,140]. The OGFC mixture was used to improve water drainage [139,141]. The AR–OGFC–13 thin overlay (25 mm thickness) project, conducted in Jiangsu province, proved effective in noise reduction [18]. In addition, the air voids of thin overlay were blocked and resulted in a decrease of permeability [142].

Furthermore, the thin overlay of RAC–G was also investigated. Huang pointed out that the particle size between 2.36 and 4.75 mm was the most significant factor in enhancing the performance of RAC–G mixtures [60]. The research results indicated that the ARAM–10 mixture had good rut resistance, excellent low-temperature resistance, and moisture sensitivity and that AR–OGFC exhibited good skid resistance [143].

13.3.5.3.2 Construction of thin overlay

When it comes to the construction of the thin overlay, the preparation before paving was important. It consists of two parts, the repair of the old road and the paving of mat coat. For the repair of the old road, the primary process is patching the subgrade [136,144,145].

The construction process of thin overlay generally includes blending, transportation, paving, rolling compaction, and joint treatment. The technologies and key details were clarified by Wang [136]. In addition, Chinese researchers also applied the warm-mix technology to the thin overlay [146]. The thin-layer

technology used rubberized asphalt in the construction and in recent years has been broadly applied in China [147].

13.3.5.4 Rubberized asphalt waterproof materials

13.3.5.4.1 Properties of rubberized waterproof materials

In China, two kinds of rubberized asphalt waterproof coatings have been widely used and studied, namely: rubber-modified asphalt sprayed quick-setting (RMASQ) waterproof coating and noncurable rubber-modified asphalt (RMANC) waterproof coating, as shown in Fig. 13.3.13.

There were similarities and differences between the two coatings during the application process. The RMASQ needed two solutions as shown in Fig. 13.3.13, while RMANC required only one. The A and B solutions of RMASQ reacted and formed a waterproof layer. RMANC formed a waterproof layer by the volatilization of the liquid filler. In addition, anionic synthetic rubber, such as neoprene latex and SBR latex, was used to improve the properties. RMASQ was also generally used to modify emulsified asphalt [148] and RMANC was added for secondary modification of rubberized asphalt [19].

As shown in Table 13.3.7, both had excellent film-forming speed, extensibility, elasticity, durability, and energy-saving performance. However, the temperature resistance, self-healing

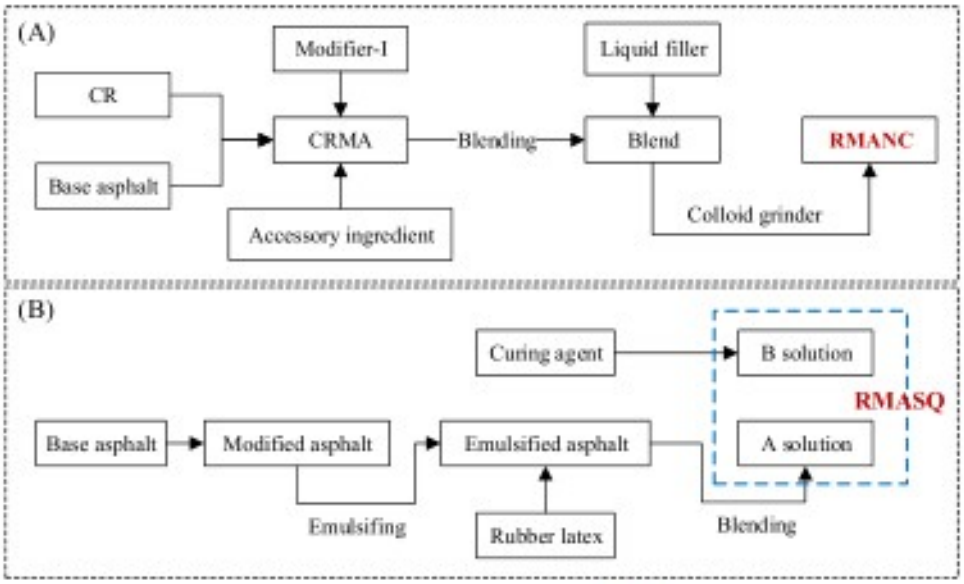


Figure 13.3.13 Production processes of waterproof coating materials [19,148].

Table 13.3.7 Comparisons of RMASQ and RMANC.

Superiority	RMASQ [149]	RMANC [148]
Speed of film form	Fast	Fast
Extensibility and elasticity	Good	Good
Durability	Good	Good
Energy-saving performance	Good	Good
Temperature tolerance	Range: 5°C ~ 35°C	Outstanding
Self-healing property	General	Outstanding
Storage property	General	Outstanding

Table 13.3.8 Optimal construction parameters of waterproof coatings.

	RMASQ [149,150]	RMANC [151]
Coverage methods	Spraying or brushing	Brushing or scraping
Thickness (mm)	1.5	1/1.5/2
Optimal dosage (kg/m^2)	1.5 ~ 2	1.3/2/2.6

property, and storage property of RMANC were better than those of RMASQ.

Jia studied the influence of three rubberized emulsions on the performance of RMASQ, and showed that emulsified asphalt with similar physical properties should be selected [150]. Styrene-butadiene latex could improve low-temperature performance of the coating, and chloroprene latex could improve the tensile strength of the coating. Moreover, Lin studied the viscosity, cryogenic flexibility, shear and bond strengths of RMASQ, and concluded that the coating had greater performance when the asphalt content was less than 10% [151,152].

13.3.5.4.2 Application of rubberized asphalt waterproof materials

In 2007, the RMASQ waterproof material was introduced from Canada and was then developed and produced in China in 2009. Since then, it has gained more and more attention and recognition in the waterproofing industry [149]. RMANC waterproof coating was introduced from Korea in 2005 and developed rapidly from 2007 to 2015 [148]. In addition, the specifications for two waterproof coating materials, referred to as "sprayed rubber asphalt waterproof coating" (JC/T 2317-2015) and

"noncured rubber asphalt waterproof coating," (JC/T 2288-2014) have been issued (see Table 13.3.8).

The coverage of waterproof material is very important during construction. Spraying and brushing are the two main methods for RMASQ. For RMANC, brushing and scraping are generally adopted. The bonding strength by brushing process was higher than that from spraying [149], whereas the spraying process was more convenient and the coating was distributed more evenly [150]. The recommended optimal dosages and thicknesses of waterproof coating are given in Table 13.3.8.

As shown in Fig. 13.3.14, rubber asphalt waterproof material is widely used. Chen produced the technical characteristics and construction technology of the composite waterproof layer [153]. In addition, Lin [151] proposed an integrated waterproof protection system from flexible to semirigid to rigid parts. The specific applications are summarized in Table 13.3.9.

Chinese researchers made great efforts to improve the performance of rubber asphalt waterproof coatings and a color-sprayed quick setting rubber waterproof coating has been developed. Liu adopted petroleum resin emulsion instead of emulsified asphalt to conduct quick-setting, waterproof, sprayed coatings [156]. In addition, the color of a waterproof coating can be adjusted by adding different color slurries.

Furthermore, flame-retardant spraying quick setting rubber asphalt waterproof coating has been used to enhance the flame

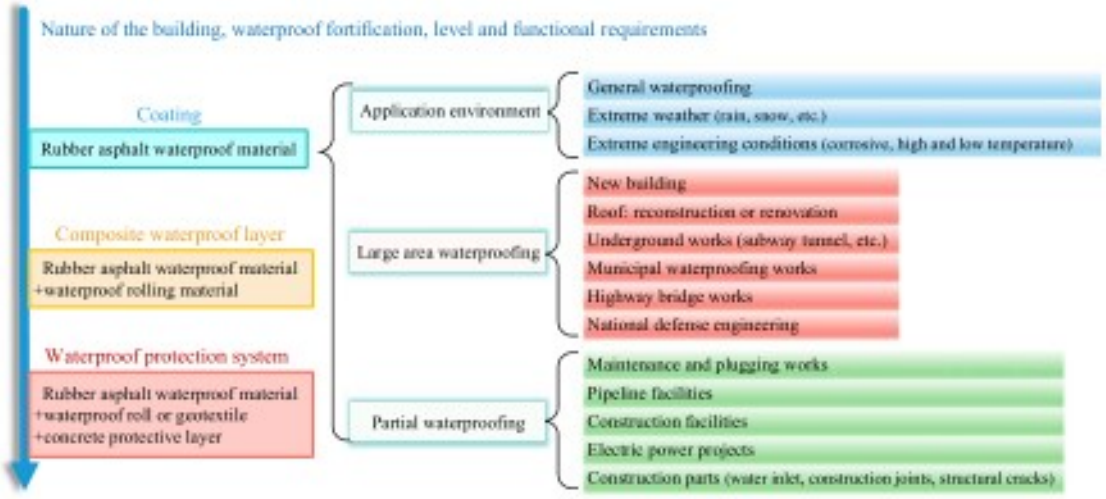


Figure 13.3.14 Application of rubber–asphalt waterproof material [148,149,151,153].

Table 13.3.9 Specific applications in China.

Site	Waterproof type	Aspects of protection	Time	cite
Beijing, Anhui, Jiangsu, Zhejiang, Liaoning, and Shaanxi province	Large area	New buildings	2005 to 2012	[153]
Beijing	Large area	National stadium	2008	[148]
Domestic enterprises	Partial	Zero-defect, zero-leakage, and zero-risk waterproofing system	2010	[148]
Changchun	Partial	Plugging the leakage of immersed tube tunnel	2017	[154]
Changsha	Large area	Subway station waterproofing	2017	[155]

retardancy of waterproof coatings [157]. The experimental results showed that rubberized asphalt waterproof material had good flame-retardant properties, bonding strength, and tensile strength when a 6% flame retardant was used. In addition, Cao applied layered double hydroxyl compound metal hydroxide (LDHs) to rubber-modified asphalt [158] for aging resistance.

13.3.5.5 Bridge deck and tunnel paving

The waterproofing of a bridge deck and tunnel is more demanding than that of the common road. Waterproof adhesive layer requires excellent deformation ability, crack resistance, high bonding strength, and stability. Rubber–asphalt binder layer and rubber–asphalt macadam seal layer are two typical waterproof layers used in bridge deck and tunnel construction.

13.3.5.5.1 Waterproofing layer

As shown in Fig. 13.3.15, the rubber–asphalt waterproof adhesive layer is used as the pavement waterproof layer in the tunnel and bridge deck. Gao found that reaction time and temperature were the most important factors affecting the properties of waterproof layer [159]. Moreover, Liu [160] carried out a finite element analysis and found that rubber asphalt had good deformation ability, suitable for bridge deck waterproofing adhesive layer [20]. For practical applications, the rubber–asphalt waterproof adhesive layer used in steel bridge deck pavement showed excellent performance with good adhesion and shearing properties [161]. In addition, Hu indicated that the rubber–asphalt binder layer in the

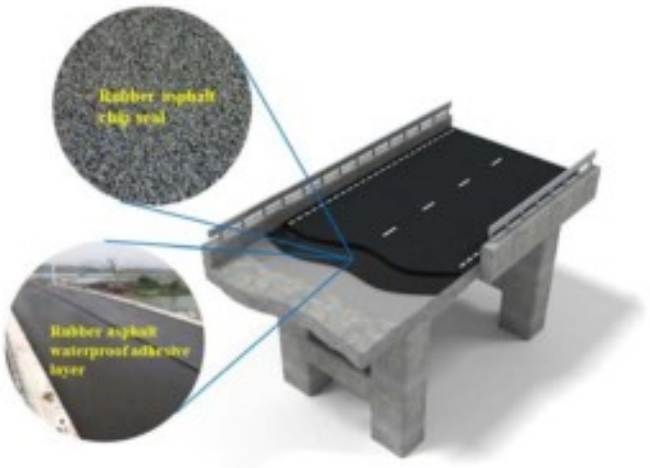


Figure 13.3.15 Applications of rubberized asphalt in the waterproof layer in the bridge deck or tunnel.

cement concrete bridge deck had high shear strength and good tolerance [162]. In addition, the cement concrete pavement with rubber–asphalt waterproof binder in the tunnel showed outstanding performance [163].

In addition, ambient temperature has the greatest influence on the shear strength of the waterproof layer. The shear strength decreased as the temperature increased [164,165]. The optimal waterproof layer was found to have a particle size of scattered gravel of 2.36 to −9.5 mm and a thickness of waterproof material of 1.5 mm [164]. In addition, when the asphalt content increased, the shear strength first increased and then decreased [165,166]. Tang showed that the cement concrete bridge with rubber–asphalt macadam seal showed good service performance [167,168].

13.3.5.5.2 Deck and tunnel pavement

Rubberized asphalt mixture is also used as surface layer in bridge and tunnel construction, and typically used in bridge deck and tunnel surface repair. Ren employed different treatment methods for various problems using rubber asphalt for the maintenance of the expressway in Chongqing City [169]. In addition, suitable bridge deck and tunnel pavement construction technology, temperature control, and rolling technology were also developed for rubber asphalt mixture [170].

Typical projects in China are summarized in Table 13.3.10. The rubber asphalt has been applied to bridge decks in China

Table 13.3.10 Examples of the bridge deck and tunnel paving.

Year and location	Pavement structure	Waterproof materials	Basic types
1994, Zhejiang [171]	Rubber–asphalt concrete (4 cm) + steel fiber concrete (6 cm)	Tack coat	Cement concrete bridge deck
1999, Guangdong [172]	Double-layer AR–SMA13 (3 cm + 5 cm)	Tack coat (5 mm)	Steel-plate floor
1999, Fujian [172]	AR–SMA16 (5 cm) + AR–SMA10 (3 cm)	Tack coat	Cement concrete bridge deck
Yunnan [173]	Gap-graded asphalt rubber (6 cm)	Rubber–asphalt SAMI (10 mm)	Cement concrete bridge deck
Guizhou [170]	AR–SMA13 (4 cm) + AC20 (6 cm)	Tack coat	Cement concrete bridge deck
Guangdong [174]	AR–AC13 (5 cm)	Tack coat	Cement concrete bridge deck
2012, Zhejiang [163]	AR–SMA13 (4 cm)	Rubber asphalt SAMI (10 mm)	Cement concrete tunnel pavement
Gansu [175]	Rubber asphalt thin overlay (2.5 cm)	Tack coat	Cement concrete tunnel pavement

SAMI, stress-absorbing membrane interlayer.

since the 1990s. Stress-absorbing membrane interlayer (SAMI) was also a choice to achieve high shear strength but suffered from high cost and complications [170]. Furthermore, rubber asphalt pavement is typically used for the surface of cement concrete and steel plate floors.

13.3.5.6 Rubberized asphalt chip seal

Chip seal was composed of asphalt binder and gravel, suitable for middle- and low-grade new pavement or pavement surface maintenance [176]. It was shown that the pull-out strengths of rubberized asphalt chip seal was higher than that of SBS emulsified asphalt seal and base asphalt seal [176].

13.3.5.6.1 Upper seal coat for roadway maintenance

The upper seal was generally used for pavement maintenance. The main types of rubberized asphalt chip seals were single-chip seal, double-chip seal, and "cape" seal as shown in Fig. 13.3.16. It was suitable for middle- and low-traffic pavements or for maintenance [22,176].

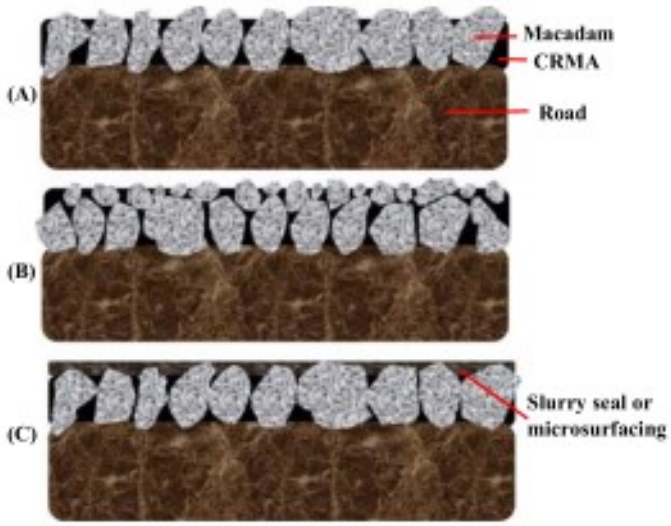


Figure 13.3.16 Types of rubberized asphalt chip seal, (A) single chip seal, (B) double chip seal, and (c) cape seal.

Table 13.3.11 Construction processes and controlled qualities of rubberized asphalt chip seal [119,177].

Order	Construction processes	
Step 1	Base layer cleanup	
Step 2	Spreading CRMA and gravel	
Controlled qualities:	CRMA spraying temperature	185 ~195°C
	Gravel spraying temperature	150 ~160°C
Step 3	Rolling with plastic core-rubber-tires	
Controlled qualities:	Gravel compaction temperature	65°C ~75°C
	First compaction	1–2 times and 2–2.5 km/h
	Recompaction	once and 2.5–3 km/h

The typical temperatures used for construction processes are shown in Table 13.3.11. Both synchronous and asynchronous construction were typically used to produce slurry seal. the synchronous sealing machine also effectively improved the production ratio and reduced the pollution to the environment [177,178]. The rubber-wheel roller was used in the process of rolling as shown in Table 13.3.11.

Furthermore, Chinese researchers have made a lot of efforts to improve the performance of single chip seal: for example, it was found that that when the particle size was 9.5 mm, the rubber asphalt chip seal showed excellent performance [179]. Wang applied rubber-emulsified asphalt to conduct two layers of

microsurfacing with a 5 mm thickness on the chip seal [180]. The test section in Shanxi showed good noise reduction and durability after 2 years of service.

Qian and Gu indicated that the addition of basalt fiber could significantly improve the tensile strength and shear strength of rubber asphalt chip seal [181,182]. In addition, preheating, precoating, and mist-sealing technologies may also improve the antispalling ability of the chip seal [179].

As shown in Table 13.3.12, the single-chip seal, the most common and basic chip seal, may meet all the functions of the seal coat. The double rubberized asphalt chip seal processed higher shear strength, better adhesive property, and longer fatigue life than a single-chip seal. "Cape" seal was a combination of chip seal and microsurfacing or slurry seal. "Cape" seal layer not only had the characteristics of a chip seal but also had the advantage of smooth surface, completely preventing the rain from permeating into the road.

Table 13.3.13 showed that the three seals provided good pavement performance in widespread application in China [177–179]. In addition, the optimal concentration, rubber size, and gravel concentration (dosage) have been recommended as well.

13.3.5.6.2 Lower-seal coat-stress absorption

When the chip seal was used for a lower layer, it was generally used as a SAMI, which could absorb the high stress caused by the horizontal displacement of the base layer and prevent cracks from propagating from lower layer to the surface. Many studies proved that the SAMI was better than polyester glass fiber seal layer [188].

Table 13.3.12 Advantages of rubberized asphalt chip seal [183,184].

Types of rubber asphalt chip seal			Advantages
Single-chip seal			Simplest process; meets all functions.
Double-chip seal	Common	Upper: small gravel Lower: large gravel	Higher shear strength; better adhesive property; better fatigue life.
	Inverted	Upper: large gravel Lower: small gravel	Make a lower seal layer closely attached to the roadbed.
"Cape" seal			Smooth surface; not peeling off; Completely prevent rain

Table 13.3.13 Examples of chip seal.

Location/year	Type	Structure		Rubberized asphalt concentration (kg/m^2)	Gravel particle size (mm)	Gravel concentration (kg/m^2)
Shanxi, 2013 [180]	Microsurfacing	Double layer (5 mm)		–	–	0
Shaanxi, 2010 [178]	Upper-seal coat	Single layer		–	10 ~ 15	–
Gansu, 2001 [177]	Upper-seal coat	Double layer	Upper layer	1.0 ~ 1.2	3 ~ 5	–
			Lower layer	2.0 ~ 2.3	10 ~ 15	–
[183]	Upper-seal coat	Inverted seal	Upper layer	2.2 ~ 2.6	2.36 ~ 4.75	7 ~ 9
			Lower layer	1.8 ~ 2.2	9.5 ~ 13.2	10 ~ 12
Guangdong, 2011 [179]	Upper-seal coat	"Cape" seal	Slurry seal	–	Grading	–
			Chip seal	2.2	9.5	6
Gansu, 2007 [119]	SMAI	Single layer		2.0 ~ 2.3	9.5 ~ 13.2	7.5
Zhejiang, 2008 [185]	SAMI	Single layer		1.75	9.5 ~ 13.2	7.6
Anhui, 2012 [186]	SAMI	Single layer		2.3	13.2 ~ 16	12
Jiangxi, 2011 [187]	SAMI	Single layer		–	9.5–13.2	–

At high temperatures, the interlayer force of rubberized asphalt SAMI was poor. Therefore it was shown that the asphalt content should be increased for the pavement surface in order to enhance the interlayer shear strength [5,188].

In 2013, composite-modified SAMI from high-density polyethylene (HDPE) and rubber powder was used on the new cement stabilized macadam base in Heilongjiang province, and was shown to exhibited good road performance [189,190]. In addition, warm-mix technology was also applied in the construction of SMAI with rubberized asphalt [191,192]. This material was also commonly used in tunnel cement pavements in Zhejiang and Jiangxi provinces, as shown in Table 13.3.13.

In addition, the large stone porous asphalt rubber mixture (LSPARM) was designed with high-temperature rutting resistance, high moisture sensitivity, high-temperature crack

resistance, and high fatigue resistance [193]. Moreover, LSPARM also had good drainage properties, offering a new idea for the development of SAMI. As shown in Table 13.3.13, the applications of SAMI with single particle size in Gansu, Zhejiang, Anhui, and Jiangxi provinces were shown to be effective.

13.3.6 Environmental and economic benefits of rubberized asphalt pavement

13.3.6.1 Environmental benefits

13.3.6.1.1 Energy conservation and emission reduction

The energy consumption and emission of greenhouse gases (GHG) occurring in the process of raw material production, including base asphalt production, crumb rubber (CR) production, and CRMA production, can be measured at different stages.

It was confirmed that in order to produce smaller particle size, more energy is required [194]. The liquid nitrogen low-temperature method consumed the most energy, followed by air-cooling and room-temperature methods [195]. Xiong [195] used liquefied natural gas (LNG) to generate the crumb rubber and indicated that the production energy consumption was reduced by 437.3 kW/t and that 276 kW h electric energy was saved. In addition, Yang developed the waste tire granule gasification and desulfurization technology to improve the desulfurization efficiency and ultimately reduce the production energy consumption [196].

As shown in Fig. 13.3.17, the energy consumption and GHG emission of rubberized asphalt were significantly

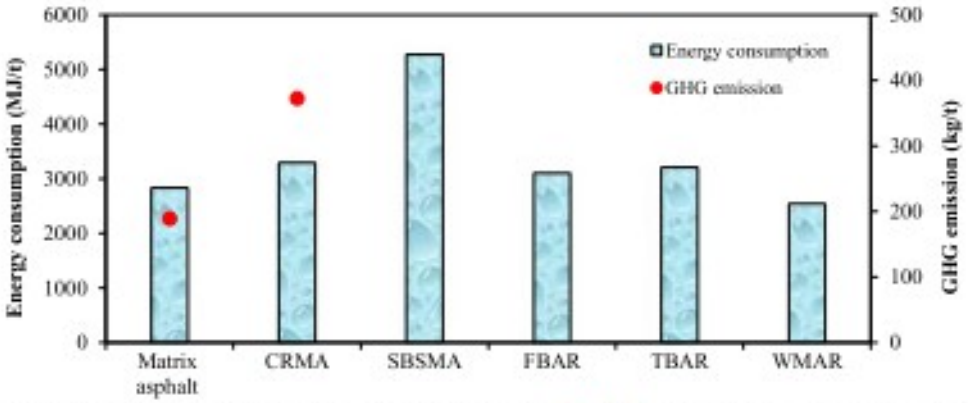


Figure 13.3.17 Energy consumption and GHG emission of binders [1,194]. SBSMA, SBS modified asphalt; FBAR, field blended rubberized asphalt; TBAR, terminal blended rubberized asphalt; WMAR, warm mix rubberized asphalt.

higher than those of base asphalt [194]. The field blended CRMA and Terminal blended CRMA consumed similar amounts of energy [1,194]. However, the energy consumption for SBSMA was much higher than for CRMA. The major reason was that the production of tire powder consumed less energy than that of the SBS modifier [1]. The WMA technology helped reduce the mixing and compaction temperatures of rubberized asphalt and thus saved approximately 20%～25% of fuel [1].

The mixing process also consumed energy consumption and also resulted in GHG emission. As shown in Table 13.3.14, the energy consumption for the base asphalt mixture was the lowest [1,197]. In addition, the SBS-modified mixture consumed more energy than the CRMA mixture due to higher energy consumption of SBS modifier processing [1]. The mixing temperature was the most significant factor affecting energy consumption. With the addition of warm-mix additive, the mixing temperature declined and thus reduced the energy consumption [83,197].

All processes of transportation, paving, and rolling of mixture consume energy and emit GHG. To reduce energy consumption

Table 13.3.14 Consumption and greenhouse gases emissions of rubberized mixtures.

Cite	Mix type	Energy consumption (MJ/ton)	Mazout consumption (ton/1000 ton)	Greenhouse gases emission (kg/ton)
[1]	Rubber asphalt mix	678.8		–
[1]	SBS asphalt mix	743.8		–
[197]	Common asphalt mix	–	8	–
[197]	Warm mixed asphalt mix	–	5.5	–
[197]	Rubber asphalt mix	–	10.5	–
[197]	WMAR mix	–	6.2	–
[83]	Common asphalt mix	384.9	–	–
[83]	TBAR mix	409.2	–	–
[83]	TB+4%Sasobit mix	388.5	–	–
[83]	TB+4%PE wax mix	398.8	–	–
[194]	RA+30%RAP mix	349.9	–	30.35
[194]	RA+40%RAP mix	338.35	–	29.45
[194]	RA+50%RAP mix	326.40	–	28.54

and emission, recycling asphalt pavement (RAP) was also used in the CRMA mixture because the energy consumption and GHG emission of CRMA were higher than for RAP [194]. Moreover, the dry process consumed more rubber powder than the wet process in mixture production, this being an important contribution to waste tire consumption and environmental protection [2].

As shown in Table 13.3.15, the energy consumption of SBS-modified asphalt pavement was the highest, followed by the rubber asphalt and then the rubber asphalt with RAP, the base asphalt with RAP. Rubberized asphalt showed the highest GHG emissions followed by SBS-modified binder and then the rubberized asphalt with RAP, the base asphalt with RAP. In general, it could be found that the base asphalt pavement was the most environmentally friendly. With the increase in the dosage of RAP, the energy consumption and GHG emission of the mixture were reduced [194].

Furthermore, life cycle assessment (LCA) was used to evaluate the entire life of the pavement; it was found that the process using crumb rubber mixture corresponded to a net energy savings of 4236 MJ/t, and resulted in a reduction of the overall energy ranging from 43% to 46% [1]. This implied that the combined application of rubberized asphalt and RAP in pavements could be considered as a sustainable development.

Table 13.3.15 Energy consumption and greenhouse gases emissions of various mixture types [194].

Serial number	Pavement type		Energy consumption (MJ/t)	Greenhouse gases emission (kg/t)
	Binder type	Mixture type		
1	Base asphalt	AC−13	554	44.03
2	SBS-modified asphalt	SMA−13	748	55.84
3	RA	SMA−13	631.1	58.93
4	Base asphalt +30%RAP	AC−13	588.66	49.03
5	Base asphalt +40%RAP	AC−13	574.34	48.16
6	Base asphalt +50%RAP	AC−13	559.59	47.26
7	RA+30%RAP	AC−13	606.36	55.57
8	RA+40%RAP	AC−13	589.49	53.75
9	RA+50%RAP	AC−13	572.22	51.93

13.3.6.1.2 Noise-reduction performance

Another advantage of using rubberized asphalt in pavement is its excellent noise-reduction performance. Viscoelasticity is one of the main factors affecting the noise of asphalt pavement [1]. The noise-reduction examples in some countries and regions are listed in Table 13.3.16 [2]. Rubberized asphalt pavement could reduce vehicle noise by more than 3 dB compared to ordinary pavement [126]. In addition, rubberized asphalt pavement continued to reduce traffic noise after six years, but other pavements could not [198].

13.3.6.1.3 Environmental safety

The fumes from asphalt pavement construction have a potential environmental impact on human health. Asphalt fumes are composed of polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and other exhaust gases [1]. As shown in Fig. 13.3.18, CO emission was significantly reduced after the use of the rubberized asphalt mixture [1]. During the process of producing and paving rubberized asphalt mixture, a bad smell was detected that resulted in irritation of the throat, nose, and eyes [1]. However, some emission studies conducted over the past two decades for rubberized mixture generally indicate that there is slight difference in emissions between rubberized mixture with the conventional HMA mixture and no identifiable risk to the health of paving personnel or the public [2,199].

It is important to reduce the emissions of rubberized asphalt. Chinese researchers have made a lot of contributions to the development of treatment methods, included combustion

Table 13.3.16 Noise-reduction examples of rubberized asphalt pavements in various countries and regions [2].

Countryand region	Time	Reducing level of the noise
Belgium	1981	8 ~ 10 dB
Canada	1981	3 ~ 4 dB
France	1984	3 ~ 5 dB
Germany	1980	3 dB
Netherlands	1988	2.5 dB
Phoenix, United States	1990	10 dB
Orange, United States	1992	3 ~ 5 dB
Los Angeles, United States	1991	3 ~ 7 dB
Hebei, China	2000	3 ~ 5 dB

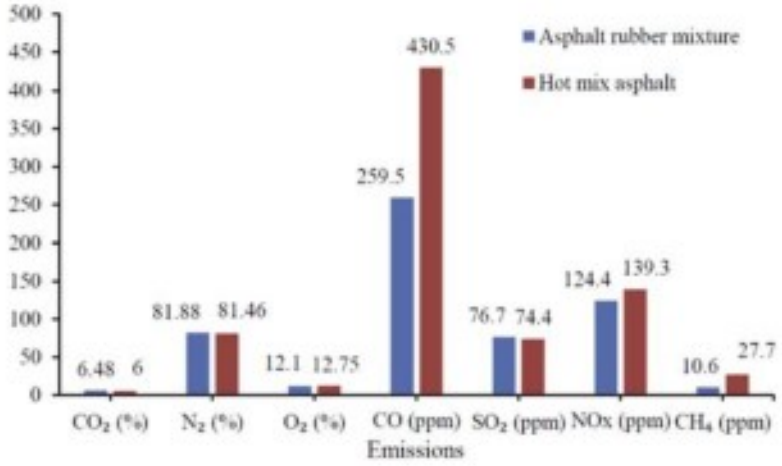


Figure 13.3.18 Emissions of the CRMA mixtures and HMA mixture [1].

Table 13.3.17 Emissions of harmful substances from asphalt mixtures [2].

Test item	Unit	HMA	WMA	Reduce rate/%
CO_2	%	2.6	1	61.5
NO_X	Mg/m^3	151	40	73.5
CO	Mg/m^3	104	91.3	12.2
SO_2	Mg/m^3	13	3.3	74.6
Asphalt fume	Mg/m^3	21.1	1.7	91.9
Benzene soluble	Mg/m^3	19.5	0.581	97.0
Benzo(a) pyrene	$\mu g/m^3$	0.0944	0.0187	80.2

method, absorption method, electrostatic method, and low-temperature plasma method [199,200]. In addition, as described before, WMA technology has been widely used to reduce emissions [201], as shown in Table 13.3.17.

13.3.6.2 Economic benefits

Life cycle analysis (LCA) of asphalt pavement is usually divided into four stages: production, placement and construction, maintenance and repair, demolition or recycling [197].

As shown in Fig. 13.3.19, it was found that SBS-modified asphalt cost more due to the higher price of SBS modifier; as a result, rubberized asphalt gained an advantage. In addition, Chinese researchers used biooil (1500–2000 yuan per ton) in rubberized asphalt to replace asphalt (5000 yuan per ton) in

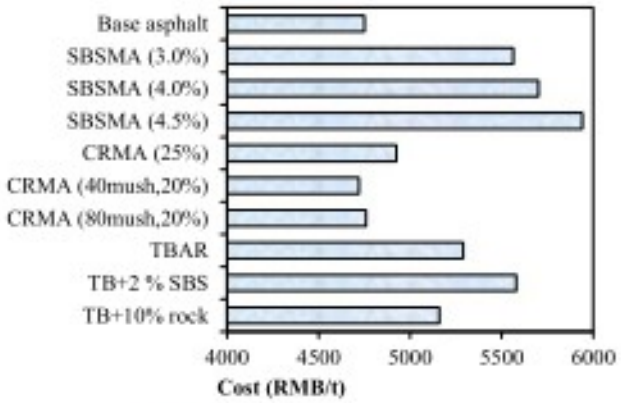


Figure 13.3.19 Costs of different binders [202–204].

Table 13.3.18 Costs of different mixtures and the life expectancies of pavements.

Cite	Binder type	Mix type	Cost	Life expectancy (years)
[206]	CRMA	SMA–13	763 RMB/ton	15
[206]	CRMA	AC–13	815 RMB/ton	–
[83]	Base asphalt	SMA–10	59.9 USD/ton	–
[83]	TBAR	SMA–10	89.9 USD/ton	–
[83]	TB+4% Sasobit	SMA–10	96.2 USD/ton	–
[203]	SBSMA	SMA–13	–	10
[203]	Base asphalt	AC–13	–	6

asphalt binder, improving the performance of rubberized asphalt and saving considerable costs at the same time [205].

The production cost of the mixture is also important in determing the whole cost, which includes the cost of asphalt, the cost of aggregate, and the energy consumption. Table 13.3.18 shows that the production cost of the rubberized asphalt mixture was higher than base asphalt mixture. In addition, the cost of CRMA with dense gradation was higher than that of rubberized SMA mixture [206]. The addition of WMA additive resulted in a higher cost for the WMA mixture [83].

In addition, the advantage of rubberized asphalt mixture was to reduce the thickness of pavement structure. It has been shown that CRMA could reduce the thickness (from 30–70% reduction) of rubberized asphalt pavement, extend the service life, and reduce maintenance costs [199]. When the rubberized asphalt stress absorption layer was applied in the pavement structure layer, the thickness could be further reduced [198].

13.3.7 Conclusions

Rubberized asphalt materials are widely used in China. This chapter covered the Chinese experience, and included the properties of rubberized asphalt and rubberized asphalt mixtures. Some typical applications of rubberized mixtures in thin overlay, waterproofing, bridge deck, tunnel paving, and chip seal were summarized. In addition, the environmental and economic benefits were also studied by Chinese researchers. The following conclusions could be made based on studies completed in China:

1. The properties of rubber powder and base asphalt significantly influence the performance of rubberized asphalt. The main influencing factors on production process have been optimized by Chinese researchers.
2. The filler type, rubberized asphalt content, and aggregate gradation may have impacts on volumetric properties of rubberized asphalt mixture.
3. Many unique methods and equipment have been developed in China to produce rubber powder, rubberized asphalt, and rubberized asphalt mixture over the past few decades.
4. Rubberized asphalt pavement has been successfully applied in many regions of China. The rubberized asphalt mixture is typically applied for the surface layer of new pavement or thin overlay to extend the service life of old pavement in China.
5. Waterproof coating by rubberized asphalt has been broadly applied in China, including bridge deck and tunnel paving.
6. Rubberized asphalt chip seal is widely used in middle and low layers of new pavement or pavement maintenance in China, and SAMI proved its feasibility in absorbing the stress to extend the service life of pavement structure, which has been broadly applied in various layers of pavement.
7. The application of rubberized asphalt mixtures generally improves the environmental safety based on life cycle analysis, including reduce noise and emissions. In addition, the costs saving is a major priority for the utilization of waste tire rubber in China.

References

[1] T. Wang, F. Xiao, X. Zhu, B. Huang, Jg Wang, S. Amirkhanian, Energy consumption and environmental impact of rubberized asphalt pavement, J. Clean. Prod. 180 (2018) 139–158.

[2] P. Li, Z. Ding, Analysis of environmental and ecological effects on new techniques for asphalt pavement materials, Proceedings of 2011 International Symposium on Water Resource and Environmental Protection, IEEE Computer Society, 2011, 3090–3092.

[3] C. Guo, Study on the application technology of ground tire asphalt rubber, Chongqing Jiaotong University, 2008.
[4] C. Dong, Production of rubber powder modified asphalt and its application in highway construction, Technol. Highw. Transp. 03 (2003) 39–45.
[5] H. Xie, Study on Application of Asphalt-Rubber in the Composite Pavement, Chongqing Jiaotong University, 2008.
[6] W. Xu, J. Kong, C. Liu, Development and application of fine rubber powder production technology, Appl. Mech. Mater. 709 (2015) 380–383.
[7] D. Sun, F. Jin, X. xu, W. Lv, Research progress of wet process and dry process for asphalt rubber pavement, Pet. Asph. 22 (06) (2008) 1–5.
[8] L. Han, M. Zheng, C. Wang, Current status and development of terminal blend tyre rubber modified asphalt, Constr. Build. Mater. 128 (2016) 399–409.
[9] B. Li, J. Wang, G. Cao, C. Wang, X. Yang, Influence mechanism of crumb rubber characteristics on high-temperature performance for rubber modified asphalt binder, J. Basic Sci. Eng. 25 (2) (2017) 347–355.
[10] X. Li, L. Ping, H. Wang, C. Zhang, Z. You, Performance test of rubber asphalt based on domestic and abroad test methods, J. Traffic Transp. Eng. 15 (1) (2015) 10–17.
[11] Y. Cui, Y. Xing, L. Wang, S. Zhang, Improvement mechanism of crumb rubber-modified asphalt, J. Build. Mater. 14 (5) (2011) 634–638.
[12] R. Cao, R. Chen, Laboratory study on process parameters of asphalt rubber and their effects on performance, J. Southeast. Univ. 38 (2) (2008) 269–273.
[13] Y. Tan, Y. Fu, L. Ji, L. Zhang, Low-temperature evaluation index of rubber asphalt, J. Harbin Inst. Technol. 48 (3) (2016) 66–70.
[14] L. He, Y. Ma, T. Ma, Research on asphalt rubber and its aging performance, J. Build. Mater. 16 (2) (2013) 370–374.
[15] X. Qiu, L. Chen, L. Xue, Effect of crumb rubber modifier on pavement performance of wearing course asphalt mixture, Adv. Mater. Res. 168 170 (2) (2011) 1145–1148.
[16] Y. Dong, Y. Tan, L. Yang, Evaluation of performance on crumb-rubber-modified asphalt mixture, J. Test. Eval. 40 (7) (2012) 20120186–20120191.
[17] Y. Zhang, K. Li, B. Liang, X. Liu, Effect of rubber particles on asphalt mixture marshall mechanical index, J. Henan Univ. Sci. Technol. 33 (4) (2012) 52–55.
[18] Q. Bai, Z. Qian, R. Cao, Mix design method of asphalt rubber open-graded friction course and its application in overlay, J. Southeast Univ. 25 (3) (2009) 395–399.
[19] H. Luo, J. Tian, J. Li, T. Huang, M. Zhang, L. Wei, et al., Study on the preparation and technology of spraying quick-setting waterproof material, N. Chem. Mater. 42 (01) (2014) 51–52+55.
[20] Y. Li, Y. Tan, The connection properties of rubber asphalt waterproofing adhesive layer in bridge deck pavement, Appl. Mech. Mater. 142 (2011) 169–172.
[21] J. Zhou, Q. Sun, X. Wu, Y. Wang, Finite element analysis on mechanic feature of crumb rubber modified asphalt waterproofing layer for bridge deck, J. Wuhan Univ. Technol. 29 (9) (2007) 38–40.
[22] J.V. Kirk, M. Shu, Application of Cape seal technology for scrap rubber asphalt, China Highway Maintenance Technology Conference, Beijing, China, 2012, 7.
[23] A. Kang, Research on the mechanism of ACRM, J. Highw. Transp. Res. Dev. 25 (7) (2008) 12–16.

[24] M. Xu, J. Liu, W. Li, W. Duan, Novel method to prepare activated crumb rubber used for synthesis of activated crumb rubber modified asphalt, J. Mater. Civ. Eng. 27 (5) (2015).
[25] S. Kocevski, S. Yagneswaran, F. Xiao, V.S. Punith, D.W. Smith Jr., S. Amirkhanian, Surface modified ground rubber tire by grafting acrylic acid for paving applications, Constr. Build. Mater. 34 (2012) 83–90.
[26] K. Yu, H. Wang, H. Han, R. Li, X. Chen, J. Du, et al., Hydrogen peroxide oxidizing modification of crumb tire rubber and its application in modified bitumen, J. Tianjin Univ. 47 (11) (2014) 949–954.
[27] F. Xiao, S. Yao, J. Wang, J. Wei, S. Amirkhanian, Physical and chemical properties of plasma treated crumb rubbers and high temperature characteristics of their rubberised asphalt binders, Road. Mater. Pavement Des. 21 (3) (2018) 587–606.
[28] J. Shen, S. Amirkhanian, F. Xiao, B. Tang, Surface area of crumb rubber modifier and its influence on high-temperature viscosity of CRM binders, Int. J. Pavement Eng. 10 (5) (2009) 375–381.
[29] X. Wang, R. Cao, Rubber asphalt modification mechanism, J. Chang'an Univ. 31 (02) (2011) 6–11.
[30] L. Zhang, C. Xing, F. Gao, T. Li, Y. Tan, Using DSR and MSCR tests to characterize high temperature performance of different rubber modified asphalt, Constr. Build. Mater. 127 (2016) 466–474.
[31] M. Liang, X. Xin, W. Fan, H. Sun, Y. Yao, B. Xing, Viscous properties, storage stability and their relationships with microstructure of tire scrap rubber modified asphalt, Constr. Build. Mater. 74 (2015) 124–131.
[32] L. He, J. Wei, L. Liu, J. Deng, Study on phase structure of rubberized asphalt binder based on Han curve, J. Highw. Transp. Res. Dev. 34 (05) (2017) 10–18+94.
[33] G. Li, F. Wang, M. Kuang, X. Zhou, Performance of SBS/crumb rubber composite modified asphalt, J. East. China Univ. Sci. Technol. 42 (1) (2016) 21–27.
[34] Y. Guo, B. Zhao, A. Shen, W. Jia, Q. Zhang, Experimental study on performance of rubber asphalt based on orthogonal design method, J. Highw. Transp. Res. Dev. 34 (02) (2017) 7–14.
[35] Z. Ye, X. Kong, J. Yu, L. Wei, Z. Jiang, Study on rubber powder modified asphalt, J. Wuhan Univ. Technol. 01 (2003) 11–14.
[36] W. Huang, X. Fu, Y. Li, S. Liu, Evaluation of low temperature performance and correlation analysis on low temperature indexes of SBS modified asphalts, J. Build. Mater. 20 (3) (2017) 460–467.
[37] M. Liang, X. Xin, W. Fan, H. Luo, H. Sun, B. Xing, et al., Study on viscoelastic behavior of crumb tire rubber modified asphalt with different particle sizes based on dynamic mechanical analysis, Acta Petrolei Sin. 31 (5) (2015) 1187–1192.
[38] Y. Liu, C. Liu, Y. Zhang, Reaction rules of crumb rubber modified asphalt, J. China Univ. Pet. 41 (03) (2017) 154–160.
[39] P. Li, Z. Ding, C. Chen, Analysis of swelling and degradation characteristics of crumb rubber in hot asphalt, J. South China Univ. Technol. 44 (12) (2016) 97–103.
[40] Z. Lv, B. Li, X. Yang, Y. Wei, Z. Zhang, Optimization of production process parameters of waste rubber powder modified asphalt based on approximation to ideal point sequencing method, J. Highw. Transp. Res. Dev. 34 (04) (2017) 1–7.
[41] G. Yang, A. Shen, Z. Chen, L. Yu, Y. Guo, Pavement performance and modified mechanism of rubber powder and SBS compound modified asphalt mixture in seasonal freezing region, J. Chang'an Univ. 35 (06) (2015) 6–15+23.

[42] Y. Cui, Y. Xing, L. Wang, S. Zhang, Micro-structure and rheological behavior of composite crumb rubber modified asphalt, Polym. Mater. Sci. Eng. 28 (2) (2012) 41–44.
[43] D. Zhang, Mechanism and application of modified asphalt, Pet. Asph. (02) (2003) 36–38.
[44] T. Wang, R. Yang, A. Li, L. Chen, B. Zhou, Comparative experimental research of elastic recovery performance indexes of rubber asphalt, J. Highw. Transp. Res. Dev. 33 (04) (2016) 32–38.
[45] L. He, A. Shen, C. Xie, L. Liu, Orthogonal test for rubber asphalt properties, J. Chang'an Univ. 34 (01) (2014) 7–12.
[46] T. Li, J. Li, W. Li, Micro-mechanism study and road engineering application of asphalt rubber, 3rd International Conference on Civil Engineering, Architecture and Building Materials, CEABM 2013, May 24, 2013–May 26, 2013, Trans Tech Publications Ltd, Jinan, China, 2013, 1817–1824.
[47] Y. Sheng, H. Li, J. Geng, Y. Tian, Z. Li, R. Xiong, Production and performance of desulfurized rubber asphalt binder, Int. J. Pavement Res. Technol. 10 (3) (2017) 262–273.
[48] L. Wang, L. Wang, C. Chang, Study on the adhesion performance of modified asphalt-aggregate composite based on the surface free energy theory, Acta Mater. Compos. Sin. 34 (9) (2017) 2061–2069.
[49] Z. Xie, Research on the relationship between clay content in aggregate and water stability of rubber asphalt mixture, Adv. Mater. Res. 639–640 (2013) 346–349.
[50] X. Yu, P. Ding, D. Xu, L. Yin, Y. Wang, Effects of fillers on the high temperature properties of CRMA mastic, New Frontiers in Road and Airport Engineering. 2015 International Symposium on Frontiers of Road and Airport Engineering, American Society of Civil Engineers, Reston, VA, USA, 2015, 122–131.
[51] Q. Chen, T. Ling, C. Mou, Influence of filler on high temperature performance of rubberized asphalt based on DSR test, Commun. Sci. Technol. Heilongjiang 41 (04) (2018) 41–42.
[52] Q. You, Z. Cong, N. Zheng, The influence of crumb rubber modified asphalt mixture to the volume of air voids, J. Wuhan Univ. Technol. 33 (6) (2011) 54–58.
[53] T. Ling, C. Xiao, W. Xia, L. Wu, Characteristics of asphalt-rubber mortar and aggregate gradation optimization based on high temperature condition, J. Civil Archit. Environ. Eng. 32 (5) (2010) 47–52.
[54] P. Guo, Study on water stability of Sasobit warm mixture asphalt, J. Zhengzhou Univ. 31 (05) (2010) 36–39.
[55] P. Cheng, P. Fan, Effect of aggregate gradation on performance of rubberized WMA, J. Highw. Transp. Res. Dev. 31 (3) (2014) 32–37.
[56] W. Huang, W. Wang, Y. Huang, Y. Li, Influencing factor research on high-temperature performance of asphalt rubber mixture, J. Tongji Univ. 38 (7) (2010) 1023–1028.
[57] H. Zhang, Z. Gao, M. Chang, H. Wang, Aggregate gradation fractal characteristic of crumb rubber asphalt mixtures, J. Wuhan Univ. Technol. 33 (1) (2011) 82–85.
[58] Y. Liu, S. Han, Z. Zhang, O. Xu, Design and evaluation of gap-graded asphalt rubber mixtures, Mater. Des. 35 (2012) 873–877.
[59] D. Xu, X. Wang, B. Chen, Research on properties of reclaimed rubber modified asphalt mixture, J. Wuhan Univ. Technol. 34 (10) (2012) 48–52.

[60] M. Huang, M. Zheng, Y. Li, W. Huang, Air void variation of asphalt rubber mixture grade RAC–G, J. Changsha Univ. Sci. Technol. 9 (1) (2012) 23–28.
[61] K. Wu, G. Yang, A. Zeng, Design of rubberized asphalt concrete by means of coarse aggregate void filling method, Adv. Mater. Res. 463–464 (1) (2012) 215–220.
[62] Y. Chen, Z. Li, Gradation design of crumb rubber asphalt mixture, J. Highw. Transp. Res. Dev. 29 (11) (2012) 19–24.
[63] W. Huang, M. Huang, M. Zheng, Y. Li, Air void variation of asphalt rubber mixture grade SAC–13, J. Tongji Univ. 40 (5) (2012) 31–36.
[64] Y. Wang, L. Liu, L. Sun, Influence of temperature on volumetric parameters of asphalt rubber mixture with warm-mix additive, J. Build. Mater. 16 (3) (2013) 539–543.
[65] P. Fan, P. Cheng, Influencing factors research on high temperature performance of warm mix rubber asphalt mixture, J. Wuhan Univ. Technol. 36 (1) (2014) 62–67.
[66] Y. Chen, Z. Li, Meso-structure of crumb rubber asphalt mixture based on discrete element method, J. Harbin Inst. Technol. 45 (4) (2013) 116–121.
[67] X. Fan, Performance of asphalt mixture made from waste tire rubber, Sci. Technol. Rev. 29 (21) (2011) 70–72.
[68] M. Yu, G. Wu, Research on the mix design of dry process crumb rubber modified asphalt mixture, J. Build. Mater. 17 (1) (2014) 100–105.
[69] X. Ding, T. Ma, W. Zhang, D. Zhang, Experimental study of stable crumb rubber asphalt and asphalt mixture, Constr. Build. Mater. 157 (2017) 975–981.
[70] W. Huang, M. Zheng, M. Huang, Fatigue performance of terminal blend rubberized asphalt mixture, J. Tongji Univ. 42 (10) (2014) 1543–1549.
[71] H. Xu, S. Dang, D. Cui, Durability test research of asphalt mixture with rubber particles under the condition of freeze-thaw cycle, Adv. Mater. Res. 919–921 (2014) 1096–1099.
[72] L. Du, S. Dang, H. Xu, B. Liang, K. Zhai, Water stability test of crumb rubber asphalt mixture based on different grades of road, J. Henan Univ. Sci. Technol. 36 (1) (2015) 67–71.
[73] L. Feng, Y. Cui, C. Li, Water stability of rubber modified asphalt mixture under salt freeze cycle, J. Build. Mater. 17 (5) (2014) 823–828.
[74] X. Lu, B. Lu, H. Huang, Q. Jiang, Structure and properties of continuously devulcanized ground tire rubber using independently designed single screw extruder, CIESC J. 65 (11) (2014) 4614–4619.
[75] Y. Zhang, D. Ren, L. Zhang, J. Shi, X. Hu, X. Lin, Modeling on the dynamic analysis of the rubber devulcanization in the counter-rotating twin screw extruder, Polym. Mater. Sci. Eng. 29 (11) (2013) 168–172.
[76] Z. Ma, Y. Lian, Production and application of rubber powder, Liaoning Chem. Ind. 02 (2003) 91–94.
[77] J. Chen, R. Zhang, M. Ji, F. Fang, Q. Wang, Y. Tong, Research of fine control technology about the tire rubber production line auxiliary machine, 2nd International Conference on Communications, Signal Processing, and Systems, CSPS 2013, September 1, 2013 - September 2, 2013, Springer Verlag, Tianjin, China, 2014, 391–399.
[78] L. Qiu, J. Yang, Waste tire free shear breaking and design of hydraulic system, 2nd International Conference on Advances in Materials and Manufacturing Processes, ICAMMP 2011, December 16, 2011 - December 18, 2011, Trans Tech Publications, Guilin, China, 2012, 497–500.
[79] S.B. Liang, Y.C. Hao, Novel cryogenic grinding system for recycling scrap tire peels, Adv. Powder Technol. 11 (2) (2000) 187–197.

[80] S.B. Liang, D.P. Hu, C. Zhu, A.B. Yu, Production of fine polymer powder under cryogenic conditions, Chem. Eng. Technol. 25 (4) (2002) 401–405.
[81] Y. Liu, X. Yin, Production method of rubber powder, China Elastomerics (03)(2001) 40–43.
[82] Y. Ni, M. Liao, X. Li, Preparation process and properties of crumb rubber modified asphalt, Acta Sci. Nat. Univ. Sunyatseni 44 (Suppl. 2) (2005) 33–35.
[83] Y. Wen, Y. Wang, K. Zhao, D. Chong, W. Huang, G. Hao, et al., The engineering, economic, and environmental performance of terminal blend rubberized asphalt binders with wax-based warm mix additives, J. Clean. Prod. 184 (2018) 985–1001.
[84] W. Huang, C. Yan, S. Liu, Z. Shan, F. Xiao, Low temperature performance comparison of terminal blend rubberized/SBS modified asphalt, J. Build. Mater. 19 (6) (2016) 1088–1091.
[85] R. Dong, C. Qi, K. Zheng, M. Zhao, Test on low-temperature performance for high-temperature pyrolytic rubber modified asphalt, China J. Highw. Transp. 30 (10) (2017) 32–38.
[86] M. Kuang, F. Wang, X. Zhou, C. Li, Effect of pre-degraded process on performance of crumb rubber modified asphalt, J. East China Univ. Sci. Technol. 41 (3) (2015) 328–334.
[87] Z. Wang, Study on the of Asphalt Rubber Equipment, Chang'an University, 2014.
[88] D. Wang, Research on Production Technology and Key Equipment of Rubber Asphalt, Chang'an University, 2010.
[89] B. Wu, J. Chen, A rubberized asphalt heating equipment.
[90] Y. Yang, Heating system of rubberized asphalt production equipment.
[91] Y. Yang, Feeding system of rubberized asphalt production equipment.
[92] Z. Wang, Performance Test of Rubber Asphalt and Research on Production Equipment, Chang'an University, 2015.
[93] N. Jiang, A rubberized asphalt kettle.
[94] N. Zhen, X. Ji, Z. Cong, X. Wang, A improved rubberized asphalt reaction still.
[95] M. Yu, G. Wu, J. Zhou, S. Easa, Proposed compaction procedure for dry process crumb rubber modified asphalt mixtures using air void content and expansion ratio, J. Test. Eval. 42 (2) (2014).
[96] W. Cao, Study on properties of recycled tire rubber modified asphalt mixtures using dry process, Constr. Build. Mater. 21 (5) (2007) 1011–1015.
[97] F. Bai, X. Yang, G. Zeng, A stochastic viscoelastic-viscoplastic constitutive model and its application to crumb rubber modified asphalt mixtures, Mater. Des. 89 (2016) 802–809.
[98] J. Shen, B. Li, Z. Xie, Interaction between crumb rubber modifier (CRM) and asphalt binder in dry process, Constr. Build. Mater. 149 (2017) 202–206.
[99] Z. Xie, J. Shen, Performance properties of rubberized stone matrix asphalt mixtures produced through different processes, Constr. Build. Mater. 104 (2016) 230–234.
[100] M. Yu, G. Wu, W. Liu, X. Wang, L. Zhang, The shaping process research on crumb rubber modified asphalt mixture, Appl. Mech. Mater. 178–181 (3) (2012) 1568–1572.
[101] Z. Xie, J. Shen, Multi-scale evaluation on the interaction between asphalt and crumb rubber, New Frontiers in Road and Airport Engineering. 2015 International Symposium on Frontiers of Road and Airport Engineering, American Society of Civil Engineers, Reston, VA, USA, 2015, 10–16.

[102] Y. Zhu, P. Jiang, Viscosity-temperature characteristics and pavement performance rubber-modified asphalt added with domestic TOR, Mater. Rev. 30 (6) (2016) 134–139.
[103] W. Cao, W. Lu, Experimental research on recycled tire rubber modified asphalt mixture using hybrid process, J. Build. Mater. 10 (1) (2007) 110–114.
[104] Y. Wang, L. Liu, Storage stability of asphalt rubber at high temperature, Fourth International Conference on Transportation Engineering, American Society of Civil Engineers, Reston, VA, USA, 2013, 1178–1183.
[105] L. He, X. Huang, Y. Ma, D. Zhuang, T. Ma, Experimental study on storage stability of crumb rubber modified asphalt, J. Southeast Univ. 41 (5) (2011) 1086–1091.
[106] W. Huang, Y. Zhang, Mechanism and process control of road-use asphalt rubber reaction procedure, J. Highw. Transp. Res. Dev. 11 (2006) 5–9.
[107] Z. Chen, Z. Zhang, H. Luo, N. Dong, Rubber modified asphalt storage stabilizer option, Adv. Mater. Res. 311–313 (2) (2011) 1136–1139.
[108] C. Wang, F. Wang, W. Zhang, Research on road performance of desulfurized rubber asphalt and mixture, Appl. Mech. Mater. 525 (2014) 546–551.
[109] G. Wang, X. Liu, L. Yao, X. Zhang, P. Dong, A rubber asphalt storage equipment.
[110] Z. Zhang, L. Chen, C. Wu, K. Liu, A. Li, J. Tang, et al., Rubberized asphalt storage equipment.
[111] C. Wu, L. Chen, Z. Guo, R. Wang, K. Liu, J. Tang, et al., Rubberized asphalt storage and heating device.
[112] L. Guo, X. Zhang, A rubberized asphalt storage heating device.
[113] C. Zhang, H. Wang, Z. You, L. Li, Correlation between workability and compaction property of rubber asphalt mixture, J. Southeast Univ. 46 (1) (2016) 202–208.
[114] L. He, A. Shen, J. Tan, L. Wang, The research on compaction characteristics of rubber asphalt mixture, Appl. Mech. Mater. 256–259 (2013) 1845–1850.
[115] M. Huang, J. Liu, X. Zhang, D. Li, Laboratory assessment of workability of asphalt rubber hot mixes using warm mix technology, Appl. Mech. Mater. 193–194 (1) (2012) 452–457.
[116] Z. Zhang, L. Song, F. Chen, Influence of different warm-mixed agent on asphalt mixture, J. Wuhan Univ. Technol. 36 (3) (2014) 53–58.
[117] L. He, T. Ling, Y. Ma, T. Ma, X. Huang, Rheological properties of warm mix asphalt rubber in wide range of pavement temperature, J. Traffic Transp. Eng. 15 (01) (2015) 1–9.
[118] W. Cao, S. Liu, Performance evaluation of asphalt-rubber stone matrix asphalt mixtures with warm mix asphalt additives, J. Test. Eval. 41 (1) (2013) 20120014–20120021.
[119] W. Wang, Application of rubber asphalt macadam and rubber asphalt concrete in Jia 'an section of G30 Expressway, J. Guizhou Univ. Financ. Econ. 9 (02) (2013) 88–91.
[120] D. Zhu, Study on application technology of rubber asphalt in pavement maintenance engineering, Chang'an University, 2014.
[121] Y. Li, N. Wang, Y. Xu, Research on the application of rubber modified asphalt in highway maintenance engineering, J. Guizhou Univ. Financ. Econ. 13 (09) (2017) 126–128.
[122] W. Jia, Study on the Road Performance of Asphalt Rubber and Its Mixture, Chang'an University, 2013.

[123] X. Wang, P. Li, Y. Wang, L. Fu, A study on the application of rubber crumb modified asphalt mixture, Appl. Mech. Mater. 193–194 (1) (2012) 500–504.
[124] H. Li, H. Jiang, W. Zhang, P. Liu, S. Wang, F. Wang, et al., Laboratory and field investigation of the feasibility of crumb rubber waste application to improve the flexibility of anti-rutting performance of asphalt pavement, Materials 11 (9) (2018).
[125] Z. Xie, J. Shen, Performance of porous European mix (PEM) pavements added with crumb rubbers in dry process, Int. J. Pavement Eng. 17 (7) (2016) 637–646.
[126] Z. Guo, G. Shen, X. Wang, L. Li, Analysis of asphalt-rubber pavement noise spectrum with close-proximity trailer method, China J. Highw. Transp. 25 (4) (2012) 22–28.
[127] Z. Zhang, W. Liu, X. Li, Research and application on the crumb rubber modified low-noise asphalt pavement, 4th International Conference on Technology of Architecture and Structure, ICTAS 2011, September 22, 2011 - September 24, 2011, Trans Tech Publications, Xi'an, China, 2012, 1351–1356.
[128] Z. Yao, Z. Chen, G. Zhang, M. Li, Research on large partical size and porous rubber modified asphalt mixture repairing techniques used in white and black pavement, Adv. Mater. Res. 1061–1062 (2015) 386–391.
[129] H. Wang, Q. Zhang, Design and comparative analysis of anti-skid surface of HMA, J. Highw. Transp. Res. Dev. 05 (2004) 15–17.
[130] L. Qing, Application of warm mix rubberized asphalt technology in old cement pavement reconstruction project, J. Guizhou Univ. Financ. Econ. 7 (12) (2011) 99–103.
[131] X. Li, R. Feng, Evaluation of long term use effect of warm mixed rubber asphalt mixture in different pavement structure, J. Guizhou Univ. Financ. Econ. 14 (04) (2018) 103–105.
[132] C. Wu, M. Yu, K. Liu, Application research on technology of scrap tire rubber asphalt regenerating old asphalt pavement, J. Chongqing Jiaotong Univ. 34 (01) (2015) 64–67+77.
[133] X. Qiu, M. Zhang, L. Xue, X. Xu, W. Wong, Evaluation on performance of porous asphalt pavement in Hong Kong, J. Shenyang Jianzhu Univ. 21 (3) (2005) 204–207.
[134] L.T. Geng, Q. Xu, R.B. Ren, C. Chazallon, Performance research of a new stabilized rubber modified asphalt and sand anti-fracture mix for semi-rigid asphalt pavement, J. Test. Eval. 45 (1) (2017) 1–8.
[135] J. Li, F. Ni, J. Jin, Z. Zhou, A comparison of rejuvenator and sryrenebutadiene rubber latex used in hot in-place recycling, Road. Mater. Pavement Des. 18 (1) (2017) 101–115.
[136] X. Wang, Research on Preventive Maintenance Technology of Rubber-Asphalt Mixture Thin Overlay, Chongqing Jiaotong University, 2017.
[137] Y. Song, D. Wang, The application of rubber asphalt in the cover project of Huibe Expressway, Hunan Commun. Sci. Technol. 36 (01) (2010) 29–32.
[138] X. Zhou, Application of rubber asphalt thin-layer overlay in expressway maintenance, West China Commun. Sci. Technol. 03 (2017) 35–37+88.
[139] H. Li, Application of rubber asphalt thin overlay in highway maintenance, Transpoworld 27 (2018) 74–75.
[140] M. Wu, J. Zhong, Research on the application of TBRA–SMA9.5 thin overlay technology in highway maintenance, East. China Highw. 04 (2014) 35–38.

[141] X. Su, A brief discussion on the technology of rubberized asphalt thin overlay, J. Guizhou Univ. Financ. Econ. 5 (05) (2009) 66–67.
[142] H. Bian, Design and consturction of AR–OGFC overlaying in thin layer, Mod. Transp. Technol. 05 (2008) 21–23.
[143] J. Zhao, T. Li, Study on the influence of gradation type on the properties of rubberized asphalt mixture used for thin overlay, Municipal Eng. Technol. 35 (03) (2017) 173–177+182.
[144] Y. Hao, Study on bonding performance of asphalt concrete thin layer cover, Urban Roads Bridges Flood Control 08 (2016). 284–287+27.
[145] T. Li, C. Li, Application study on the composite technology of impact compaction, asphalt rubber and stress absorbing membrane interlayer in road engineering, J. Univ. Sci. Technol. Beijing 33 (2) (2011) 244–249.
[146] P. Fan, Study on Thin Overlay Technology of Warm Mix Rubber Asphalt Mixture, Northeast Forestry University, 2014.
[147] X. Wang, Y. Lin, Y. Hou, Brief introduction of synchronous thin overlay technology, J. Guizhou Univ. Financ. Econ. 6 (01) (2010) 6–8.
[148] J. Chu, C. Shen, Product research and engineering application of non-curable rubberized asphalt waterproof coating products, N. Build. Mater. 42 (08) (2015) 56–58+69.
[149] F. Lu, L. Zhao, Z. Zhu, G. Fang, X. Liu, Study on the characteristics and application of quick setting rubber asphalt waterproof coating, N. Build. Mater. 43 (05) (2016) 120–122.
[150] H. Jia, H. Li, T. Wang, Z. Wei, S. Wu, Study on the influence of rubber emulsion on the properties of spray rubberized asphalt waterproof coating, China Build. Waterproofing 02 (2018) 9–11.
[151] X. Lin, DSTD Series of No-Curing Rubber Asphalt Waterproof Coating in the Engineering Application, Hubei University of Technology, 2017.
[152] S. Li, Y. Chang, W. Li, J. Liu, W. Duan, Y. Ma, Study on the influence of viscosity on the construction performance of non-curable rubberized asphalt waterproof coating, China Build. Waterproofing 20 (2014) 54–57.
[153] B. Chen, H. Su, H. Niu, Application of BST non-curable rubber asphalt composite waterproofing system in building waterproofing engineering, N. Build. Mater. 42 (10) (2015) 78–81.
[154] X. Yang, Y. Lou, C. Zhen, L. Qiao, Application of non-curable rubberized asphalt waterproof coating in waterproof treatment of pile head, North Architecture 2 (05) (2017) 58–62.
[155] C. Tian, j Chen, W. Liu, Y. Li, Y. Cui, X. Liu, et al., Application of quick setting rubberized asphalt waterproof coating in open excavation subway station, N. Build. Mater. 44 (03) (2017) 131–134.
[156] J. Liu, Development of quick setting rubber waterproof coating by color spraying, China Build. Waterproofing 12 (2018) 5–8.
[157] H. Li, Y. Wang, S. Wang, Preparation of flame-retardant spray quick-setting rubberized asphalt waterproof coating, China Buikl. Waterproofing 13 (2018) 14–17.
[158] C. Peng, H. Zhang, Z. You, F. Xu, G. Jiang, S. Lv, et al., Preparation and anti-icing properties of a superhydrophobic silicone coating on asphalt mixture, Constr. Build. Mater. 189 (2018) 227–235.
[159] J. Gao, X. Fan, Reaction mechanism of rubber asphalt based on deck pavement material, Bull. Chin. Ceram. Soc. 36 (05) (2017) 1582–1589.
[160] Y. Liu, J. Wu, J. Chen, Mechanical properties of a waterproofing adhesive layer used on concrete bridges under heavy traffic and temperature loading, Int. J. Adhes. Adhesives 48 (2014) 102–109.

[161] L. Di, Y. Zhu, S. Cong, Application study on solvent rubber modified asphalt waterproofing adhesive layer in steel bridge deck pavement, China Build. Waterproofing 05 (2018) 37–40.
[162] X. Hu, Study on the performance tolerance of bridge deck pavement waterproof bonding layer, Subgrade Eng. 02 (2018) 122–125.
[163] W. Wu, H. Xiong, Discussion on "white to black" construction technology of cement pavement of expressway tunnel, China High-Tech Enterp. 25 (2014) 92–94.
[164] H. Jiang, J. Lan, B. Han, Experimental research on mechanic feature of crumb rubber modified asphalt waterproofing layer for bridge deck, J. Wuhan Univ. Technol. 29 (9) (2007) 77–80+94.
[165] L. Ji, Y. Li, J. Ren, Y. Tan, S. Zhang, Method of determining the spraying amount of waterproof binder for bridge deck pavement, J. Harbin Inst. Technol. 46 (4) (2014) 57–62.
[166] Z. Li, J. Wu, X. Song, Test analysis on shear resistance performancebetween rubber-asphalt waterproofing adhesive layers, Appl. Mech. Mater. 97–98 (2011) 352–359.
[167] Z. Tang, Y. Cong, Y. Hong, Application of rubber asphalt sand gel in concrete bridge deck laying, Technol. Highw. Transp. 04 (2006) 45–47+74.
[168] G. Tao, The Application Research on the Rubber Asphalt Crushed Stone Sealing as Cement Concrete Bridge Deck Waterproofing Layer, Shenyang Jianzhu University, 2015.
[169] G. Ren, Study on the Key Technology for Overhaul of Asphalt Pavement in Mountain Freeway, Chongqing Jiaotong University, 2012.
[170] Q. Gao, M. Yu, C. Liu, Application of finished rubberized asphalt in bridge deck pavement of Dasi Section of Hang-Rui Expressway, Mod. Transp. Technol. 11 (05) (2014) 5–8.
[171] H. Chen, W. Lv, Discussion on rubberized asphalt pavement of Qiantang River Bridge, East China Highw. 01 (1995) 64–66.
[172] W. Zhu, A. Li, Study on the structure of SMA double deck finished rubber asphalt bridge deck pavement, East China Highw. 02 (2014) 74–77.
[173] B. Zhang, Y. Peng, W. Wu, Application of rubberized asphalt in suspension bridge deck pavement, J. China Foreign Highw. 03 (2008) 139–143.
[174] S. Chen, J. Huang, N. Jin, S. Du, J. Zhang, Research on the application of rubber asphalt in cement bridge deck pavement, Urban. Roads Bridges Flood Control. 07 (2009). 145–147+259–145–147+260.
[175] T. Liu, Research on Ultra-Thin Surface Anti-Sliding Treatment of Gansu Province Highway Tunnel Cement Concrete Pavement, Lanzhou Jiaotong University, 2016.
[176] Z. Li, Research on Application of Rubber-Asphalt in Chip Seal, Dalian University of Technology, 2013.
[177] H. Zhu, Application analysis of double-layer rubberized asphalt macadam surface treatment structure in cold and damp area, J. Guizhou Univ. Financ. Econ. 9 (12) (2013) 92–95.
[178] X. Deng, Y. Yin, H. Ling, Applied research of asphalt-rubber chip seal in urban road maintenance, Municipal Eng. Technol. 29 (04) (2011) 33–36.
[179] S. Qu, Performance Evaluation and Optimization of Asphalt Pavement Preventive Maintenance Treatments, South China University of Technology, 2011.
[180] H. Wang, Noise reduction characteristics and durability of crumb rubber modified emulsified asphalt mixture for micro-surfacing, Road Mach. Constr. Mech. 34 (04) (2017) 60–65.

[181] Z. Qian, Y. Xue, J. Sun, Shear performance of waterproof cohesive layer of rubber epoxy asphalt stone, J. Hunan Univ. 43 (7) (2016) 82–87.
[182] X. Gu, X. Zhang, J. Lv, Z. Huang, B. Yu, X. Zou, Laboratory performance evaluation of reinforced basalt fiber in sealing asphalt chips, J. Test. Eval. 46 (3) (2018) 20160186–20160197.
[183] Z. Zang, A. Shen, Y. Guo, Study on the pavement performance of rubber asphalt inverted seal, 11th International Conference of Chinese Transportation Professionals: Towards Sustainable Transportation Systems, ICCTP 2011, August 14, 2011–August 17, 2011, American Society of Civil Engineers (ASCE), Nanjing, China, 2011, 3544–3553.
[184] Y. Cai, A. Shen, G. Yang, Bonding properties of rubber asphalt underbody chip seal, J. Build. Mater. 16 (4) (2013) 678–682.
[185] C. Jin, X. Sun, L. Chen, Application of asphalt rubber stress absorbing memberane interlayer in the rehabitation of tunnel concrete pavement, Mod. Transp. Technol. 03 (2008) 14–16.
[186] B. Cai, S. Yuan, X. Li, J. Wang, Study on the application of rubberized asphalt stress absorbing layer on Sixu Expressway, J. Guizhou Univ. Financ. Econ. 8 (07) (2012) 11–14.
[187] Q. Li, X. Chen, Z. Huang, M. Xue, S. Wu, Study on the mechanism and construction technology of rubberized asphalt stress absorbing layer, J. Guizhou Univ. Financ. Econ. 7 (04) (2011) 115–118.
[188] J. Gao, T. Ji, Study of mechanical and fatigue properties for stress absorbing membrane interlayer in asphalt rubber, J. Exp. Mech. 24 (04) (2009) 341–346.
[189] P. Cheng, S. Shi, H. Hong, Composite modified asphalt with HDPE and rubber powder and its performance of mixture for stress absorbing layer, J. Highw. Transp. Res. Dev. 31 (2) (2014) 32–36.
[190] H. Hong, P. Cheng, Fatigue performance of stress absorbing layerasphalt combining HDPE and rubber powder, J. Harbin Inst. Technol. 46 (12) (2014) 125–128.
[191] R. Pan, P. Cheng, Grading design and road use performance of warm mix rubber asphalt mixture suitable for stress absorbing layer in cold region, World Earthq. Eng. 31 (1) (2015) 161–166.
[192] W. Huang, J. Tian, B. Li, Y. Li, Research on stress absorbing interlayer of continuous dense-graded asphalt rubber mixture, J. Build. Mater. 17 (5) (2014) 856–861.
[193] W. Cao, Z. Yao, Q. Shang, Y. Li, Y. Yang, Performance evaluation of large stone porous asphalt-rubber mixture, 2010 International Conference on Advances in Materials and Manufacturing Processes, ICAMMP 2010, November 6, 2010 - November 8, 2010, Trans Tech Publications, Shenzhen, China, 2011, 1184–1190.
[194] J. Chen, Z. Lv, K. Liu, Research on energy conservation and emission reduction of rubberized asphalt recycled pavement based on LCA, Highway 61 (05) (2016) 204–211.
[195] Y. Xiong, B. Hua, Y. Li, D. Jia, Integration analysis of LNG cold energy utilization in cryogenic pulverization of waste rubber, J. South China Univ. Technol. 37 (12) (2009) 58–63.
[196] C. Yang, W. Zhang, Study on gasification and desulphurization of ground rubber tire, J. Zhengzhou Univ. Eng. Sci. 32 (3) (2011) 15–18.
[197] Y. Yang, Structural design and social and economic benefit analysis of warm mix rubberized asphalt pavement, Low Carbon World 10 (2014) 275–278.

[198] L. Chen, Environmental impact and technical and economic feasibility analysis of asphalt rubber, China Popul. Resour. Environ. 20 (S1) (2010) 391–394.
[199] H. Wang, X. Liu, P. Apostolidis, T. Scarpas, Review of warm mix rubberized asphalt concrete: towards a sustainable paving technology, J. Clean. Prod. 177 (2018) 302–314.
[200] J. Ma, S. Sun, H. Rui, L. Wang, Y. Ma, W. Zhang, et al., A review of academic research on road building machinery in china, China J. Highw. Transp. 31 (06) (2018) 1–164.
[201] Q. Wu, Research on Warm Mix Technology of Rubber Asphalt Mixture, Chang'an University, 2011.
[202] Q. Liu, Z. Hao, Application and Exploration of waste tire rubber asphalt pavement in urban road, J. Guizhou Univ. Financ. Econ. 10 (08) (2014) 118–121.
[203] X. Li, Research on Rubber Asphalt Machining Equipment and Environmental Asphalt Rubber, South China University of Technology, 2016.
[204] W. Huang, Q. Lu, C. Chai, Research on composite modification by Terminal Blend asphalt, J. Build. Mater. 19 (1) (2016) 111–118.
[205] F. Ma, X. Li, Z. Fu, Research progress in road performance of bio-modified asphalt rubber and the mixture, J. Wuhan Univ. Technol. 37 (2) (2015) 55–62.
[206] L. Wu, Asphalt Rubber Application in the SMA, Chongqing Jiaotong University, 2009.

13.4

Quiet pavements: a novel approach of utilizing rubberized asphalt mixtures

Krishna Prapoorna Biligiri
Civil & Environmental Engineering, Indian Institute of Technology Tirupati, India

13.4.1 Introduction

In an attempt to build excellent infrastructure and improve "quality-of-life" across several spectra, there is often a propensity to discount the effects of the development that could be disruptive and pose as a challenge to sustainable growth. One such effect is traffic noise, which embraces both materials- and environmental-related features directly targeting quality-of-life issues. Of the various components within the traffic noise, highway noise (also called roadway or tire/pavement noise) characterization and evaluation have intrigued many engineers and scientists chiefly due to its relation with human ergonomics. In fact, The World Bank notes that chronic exposure to road noise can affect human health, when exposed both consciously and unconsciously [1]. Fig. 13.4.1 shows the sound levels of typical noise sources observed in actual ambience [2].

Industry has been proactive in providing solutions to mitigate roadway noise by offering various designs of sound barrier walls across highways in the vicinity of neighborhoods. Further, the typical cost of the product and construction has been found to be in the range of US $1–2 Million/km [4]. However, a smart and possibly worthwhile (economical) solution would be to mitigate the roadway noise at source. In this direction, the creation of "quiet pavements" or "silent roads" ensued as a sustainable mitigation strategy [5]. It is thought-provoking to perceive that tire/pavement noise is predominantly observed at speeds greater than 40 km/h, and that there are several factors (Fig. 13.4.2) influencing the process such as structural and functional characteristics of both tire and pavement systems as well as a combination of these two governing arrangements [3,6–17].

It is estimated that about 1 billion scrap tires are produced annually worldwide [18]. If left untreated/unused, these scrap

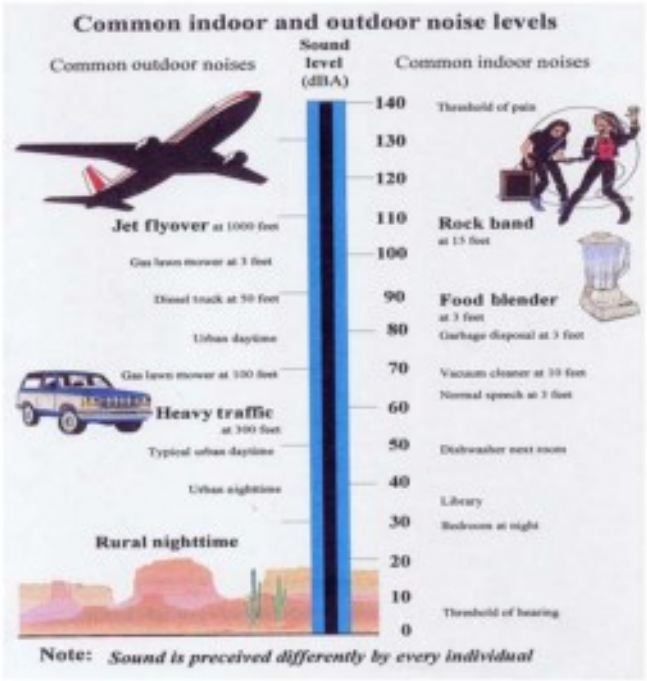


Figure 13.4.1 Sound pressure levels of typical noise sources [2,3].

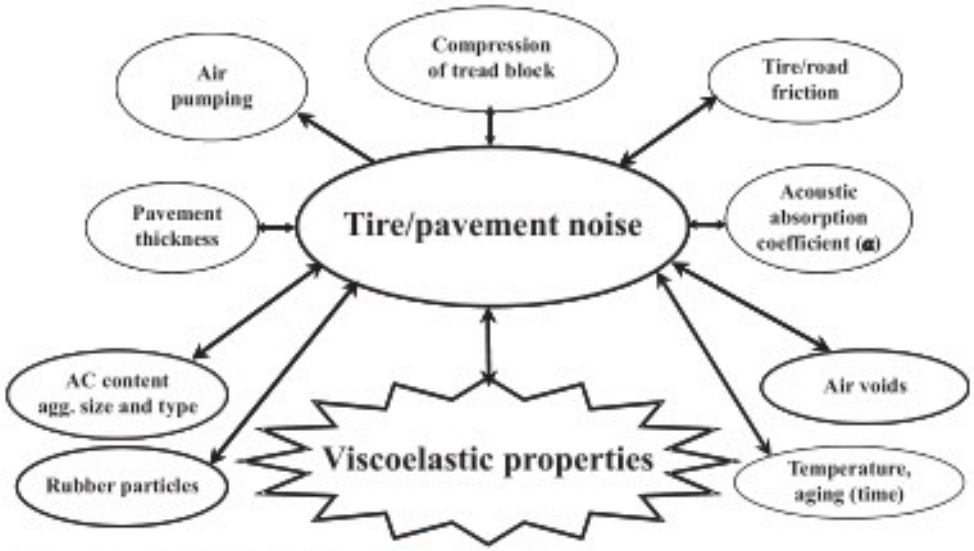


Figure 13.4.2 Typical tire/pavement noise factors [3].

tires can become a hazardous lot for mosquito breeding, contributing to an unhealthy environment. Further, if burned down, they can cause massive release of noxious gases into the atmosphere. Therefore one of the best solutions to reduce the environmental threat due to the disuse/misuse of scrap tires is to recycle the tire material in asphalt pavements by producing rubberized asphalt/asphalt–rubber (AR) products. In simple words, AR is a combination of asphalt cement (bitumen), crumb rubber inclusions, and aggregates (rocks) in varying proportions [19,20].

Worldwide experience has shown that a wide variety of AR materials have successfully helped mitigate tire/pavement noise by about 3–15 decibels in comparison with conventional asphalt concrete and cement concrete sections [3,18,21–27]. Two major types of AR have been designed and used as surface-wearing course layers, chiefly as overlays on existing asphalt concrete and/or cement concrete structural base/binder course layers: AR open-graded (AR–OG) or AR friction course (ARFC) and AR gap-graded (AR–GG) or AR asphalt concrete (ARAC). Specifically, the state of Arizona in the United States has extensively implemented AR since the late 1980s as a pavement preservation treatment and tire/pavement noise mitigation strategy. Based on performance monitoring undertaken by both maintenance engineers and researchers over more than two decades, the ARFC sections have experienced least cracking and wear, and have been the quietest pavement surfaces. Fig. 13.4.3 shows the actual field noise measurement readings of several different types of pavement surfaces in California and Arizona in the United States. As observed, the least noise-producing pavement type was ARFC, about 14 decibels quieter than the cement concrete section.

While it is true that AR mixtures have been considered as low-noise pavement surfaces, it is also significant that researchers worldwide have strived hard to understand the science behind the special material qualities that qualify it worthy of investigation. Thus this chapter in the book is an assemblage of excerpts exclusively related to the many laboratory and field investigations conducted on different asphalt paving mixtures designed across continents to characterize and evaluate viscoelastic-vibroacoustic-damping properties. Further, the scientific analogies derived from the fundamental principles regarding tire/pavement noise have been briefly described with recommendations for further research and implementation. This chapter also provides some simple toolkits that could be well-utilized by engineers and practitioners to design low-noise road surfaces, with all results and findings stemming from state-of-the-art experimentation and testing.

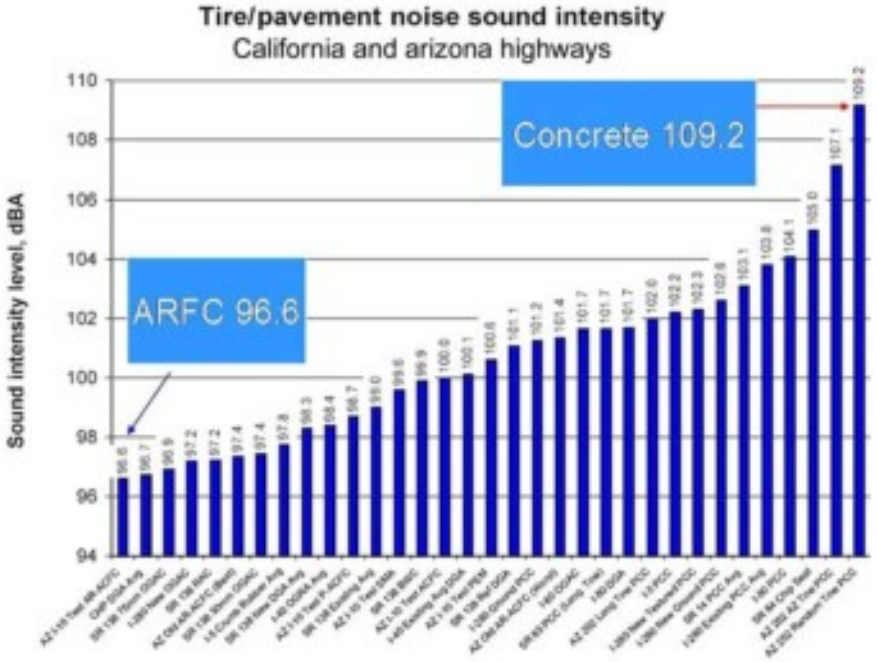


Figure 13.4.3 Field noise measurements on actual roadway stretches in the states of California and Arizona highways (United States) with ARFC depicting the case of "quiet" pavement [18].

13.4.2 Asphalt–rubber as a tire/pavement noise mitigation strategy

13.4.2.1 Laboratory evaluation and technologies

13.4.2.1.1 Viscoelastic properties of AR influencing pavement noise characteristics

One of the parameters of interest that acts as a major input in the US-based mechanistic-empirical pavement design guide is the $|E^*|$ dynamic modulus test [28]. Along with $|E^*|$, one of the other outputs emanating from the test includes phase angle, ϕ. Studies have acknowledged that ϕ is a significant performance assessor that can distinguish asphalt mixtures' viscoelastic characteristics [3,26,29]. Furthermore, ϕ is also considered as a tire/pavement noise metric capable of discerning materials' acoustic absorptive capacity in conjunction with material characteristics.

Although it is well-known that AR open-graded mixtures act as quiet pavements, there also exist diverse views that these materials perform as dampers and acoustic absorption units due to rubber inclusions, small top-size aggregates, open

texture, and rich asphalt binder content in concert with augmented viscoelastic nature. Historically, investigators have promulgated that a high amount of air pockets is key to increased damping in porous asphalt mixtures [17], which also perhaps includes AR and associated products.

In order to further appreciate the viscoelastic prowess of AR mixtures, ϕ was utilized to explain the noise-damping characteristics of various asphalt mixtures, which entailed deriving relationships [26] between average peak ϕ and actual field-measured highway noise collected using a sound intensity measurement technique by other researchers [2,8]. In summary, a nonlinear trend was observed between the two parameters in that the higher the value of ϕ, the lower the field sound intensity (Fig. 13.4.4).

In a continued research [30] several vibroacoustical damping relationships were developed and quantified for many asphalt mixtures (refer to the published document for the various parameters and relationships). The viscoelastic ϕ properties and relationships obtained previously were utilized to estimate damping ratios, dynamic magnification factors, and transmissibility at resonance. In a nutshell, ARFC mixtures provided higher noise-damping responses than conventional dense-graded asphalt mixes due to the existence of rubber inclusions along with higher asphalt cement and porosity, thereby portraying AR

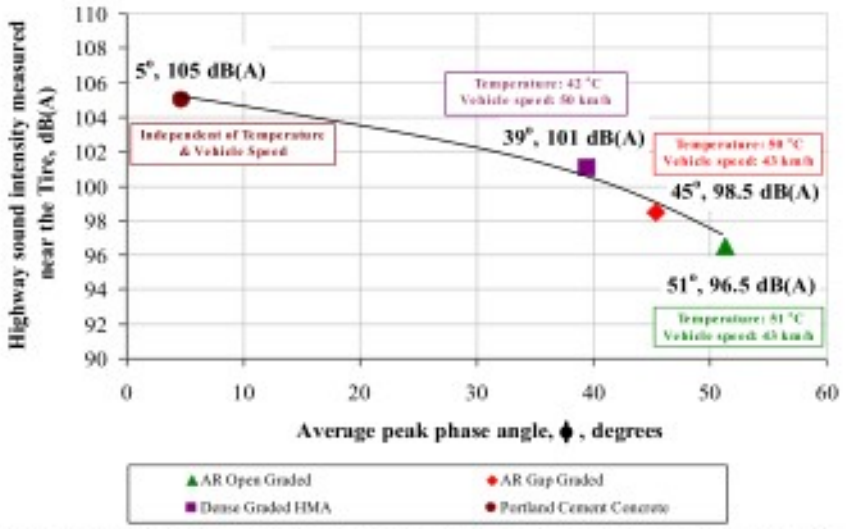


Figure 13.4.4 Relationship between highway sound intensity and average peak ϕ of paving mixtures measured in the dynamic modulus E^* test [26].

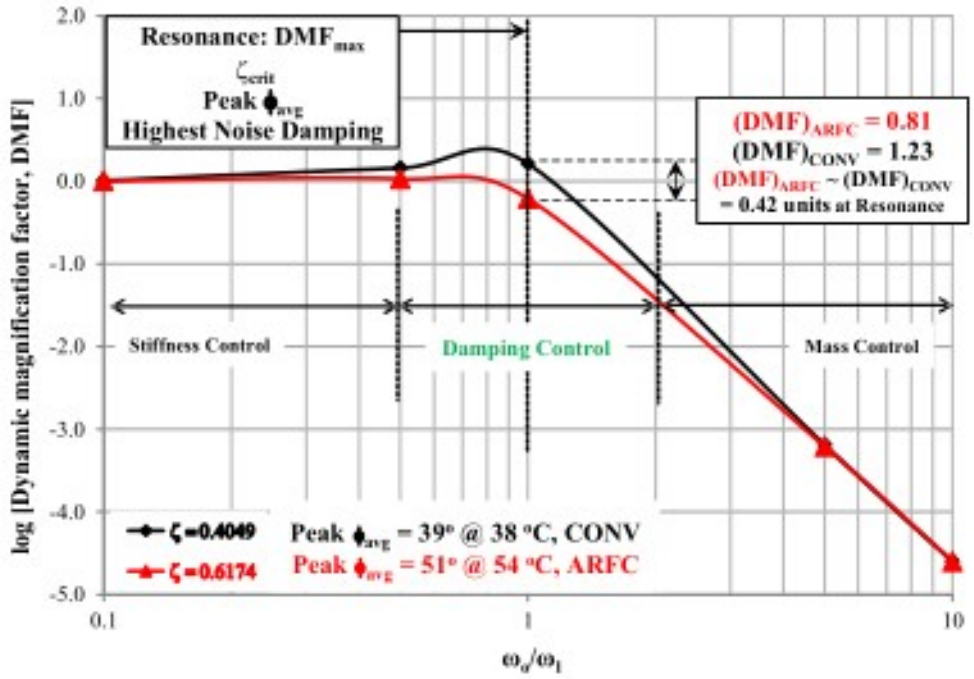


Figure 13.4.5 For particular damping ratios, the relationship between the estimated actual dynamic magnification factor vs. frequency ratio for conventional dense-graded asphalt (CONV) and asphalt rubber friction course (ARFC) mixtures [30].

mixtures to possess higher vibroacoustical damping capacity (Fig. 13.4.5). For a ϕ_{peak} difference of about 10° between the conventional dense-graded asphalt and ARFC mixtures, a difference of about 0.21 units of critical damping ratio was observed between the two mixes, translating into a difference of 0.42 units of maximum dynamic magnification factor between a "quiet" ARFC (noise level = 96 dB) and a conventional dense-graded (noise level = 101 dB) mix.

13.4.2.1.2 Science of pavement material damping

In another study [25,31], a host of pavement materials were characterized for their dampening properties using an ultrasonic pulse velocity testing method [32]. Over 30 laboratory specimens and 50 field cored samples covering actual test sections from the United States and Sweden were used for experimentation, which culminated in the development of a mathematical model to estimate ultrasonic pulse time (UPT) and effective flow resistivity (EFR). Note that the mathematical model was

established using material properties and volumetrics of pavement mixtures. It was interesting to note that the correlation between the model prediction and laboratory-measured UPT was excellent. Furthermore, a relationship between field tire/pavement noise and EFR was established, which also yielded excellent correlation between the two parameters. Very importantly, open-graded AR mixtures depicted the lowest field pavement noise while also inherent of lowest laboratory-measured EFR magnitude compared to the other mixtures (Table 13.4.1).

In a continued study [6] with the different laboratory and field-cored specimens, a novel noise-damping performance metric was established called damping acoustical measurement parameter (DAMP). DAMP was defined as the inverse relationship of impedance estimated in a previous work [31]. It was observed that mixtures with higher DAMP magnitudes were typical characteristics of low-noise pavements. For instance, open-graded AR had the highest DAMP (~20%), which was also the quietest material when actually measured in the field. Incidentally, cement concrete exhibited the lowest DAMP (12%) while also depicting highest field noise magnitudes. Further, DAMP noise-distinguishing bands were created that spanned across three unique noise-damping characteristics. Fig. 13.4.6 (published elsewhere) shows which ARFC had the "quiet" band. Many asphalt mixtures were placed in the zone of noise lessening or "perturbed" band, which may have potential to be engineered as quieter materials either through modifications of material properties or change in the type of materials used to produce a mixture. Based on what was observed for cement concrete material with respect to its low DAMP magnitude, it was consigned to the "noisy" band. Intriguingly, there are other special cement concrete materials such as pervious concrete

Table 13.4.1 Ranges of EFR (cgs Rayls) and field-measured tire/pavement noise of asphalt paving mixtures (recreated using [3,31]). (Note: the rayl unit can be converted to the SI system of units of kg/m^2 s by multiplying by 10.)

Mixture type	Laboratory-measured EFR (cgs Rayls)	Field-measured tire/pavement noise (dB)
AR Open-graded (Typical)	5700–6500	99–101
Open-graded (Typical)	7300–7400	102–103
Gap-graded (Typical)	6700–7500	101.5–102
AR Gap-graded (Typical)	7800–7900	102–103
Dense-graded	8000–10,000	103–104

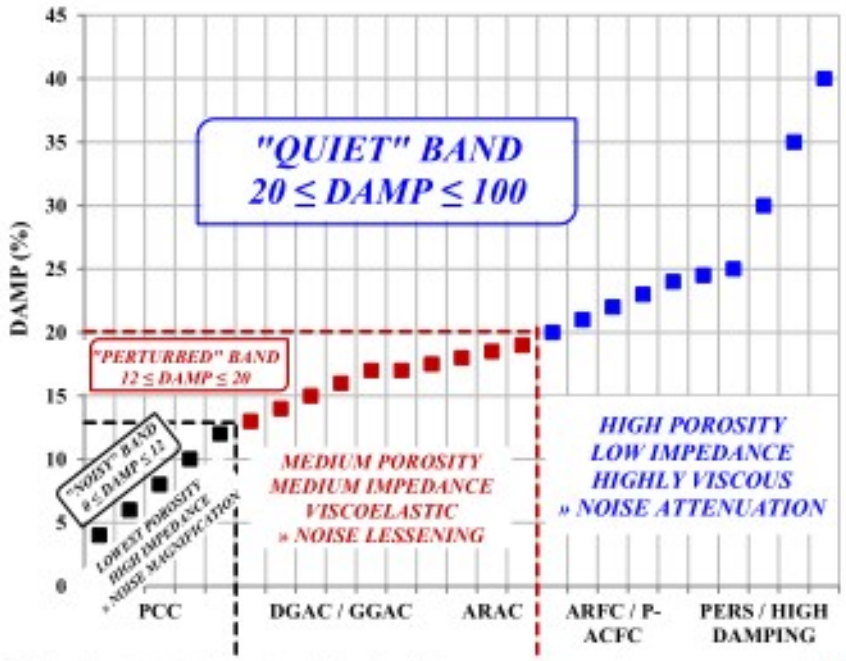


Figure 13.4.6 DAMP noise-distinguishing bands for the different pavement surface course materials [6].

that can also be positioned in the "quiet" band due to very high porosity, but that needs to be examined in the future before giving it a specific noise-band status. It is envisioned that many more paving materials could be developed and studied for their noise-damping characteristics but without compromising their durability properties and the intention for which they are primarily used.

13.4.2.2 Field noise measurement studies on AR mixtures

Field noise measurements have been carried out extensively to study sound intensities of various asphalt mixtures using different techniques. A preventative maintenance pavement preservation experiment was conducted by the Arizona Department of Transportation on a heavily trafficked interstate in the late 1990s encompassing 32 test sections and five major types of asphalt mixtures with replicate cells [6,33–35]. The five types of pavement surfaces were permeable European mix, stone matrix asphalt, AR friction course (ARFC), polymer modified friction course (P–ACFC), and asphalt concrete friction course (ACFC). The properties of these mixtures can be found elsewhere.

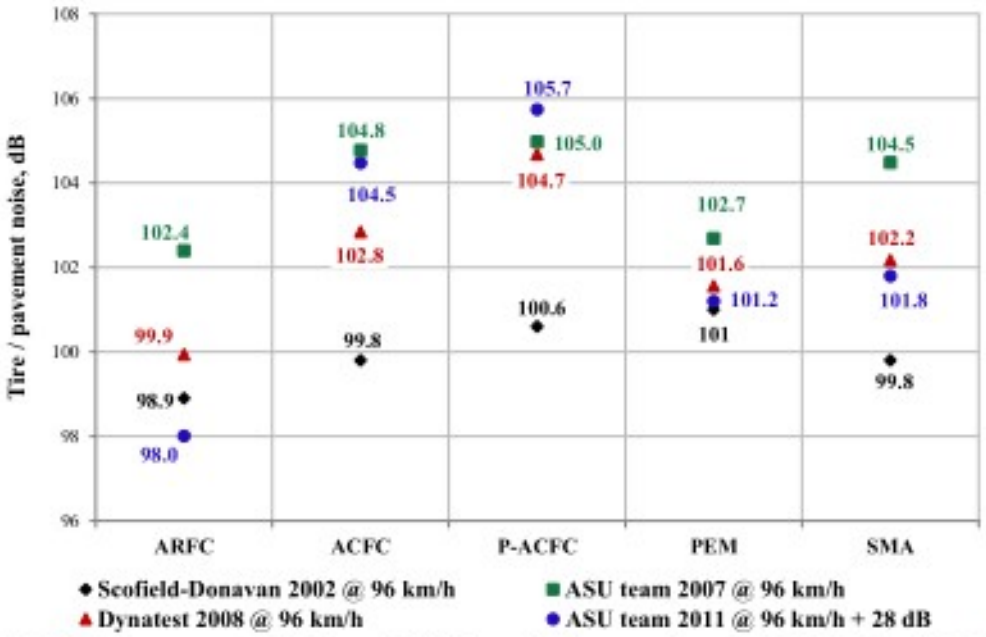


Figure 13.4.7 Noise measurements for Arizona (United States) field test sections: 2002, 2007, 2008, and 2011 [6].

Field noise measurements on these five different wearing courses were conducted using an on-board sound intensity method during 2002 [2], 2007 [34], 2008 [36], and 2011 [6], whose summaries are shown in Fig. 13.4.7 [6]. As can be seen, ARFC was the quietest among the five mixes in all four years, while interestingly ARFC also experienced the least amount of cracking and surface wear compared to the other sections that showed serious distresses during the design period. Note that field cored samples were collected from the road test sections, which were used to obtain laboratory damping characteristics, as explained previously (Section 13.4.2.1.2).

13.4.3 Discussion and way forward

As is known, enhanced viscoelastic property complemented by higher asphalt cement content, inclusions of crumb rubber in large quantities, and the presence of a large amount of air pocket (porosity) in the AR mix matrix are the main factors that reduce tire/pavement noise in comparison with other paving surfaces. Yet, there is no point-blank clarity that one or more of several parameters are truly supportive of this noise reduction trait of AR

mixtures. Thus there is expansive scientific scope to investigate the theory behind the acoustical characteristics (and performance metrics) of the different pavement surface courses and their relationships with actual field noise-damping properties.

Furthermore, the fundamental noise-damping parameters that assist in noise generation and attenuation in pavement materials needs to be studied further. More research in the vibro-acoustics area also needs to be accomplished to quantify the contribution of pavement types to the overall vibro-acoustic path while also being able to measure the variation in a pavement's contribution to the overall traffic noise. Essentially, it is envisaged that an in-depth methodical understanding of the basic noise-damping principles of the various road surfaces would help develop a framework that embodies assessment of acoustical energy stored in the massive "quiet" pavement system such as AR or many other novel materials that are being developed worldwide.

Acknowledgments

The author would like to thank his former Professor Dr. Kamil E. Kaloush, Professor at Arizona State University, United States who assigned him to work on the various asphalt material characterization programs (2004–08), during which period he was introduced to the fascinating AR product, which is still one of the key areas of his research. Further, the author would like to thank many colleagues who were part of collaborative research: Mr. George B. Way (United States), Dr. Jorge B. Sousa (Portugal), Mr. Douglas D. Carlson (United States), Mr. Ali Zareh (United States), and Dr. Ulf Sandberg (Sweden).

References

[1] K. Tsunokawa, C. Hoban, World Bank Technical Paper No. 376. Roads and the Environment, A Handbook, The World Bank, Washington, DC., USA, 1997, p. 1997.

[2] Scofield, L., and P. Donovan, Development of Arizona's Quiet Pavement Research Program, Proceedings of Asphalt Rubber 2003, Brasília, Brazil, December 2003.

[3] K.P. Biligiri, Asphalt Mixtures' Properties Indicative of Tire/Pavement Noise (Ph.D. dissertation). Department of Civil and Environmental Engineering, Arizona State University, December 2008.

[4] D. Gibbs, R. Iwasaki, R. Bernhard, J. Bledsoe, D. Carlson, C. Corbisier, et al., Quiet Pavement Systems in Europe, Report No. FHWA-PL-05–011, Submitted by American Trade Initiatives, Virginia, Sponsored by Federal Highway Administration, American Association of State Highway and Transportation Officials, USA, 2005. May.

[5] P.R. Donavan, Foreword to the special issue on tire/pavement noise, Noise Control. Eng. J. 57 (2) (2009) 49.

[6] K.P. Biligiri, G.B. Way, Noise-damping characteristics of different pavement surface wearing courses, J. Road Mater. Pavement Des. Taylor & Francis, UK. 15 (4) (2014) 925–941. Available from: https://doi.org/10.1080/14680629.2014.
[7] G. Descornet, and U. Sandberg, Road surface influence on tire/road noise – Part 2, Proceedings of Internoise 1980, Noise Control Foundation, New York, USA, 1980.
[8] P. Donavan, and B. Rymer, Measurement of tire pavement noise sound intensity methodology, Proceedings of Asphalt Rubber 2003, Brasilia, Brazil, December 2003.
[9] M. Losa, P. Leandri, R. Bacci, Empirical rolling noise prediction models based on pavement surface characteristics, Road Mater. Pavement Des. 11 (Suppl. 1) (2010) 487–506. Special Issue on EATA 2010.
[10] R.J. Bernhard, R.L. Wayson, An Introduction to Tire/Pavement Noise, Final Report, SQDH 2005-1 HL 2005-2, Institute for Safe, Quiet, and Durable Highways, Purdue University, West Lafayette, IN, 2005. January.
[11] Q. Lu, J.T. Harvey, E. Kohler, B. Rymer, L. Motumah, Comparison of tire-pavement noise characteristics of rubberized and conventional asphalt concrete mixes, Noise Control. Eng. J. 59 (3) (2011) 219–227.
[12] P.A. Morgan, P.M. Nelson, and H. Steven, Integrated assessment of noise reduction measures in the road transport sector, TRL Project Report No. PRSE/652/03, Crowthorne, U.K., 2003.
[13] A. Ongel, E. Kohler, Q. Lu, J. Harvey, Comparison of surface characteristics and pavement/tire noise of various thin asphalt overlays, Road Mater. Pavement Des. 9 (2) (2008) 333–344.
[14] A. Ongel, E. Kohler, J. Harvey, Principal components regression of onboard sound intensity levels, ASCE J. Transp. Eng. 134 (11) (2008) 459–466.
[15] A. Ongel, J.T. Harvey, Pavement characteristics affecting the frequency content of tire/pavement noise, Noise Control Eng. J. 58 (6) (2010) 563–571.
[16] R.O. Rasmussen, R.J. Bernhard, U. Sandberg, and E.P. Mun, The Little Book of Quieter Pavements, Final Report, FHWA-IF-07-XXX, Federal Highway Administration and The Transtec Group, July 2007.
[17] U. Sandberg and J. Ejsmont, Tyre/Road Noise Reference Book, INFORMEX, 2002.
[18] G.B. Way, K.E. Kaloush, K.P. Biligiri, Asphalt-Rubber Standard Practice Guide, Rubber Pavements Association, Tempe, Arizona, USA, 2012, p. 2012.
[19] V.H. Nanjegowda, K.P. Biligiri, Recyclability of rubber in asphalt roadway systems: a review of applied research and advancement in technology, Resour. Conserv. Recycl. 155 (2020) 104655Elsevier, UK. Available from: https://doi.org/10.1016/j.resconrec.2019.104655.
[20] V. Venudharan, K.P. Biligiri, J.B. Sousa, G.B. Way, Asphalt-rubber gap-graded mixture design practices: a state-of-the-art research review and future perspective, Road Mater. Pavement Des. Taylor and Francis, UK. 18 (3) (2017) 730–752. Available from: https://doi.org/10.1080/14680629.2016.1182060.
[21] WRI First Year Work Plans for June 18–December 25, 2007. Prepared for Federal Highway Administration, Contract No. DTFH61-07-H-00009, Asphalt Research Consortium, May 2007.
[22] K.E. Kaloush, and K.P. Biligiri, Understanding Noise Mitigation of AR-ACFC Mixes through Laboratory Evaluation of Storage and Loss Moduli, Final Report Submitted to Arizona Department of Transportation, June 2006.

[23] Quiet Pavement Pilot Program, Progress Report No. 2, Arizona Department of Transportation, December 20, 2005, Revised December 28, 2006.
[24] G.B. Way, D.D. Carlson, J.B. Sousa, K.E. Kaloush, and K.P. Biligiri, Introduction to asphalt-rubber pavement noise reducing characteristics, INTER-NOISE 2010, 39th International Congress and Exposition on Noise Control Engineering, ISBN: 978-1-61782-396-1, Lisbon, Portugal, 13–16 June 2010, pp. 7408–7417.
[25] K.P. Biligiri, K.E. Kaloush, Laboratory Evaluation of Noise - Dampening Properties of Asphalt Mixtures, INTER-NOISE 2010, 39th International Congress and Exposition on Noise Control Engineering, Lisbon, Portugal, 2010, pp. 7298–7307. 13–16 June 2010, ISBN: 978-1-61782-396-1.
[26] K.P. Biligiri, K.E. Kaloush, J. Uzan, Evaluation of asphalt mixtures' viscoelastic properties using phase angle relationships, Int. J. Pavement Eng. 11 (2) (2010) 143–152. Taylor & Francis, UK.
[27] K.P. Biligiri, G.B. Way, and A. Zareh, Asphalt-Rubber Properties Indicative of Noise Dampening Characteristics, Asphalt Rubber 2012 Conference, Munich, Germany, 23–26 October 2012.
[28] M.W. Witczak, K.E. Kaloush, T. Pellinen, M. El-Basyouny, and H. Von Quintus, Simple Performance Test for Superpave Mix Design, NCHRP Report 465, Transportation Research Board, National Research Council, Washington, DC. USA, 2002.
[29] K.P. Biligiri, A. Sotil, K.E. Kaloush, and J.S. Golden, 2006. Tire/road noise relationship with viscoelastic properties of asphalt mixtures. Asphalt Rubber 2006 Conference, Palm Springs, California, USA, October 2006 (Conference Proceedings, ISBN 962-405-091-0).
[30] K.P. Biligiri, Effect of pavement damping properties on tyre/road noise characteristics, Constr. Build. Mater. December. 49 (2013) 223–232. Available from: https://doi.org/10.1016/j.conbuildmat.2013.08.016.
[31] K.P. Biligiri, K.E. Kaloush, Prediction of pavement materials' impedance using ultrasonic pulse velocity, J. Road Mater. Pavement Des. 10 (4) (2009) 767–787.
[32] ASTM C597-02, Standard Test Method for Pulse Velocity through Concrete, 2002.
[33] D.D. Carlson, G.B. Way, A. Zareh, K.P. Biligiri, and K.E. Kaloush, Tire/pavement noise characteristics of wearing course asphalt mixtures, SURF 2008, 6th Symposium on Pavement Surface Characteristics, Portoroz, Slovenia, Europe, 20–22 October 2008.
[34] D.D. Carlson, G.B. Way, A. Zareh, K.E. Kaloush, and K.P. Biligiri, Noise Characteristics and Field Performance of Five Different Wearing Courses in Arizona, Asphalt Rubber 2009 Conference, Nanjing, China, 2–4 November 2009 (Conference Proceedings, ISBN 978–988-18681-1-4).
[35] L. Scofield, Arizona's Pavement Preservation Experiment, Arizona Department of Transportation Report, 2000.
[36] E. Kohler, A. Ongel, J. Harvey, and B. Rymer, OBSI measurements at the UC Pavement Research Center, Presentation made at the Transportation Research Board Summer Meeting, San Luis Obispo, California, USA, 22–25 July 2007.

13.5

Utilization of crumb rubber modifiers in producing polymer asphalt emulsions

Amanda Koh
Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL, United States

13.5.1 Introduction

The building and maintenance of civil infrastructure is a critical piece of developing and maintaining societies, but it is also a large source of energy use and a contributor to climate change [1]. As such, there has been a significant push to move toward more sustainable infrastructure construction methods and materials that consume less energy, are safer for workers, and use renewable or recycled resources. This is particularly true for roadway construction, where not only do developing countries rely on continuously improving access amongst the population to grow and thrive, but developed countries must maintain the quality of roads subject to high traffic loads that may not have been initially planned for as well as those in communities that are more remote and less trafficked. While many strategies are being developed and tested both in academia and in industry, [2] two particularly successful strategies have been the implementation of crumb rubber (CR) as a polymer modifier in asphalt and cold-application asphalt, which uses emulsions of asphalt [3–5]. As there has been proven benefits to each technology individually, work has also been done on combining them to maximize sustainability and minimize environmental impact. In this chapter, the merits and methods of use of each will be discussed as well as highlighted applications of CR-modified asphalt emulsions.

13.5.1.1 Crumb rubber as asphalt modifier

Asphalt, or bitumen, is a complex mixture of petroleum-derived organic compounds ranging from lighter hydrocarbons,

of varying saturation and aromaticity, to heavy fractions that can include inorganic elements like sulfur and nitrogen often as a part of asphaltenes (large molecules defined by their insolubility in alkanes by solubility in toluene) [6]. While asphalt has long been used as a cement binder, the incorporation of polymers (poly- meaning many, -mer referring to a repeating moiety) has shown an improvement in binder mechanical properties such as elasticity and fatigue resistance. Rubber has been a particularly well-studied and successful binder modifier. Rubber has been used in two forms: synthetic rubber (SR), generally composed of a styrene-butadiene block copolymer, and natural rubber (NR), which is harvested from rubber trees and is a mixture based largely off of isoprene [3]. Structures of these rubbers and their monomers are shown in Fig. 13.5.1.

These rubbers are the same components found in tires, although the composition of NR versus SR depends on the tire usage (cars vs trucks) as well as the region of manufacture. While SR and NR are high viscosity fluids on their own, they are cross-linked (also called vulcanized) in order to create the highly elastic and ductile ("rubbery") materials that are needed to create tires. The process of cross-linking is a chemically induced transformation of the rubber from liquid to solid that involves creating new chemical links between polymer chains. Cross-linking can be done in many ways, including heat treatment and UV-light exposure, but it generally considered an irreversible process as breaking the formed cross-links requires extremely high heat or harsh conditions, which may also break down the rubber polymer itself. As such, after tires are used and worn down past their potential for usefulness (called end-of-life

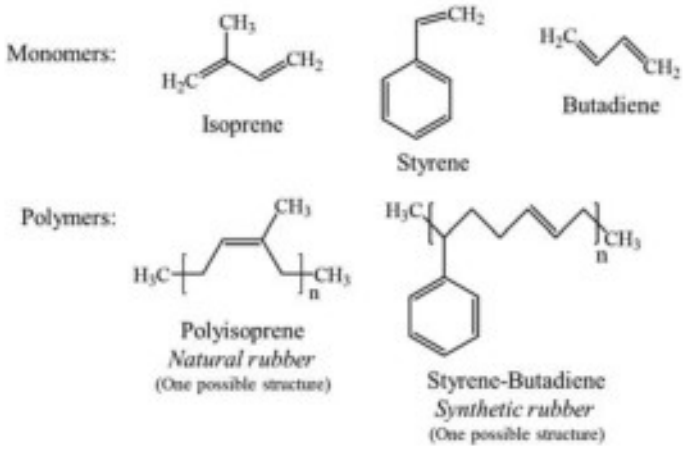


Figure 13.5.1 Monomer structure of isoprene, styrene, and butadiene, as well as possible structures for the NR and SR polymers.

tires, or ELTs), their disposal is difficult. Nonrecovered (i.e., not used further for fuel or material) ELTs have traditionally ended up in landfills, but as regulations pose stricter conditions on the disposal of tires or ban it altogether, alternative uses for ELT have become more economically attractive and feasible. One method of utilizing ELT is through the use of CR as an asphalt binder modifier [7].

Like typical polymers, CR is incorporated into asphalt to increase mechanical properties, in particular to improve fatigue and durability, rutting resistance, and thermal stability. CR-modified asphalt (CRMA) is typically made in one of two processes: a wet process where CR and asphalt are blended at high temperature (greater than 200°C)[3] such that the asphalt light fractions swell the CR and sometimes lead to devulcanization [8], and a dry process where the interaction (sometimes call "reacting") of asphalt and CR is limited [9]. The advantages and disadvantages of each process as well as the chemical and physical mechanisms underpinning the blending have been studied and documented extensively [10,11], but the end result is a modified binder that leads to road and other surfaces that show improved durability to weather and temperature as well as reduced maintenance. This, along with the use of recycled materials that will not get landfilled or burned, has shown great potential to improve the sustainability and expense of road building and maintenance.

13.5.1.2 Asphalt emulsions

Asphalt emulsions are another example of an "environmentally friendly construction technology." [12]. The polymer-modified asphalts (neat polymer or CR) described in the previous section are created and worked with at high temperatures in order to reduce viscosity and improve workability. Not only is this process energy intensive due to the high temperature requirements, but it often creates unsafe work environments for those laying the asphalt due to the volatility of the asphalt hydrocarbon fractions (which are toxic to breathe). In order to overcome these health and environmental concerns, certain asphalt applications (which will be discussed later in this chapter) have turned to cold-application asphalt, or asphalt that is used in the form of an emulsion.

Emulsions are used in almost every industry including energy, pharmaceuticals, food, and personal care. An emulsion is a stabilized mixture of two immiscible liquids. While these two liquids can be anything, most commonly one of the two

liquids is water. For asphalt emulsions, asphalt being a highly nonpolar (or hydrophobic) fluid, asphalt is the second immiscible liquid. Immiscible liquids will not mix homogenously (i.e., they will not mix to form one new continuous fluid, due to high free energy of mixing. This is often discussed between a polar and nonpolar liquid or a hydrophobic and hydrophilic liquid). Similar to common household items like oil and vinegar for a vinaigrette, if one were to simply mix asphalt and water, the two would quickly separate into two distinct phases, rather than form an emulsion. The tendency to decrease interfacial area (two bulk liquids rather than droplets of one in the other) between the two liquids is due to the high free energy of the system. In order to overcome this energetic barrier a chemical stabilizer must be added to the system that decreases the interfacial free energy between asphalt and water. For asphalt emulsions, this generally takes the form of a surface-active agent, or surfactant (also referred to as an emulsifier, a stabilizer, or a dispersant).

Surfactants are classically drawn as the cartoon in Fig. 13.5.2. In a water and asphalt emulsion, one end of the surfactant will be hydrophilic (often referred to as the surfactant "head") and one end will be hydrophobic (often referred to as the surfactant "tail"). While both the surfactant head and tail can be have many different structures, surfactants are classically categorized by the structure of the hydrophilic head. A surfactant that carries a positive charge on the hydrophilic head will be labeled as cationic (and in asphalt literature, the

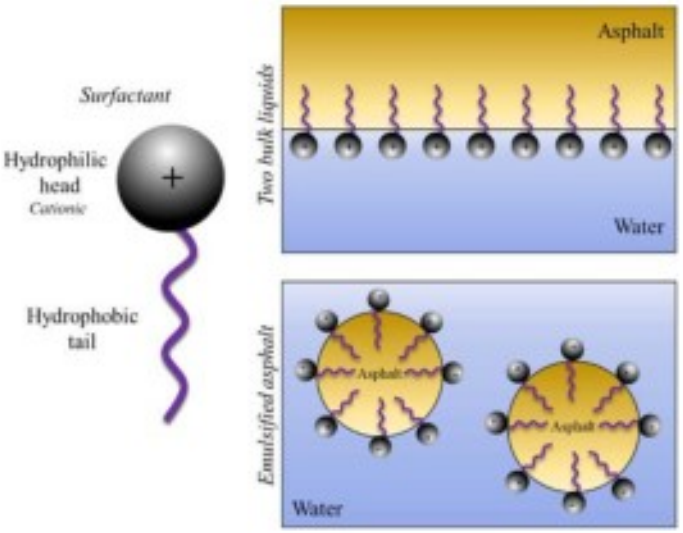


Figure 13.5.2 Cartoon of a surfactant and illustration of how a surfactant stabilizes and interface of two immiscible liquids.

resulting emulsion will be called a "cationic" emulsion, although the charge originates from the surfactant). Cationic surfactants are the most common type of surfactant used in asphalt emulsions. Other types of surfactants are anionic, carrying a negative charge, nonionic, carrying no charge, and zwitterionic, which are surfactants that simultaneously carry a negative and positive charge. These charges can be measured using zeta potential, which is an expression of a surfactant's electrophoretic mobility in a known electric field. Surfactants may be nonionic or neutral at some pH but charged at others, so asphalt emulsions also commonly use pH modifiers like limestone to render a surfactant charged. Surfactants will preferentially adsorb to water/asphalt interfaces and decrease interfacial free energy (measured as interfacial tension commonly using an instrument such as force tensiometer, capillary tensiometer, or optical analysis with a pendant drop tensiometer). This can occur at the interface of two bulk liquids, or at the interface of a droplet of asphalt suspended in water.

Emulsions are also categorized by the identity of the continuous phase, which is often the majority volume phase, and the discrete or internal phase, which is inside of the dispersed droplets. As water is most commonly one of the two phases, the two most common emulsion categorizations are oil-in-water (O/W), meaning that the internal phase is hydrophobic and the continuous phase is water, or water-in-oil (W/O), meaning that the hydrophobic phase is the continuous phase and water is suspended as droplets (shown in Fig. 13.5.3). Asphalt emulsions

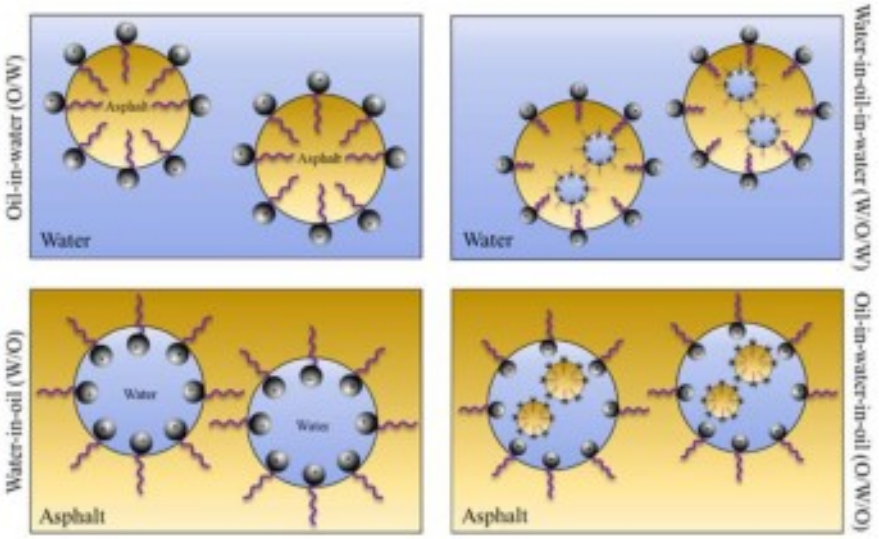


Figure 13.5.3 Emulsion phase configurations, clockwise from top left: O/W, W/O/W, O/W/O, and W/O.

are O/W emulsions, as asphalt droplets are emulsified in water using a surfactant. More complex emulsions may occur, particularly when a hydrophobic phase contains some hydrophilic components such as asphaltenes in asphalt. This may result in oil-in-water-in-oil emulsions (O/W/O) or water-in-oil-in-water (W/O/W), which is common in asphalt emulsions.

Emulsions are thermodynamically unstable systems, meaning that energy must be used to create them. For asphalt emulsions, the most common way of making emulsions is using a colloidal mill. Asphalt and water are mixed together at high energy until the desired asphalt droplet size is reached. Asphalt emulsion droplet sizes are usually on the order of 5–10 μm, but this will depend on duration and intensity of mixing, composition of the asphalt, structure and concentration of the surfactant, and other mixing parameters such as temperature of mixing. Asphalt volume fractions in the emulsion depend on the formulation and the necessary final properties.

One of the most important characterizations of asphalt emulsions once they are formed is the measurement of viscosity. As mentioned previously, neat asphalt must be heated to high temperatures in order to be at a low enough viscosity to pour and work with for a new roadway or maintenance. Asphalt

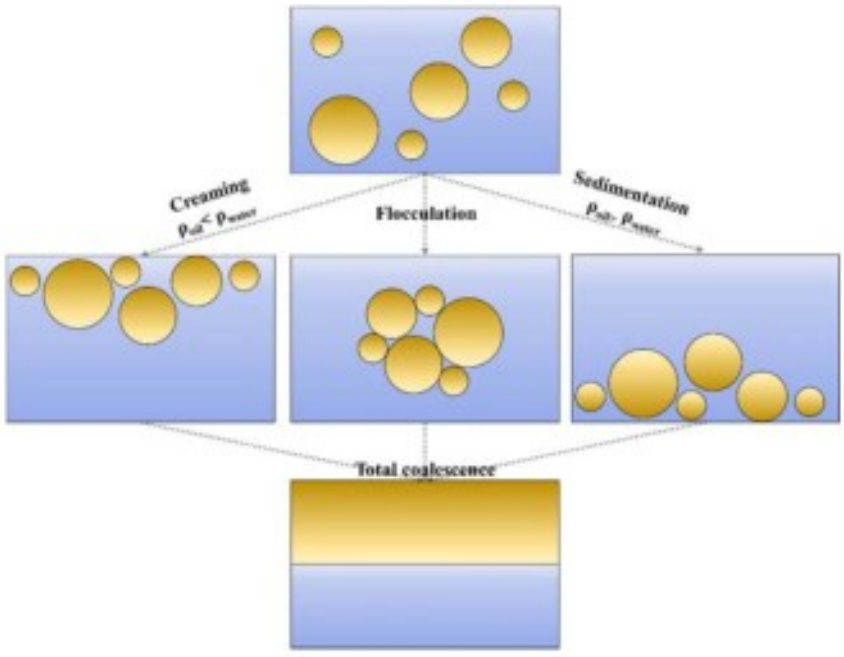


Figure 13.5.4 Pathways of colloidal instability, both reversible and irreversible.

emulsions, however, have a viscosity that is much closer to that of water making them significantly easier, cheaper, and safer to work with. Typically, asphalt emulsions may be used at a temperature up to 50°C (rather than 200°C or higher). The volume fraction of asphalt in an asphalt emulsion, the charges carried by the stabilizing surfactants in the emulsion, and the emulsion droplet sizes all impact the final viscosity, so optimizing the working viscosity of an emulsion while maintaining the required binder performance is critical.

Other common characterizations for asphalt emulsions are droplet size, water stability (i.e., water evaporation rate or water breakout), and colloidal stability. Colloidal stability is often defined as the difference in the fraction of asphalt at the top of a tank vs. the bottom of the tank (or a specific depth) [13]. Depending on the density of the asphalt (either neat asphalt or asphalt with modifiers) it is expected that emulsion droplets will either cream (i.e., float to the top) or sediment (i.e., sink to the bottom). Lack of colloidal stability requires additional mixing, energy, and time often at the road site. Improving colloidal stability is a common target for asphalt emulsion research, and often involves the use of better or more surfactants as well as additional asphalt and emulsion modifiers. In addition to the density difference between asphalt and water, colloidal stability is also affected by the repulsive and attractive forces between emulsion droplets due to electrostatics (opposite charges will lead to repulsion between droplets and improved stability) and van der Waals forces or hydrogen bonding (which can promote attraction). Asphalt emulsions that have stronger attractive forces than repulsive forces will tend to flocculate and eventually coalesce. Flocculation is a reversible process by which emulsion droplets stick together and move in unison, exacerbating the density difference between asphalt and water and decreasing colloidal stability. Coalescence is the irreversible joining of two droplets into one larger droplet and is along the thermodynamic pathway to complete emulsion separation. An illustration of colloidal instability along the path to emulsion separation can be found in Fig. 13.5.4.

While the water content in asphalt emulsions is necessary for low temperature workability and viscosity, it is not desired in the final asphalt–aggregate composite. As such, the water must be removed when used in the roadway application after being mixed with the aggregate. There are two common pathways for this to occur. First, the water in the asphalt emulsion could simply evaporate, which leads to the breaking and coalescence of emulsion droplets. This method, which is more

common with anionic surfactant-stabilized emulsions, relies on favorable weather conditions such as humidity and temperature and is generally better for very thin coatings. The second method is the gel contraction of the asphalt emulsion. In this method, the asphalt emulsion droplets "react" to aggregate surfaces, either due to the asphalt itself or more commonly the surfactant, and the emulsion droplets break and coalesce around the aggregate. The rate at which asphalt emulsions gel and break is related to the droplet size, water/asphalt interfacial tension, and the viscosity of the emulsion. The rate can also be manipulated through the addition of emulsion breakers, which typically alter the charges present on emulsion droplets and thus the overall stability of the emulsion. This gelation method of asphalt emulsion breaking is not dependent on the weather, although higher environmental temperatures will reduce emulsion viscosity, so it is often the more preferred method. The gelation method of emulsion breaking does sometimes lead to entrapment of water in the resulting asphalt/binder coating and is often the source for asphalt W/O/W emulsions.

13.5.2 Crumb rubber-modified asphalt emulsions

The previous section of this chapter detailed the benefits of CRMA and asphalt emulsions in terms of safety and ecological benefit. By combining these two technologies, researchers and industry have been able to move toward a solution for roadway maintenance based on CR-modified asphalt emulsions that benefits from the advantages of both. There are two main ways that CR has found a use in asphalt emulsions: as a binder modifier, essentially creating emulsions of CRMA, and as a filler/aggregate replacement, used in conjunction with asphalt emulsions. This section will detail the methods of manufacture, usage, and advantages of each type of CR-modified asphalt emulsion.

13.5.2.1 CR as asphalt emulsion binder modifier

CR-modified asphalt emulsions (E–CRMA) are often used in road maintenance applications that require relatively thin coatings such as chip/slurry seals, cold regeneration, and microsurfacing [14]. Polymer-modified asphalt emulsions, particularly emulsions of asphalt mixed with latex, are already common in industry. Utilizing CR instead of virgin polymer improves the environmental impact of road maintenance. One of the main

issues associated with E–CRMA is the incorporation of CR into the asphalt. For E–CRMA, the CR is dispersed in the asphalt before emulsification.

13.5.2.1.1 Improving CR dispersibility

As discussed earlier (and in previous chapters) CR is a vulcanized polymer that physically disperses into asphalt by the absorption of light asphalt fractions, which can be sped up through increased temperature, and causes partial to full devulcanization, depending on the temperature of the blend. The resulting CRMA is typically highly viscous and does not emulsify well (particularly as heating up the CRMA to temperatures above 100°C cannot be done in conjunction with water). Any resulting emulsions, if they can be formed, typically are colloidally unstable and do not give the desired final rheological or application properties. In order to form an adequate emulsion, in terms of stability or viscosity, CR cannot be directly dispersed into the asphalt without any treatment or additives. As such, a significant amount of work has gone into understanding how to treat the CR before asphalt dispersion in order to create optimal emulsions. While many techniques similar to those used for CRMA such as alteration of rubber composition and particle size, two common techniques for CR–asphalt modification are surface treatments and the addition of additives.

When a solid or semisolid disperses into a liquid, the compatibility between the solid surface and the liquid often dictates the extent to which a stable dispersion is created or if a dispersion is created at all. As such, one method of improving CR and asphalt blending is to modify the CR surface chemistry [15,16]. However, as CR is a highly cross-linked largely hydrocarbon solid, the material surface is largely inert and does not lend well to typical surface functionalization chemistry. Instead, one of the more common ways of altering CR surface chemistry is through irradiation. Irradiation subjects the CR surface to high energy in a concentrated dose, which is enough to cleave surface carbon–carbon, carbon–oxygen, carbon–sulfur, sulfur–oxygen, and sulfur–sulfur bonds (irradiation penetration will depend on duration and intensity of dosage). A typical analytical technique to monitor this transition is Fourier transform infrared spectroscopy (FT–IR). Examples of FT–IR spectra from CR with surface treatments including irradiation are shown in Fig. 13.5.5. Breaking these bonds not only improves the chemical compatibility of asphalt with CR, but also frees the CR to swell further and absorb more of the asphalt. Frequent sources of irradiation are gamma and microwave radiation [17,18].

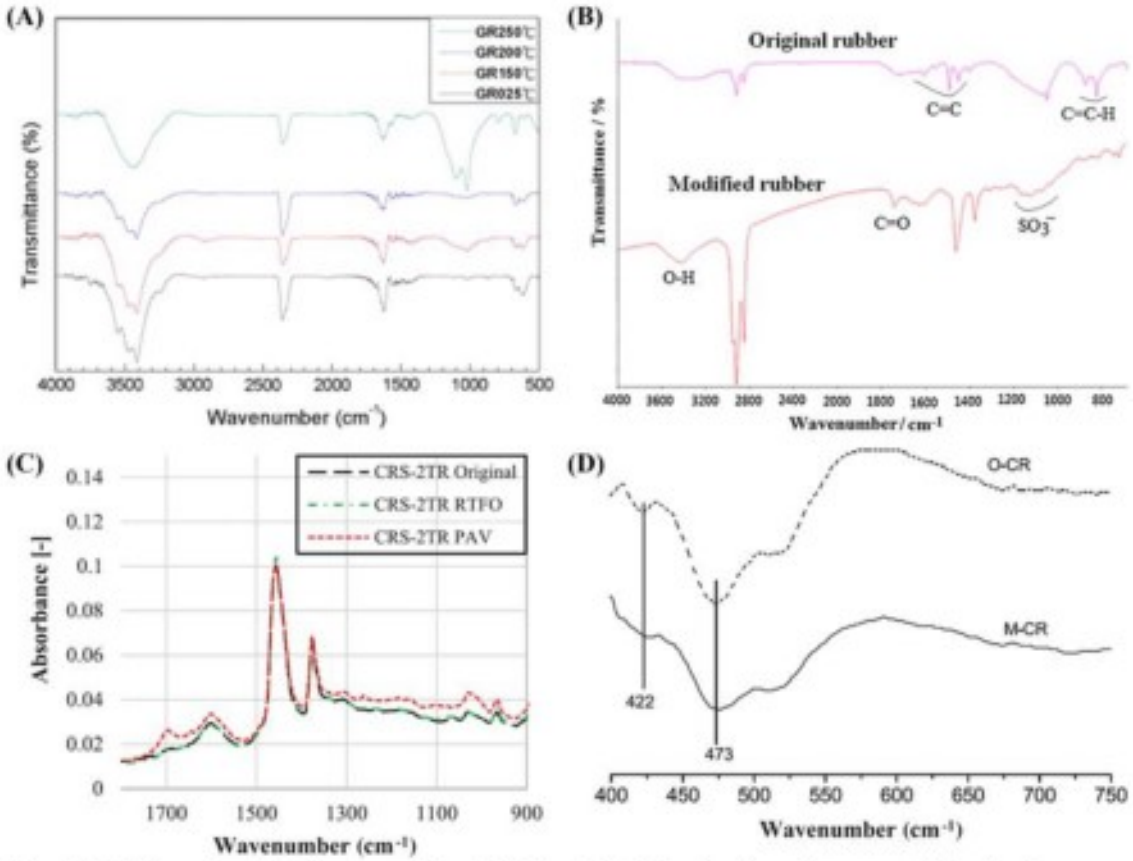


Figure 13.5.5 Examples of FT–IR spectra of crumb rubber after (A) varying thermal treatment; (B) oxidative treatment; (C) treatment in a rolling thin film oven (RTFO) and a pressure aging vessel (PAV); and (D) microwave treatment. Adapted from Chou et al. [16], He et al. [15], Sarkar et al. [22], and Yu et al. [18].

The second way to improve asphalt/CR compatibilization is through the addition of additives such as hydrocarbons (e.g., alkanes, toluene, aromatics), petroleum derivatives, or acids (e.g., polyphosphoric acid) blended with the CRMA to improve asphalt absorption and CR devulcanization. Acids, however, can interfere with the stability provided by cationic surfactants by altering the surface charge of emulsion droplets. But even the addition of fluid additives is sometimes not enough to reduce the viscosity of the CRMA enough to emulsify it, as a gel network may be formed that can not be mixed except at high temperatures. In this case, some researchers have looked at the dual modification of E–CRMA through microwave surface treatment as well as the addition of additive colloidal/viscosity modifiers [14,19].

13.5.2.1.2 E–CRMA characterization and performance

E–CRMA are generally characterized at three stages: (1) the initial CRMA blend, (2) the E–CRMA, and (3) the resultant coating from dried E–CRMA. The initial CRMA is typically characterized in terms of viscosity (particularly with respect to temperature), softening temperature, modulus, and ductility. Chemical analysis may also be done through FT–IR and gel permeation chromatography to determine the absorption of asphalt fractions into the CR.

The most common analyses for the E–CRMA are droplet size (and dispersity); evaporation (also called water breakout); emulsion viscosity or workability; and stability. Workability refers to the densification of the emulsion upon use, often after being compacted using a gyratory compactor or similar equipment [20]. Densification indicates the ease with which the emulsion can be broken into a continuous binder/aggregate film. Stability refers to the physical inhomogeneity of the emulsion from the top to the bottom of the tank (as shown in Fig. 13.5.4), and is generally measured by taking the difference in nonaqueous weight percent concentration at the top and bottom. This analysis often follows standards such as ASTM D244 (United States) or T0607–2011 (China). The typical specification is less than 1% change in 1 day. Also, frequently of interest are zeta potential, describing the emulsion surface charge and an indicator of stability, and breaking index, which describes the reactivity of the emulsion to aggregate surfaces and the speed with which emulsions will break to form complete films.

The analysis of dried E–CRMA, also frequently described as E–CRMA residue, is of critical importance as this is the form that will be used in application. Emulsions can be broken through compaction (using equipment as similar as possible to what would be used on the road) or evaporation [using methods such as those described in ASTM D255 (United States), T0651–1993 (China), or AASHTO R 78 (American Association of State Highway and Transportation Officials)].

To understand the viscoelasticity of E–CRMA residue, a rheometer is often used to measure G^* (complex modulus) and δ (phase angle). G^* is a measure of the residue's stiffness and resistance to deformation under stress. This is often measured dynamically such that the complex modulus can be broken down into the storage (G') and loss (G") modulus. G' denotes the elastic or "solid-like" characteristics of a material while G" denotes the viscous or "liquid-like" characteristics of a material. The dominance of one over the other describes the transitions

between solids liquids such as when CRMA is heated or E–CRMA is dried. The phase angle is a description of how far in either direction the material is, as a phase angle of 0 degrees means a perfectly elastic solid and a phase angle of 90 degrees means a perfectly viscous liquid. More commonly used to describe this is tanδ, which is equal to G"/G'. A higher tanδ refers to a more viscous material and a lower tanδ refers to a more elastic material. These viscoelastic terms allow for a better understanding of the effect of CR and emulsion parameters on the stiffness and durability of the final binder–aggregate coating. Improved elasticity is expected to lead to improved durability as the material is expected to better resist deformation under load.

Viscoelasticity is also used to understand the rutting resistance of the final coating. The term $G^*/\sin\delta$ is used as a "rutting resistance factor." The higher the rutting resistance factor the better the coating's resistance to tire deformation and the creation of ruts, grooves, or depressions in the road. A multiple stress creep recovery test is also used to determine rutting resistance without needing to measure complex modulus and phase angle first using standard methods such as AASHTO TP70. Rutting resistance can also be measured directly using a wheel tracking test, as load is applied through a wheel and deformation is tracked.

The previously described viscoelasticity is generally measured in shear, testing material modulus vs. shear stress, or shear frequency (angular frequency). Modulus and mechanical properties can also be measured in tension, compression, and bending. An illustration of these four means of measurement can be found in Fig. 13.5.5. Indirect tensile strength (ITS) and indirect tensile stiffness modulus (ITSM) are two of the most common means of determining mechanical resistance to deformation of binder–aggregate composites and the effects of temperature, curing time, CR concentration, and emulsion parameters (droplet size, breaking, etc.). Both tests demonstrate the material resistance to cracking and ability to handle deformation under load and are demonstrated in Fig. 13.5.6. Analytical models describing the effects of temperature and time on ITSM are shown here [21]:

$$\log S = -\alpha T + \beta \tag{13.5.1}$$

$$S_t = S_{max} - (S_{max} - S_i)\cdots e^{-b(t-t1)} \tag{13.5.2}$$

where S refers to stiffness, t refers to curing time, T refers to temperature, and α and β are fitting parameters. Thermal sensitivity can be judged based on Eq. (13.5.1), as α increases as temperature sensitivity increases.

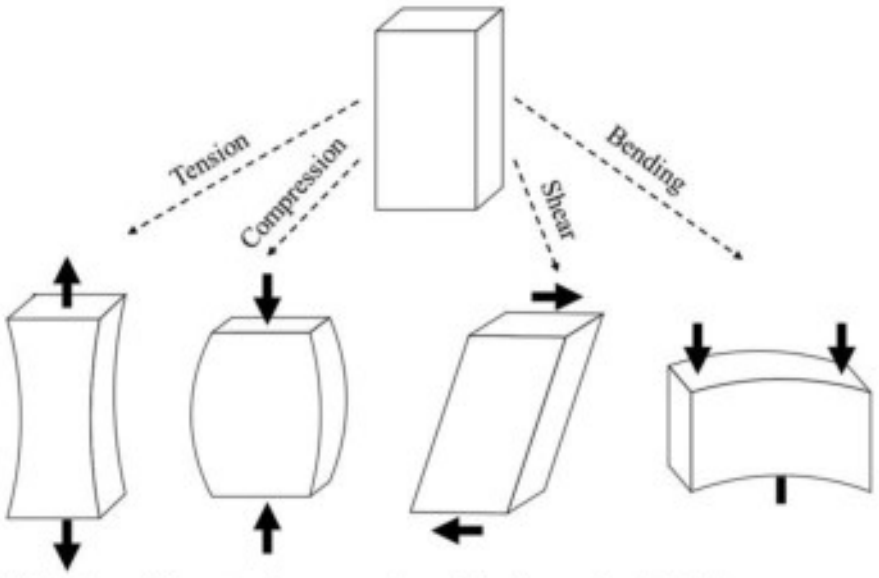


Figure 13.5.6 Illustrations of shear, tensile, compressive, and bending mechanical testing.

Fatigue is also an important measurement of E–CRMA coatings, as the addition of CR is expected to generally increase fatigue resistance, particularly with respect to temperature. E–CRMA fatigue residue is often measured both in tension and in bending. The indirect tensile fatigue test (ITFT) measures resistance to cracking by repeatedly applying a load to the material and determining how many loads the residue can withstand before a crack initiates. The fatigue resistance is expressed with respect to initial applied deformation and the number of loads required to show cracking and material failure. Fatigue can also be measured in bending, using a three- or four-point bending geometry on a mechanical load frame. Both measurements are frequently done with respect to temperature, CR or additive content/composition, and emulsion parameters. Fracture toughness, another indicator of resistance to cracking, can also be measured directly using the semicircular bonding test (ASTM D8044, EN12697-44), although this is a much newer test method than those previously described.

Lastly, the final E–CRMA residue may be tested with a bitumen bond strength test. This test measures the pull off tensile strength and moisture susceptibility of the residue, which is a critical parameter to understanding the long-term viability and durability of the coating.

The final effects of CR on asphalt emulsions, and the comparison of these emulsions with hot CRMA, will depend on many factors such as the emulsification method, surface treatment and composition of the rubber, the size of the rubber particles, etc. A few generalizations about expected performance can be made, however. E–CRMA residues are expected to be stiffer than those from neat asphalt emulsions, resulting in higher G^* [14,17]. Rutting resistance and fatigue life of the E–CRMA is also expected to be improved vs. the neat asphalt emulsion across temperatures. In general, thermal sensitivity is expected to be improved as well as chemical degradation, the latter in part due to the additives used in the production of tires such as antioxidants and antiozonants that prevent chemical rubber breakdown [22]. Available comparisons of E–CRMA to hot-mix CRMA or emulsions of polymer (latex or SR)-modified asphalt are mixed but show promising signs of comparable performance while improving worker safety and environmental impact.

13.5.2.2 CR as replacement filler for asphalt emulsions

As discussed previously, asphalt emulsions are most commonly used for microsurfacing or for chip seals (although they may be the primary surface for low traffic volume roads). The important characteristics of these chip seals are based on their ability to protect the lower asphalt layers from weather, generally by sealing cracks and providing improved water resistance, acid resistance, impact resistance, and sound/thermal insulation, as well as providing improved friction and skid resistance. A chip seal, or other types of microsurfacing, is a blend of asphalt and typically one stone layer of aggregate. The two components are compacted to create a final surface that has adequate friction, durability, and strength.

While CR has shown promise as an asphalt binder modifier in the emulsion itself (meaning that asphalt and emulsion are preblended) for these road surfaces, this use of CR requires fairly low concentrations of CR. Instead, replacing the mineral filler of an asphalt emulsion-aggregate coating with reused CR uses significantly higher concentrations of the recycled material, thus optimizing the environmental impact of recycling CR. It is important then to understand the impact of CR as replacement filler for asphalt emulsion-based chip seals and microsurfacing applications.

13.5.2.2.1 Characterization of CR filler asphalt emulsion coatings

In order to understand and optimize the potential of CR as a filler replacement, one of the first tests often done to compare CR to traditional filler is the Los Angeles abrasion test. This test determines the strength of the aggregate itself in terms of resistance to abrasion and is often run according to AASHTO T 96 or ASTM C 131. A more abrasion-resistant filler is more robust to road traffic and is more likely to provide increased friction to tires over sustained periods of time.

Optimum asphalt binder content is also frequently evaluated to determine the concentration of asphalt in the final coating that will have the maximum Marshall properties. These properties typically include porosity, void in mixture (VIM), and Marshall stability, which is the maximum load a specific shape and size of the aggregate/binder composite can handle (test specimen specifications chosen according to the designated standard). Maximizing stability while minimizing porosity and VIM is typically the goal of Marshall tests to optimize the asphalt binder content.

Final, cured coatings are generally subjected to some of the same mechanical and compaction evaluations described in Section 13.5.2.1. In particular, these evaluations include, measurements of maximum density and the difference between maximum and dry density as well as ITS, ITSM, and ITFT. Increased density of the chip seal indicates improved cohesion between the aggregate and the binder and is likely to lead to a more fatigue- and weather-resistant road. ITS, ITSM, and ITFT similarly indicate resistance of the road coating to deformation and fatigue resistance to cracking under repeated loads and under various environmental conditions.

Unique to measurements of chip seals with filler replaced with CR are evaluations of aggregate texture, friction, and aggregate adhesion. One of the primary purposes of the aggregate in a chip seal is to increase the friction and skid resistance of a road by increasing energy dissipation between the tire and road surface. Quantifying the ability of a chip seal surface to increase friction generally relies on the measurement of road texture, specifically what has been called the road "macrotexture" and "microtexture" [23,24].

Surface microtexture is defined as roughness on the scale of less than 0.5 mm and is generally dominated by the degree to which aggregates jut out from the asphalt binder. This is dependent on the penetration depth of the aggregates as well as their average size. While there is no consensus formulation for chip

seals, it is generally understood that aggregate penetration depth should range from 50%–80% (based on average aggregate size) so as to not be completely enveloped by the binder but also not stick so far out that they break off easily. Microtexture, due to the small-scale nature of the texture, is characterized using microscopy and image analysis.

Surface macrotexture, which is defined as roughness on the scale of 0.5–50 mm, is affected by the aggregation of mineral aggregates and their pattern/organization on the cured surface. The most common method for measuring surface macrotexture is the measurement of the mean texture depth (MTD) using the sand patch method (ASTM E965). This involves spreading a uniform volume of sand on various chip seal surfaces in a circular pattern and determining how far that sand can be spread. The smaller the circle the greater the MTD, and the rougher the surface of the chip seal. Other examples of measurements of macrotexture include the outflow meter test as well as more precise, quantitative analytical methods, which involve closer inspection and image analysis.

Lastly, as the friction, drainage, and texture of the chip seal rely on the asphalt embedded aggregates it is critical to measure the adhesion of the aggregate to the binder particularly when partially exposed. A common way of testing this is the Vialit test. This involves creating a uniform grid of aggregate in binder, curing the composite in a frame, flipping the frame over, and, while keeping the temperature at a low set point (such as −10°C), repeatedly dropping a steel ball on the composite. A visual example of this

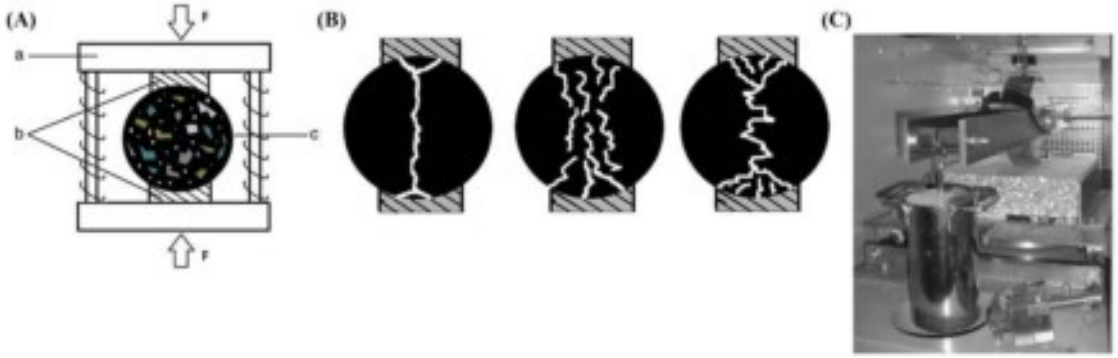


Figure 13.5.7 Example of setup and testing for measurement of (A) indirect tensile stiffness modulus [a, test frame, b, holding apparatus, c, test sample]; (B) modes of tensile fracture; and (C) wheel tracking for rutting resistance. Figures adapted from F.M. Navarro, M.C.R. Gámez, Influence of crumb rubber on the indirect tensile strength and stiffness modulus of hot bituminous mixes, J. Mater. Civ. Eng., 24 (6) (2012) 715–724 [25] [a and b] and L.P.T.L. Fontes, G. Trichês, J.C. Pais, P.A.A. Pereira, Evaluating permanent deformation in asphalt rubber mixtures, Constr. Build. Mater. 24 (7) (2010) 1193–1200 [26] [c].

test being performed is shown in Fig. 13.5.7 [31,32]. The amount of aggregate that remains in the cured composite is evaluated as a measure of how well the aggregate is embedded and the cohesion between cured binder and aggregate.

13.5.2.2.2 General results from asphalt emulsion chip seals with CR replaced filler

Prior to adding CR to a chip seal, it is important to understand the abrasion resistance of the CR on its own compared to traditional aggregate. Generally, it has been found in the literature that CR has less mass loss after undergoing the Los Angeles test than mineral aggregates. This is likely due to CR's increased elasticity and ductility, allowing it to deform rather than crack when under an applied load.

CR is also found to improve compaction in chip seal coatings, with higher concentrations of CR leading to an increase in chip seal density. Current research does not agree as to the relationship between compaction cycles and density with respect to CR concentration, although when used under realistic situations it has been found that not all common equipment is compatible with CR-filled chip seals. In particular, it was found that using rubber compactor tires was not compatible with a chip seal using rubber aggregate and a steel roller compactor had to be used instead [27]. CR particle size also impacts compaction, as smaller CR particles used with asphalt emulsions tend to result in increased compaction and requires less compaction to achieve the same density as larger particles [28].

As would be expected, increasing the CR concentration of chip seals (i.e., replacing traditional rigid aggregates with an elastic, flexible filler) tends to decrease ITS, ITSM, and Marshall stability. This is due to the increased deformation of rubber under load when compared with common cementitious aggregates [29–31]. The final strength and stability of the chip seal using CR can be modified by altering the CR particle size, as smaller sizes tend to show smaller reductions in strength and stiffness as compared to larger CR particles. This has been demonstrated in comparisons between traditionally ground CR versus cryogenically ground CR as well as traditionally ground CR sieved to different mean sizes [30]. This may be due to reduced cohesion between the binder and CR aggregate as particle sizes increase. Some have suggested that this conclusion should promote the replacement specifically of fine aggregates with CR, rather than aggregates in general. Increasing the concentration of asphalt in the asphalt emulsion can overcome these

decreases in mechanical strength while improving the chip seal environmental impact [32].

Additionally, as seen with E–CRMA, the addition or replacement of filler with CR increases the fatigue resistance of the chip seal, likely due to the elastic nature of the rubber and improved temperature insensitivity. This also extends to improved rut resistance seen in chip seals where mineral aggregate is replaced with CR [19].

CR tended to improve micro- and macrotexture in asphalt emulsion chip seals, particularly when considering the inherent roughness of the CR particle. Microtexture improves with the use of CR, particularly if the surface area and roughness of the CR are high. This tends to be the case for traditionally ground CR rather than cryogenically ground CR, as larger particle sizes as well as the method itself lead to rougher particles. Traditionally ground CR particles also tend to be rougher than many mineral aggregates, which are subject to smoothening by water either naturally in rivers or industrial cleaning processes. Traditionally ground CR also tends to increase the MTD of the chip seal, due to the roughness of the rubber and aggregation in the binder composite [23].

CR has been found to dramatically improve stone retention when studied using the Vialit test over traditional mineral aggregates [19,27]. A demonstration of a standard Vialit test is shown in Fig. 13.5.8. Asphalt emulsions also have shown dramatic improvement in stone retention over typical aggregate–asphalt composites. This may be due to improved thermal resistance at cold temperatures as compared to the traditional composite, as shrinkage of the asphalt–aggregate weakens the adhesion of the binder on the aggregate and allows for easier release of the aggregate from the composite. Improved thermal resistance is a common benefit of CR-modified asphalts as well as asphalt emulsions.

13.5.3 Conclusions and future directions for CR-modified asphalt emulsions

It is widely recognized that while infrastructure improvement and maintenance is a large user of energy and can be quite expensive it can also push forward a strong agenda of improved ecological and environmental sustainability. Two means of doing this that have been studied and are being implemented are the use of CR and the use of asphalt emulsions. End-of-life tires are a steadily increasing problem around the world, and

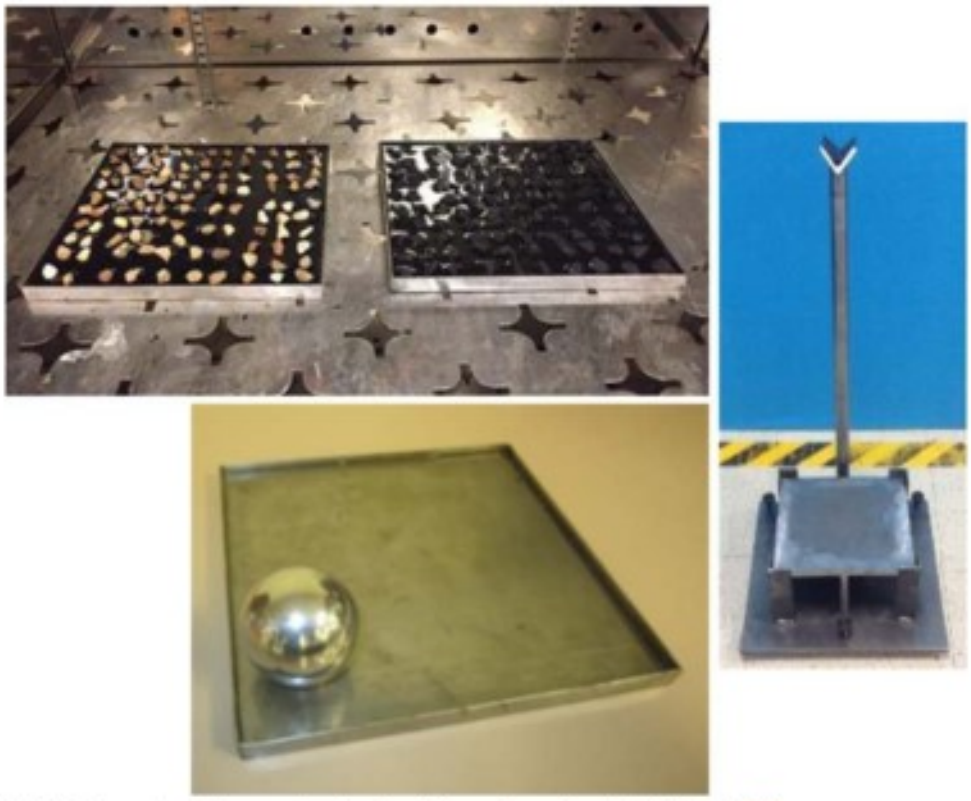


Figure 13.5.8 Test samples, setup, and application of force for a standard Vialit test [27].

the recycling of these tires as CR has the potential to dramatically decrease the number of tires ending up in landfills or otherwise creating pollution. The CR can be directly incorporated into asphalt in order to improve elasticity, fatigue, and thermal resistance as well as used as a replacement for mineral aggregate. The cold application of asphalt by using the asphalt as an emulsion reduces the energy burden of the process, as the asphalt does not need to be heated as high to be workable, and reduces the health burden on workers who may breathe in the volatile fractions of the asphalt. In combining these two methods, improved roadway surface composites can be made that provide for community needs and protect the safety and sustainability of the community.

In order to understand the performance of CR with asphalt emulsions, a number of characterization methods are used. These often look at changes in mechanical performance, volumetric performance, chemical stability, thermal stability, and performance

while in use such as rutting resistance, friction, and abrasion. Using CR with asphalt emulsions, either as a binder modifier or as an aggregate replacement does present new challenges such as difficulty in emulsification due to higher binder viscosity and reduced stiffness. However, ongoing work has shown that with proper formulation CR-modified asphalt emulsions can be competitive with hot-poured polymer-modified asphalt.

Innovation in this space moving forward will be dictated by how well the academic and industrial communities work together to develop asphalt technologies that not only improve performance but also reduce cost and do not require additional equipment or technical burden on roadway workers. Much of the work thus far on asphalt emulsions has been done with relatively little collaboration with the surface chemistry community, but specific focus on the surfactants used for asphalt emulsions, particularly within the domain of the plethora of existing commercial surfactants, could improve control over the setting rate and breaking of asphalt emulsions as well as asphalt emulsion size. The surface chemistry of rubber particles could also be altered through more inexpensive and simple methods than solely irradiation and may show improved compatibilization with asphalt for greater workability. While some fundamental models have been proposed to understand phenomena such as the relationship between particle size and compaction [27], better understanding of the small-scale physical and chemical properties that lead to the macroscopic changes that are being studied could also help push forward the state of the art.

References

[1] A. Schweikert, P. Chinowsky, X. Espinet, M. Tarbert, Climate change and infrastructure impacts: comparing the impact on roads in ten countries through 2100, Proc. Eng. 78 (2014) 306–316.
[2] Y. Huang, R.N. Bird, O. Heidrich, A review of the use of recycled solid waste materials in asphalt pavements, Resour. Conserv. Recycl. 52 (1) (2007) 58–73.
[3] S. Bressi, N. Fiorentini, J. Huang, M. Losa, Crumb rubber modifier in road asphalt pavements: state of the art and statistics, Coatings 9 (6) (2019) 384.
[4] D. Lo Presti, Recycled tyre rubber modified bitumens for road asphalt mixtures: a literature review, Constr. Build. Mater. 49 (2013) 863–881.
[5] A. James, G. Baumgardner, A. Kadrmas, P. Simpson, Asphalt emulsion technology, Transp. Res. Circ. (2006) 1–15.
[6] J. Johnston, K. Gayle, Polymer Modified Asphalt Emulsions: Composition, Uses and Specifications for Surface Treatments. HWA Publication No. FHWA-CFL/TD-08-00x, 2009.

[7] Global ELT Management – A global state of knowledge on regulation, management systems, impacts of recovery and technologies; WBCSD – Tire Industry Project, 2019.
[8] L. Zanzotto, G.J. Kennepohl, Development of rubber and asphalt binders by depolymerization and devulcanization of scrap tires in asphalt, Transp. Res. Rec. 1530 (1) (1996) 51–58.
[9] I. Gawel, R. Stepkowski, F. Czechowski, Molecular interactions between rubber and asphalt, Ind. Eng. Chem. Res. 45 (9) (2006) 3044–3049.
[10] G. Morrison, H. Hedmark, S. Hesp, Elastic steric stabilization of polyethylene-asphalt emulsions by using low molecular weight polybutadiene and devulcanized rubber tire, Colloid Polym. Sci. 272 (4) (1994) 375–384.
[11] NCHRP Report 459—Characterization of Modified Asphalt Binders in Superpave Mix Design; 459; Transportation Research Board—National Research Council—National Academy Press, Washington D.C., 2001.
[12] D. Lesueur, Polymer modified bitumen emulsions (PMBEs), in: T. McNally (Ed.), Polymer Modified Bitumen, Woodhead Publishing, 2011, pp. 25–42.
[13] F. Navarro, P. Partal, F. Martınez-Boza, C. Gallegos, Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens, Fuel 83 (14–15) (2004) 2041–2049.
[14] X. Zhou, F. Wang, X. Yuan, M. Kuang, Y. Song, C. Li, Usage of slurry oil for the preparation of crumb-rubber-modified asphalt emulsions, Constr. Build. Mater. 76 (2015) 279–285.
[15] L. He, Y. Ma, Q. Liu, Y. Mu, Surface modification of crumb rubber and its influence on the mechanical properties of rubber-cement concrete, Constr. Build. Mater. 120 (2016) 403–407.
[16] L.-H. Chou, C.-K. Yang, M.-T. Lee, C.-C. Shu, Effects of partial oxidation of crumb rubber on properties of rubberized mortar, Compos. Part. B Eng. 41 (8) (2010) 613–616.
[17] I. Ibrahim, A. Abd El Rhman, M. El-Shafie, Effect of irradiated crumb rubber on cold recycled bitumen emulsion mixes properties, Am. Sci. Res. J. Eng. Technol. Sci. 15 (1) (2016) 76–87.
[18] G.-X. Yu, Z.-M. Li, X.-L. Zhou, C.-L. Li, Crumb rubber–modified asphalt: microwave treatment effects, Pet. Sci. Technol. 29 (4) (2011) 411–417.
[19] G. Holleran, J. Reed, J. Van Kirk, *The use of crumb rubber in slurry and microsurfacing and chip seals*, AAPA International Flexible Pavements Conference, 10th, 1997, Perth, Western Australia, Vol. 1, 1997.
[20] M. Pettinari, G. Dondi, C. Sangiorgi, O. Hededal, The effect of cryogenic crumb rubber in cold recycled mixes for road pavements, Constr. Build. Mater. 63 (2014) 249–256.
[21] M. Bocci, A. Grilli, F. Cardone, A. Graziani, A study on the mechanical behaviour of cement–bitumen treated materials, Constr. Build. Mater. 25 (2) (2011) 773–778.
[22] M.T.A. Sarkar, M.N. Rahman, M.A. Elseifi, C. Mayeux, S.B. Cooper III, Rheological and molecular characterizations of tire rubber modified asphalt emulsion, Transp. Res. Rec. (2020). 0361198120908871.
[23] A.A. Gheni, O.I. Abdelkarim, M.M. Abdulazeez, M.A. ElGawady, Texture and design of green chip seal using recycled crumb rubber aggregate, J. Clean. Prod. 166 (2017) 1084–1101.
[24] B. Aktaş, M. Karaşahin, M. Tiğdemir, Developing a macrotexture prediction model for chip seals, Constr. Build. Mater. 41 (2013) 784–789.
[25] F.M. Navarro, M.C.R. Gámez, Influence of crumb rubber on the indirect tensile strength and stiffness modulus of hot bituminous mixes, J. Mater. Civ. Eng. 24 (6) (2012) 715–724.

[26] L.P.T.L. Fontes, G. Trichês, J.C. Pais, P.A.A. Pereira, Evaluating permanent deformation in asphalt rubber mixtures, Constr. Build. Mater. 24 (7) (2010) 1193–1200.
[27] A.A. Gheni, M.A. ElGawady, Crumb rubber as a sustainable aggregate in chip seal pavement, Congrès International de Géotechnique–Ouvrages–Structures, Springer, 2017, pp. 392–401.
[28] P.S. Wulandari, D. Tjandra, The use of crumb rubber for replacing fine aggregate in cold mixture asphalt, IOP Conf. Ser. Mater. Sci. Eng. (2019) 012119. IOP Publishing:.
[29] P. Wulandari, K. Kertorahardjo, A. Thesman, D. Tjandra, Effect of crumb rubber as fine aggregate replacement in cold mixture asphalt, Civ. Eng. Dimens. 21 (2019) 107–112.
[30] G. Dondi, P. Tataranni, M. Pettinari, C. Sangiorgi, A. Simone, V. Vignali, Crumb rubber in cold recycled bituminous mixes: comparison between traditional crumb rubber and cryogenic crumb rubber, Constr. Build. Mater. 68 (2014) 370–375.
[31] M. Pettinari, A. Simone, Effect of crumb rubber gradation on a rubberized cold recycled mixture for road pavements, Mater. Des. 85 (2015) 598–606.
[32] Z. Chen, S.P. Wu, T. Zhang, L. Pang, Experimental investigation on fracture and tensile characteristics of micro-surfacing containing crumb rubber, Key Eng. Mater. Trans. Tech. Publ. (2008) 489–492.

13.6

Utilization of rubberized asphalt in the Europe

Davide Lo Presti[1,2], Juan Gallego Medina[3], Jorge Carvalho Pais[4], Lily Poulikakos[5], Moises Bueno[5], Davide Dalmazzo[6] and Ezio Santagata[6]

[1]Department of Engineering, University of Palermo, Palermo, Italy [2]Nottingham Transportation Engineering Centre, University of Nottingham, Nottingham, United Kingdom [3]Dpto. Ingeniería del Transporte, Territorio y Urbanismo Universidade Politecnica de Madrid, Madrid, Spain [4]ISISE, Department of Civil Engineering, University of Minho, Guimarães, Portugal [5]Empa—Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland [6]Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Torino, Italy

13.6.1 Introduction

The first appearances of rubberized asphalt in Europe occurred 60 years ago, but its widespread adoption has not yet happened. In the last decade, substantial changes in terms of technical and governance solutions, together with the global interest in implementing sustainable development and a circular economy, are allowing new high peaks of interest for rubberized asphalt mixtures.

In the following sections we will provide an overview of the rubberized asphalt technologies currently used in Europe and then provide readers with details about history, case studies, and prospective from countries who are pioneers of these technologies in Europe: Spain, Portugal, and Italy, as well as from a newcomer like Switzerland. These summaries are offered thanks to a cooperation with estimeed colleagues who in the last 10–15 years have all played a significant role for introducing rubberized asphalt technologies into the road industry by performing successful research/validation projects often funded by government bodies and carried out by the major academic and industrial stakeholders. A final section will then provide readers with lessons learned together with perspectives and recommendations for the future use of rubberized asphalt in Europe.

13.6.2 Rubberized asphalt mixtures: an overview of technologies currently used in Europe

In the 1960s scrap tires were processed and used as a secondary material in the pavement industry. One application was introduced by two Swedish companies that produced a surface asphalt mixture with the addition of a small quantity of ground rubber from discarded tires as a substitute for a part of the mineral aggregate in the mixture, in order to obtain asphalt mixture with improved resistance to studded tires as well as to snow chains, via a process known as the "dry process." In the same period Charles McDonalds, a materials engineer of the city of Phoenix in Arizona (USA), was the first to find that after thoroughly mixing crumbs of RTR with bitumen (CRM) and allowing it to react for a period of 45 min to an hour, this material captured beneficial engineering characteristics of both base ingredients. He called it Asphalt Rubber and the technology is well known as the "wet process". In the early 1990s, the patent of the McDonald's process expired making the wet process of public domain [1]. Since then, an overwhelming amount of research is still ongoing worldwide to validate and improve technologies related to rubberized asphalt pavements. In Europe, in order of first applications, Spain, Portugal, and Italy have been playing a major role with thousands of kilometers of road paved, in some cases supported by tailored specifications. This has been possible since in these countries specific consortiums have been created for systemic management and promotion of the reuse of recycled tire rubber: Signus ecovalor in Spain, Valorpneu in Portugal, and Ecopneus in Italy. These organizations have been formed as a consequence of the adoption by these countries of the Extended Producer Responsibility (EPR) regime, explained in the 2008 EU Waste Framework Directive [2]. Also thanks to these initiatives, the scientific progress in the development of rubberized asphalt went on and both academia and private sector, often in collaboration, developed methodologies and technologies that significantly improved the knowledge of the stakeholders and provided increased confidence for their use.

Rubberized asphalt is a family of materials and technologies and today Europe is witnessing an exponentially increased interest in them due to several policies, at both national and continental levels, that are pushing innovation to be greener. In 2019, some members of the European Asphalt Pavement Association prepared a draft of a dedicated European standard for rubberized asphalt materials. That draft standard was finally rejected but for the first

time, discussions are ongoing at continental level. The recent increased interest is also resulting in a wide range of technologies developed and trialed in several parts of Europe. These can be categorized and summarized within two well-known macrocategories (1) "wet process" and (2) "dry process." In both categories processing conditions and/or materials are engineered and optimized to allow improvements of the asphaltic material performance by minimizing changes in material manufacturing and paving operations. The following is a short description of the rubberized asphalt technologies (not including slurries), while Table 13.6.1 provides an overview of their utilization in Europe.

(1) *Wet process—McDonald, continuous blending (CB), terminal blending (TB), bitumen–rubber concentrate, hybrid rubberized binder*

The "wet process" is used to describe a whole group of technologies tailored to modify the bituminous binder. Excellent performance has been recorded over the years and in many countries worldwide [1]. The main issues in widespread adoption relate to adaptation of the manufacturing

Table 13.6.1 Overview of the use of rubberized asphalt technologies in Europe (August 2020).

	Research	Trials/validation	Marketed
Wet process			
McDonald	Belgium, Czech Republic, France, Germany, Greece, Italy, The Netherlands, Spain, Poland, Portugal, United Kingdom	Czech Republic France, Greece, Italy, Poland, Portugal, Spain, Slovenia, Sweden	Czech Republic, France, Italy, Portugal, Spain, Sweden
Continuous	Czech Republic, Spain	Spain	Spain
Terminal blend	Austria, France, Spain	Austria, Czech Republic, Spain	Czech Republic, Spain
Hybrid rubberized binder	Austria, Czech Republic, Italy, Spain	Austria, Italy, Spain	Italy, Spain
Dry process			
Tire-derivate aggregate	France, Germany, Italy, The Netherlands, Poland, Portugal, Spain, Sweden, United Kingdom	Czech Republic, France, The Netherlands, Poland, Portugal, Spain, Sweden, United Kingdom	Czech Republic, France, Poland, Spain
Hybrid rubberized mixture	France, Italy		
Semiwet	Czech Republic, Germany, Poland, Serbia, Spain, Switzerland	Czech Republic, Denmark, Germany, Serbia, Slovenia, Spain, United Kingdom	Czech Republic, Germany, Spain, United Kingdom

process, which requires specialized and expensive equipment, and lack of storage stability at high temperatures.

One of the first commercial binder systems exploiting this route was developed in the 1960s in the United States by McDonald and consisted of the dissolution of the crumb rubber in bitumen as a modifying agent. This technology is the original wet process, also commonly called asphalt rubber (AR) or wet process high viscosity, where the bitumen–rubber binder is fabricated in a blending tank, mixing crumb ubber (15%–22%) and bitumen at a high speed for 1–2 min. Afterward, the modified binder is collected in another tank and mixed with augers, where the blend stays for a sufficient period of time (45–60 min) to allow the circulation and consequently the reaction of the blend [3,4]. The resulting binder is then used to produce bituminous mixtures.

The second method, CB, was developed in Florida and describes a wet process in a continuous operation rather than a batch procedure. This technology differs from the McDonald process in several aspects: the reaction occurs during the blending using a unique unit with agitators and lower percentages of crumb rubber modifier (CRM) (from 8% to 10% rubber) with a smaller size are incorporated into the bitumen. Moreover, the CB system requires lower mixing temperature and shorter reaction time [5].

A third method, commonly called TB, was introduced in the United States in the 1980s "as a form of the wet process where CRM (from 10% to 12%) is blended with bitumen at the refinery or at an asphalt binder storage and distribution terminal and transported to the asphalt mixing plant or job site for use." However, while performance is satisfactory due to the inferior amount of CRM it is not yet comparable with the McDonald wet process [6,7].

The last and most recent method is the hybrid binder modification that consists of incorporating two or more polymeric modifiers of different nature to a bitumen, in order to take advantage of their complementary features. For rubberized asphalt this usually happens by adding compounds of CRM and synthetic polymers such as stirene-butadiene-stirene (SBS) and/or ethylene-based copolymer [8,9].

(2) *Dry process—Tire-derivate aggregate, hybrid rubberized mixtures, semiwet*

The "dry process" is a family of technologies aimed at modifying asphalt mixtures directly.

Despite the unstable performance, compared to the wet process, the dry process presents certain advantages, such as

avoiding modifications to the existing asphalt plant's setup. The size of CRM is variable: today is comparable to the wet process ranging from 0.5 to 2 mm, but for certain applications the dry process allows for coarser particle size. The amount of CRM used in the dry process can be significantly higher (the dry process can use from 2 to 4 times as much as the wet process), increasing the rate of the recycling material, and the incorporation in the mixture is usually done directly in the mixer with no need for specialized equipment. However, the main issue is lack of control of the CRM swelling/digestion process, which usually last even hours after mixing and could cause serious issue such as premature cracking and raveling.

Originally, this process was developed in Sweden in the late 1960s and defined as any method that mixes CRM with the heated aggregates before blending the hot bitumen in the mixing chamber. The modification of the asphalt mixture consists of enriching and/or replacing portions of the aggregate skeleton with tire-derivate aggregates to provide the mixture with more flexibility. Performance has always been uncertain with some successful examples and as many problems due to early damage of roads [10–12].

Since the early 1990s, evolutions of the dry process have been introduced and consist of hybrid-mixture technology including the use of tire-derivate aggregate together with other complementary ad mixtures (i.e., plastic) and/or bitumen modified with synthetic polymers and/or wet-process technologies [13,14].

Finally, the most recent technology, introduced in the early 2010s and also known as a semiwet process, aims to match the well-known good performance of the wet process with the user-friendliness of the dry process. This technology delivers rubberized asphalt mixtures through the dry process but uses engineered CRMs to allow for a controlled swelling/digestion process. This process is possible thanks to predigestion of the rubber particles with bitumen or modification of the CRM surface to promote the reaction with the bitumen. The former can also be obtained through preliminary manufacturing of a bitumen–rubber concentrate (between 15% and 50% of rubber) at specialized industrial premises. The concentrate is then cooled down and grinded or, by following other procedures, it can also be turned into granules or pellets [15]. Several patented semiwet technologies are being marketed mainly in the United States and Europe and so far promising performance has been seen worldwide [16].

13.6.3 Experience and lessons learned—Spain

13.6.3.1 History

In Spain, the yearly consumption of tires accounts up to 300,000 tons/year. The whole amount is correctly managed to prevent landfills and promote the valorization of this potential waste. In recent years, material valorization to produce secondary raw material has exceeded 40% of the processed end-of-life tires (ELTs). This achievement has been possible thanks to the EPR regime, an integrated management system based on not-for-profit organizations regulated by law, in charge with the management of the used tires, and financed by the tax applied to tires at the point of sale to the final consumer.

A part of the granulated rubber is dedicated to the production of asphalt paving materials. The first attempts to pave a road with a rubberized material started between 1994 and 1997. Several projects carried out by the dry process were performed with semidense asphalt mixtures including 2% of crumb rubber 0.8 mm particle size. In general terms, the performance of these test sections was fair to good. The first rubber-modified binders at industrial scale were produced in Madrid and Seville. The binders were manufactured by the TB system incorporating 12% of rubber over the bitumen. The properties and performance of these rubber binders were similar to those of a low-content ethylene vinyl acetate-modified binder.

In 2002 two AR units made in the United States, but operated by a Spanish company, started producing high-viscosity rubber-modified binders (McDonald system). Soon afterward an asphalt–rubber unit made in Spain started operating. In this case, the equipment worked according to the CB scheme. The availability of these production units allowed the companies involved to experiment with different formulas: high-viscosity binders (18% rubber), binders with medium content (8%–12% rubber), and different combinations of rubber and SBS polymers, with the economic target of reducing the cost for polymer-modified binders. Although at first, these machines were used for research test sections, the good results obtained allowed them to become an alternative to traditional binders in real projects. The success of these technologies promoted the elaboration by the Spanish Ministry of Public Works of the Manual for Incorporation of Crumb Rubber in Asphalt Mixtures (Spanish) [17]. Moreover, new technical specifications were enacted in the Advisory Circular 21/2007 (Spanish) to regulate the characteristics of several categories of rubber-modified

binders, based on the experience acquired over the years [18]. The aim of these specifications was to integrate these new modified binders in the regular specifications for net- and polymer-modified binders so that the inclusion of the rubber binders in new projects was easy. Three categories of rubber binders were defined in the specifications: (1) "bitumens improved with rubber," usually with 6%–12% rubber; (2) "hybrid rubber-polymer-modified binders," with 4%–12% rubber + polymers; and (3) "high-viscosity AR binders," with usual contents of rubber above 18%, and polymer in a few cases. Figs. 13.6.1–13.6.3 show the specifications that used in the design and production of rubber binders since 2007. More than 1000 kms of roads have been paved in Spain according to these specifications.

As for the dry process, the Advisory Circular 21/2007 relegated its production to medium-low volume roads because of the difficulties in conciliating the needed digestion time with high production rates at the job site.

13.6.3.2 Research projects and latest developments

Applications of rubberized asphalt in Spain and development of technologies have come a long way since the early 2000s. About

Characteristics		Reference Standard	Unit	BC35/50	BC50/70
Penetration, 25°C		EN 1426	0.1 mm	35-50	50-70
Softening point		EN 1427	°C	≥ 58	≥ 53
Fragility point Fraass		EN 12593	°C	≤ -5	≤ -8
Force - ductility (5 cm/min)	5°C	EN 13589 EN 13703	J/cm^2	≥ 0.5	
Elastic recovery at 25°C		EN 13398	%	≥ 10	
Storage stability (*)	Softening point difference	EN 13399	°C	≤ 10	
	Penetration difference		0.1 mm	≤ 8	≤ 10
Solubility		EN 12592	%	≥ 92	
Inflamation point o/v		EN ISO	°C	≥ 235	
Residues from RTFOT: UNE EN 12607-1					
Mass Variation		EN 12607-1	%	≤ 1.0	
Retained Penetration		EN 1426	% o.p.	≥ 65	≥ 60
Softening point Variation		EN 1427	°C	min -4 máx +8	min -5 máx +10

Figure 13.6.1 Spanish specifications for bitumens enhanced with rubber. (*) Only required by binders that are not produced "in situ."

Denomination EN 14023				PMB 10/ 40-70 C	PMB 25/ 55-65 C	PMB 45/ 80-60 C	PMB 45/ 80-65 C	PMB 45/ 80-75 C	PMB 75/ 130-60 C
Characteristics		EN		Ensayos sobre el betún original					
Penetration at 25°		1426	0.1 mm	10-40	25-55	45-80	45-80	45-80	75-130
Softening point		1427	°C	≥ 70	≥ 65	≥ 60	≥ 65	≥ 75	≥ 60
Force-ductility (5 cm/min)		13589 13703	J/cm²	≥ 2 (15°C)	≥ 2 (10°C)	≥ 2 (5°C)	≥ 3 (5°C)	≥ 3 (5°C)	≥ 1 (5°C)
Fragility point Fraass		12593	°C	≤ -5	≤ -7	≤ -12	≤ -15	≤ -15	≤ -15
Elastic recovery at 25°C		13398	%	TBR(**)	≥ 50	≥ 50	≥ 70	≥ 80	≥ 60
Storage stability(*)	Softening point difference	13399 1427	°C	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5
	Penetration difference	13399 1426	0.1 mm	≤ 9	≤ 9	≤ 9	≤ 9	≤ 13	≤ 13
Ignition point		ISO 2592	°C	≥ 235	≥ 235	≥ 235	≥ 235	≥ 235	≥ 220
Durability – Resistance to RTFOT EN 12607-1									
Mass change		12607-1	%	≤ 0.8	≤ 0.8	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Retained penetration		1426	%	> 60	> 60	> 60	> 60	> 60	> 60
Softening point increase		1427	°C	≤ 8	≤ 8	≤ 10	≤ 10	≤ 10	≤ 10
Softening point decrease		1427	°C	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5

Figure 13.6.2 Spanish specifications for hybrid rubber–polymer-modified binders. (*) Only required by binders that are not produced "in situ."

1,639 km of highways, roads, and streets were paved with rubberized asphalt mixtures by 2017, consuming 16,745 tons of ground tire rubber [19]. As shown in Fig. 13.6.4, in most cases, wet-process technology was selected, mainly with in-situ blending, while the dry process was used only in 13% of the cases.

Several investigation projects have been carried out to offer more in-depth knowledge of these technologies as well as provide technical guidance to promote the use of rubberized asphalt in road pavements. Some of the projects have been supported by the Ministry of Public Works. Other projects have been financed by the Spanish EPR consortium Signus Ecovalor. Signus Ecovalor has requested several universities to collaborate in research investigations and to generate technical guidelines to promote practical applications, as the Guide for the Production of Rubberized Binders [20] and the Guide for the Production and Installation of Asphalt Mixtures with Crumb Rubber from End of Life Tires.

Characteristics		Reference standard	Unit	BMAVC-1	BMAVC-2	BMAVC-3
High viscosity rubber modified binder						
Penetration, 25°C		EN 1426	0.1	15-30	35-50	55-70
Softening point		EN 1427	°C	≥ 75	≥ 70	≥ 70
Fragility point Fraass		EN 12593	°C	≤ -4	≤ -8	≤ -15
Force-Ductility (5 cm/min)	5°C	EN 13589 EN 13703	J/cm²	-	≥ 2	≥ 3
	10°C			≥ 2	-	-
Consistency (Flender, 60°C)		NLT 183	s	≥ 3000		
Dynamic viscosity	135°C	EN 13302	mPa·s		≤ 7500	≤ 5000
	170°C			≥ 2000	≥ 1200	≥ 800
Elastic recovery	25°C	EN 13398	%	≥ 10	≥ 20	≥ 30
Storage stability (*)	Ring and ball Difference	EN 13399	°C	≤ 5		
	Penetration Difference		0.1 mm	≤ 20		
Ignition point o/v		ISO 2592	°C	≥ 235		
Durability – Resistance to RTFOT EN 12607-1						
Mass variation		UNE EN 12607-1	%	≤ 0.8	≤ 0.8	≤ 1.0
Retained penetration		UNE EN 1426	% p.o	≥ 60		
Softening point variation		UNE EN 1427	°C	min -4 max +10		min -5 max +12

Figure 13.6.3 Spanish specifications for high-viscosity asphalt–rubber binders. (*) Only required by binders that are not produced "in situ."

In terms of innovation, the first one of the drawbacks usually mentioned for rubberized asphalt mixtures is the manufacturing temperature required, which is 5°C–10°C above that of conventional asphalt mixtures. Efforts to reduce the working temperatures for rubberized asphalt mixtures has been made in several investigation projects in Spain. Signus project produced a document with the methodological guidance and study cases for Warm Rubberized Asphalt Mixtures [21].

The second innovation that deserves mention is the so-called semiwet process with predigested rubber. As the manufacturing process of the rubberized binders (wet process) have difficulties to accomplish the storage stability requirements, and the dry process demands strict digestion times, this new concept, the

semiwet process, has emerged. Through this technology, a Spanish company is producing a pretreated ground tire rubber that achieves quick digestion when it is added to asphalt mixtures in the mixer of the asphalt plant. This technology is a promising way to incorporate CRM into asphalt mixtures as it prevents the need for different plant setups. The mechanical performance of the mixtures produced by this new pretreated crumb rubber is similar to that of the traditional wet process, as reported in Ref. [16]

13.6.3.3 Lessons learned and prospective

The experience with rubberized asphalt materials in Spain provided some valuable lessons: in technical terms, rubberized asphalt materials have a good performance, ranging from the conventional mixtures to the polymer-modified mixtures, depending on the percentages of rubber and the process used. Additionally, it is possible to use warm-mix technologies to work at reduced temperatures. Although the wet process is generally preferable, a new process is emerging: the semiwet process. This promising technology prevents the lack of digestion by the dry process as well as the potential problems with storage stability by the wet process. It must be noted that a favorable administrative framework is essential for the promoted use of rubberized asphalt paving materials. In this sense, currently the Spanish

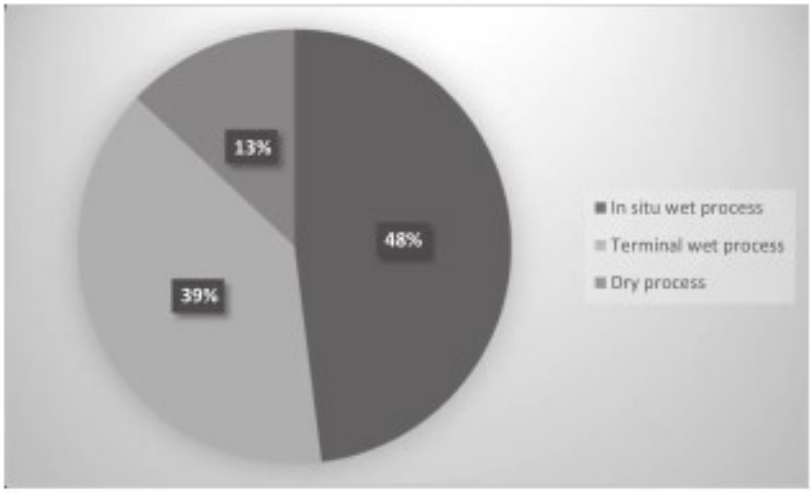


Figure 13.6.4 Technologies for rubberized asphalt in Spain. Adapted from L.A. De Leon, L. Saiz, R. Pérez, 20 years of rubberised asphalt mixtures in Spanish roads. Signus Ecovalor. https://www.signus.es/mezclas-asfalticas-con-polvo-de-neumatico, 2018 (accessed May 2020).

Ministry of Public Works is preparing new specifications for rubberized asphalt paving materials. Furthermore, there is also a new framework for the public procurement of civil engineering projects: the program for green and sustainable public procurement. This policy provides award criteria for public works proportional to the amount of waste valorized in a project. The new legal regulations define not only the rubberized binder's properties but also the criteria to assess the sustainability of projects that include this family of materials.

13.6.4 Experience and lessons learned—Portugal

In Portugal, since 2003, on average, 80,000 tons of used tires are collected and processed and the tires in stockpiles have been eliminated in the last four years [22]. Presently, more than 60% of used tires have been recycled, 25% are used for energy valorization, and about 12.5% are used for retreading, as indicated in Fig. 13.6.5. This was possible thanks to the adoption of the EPR though a nonprofit company, Valorpneu, that since 2002, has organized and managed the collection system and final destination of used tires.

One of the main applications of recycled tires in Portugal is the production of crumb rubber for asphalt modification, playground pavements, or rubber for synthetic grass. This production is carried out using a mechanical grinding and cryogenic process.

13.6.4.1 History

The application of rubberized asphalt in Portugal started in 1999 with the rehabilitation of two stretches of national roads with a total extension of approximately 30 km. The pavements under rehabilitation were in very bad condition, with severe alligator cracking in extensive areas. The solution designed for the rehabilitation of the two pavements comprised the placement of an asphalt-leveling course with variable thickness, followed by a gap-graded asphalt-wearing course using wet-process AR. Because it was the first experiment with AR in Portugal, the rehabilitation was monitored to gather as much information as possible to help develop recommendations for the use of this type of technique in Portugal. The monitoring comprised the laboratory characterization of the asphalt–rubber binder and the mechanical characterization

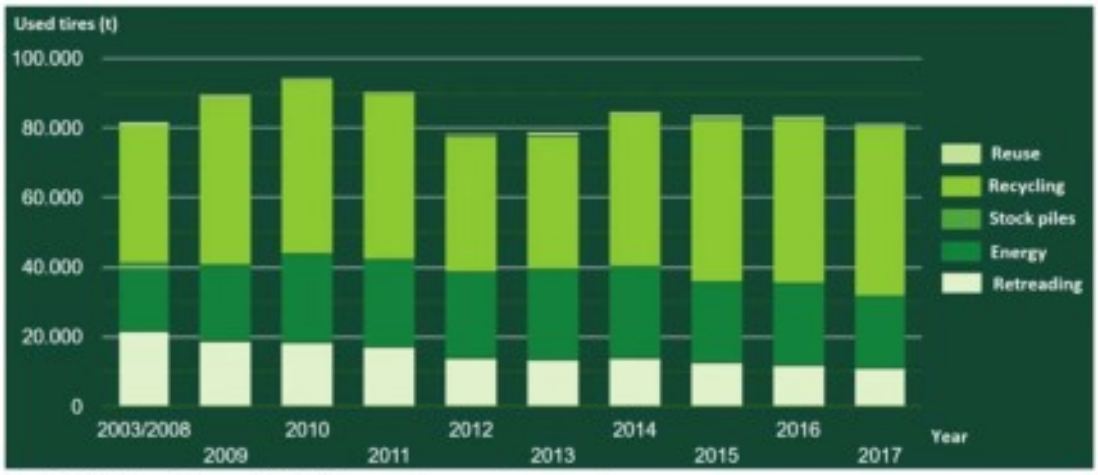


Figure 13.6.5 Destination of ELTs in Portugal (www.valorpneu.pt).

of the asphalt–rubber mixtures (more details in the next paragraph).

The first application of the dry process in Portugal was carried out in 2011 in a 5 km stretch of a national road using a fine crumb rubber (0.6 mm nominal size) typically used in the wet process to promote some interaction between the rubber and the bitumen [23]. Mechanical characterization of the asphalt mixes, including stiffness modulus, fatigue life, and permanent deformation resistance, was assessed for comparison with conventional mixes, considering the influence of the testing temperature. The results for the mechanical properties of dry AR mixes compare well with the wet process, and after five years of service, the pavement shows satisfactory performance, both in terms of structural performance and functional performance.

The main contribution of this project for the application of rubberized asphalt in Portugal was the introduction of specifications for the asphalt–rubber binder as well as for asphalt–rubber mixes. The first step included the creation of two technical assessment documents for the design and application of high-rubber content asphalt mixes, whereas the second step was the creation of Portuguese specification for low, medium, and high rubber content-modified bitumen and their corresponding asphalt–rubber mixes.

For example, Fig. 13.6.6 shows the specifications for the bitumen modified with high rubber content where viscosity, penetration, softening point, durability, elastic recovery, and storage stability are specified for two base asphalts, namely 35/50 and

50/50 pen asphalt. For asphalt mixes, the specifications define the mechanical characteristics such as the stiffness modulus, fatigue, and permanent deformation resistance, as illustrated in Fig. 13.6.7.

13.6.4.2 Case study

As mentioned earlier, Portugal was a pioneer of rubberized asphalt technology beginning in 1999 with its first experiment with AR. This rehabilitation project was monitored to gather as much information as possible to help develop recommendations for the use of this type of technique in Portugal. The monitoring comprised the laboratory characterization of the asphalt–rubber binder and the mechanical characterization of the asphalt–rubber mixtures.

The asphalt–rubber binder for this project was produced at a temperature of 180°C, using 18% of crumb rubber, and the digestion time was studied from 45 min to 6 h and viscosities below 5000 cP were obtained as illustrated in Fig. 13.6.8 [24].

In terms of mechanical behavior, the asphalt–rubber mixes' stiffness, fatigue, and permanent deformation tests were carried

Bitumen modified with high rubber content (BBA)					
Specification		Standard	Unit	BBA 35/50	BBA 50/70
Apparent Viscosity at 175ºC, min. (Brookfield viscometer with thermosel, handle SC4-27, 20rpm)		EN 13302	mPa.s	2500 - 4500	2500 - 4500
Apparent Viscosity at the exit of reaction tank, at 175ºC, min.		-	cP	3500 - 5000	3500 - 5000
Penetration, 25ºC, 100g, 5 s		EN 1426	0,1 mm	15 - 30	20 - 35
Softening Point, min.		EN 1427	ºC	68	65
Durability (Resistance to hardening) after RTFOT, 163ºC, max.	Change of mass, máx.	EN 12607-1	%	+ 0,8	+ 1,0
	Retained Penetration, 25ºC, 100g, 5s, min.		%	70	65
	Increase of Softening Point, max.		ºC	12	12
Elastic Recovery, elongation of 10 cm, at 25 ºC, min.		EN 13398	%	75	75
Storage Stability	Difference in Softening Point, max.	EN 13399	ºC	5	5
	Difference in Penetration, max.		0,1 mm	8	10

Figure 13.6.6 Portuguese specification for bitumen modified with high rubber content.

MBR-BMB® - Gap-graded Asphalt Rubber mixtures				
Property		Test method	BBA produced with 35/50 pen grade bitumen	BBA produced with 50/70 pen grade bitumen
Stiffness modulus, MPa		EN 12697-26: 2004 (4PBT, 20°C, 10Hz)	3000 - 4500	2500 - 3500
Resistance to fatigue	ε6	EN 12697-24:2004 (4PBT, 20°C, 10Hz)	≥ 200	≥ 250
	p		-6 to -4	
Resistance to permanent deformation	Deformation rate between 105 and 120 min., µm/min.	NLT 173/84 (wheel tracking test, 60°C)	≤ 10	≤ 14
	WTS_{AIR}, $mm/10^3$ cicles	EN 12697-22:2003 (wheel tracking test, Small size device, procedure B, Air,60°C)	≤ 0,08	≤ 0,09
	PRD_{AIR}, %		≤ 6,0	≤ 7,0

Figure 13.6.7 Portuguese specification for gap-graded asphalt–rubber mixes (wet process).

out that allowed to obtain values for further consideration in the design of pavements with asphalt–rubber mixes.

Since then, 14,000 km^2 of roads have been paved with AR containing about 18%–19% of crumb rubber, which corresponds to 1500 tons of rubber/year used in the rehabilitation of road pavements in Portugal. The quality control of these rehabilitations include mechanical tests to assess the stiffness and fatigue resistance of the applied asphalt–rubber mixes. For gap-graded asphalt–rubber hot mixes, stiffness and fatigue resistance are presented in Figs. 13.6.9 and 13.6.10, respectively.

13.6.4.3 Lessons learned and prospective

Portugal has established a policy for the management of used tires and received encouragement from the national road administration for the application of crumb rubber in road pavements. These steps contributed to the construction of more than 14,000 km^2 of asphalt–rubber pavements with great success in terms of structural and functional performance in the rehabilitation of road pavements. The different applications of asphalt–rubber mixes were also used to the establishment of practical rules and specifications for the use of crumb rubber-modified asphalt mixes that has allowed to obtain parameters for the design of the rehabilitation of road pavements with these mixes. Among others, stiffness, fatigue, and permanent

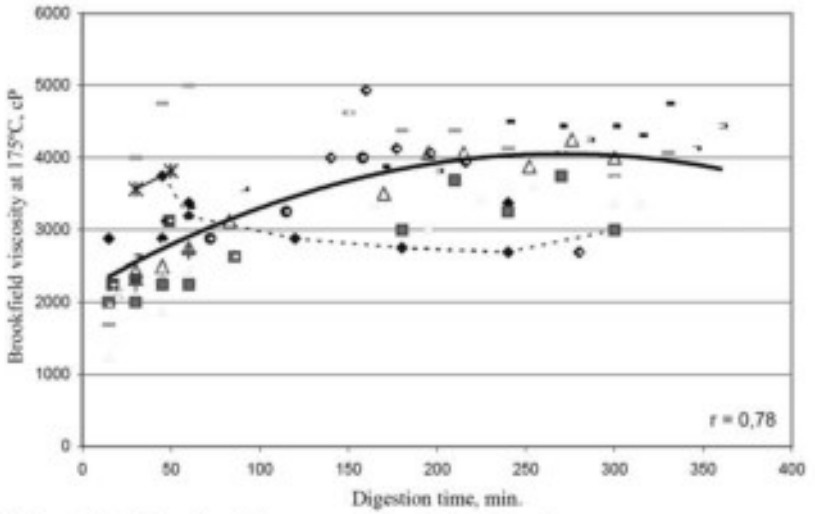


Figure 13.6.8 Evolution of the viscosity of bitumen–rubber during digestion. Adapted from I. Antunes, Asphalt Rubber: Study of the Rheology of Modified Bitumen with Recycled Tire Rubber Powder (Ph.D. thesis). Università degli studi di Parma (in Italian), 2006.

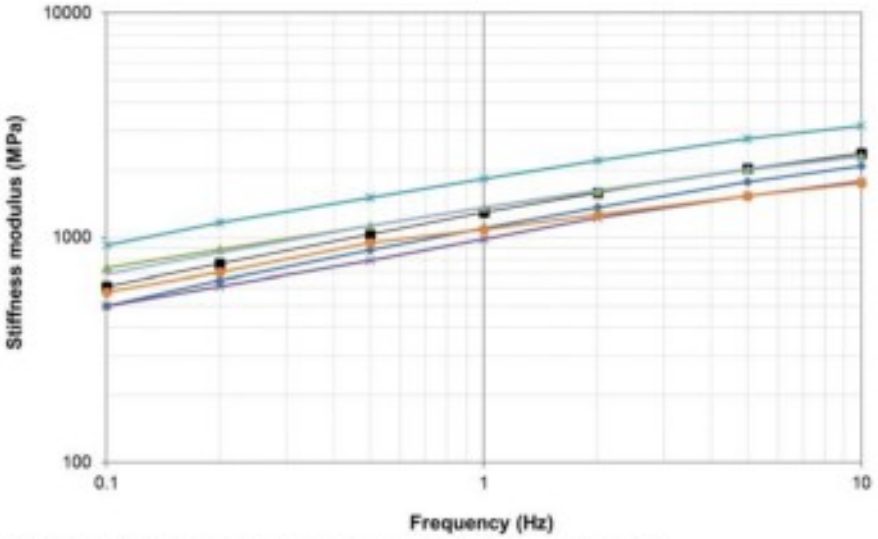


Figure 13.6.9 Stiffness modulus for Portuguese gap-graded asphalt–rubber mixes.

resistance have been assessed. Despite a significant decrease in the use of asphalt–rubber mixes after the 2010 crisis, Portugal has practical and technical conditions for successful application

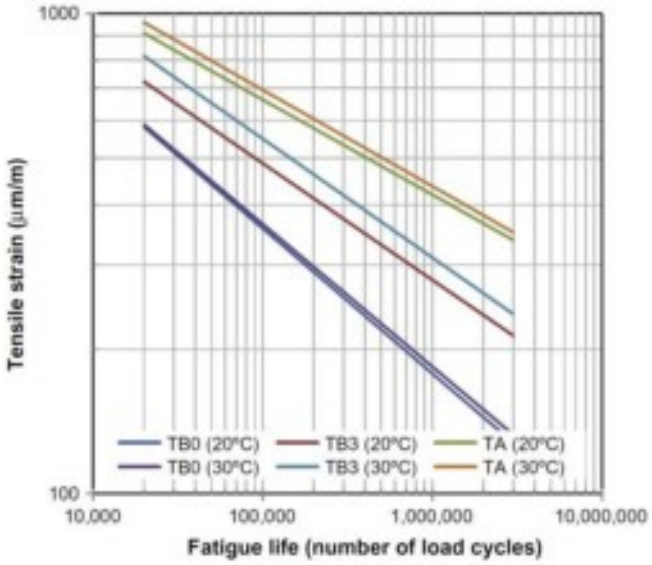


Figure 13.6.10 Fatigue life for Portuguese gap-graded asphalt–rubber mixes.

of asphalt–rubber mixes in the rehabilitation of road pavements contributing to sustainable utilization of ELTs.

13.6.5 Experiences and lessons learned—Italy

13.6.5.1 History

In Italy, the annual yield of ELTs is of the order of 350,000 tons. While in the past their management involved massive landfilling, European legislation acts in force since the late 1990s have promoted energy production or matter recovery, and significant efforts have been made to identify the most efficient destinations. In such a scenario, the use of processed ELTs in pavement applications was at first considered controversial. However, the situation has radically changed in the last 20 years as a result of the evolution of national legislative constraints related to the management of ELTs [25,26], of the introduction in civil engineering of sustainability concepts, and of the creation of focused industrial initiatives. Thus private companies have developed specific ELT-related paving technologies in order to gain opportunities in the market, and public administration has opened up to these innovations with continuously growing interest. Academic institutions

have also contributed to such an evolution by means of focused research initiatives and investigations.

Early full-scale applications starting in 2006 focused on the use of crumb rubber (CR) derived from ELTs as a bitumen modifier in the context of the classical "wet" technology, leading to the production of "AR." In particular, such a technology was adopted as part of maintenance and construction works carried out mainly on municipal and provincial roads. By following the reference guidelines developed in the United States, the corresponding bituminous mixtures that were generally employed for the formation of wearing courses were for the most part the "open-graded" and "gap-graded" type. Moreover, in a few applications AR was also used in stress-absorbing membrane interlayers. Unfortunately, road administrations adopted the abovementioned paving solutions in isolated cases, with no planned and systematic use at the network level.

13.6.5.2 Case studies and research activities

A significant contribution to the diffusion at the national scale of asphalt–rubber technology occurred in 2008 with the initiatives of the Province of Torino, which financed the construction of a pilot section on the newly built Borgaro–Venaria ring road and thereafter supported several research and implementation activities carried out as part of national and European funding schemes [27,28]. These were developed with the involvement of the Politecnico di Torino and with the aid of Ecopneus, a nonprofit national consortium created in 2009 for the overall management of the recovery and treatment of ELTs.

The Borgaro–Venaria experiment involved the placement of 16,000 m^2 of wearing course mixture of the gap-graded type containing AR, fully integrated by laboratory design studies, field monitoring, and modeling activities [29]. The outcomes of such an application were functional for the definition of further technological solutions, which were trialed on other provincial roads. These included AR wearing course mixtures of the gap graded and dense-graded type, also containing reclaimed asphalt and viscosity-reduction additives.

Further activities focused on training of technical staff, development of draft performance standards, and layout of strategies for the satisfaction of the dictates of the so-called green public procurement policy (Green Public Procurement).

With the involvement of industrial partners, trials and experiments were also performed in order to explore the possibility of implementing the "dry" technology, which had been previously employed in sporadic construction works, with limited extension and often not entirely satisfactory in terms of durability.

In the course of time, several academic research groups carried out experimental investigations and analyses on bituminous binders and mixtures containing CR from ELTs, covering both fundamental characterization and performance-related issues. The obtained results were in line with those shared by the international community, with some additional original contributions of significant scientific value.

The earlier works focused on rheology of asphalt–rubber binders, which was assessed in comparison to polymer-modified and terminal blend binders [24,30], either with classical laboratory tests or with more advanced characterization protocols for the evaluation of resistance to permanent deformation and fatigue damage [31], resistance to aging, and to the aggressive action of kerosene. In the more mature phase of research, innovative investigations were carried out on the subject of CR–bitumen interactions, with the development of models for the prediction of the time-dependent viscosity characteristics and for the full description of viscoelastic properties [32,33]. These studies were supported by a significant amount of research work done for the physical, morphological, and chemical characterization of CR coming from different Italian ELT processing plants [34]. More recent research work has considered the potential use of bitumen extenders in combination with CR and has also focused on the effects of ultraviolet aging [35,36].

With respect to bituminous mixtures, most of the initial work was carried out on asphalt–rubber gap-graded and open-graded mixtures, which were characterized by making use of both traditional and more advanced techniques in terms of their stress–strain behavior, moisture sensitivity, and durability [37,38]. Specific studies have also been performed with the goal of assessing the acoustic performance in service of these mixtures and in developing criteria for the optimization of their surface texture. More recent studies have entailed the construction of full-scale test sections as part of a European project, with the evaluation of multiple paving solutions, which have included the adoption of the warm technology and the use of reclaimed asphalt [39].

Innovative studies have been performed on the topic of life cycle assessment (LCA) and on the evaluation of the potential health impact on workers of gaseous emissions produced

during paving operations. LCA analyses have been carried out by referring to selected environmental indicators and models, comparing CR technologies (wet and dry) with other paving options with the purpose of identifying the most sustainable solutions [40,41]. With respect to the topic of emissions, investigations have included sampling of fumes in construction sites for the determination of the concentration of volatile organic compounds (VOCs) and PAHs, and subsequent interpretation of laboratory data in the context of a differential risk assessment procedure [42]. Further studies have also been done for the development of a laboratory procedure for the simulation of site emissions in controlled conditions [43].

Initial investigations performed on bituminous mixtures produced with the dry technology considered volumetric and mechanic characteristics [44,45] and the vibration attenuation potential [46]. More recent studies considered the effects of different types of CR (of the fine and coarse type), analyzing the overall performance of several dry formulations prepared in a purposely developed double-drum asphalt mixer [47]. Finally, specific investigations have been carried out to assess the possibility of employing the dry technology for the production of high-performance porous asphalt and stone mastic asphalt mixes [48,49].

With respect to entrepreneurial activities, in the last 20 years several companies have invested in CR-related products and technologies. A remarkable pioneering work was done in Tuscany, where the first asphalt–rubber production plant was installed in 2006, thereafter acting as a reference for many full-scale applications throughout the country. Other private companies have chosen different technological solutions and commercial strategies to promote the use of CR in paving applications. These include the "rubberized asphalt" technology (that yields polymer-modified binders in which CR is employed as a modifier in combination with other selected synthetic polymers); the so-called "hybrid dry" technology (which entails the combined use of fine CR and polymer-modified bitumen); and other technologies based on the use of meltable compounds containing CR to be mixed in bitumen tanks or directly in the asphalt-mixing chamber.

13.6.5.3 Lessons learned and prospective

As a result of the efforts and initiatives described above, it has been estimated that by January 2020 in Italy there are approximately 520 lane km of pavements containing CR products distributed throughout the country. Interest in CR-related technologies is

still growing, but widespread and systematic use of these paving solutions is still prevented by the absence of official national technical specifications. The national research community has proven to be extremely active and it is envisioned that further significant achievements will be gained in the near future.

13.6.6 Experience and lessons learned—Switzerland

13.6.6.1 History

In Switzerland, every year 70,000 tons of waste tires are produced and transported mostly to the cement industry for incineration or exported for further processing. The use of crumb rubber in asphalt mixtures has only been rudimentarily tried with no concrete results or reports. In fact, rubber-modified mixtures have been used in Switzerland mainly in the framework of the low-noise pavement project *Lärmarme Strassenbeläge Innerorts* (2011). Test sections were constructed in urban environments. Two special designs with semidense mixtures were constructed with 4 mm maximum aggregate size incorporating steel slag and crumb rubber. The main result of the project was the achievement of acoustic data for a period of six years of pavements with this type of asphalt mixes. In addition, there were different attempts involving this technology. Unfortunately, most of these works have not been reported and the outcomes are not available. However, a recently completed project in Switzerland funded by the federal government is allowing dry-process rubberized asphalt to gain interest.

13.6.6.2 Case study

The project led by Empa and including crumb rubber manufacturer (TRS), two mixing plants (FBB and Weibel), and Ammann who produces the asphalt mixing plants generated interest in the technology. The goal of the project was to use crumb rubber in asphalt mixes to improve its performance as well as and as an important waste reduction measure. To this end, the project developed novel manufacturing methods and materials to further explore the valorization potential of crumb rubber from waste tires, with their reuse in asphalt road pavements. This project also demonstrated and developed eco-innovative technologies in real-life environments in terms of their

mechanical performance, environmental and economic viability in order to promote their widespread market uptake and replication validated.

For the sake of faster uptake from industry, in this project the dry method of fabrication was adopted. Using a multiscale approach, the performance of seven types of crumb rubber obtained from different grinding techniques with and without chemical modifications were investigated in a first phase. At the microscale, using electron microscopy it was shown that the conditioning time of RMA mixtures plays an important role in the morphology of the rubber in asphalt. Longer conditioning times lead to the digestion of the rubber particles. RMA mixtures were investigated based on two types of mixtures: a semidense asphalt wearing course (SDA 4) and a dense binder course (AC B 22 H). During the optimization phase, volumetric properties were measured and conventional tests such as water susceptibility were conducted. Results showed that the performance of these mixtures clearly depends on the type of rubber and modification [50].

One type of chemically modified rubber with good in situ results in the United States was chosen for plant production. Batches of 2–3 tons of three variations of the optimized two mixture types (six mixtures) were produced in the two partner mixing plants and samples delivered to Empa for further investigation. Concerning the mechanical performance, it was observed that the RMA mixtures met the Swiss requirements regarding water sensitivity and rutting. Furthermore, additional tests not required by the standards were performed to assess water stripping (boiling water and Hamburg tests), scuffing, particle loss, and low-temperature cracking. The results indicated that in comparison to conventional polymer-modified asphalt mixtures the performance depended on the test type, and sometimes inferior, sometimes equal, and sometimes better (Fig. 13.6.11). The response was also found to be dependent on the rubber content and type of mixture but mostly remained within the requirements or the industry acceptable values where none existed.

In addition, larger specimens were rolling compacted from each mixture and a traffic simulator was used to assess their performance in m-scale under rolling wheel loads. It was confirmed that also at large scale the resistance against deformation of the experimental mixtures showed acceptable values for high CR concentrations as well as for dense mixtures comparable to the reference PmB (Fig. 13.6.12). As a main conclusion, it was observed that the design of the modified mixture (i.e.,

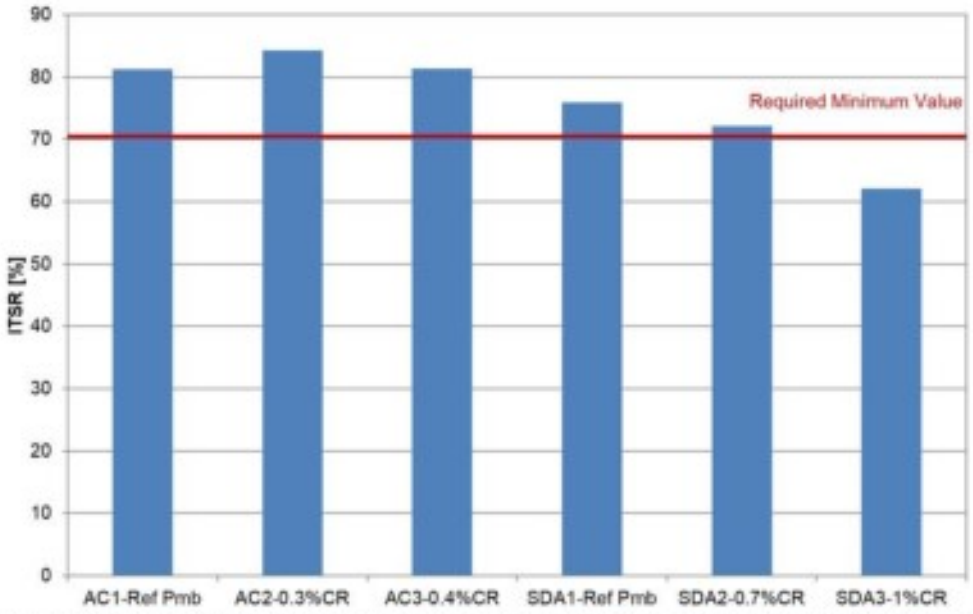


Figure 13.6.11 Indirect tensile strength ratio (ITSR) for all mixtures, with the minimum requirement of 70% shown in red.

asphalt binder properties and content regarding the type and amount of CR to be used) is a central factor for the optimization of performance.

Also, during the production of the rubberized asphalt mixtures in the asphalt plants, the VOC emissions in the mixer and exhauster were measured. Results showed that at the same mixing temperature, mixer VOC peak height concentrations were slightly higher with CR mix batches than with the reference PmB mix batches. This difference was deemed small, but further measurements during full production are needed and planned. In addition, an environmental assessment of the plant produced mixtures was done using leaching tests. The results showed that poly PAHs in leachates are only asphalt-related, CR contributions for PAH were small, and leaching of zinc compounds from CR-asphalt was slow. More polar, ionizable constituents of CR such as benzthiazole-based vulcanization accelerators quickly leached from CR-modified asphalt. Although not measured, it could be expected that other polar compounds present in CR, with similar physicochemical properties, can potentially leach from CR-modified asphalts as well. To prevent this issue, a water-based extraction procedure of CR might remove such polar compounds before implementing

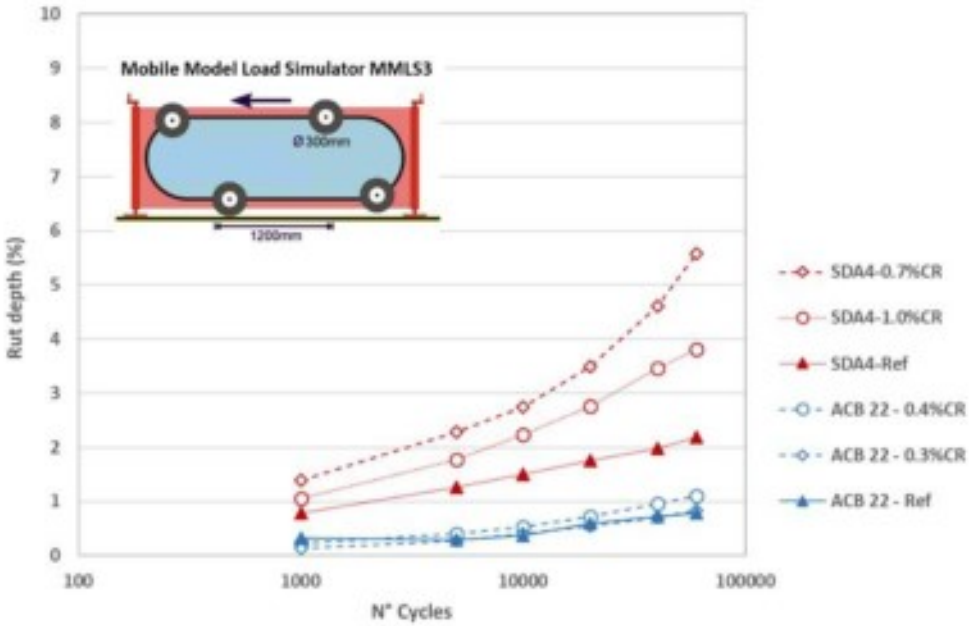


Figure 13.6.12 Evolution of permanent deformation after loading with the MMLS3.

them in asphalt. Finally, a preliminary LCA of the produced mixtures was performed using two methods. The results show that the CR wearing courses have slightly higher energy demands, while considerably lower emissions of greenhouse gases than that of the reference Pmb. Therefore it can be preliminarily concluded that using CR in the wearing course of SDA pavement is an environmentally promising option to dispose of waste tires in Switzerland.

13.6.6.3 Lessons learned and prospectives

Upon the completion of the research project on the use of the dry process, overall the rubberized asphalt mixtures showed good mechanical, environmental, and economical performance. As a result of the positive performance tests at the laboratory scale, various test sections are currently planned in Switzerland.

13.6.7 Conclusions

Experience in a number of countries and a significant amount of research have shown that rubberized asphalt provides a

number of advantages, but widespread adoption in Europe is still far from being a reality. Nevertheless, the push toward a circular economy and cost-effective green solutions are allowing European industry, academia, and government to engineer new solutions to solve old practical limitations and favoring a revival of interest for this family of technologies. This chapter offered an overview of these solutions through detailed descriptions of the lessons learned in pioneering countries such as Portugal, Spain, and Italy, as well as from a newcomer such as Switzerland. The described solutions can be summarized as follows:

1. Technical: the historical division in wet and dry process is still valid, but in Europe a wide range of new technologies, as presented in the first section chapter, are being researched, validated, and marketed to address issues such as storage stability of wet process, lack of control of the swelling for the dry process, and generation of fumes during material manufacturing and road pavement laying and compaction.
2. Governance: The countries that are witnessing successful uptake of rubberized asphalt are those where significant research and validation are being carried out. This is usually favored by a systemic approach in governance, such as the EPR, and from the adoption of tailored specifications to favor an easier uptake from industry.

The revival of rubberized asphalt in Europe is not free from issues, in fact both asphalt manufacturers and road authorities are still reluctant to trust this family of technologies until issues such as the multirecyclability of these materials and the quality of runoff/subsurface water from related road pavements are solved. Furthermore, the increased use of secondary materials in asphalt mixtures highlights the limitations of conventional testing of binders and mixtures and is pushing asphalt technologists to look for new testing procedures and classifications. In order to help in this sense, the rubber industry should provide asphalt mixture manufacturers with a consistent and classified CRM/tire derivate aggregate.

Acknowledgments

The authors want to acknowledge the support and the precious information received by the following colleagues: Bernard Hofko from Technical University of Wien (Austria), Jan Valentin from Czech Technical University in Prague (Czech Republic), Erik Nielsen from Danish Road Directorate (Denmark), Yasmina Mahmoudi from University of Lyon (France), Katerina Varveri from TU Delft (Greece and The Netherlands), Michael Witsuba from University of Braunschweig (Germany), Marko Oreskovic from University of Belgrade (Serbia), and Marjan Tusar from ZAG (Slovenia).

References

[1] Lo Presti D. Recycled tyre rubber modified bitumen for road asphalt mixtures: a literature review, Construction and Building Materials Elsevier, (2013) ISSN: 0950-0618 https://doi.org/10.1016/j.conbuildmat.2013.09.007.

[2] Directive 2008/98/EC on waste (Waste Framework Directive), https://ec.europa.eu/environment/waste/framework/ (accessed August 2020).

[3] Dantas-Neto, S.A., Farias, M.M., Pais, J.C., Pereira, P.A.A., Influence of crumb rubber and digestion time on the asphalt rubber binders, Road Materials and Pavement Design. vol 7, no 2, 2006, p. 131-148.

[4] Thives, L., Pais, J.C., Pereira, P.A.A., Trichês, G., Amorim, S., Assessment of the digestion time of asphalt rubber based on microscopy analysis, Construction and Building Materials, Volume 47, October 2013, Pages 431–440.

[5] S. Bressi, N. Fiorentini, J. Huang, M. Losa, Crumb Rubber Modifier in Road Asphalt Pavements: State of the Art and Statistics, Coatings, MDPI (2019).

[6] PCCAS, Pacific Coast Conference for Asphalt Specifications Minutes, PCCAS, Portland, OR, USA, 2012.

[7] C. Wu, K. Liu, J. Tang, A. Li, Research on the terminal blend rubberised asphalt with high-volume of rubber crumbs and its gap graded mixture, Munich Asph. Rubber (2012).

[8] B. Kök, H. Çolak, Laboratory comparison of the crumb-rubber and SBS modified bitumen and hot mix asphalt, Constr. Build. Mater. 25 (2011) 3204–3212.

[9] N. Mashaan, M. Karim, Investigating the rheological properties of crumb rubber modified bitumen and its correlation with temperature.

[10] D. Fornai, C. Sangiorgi, F. Mazzotta, J.M. Bermejoc, L. Saizc, A new era for rubber asphalt concretes for the green public procurement in road construction, 1st European Road Infrastructure Congress | 18–20 October 2016 | Leeds, United Kingdom.

[11] M.A. Heitzman, State of the Practice for the Design and Construction of Asphalt Paving Materials with Crumb Rubber Additive. Report No. FHWA-SA-92-022; Office of Engineering; Pavement Division, Federal Highway Administration, Washington, DC, USA, 1992.

[12] H. Takallou, I. McQuillen, R.O. Hicks, Effect of Mix Ingredients on Performance of Rubber-Modified Asphalt Mixtures, Transportation Research Institute, Fairbanks, AK, USA, 1985.

[13] S. Kocak, M.E. Kutay, Effect of addition of dry crumb rubber on the performance of terminal blend crumb rubber modified asphalt mixtures, Transp. Res. Rec. 2633 (1) (2017) 90–97. Available from: https://doi.org/10.3141/2633-11.

[14] V. Vignali, F. Mazzotta, C. Sangiorgi, A. Simone, C. Lantieri, G. Dondi, Incorporation of rubber powder as filler in a new dry-hybrid technology: rheological and 3D DEM mastic performance evaluation, Materials 9 (2016) 842.

[15] Dantas-Neto, S.A., Farias, M.M., Pais, J.C., Pereira, P.A.A., Dense graded hot mixes using asphalt-rubber binders with high rubber contents, Road Materials and Pavement Design. vol 7, nº 1, 2006, p. 29-46.

[16] F. Chavez, J. Marcobal, J. Gallego, Laboratory evaluation of the mechanical properties of asphalt mixtures with rubber incorporated by the wet, dry, and semi-wet process. 205 (2019) 164–174, 30 April 2019. https://doi.org/10.1016/j.conbuildmat.2019.01.159.

[17] Cedex, Manual for Incorporation of Crumb Rubber in Asphalt Mixtures. Spanish Ministerio de Fomento and Ministerio de Medio Ambiente. ISBN 978-84-7790-450-2. http://www.cedex.es/NR/rdonlyres/27EDCC96-7C3A-42B5-96B7-F6B87D0BD3DF/116371/Manual_NFU.pdf, 2007 (accessed May 2020).
[18] Spanish Ministry of Public Works, Advisory Circular 21/2007. Specifications for rubberised binders. Spanish. http://www.carreteros.org/normativa/noc/pdfs/0_100ne/021_2007.pdf, 2007 (accessed May 2020).
[19] L.A. De Leon, L. Saiz, R. Pérez, 20 years of rubberised asphalt mixtures in Spanish roads. Signus Ecovalor. https://www.signus.es/mezclas-asfalticas-con-polvo-de-neumatico, 2018 (accessed May 2020).
[20] J.M. Bermejo, J. Gallego, L. Saiz, Guide for the Production of Rubberised Binders. Spanish. ISBN 13 978-84-616–9263-7. https://www.signus.es/wp-content/uploads/2017/06/Guia_betunes_signus_def.pdf, 2014 (accessed May 2020).
[21] J. Gallego, A.M. Rodriguez-Alloza, L. Saiz-Rodriguez, R. Pérez-Aparicio, F. Moreno, M.C. Rubio, Warm Rubberised Asphalt Mixtures. Spanish. ISBN: 978-84-09–11306-4. https://www.signus.es/wp-content/uploads/2019/05/mezclas_bituminosas_semicalientes.pdf, 2019 (accessed May 2020).
[22] J. Pais, D. Lo Presti, C. Santos, P. Pereira, L. Thives, The effect of prolonged storage time on asphalt rubber binder properties, Construction and Building Materials 210 (2) (2019) 242–255. Available from: https://doi.org/10.1016/j.conbuildmat.2019.03.155.
[23] J.L. Feiteira Dias, L.G. Picado-Santos, S.D. Capitão, Mechanical performance of dry process fine crumb rubber asphalt mixtures placed on the Portuguese road network, Constr. Build. Mater. 73 (2014) 247–254. Available from: https://doi.org/10.1016/j.conbuildmat.2014.09.110.
[24] I. Antunes, Asphalt Rubber: Study of the Rheology of Modified Bitumen with Recycled Tire Rubber Powder (Ph.D. thesis). Università degli studi di Parma (in Italian), 2006.
[25] Decreto legislativo, n. 152. Norme in materia ambientale, 3 aprile 2006.
[26] Decreto Ministeriale, n. 82 - Regolamento per la gestione degli pneumatici fuori uso (PFU), ai sensi dell'articolo 228 del decreto legislativo 3 aprile 2006, n. 152 e successive modificazioni e integrazioni, recante disposizioni in materia, 11 aprile 2011.
[27] E. Santagata, M. Lanotte, D. Dalmazzo, and M.C. Zanetti, Potential performance-related properties of rubberised bituminous mixtures produced with dry technology, Proceedings, 12th International Conference on Sustainable Construction Materials, Pavement Engineering and Infrastructure, Liverpool, UK, 27–28 February, 2013.
[28] E. Santagata, O. Baglieri, M. Alam, M. Lanotte and P.P. Riviera, Evaluation of rutting resistance of rubberised gap-graded asphalt mixtures, Proceedings, 6th International Conference Bituminous Mixtures and Pavements, Thessaloniki, Greece, 10–12 June, 2015, pp. 407–412.
[29] E. Santagata, P.P. Riviera, D. Dalmazzo, M. Lanotte, M.C. Zanetti, S. Fiore, et al., Design and construction of a full-scale test section with asphalt rubber gap-graded wearing course mixture, Proc. Soc. Behav. Sci. 53 (2012) 524–534. Available from: https://doi.org/10.1016/j.sbspro.2012.09.903.
[30] D. Lo Presti, Rheology and Curing of Tyre Rubber Modified Bitumens (Ph.D. thesis). University of Palermo, 2011.
[31] F. Merusi, Metodi reologici avanzati per l'analisi del comportamento dei bitumi stradali negli stati critici di esercizio (Ph.D. thesis). University of Parma (in Italian), 2009.
[32] M. Lanotte, Studio dell'interazione tra polverino di gomma e bitume nei leganti modificati con tecnologia wet (Ph.D. thesis), Politecnico di Torino (in Italian), 2014.

[33] E. Santagata, D. Dalmazzo, M. Lanotte, M.C. Zanetti, and B. Ruffino, Relationship between crumb rubber morphology and asphalt rubber viscosity, Proceedings, AR2012, 5th Asphalt Rubber "Roads of the Future" International Conference, Munich, Germany, 23–26 October, 2012, pp. 513–532.
[34] M.C. Zanetti, S. Fiore, B. Ruffino, E. Santagata, D. Dalmazzo, M. Lanotte, Characterization of crumb rubber from end-of-life tires for paving applications, Waste Manage. 45 (2015) 161–170. Available from: https://doi.org/10.1016/j.wasman.2015.05.003.
[35] G. Tarsi, P. Caputo, M. Porto, C. Sangiorgi, A study of rubber-REOB extender to produce sustainable modified bitumens, Appl. Sci. 10 (2020) 1204. Available from: https://doi.org/10.3390/app10041204.
[36] M. Zadshir, D. Ploger, X. Yu, C. Sangiorgi, H. Yin, Chemical, thermophysical, rheological, and microscopic characterisation of rubber modified asphalt binder exposed to UV radiation, Road Mater. Pavement (2020) 1–17. Available from: https://doi.org/10.1080/14680629.2020.1736606.
[37] M.N. Partl, E. Pasquini, F. Canestrari, A. Virgili, Analysis of water and thermal sensitivity of open graded asphalt rubber mixtures, Constr. Build. Mater. 24 (3) (2010) 283–291. Available from: https://doi.org/10.1016/j.conbuildmat.2009.08.041.
[38] E. Santagata, M.C. Zanetti, A. Fortunato, The European project Tyrec4Life, Strade Autostrade 111 (3) (2015) 22–28 (in Italian).
[39] P. Leandri, P. Rocchio, M. Losa, A SWOT analysis of innovative high sustainability pavement surfaces containing crumb rubber modifier, Road Mater. Pavement (2020) 1–20. Available from: https://doi.org/10.1080/14680629.2020.1736132.
[40] A. Farina, M.C. Zanetti, E. Santagata, G.A. Blengini, Life cycle assessment applied to bituminous mixtures containing recycled materials: crumb rubber and reclaimed asphalt pavement, Resour. Conserv. Recycl. 117 (part B) (2017) 204–212. Available from: https://doi.org/10.1016/j.resconrec.2016.10.015.
[41] S. Bressi, J. Santos, M. Orešković, M. Losa, A comparative environmental impact analysis of asphalt mixtures containing crumb rubber and reclaimed asphalt pavement using life cycle assessment, Int. J. Pavement Eng. (2019) 1–15. Available from: https://doi.org/10.1080/10298436.2019.1623404.
[42] M.C. Zanetti, S. Fiore, B. Ruffino, E. Santagata, M. Lanotte, Assessment of gaseous emissions produced on site by bituminous mixtures containing crumb rubber, Constr. Build. Mater. 67 (2014) 291–296. Available from: https://doi.org/10.1016/j.conbuildmat.2014.03.030.
[43] M.C. Zanetti, E. Santagata, S. Fiore, B. Ruffino, D. Dalmazzo, M. Lanotte, Evaluation of potential gaseous emissions of asphalt rubber bituminous mixtures. Proposal of a new laboratory test procedure, Constr. Build. Mater. 113 (2016) 870–879. Available from: https://doi.org/10.1016/j.conbuildmat.2016.03.101.
[44] M. Pasetto, and N. Baldo, Recycling of tire rubber in porous asphalts using the dry process: Mechanical characterisation and performance evaluation of mixes, Proceedings, 2008 Global Symposium on Recycling, Waste Treatment and Clean Technology, REWAS 2008, 559–564.
[45] B. Celauro, C. Celauro, and A. Di Francisca, Studio sperimentale sull'impiego di CRM (Crumb Rubber Modifier) nei conglomerati bituminosi secondo processo dry, Proceedings, XIII SIIV National Conference, Padova, Italia (in Italian), 2003.

[46] A. D'Andrea, T. Loisi, and L. Urbani, Fenomeni vibratori da traffico stradale in presenza di strati con granulato di gomma, Proceedings, XVI SIIV National Conference, Campus di Arcavacata di Rende (CS), Italia, 2006.
[47] E. Santagata, M.C. Zanetti, G. Corbetta, D. Fornai, POLIPNEUS Project. Science and technology of bituminous binders and mixtures containing crumb rubber from end-of-life tyres, Strade Autostrade 97 (1) (2013) 62–68 (in Italian).
[48] M. Pettinari, G. Dondi, C. Sangiorgi, F. Petretto, The use of cryogenic crumb rubber in the cold recycling technique, Airfield Highw. Pavement 2013 (2013) 1088–1099. Available from: https://doi.org/10.1061/9780784413005.091.
[49] C. Sangiorgi, S. Eskandarsefat, P. Tataranni, A. Simone, V. Vignali, C. Lantieri, et al., A complete laboratory assessment of crumb rubber porous asphalt, Constr. Build. Mater. 132 (2017) 500–507. Available from: https://doi.org/10.1016/j.conbuildmat.2016.12.016.
[50] I. Rodríguez-Fernández, F. Tarpoudi Baheri, M.C. Cavalli, L.D. Poulikakos, M. Bueno, Microstructure analysis and mechanical performance of crumb rubber modified asphalt concrete using the dry process, Constr. Build. Mater. 259 (2020) 119662.

This page intentionally left blank

14

Sports and leisure infrastructure and applications: styrene butadiene crumb rubber infill in artificial turf sports fields

Nicolas Evans
FIFA-Strasse 20, 8044 Zurich, Switzerland

The chapter title suggests a number of possibly not so intuitive matches between tire waste and sports but looking at "leisure infrastructure" does give a clue as to the concrete applications that we see in sports today. While many applications that are more generic in terms of using recycled materials in construction of infrastructure (fencing, seating, flooring) also apply to sports environments, the main focus of this chapter will be on one hugely specific application, which is artificial turf fields where tire waste is used as a component offering performance characteristics through its elastic and durable nature. It is fair to say that many sports would not have the participation numbers today if it was not for those crumb rubber-filled fields but as conscience over circular economies, environmental impact, and climate change grows, so will the cry for greener, more "sustainable" alternatives.

14.1 How tire waste and sports infrastructure fit together — the role of artificial turf in football and football development

14.1.1 Artificial turf system

For those not familiar with artificial turf fields, the illustration in Fig. 14.1 shows a generic build of an artificial turf system. The main point to understand is that it is most meaningful to be speaking of "systems" rather than individual product parts (such as carpet, sand, or rubber infill) or components as the final characteristics of the surface that the players

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00011-9
© 2021 Elsevier Inc. All rights reserved.

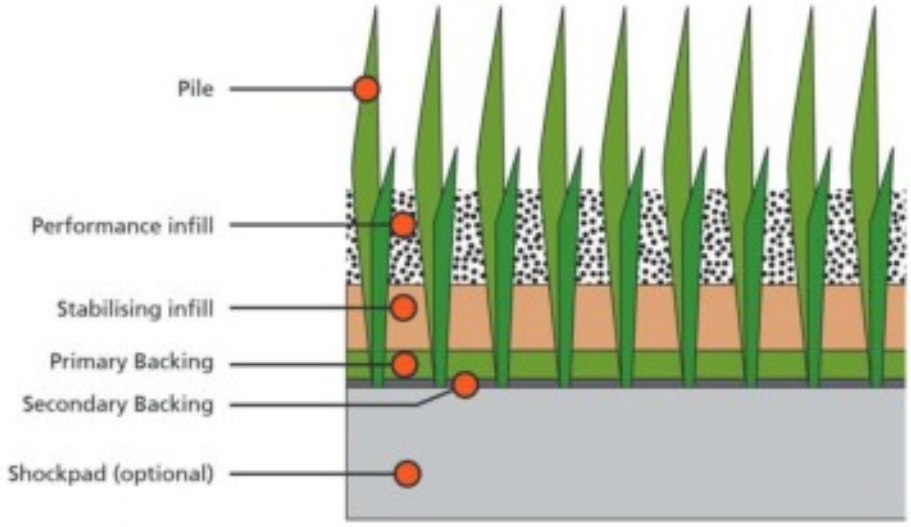


Figure 14.1 Typical artificial turf system.

will experience are an interplay of the properties of all the materials that constitute the synthetic sports field. This distinction is critical at the beginning to understand that each material plays a part but that – for instance – granule infill is only one part of the equation.

The main components of such a system are bottom up:

- a shock pad (sometimes also called e-layer), which is an elastic layer that may be installed underneath the carpet system and provides the shock absorbing layer in the construction. Not all systems will have this component but it is growing in demand.
- The carpet, which is generally a latex or PU backing holding artificial yarns in place that are either woven or tufted into a primary backing that can be made of a number of materials typically polypropylene based and commonly reinforced with fiber glass and similar materials.
- Stabilizing infill that is used to weigh down the carpet – mostly by applying sand.
- Performance infill, which – as the name suggests – offers the final performance characteristics for the ball and player to the field and is most frequently some form of rubber granules.

The Fédération Internationale de Football Association (FIFA), the world governing body of association football, is among a number of sports organizations – Fédération International de Hockey (FIH) to be named alongside World Rugby as the two major other federations championing use of artificial turf – that has allowed its game to be played on

such synthetic surfaces in order to provide as many players as possible a viable playing surface even when climate, geography, or natural resources do not allow for good natural turf to be grown. In order for this to be possible, however, there is a comprehensive testing scheme in place that requires products and installed fields to meet strict criteria with regards to player safety, player performance, and ball performance. Several decades of research have gone into determining the "correct" values that such an engineered synthetic surface must provide in order to be as similar as possible to what most athletes consider the ultimate gold standard: good-quality natural turf. The abovementioned organizations have each developed their specific requirements [1–3] around key elements of their games such as minimum and maximum ball roll (often attributed to the stiffness of the artificial turf fibers) but equally around player grip, ball rebound height, and energy loss and restitution reflecting the elasticity of the surface (much more frequently the part influenced by the rubber infill). Many studies ranging from biomechanical and psychological experimental research with elite players down to chemical evaluations of individual product components have given an informed range of criteria that any given surface must perform to in order to be certified by the sport's governing bodies or the national standards' associations (European Normalisation Committee (CEN), American Society for Testing and Materials (ASTM), International Standardisation Organisation (ISO), etc.). Summing up a multidisciplinary decade of research, the playing surface must be hard enough to allow players good grip and fast running speeds but equally elastic to ensure players are comfortable on the surface (and possibly reduce the risk of injury) and that the ball does not bounce too high differing from good natural turf (as noted from earlier generations of artificial turf without performance infill). Finding the right balance is the endgame of the artificial turf system manufactures whose R&D efforts are focused on mixing the right components to solve for both the technical specifications and the customers' needs that are often driven by financial considerations. To put these efforts into context: at the time of writing, FIFA lists in excess of 4000 products tested to its standards that have shown to meet the comprehensive criteria. It should be noted that there was an update to regulations in 2015, meaning this number is reflective of the 2015–2020 period. To put it further into context, around 2000 fields – mostly used in elite or training environment at a higher level – meet the criteria and

are eligible for hosting official matches, with well over 10,000 fields having been certified under the program since 2001. This comes to show that there is a huge heterogeneity around product composition, which can be attributed to the six different elements portrayed above creating vast amounts of possible combinations due to available components, local legislation, and individual customer preferences.

This introduction is necessary to explain the crucial role that "tire waste" (to quote this book's main focus) plays within the artificial turf system, which will be elaborated on later. The recycled tires have proven to be a very useful performance infill (often referred to as crumb rubber or styrene butadiene rubber (SBR)) with some cases of bound granules used for shock pads too. The majority of this chapter will therefore focus on the infill application due to the much larger proportion of this use compared to the shock pads but will lead into how there could be a shift toward the use within elastic underlayers too.

14.1.2 Market potential for recycled tires in artificial turf fields

Elaborating on the product composition described in Fig. 14.1, the pie chart in Fig. 14.2 shows why SBR and other performance infills are so critical to the end product: in the most economical systems available (and hence the most frequently found) SBR accounts for 44% of the entire system almost matching the 49% that stabilizing infill (sand) accounts for [4]. Taking the reasonable assumption of a total weight of 36 kg/m^2 for a full-size football field measuring 106 m × 71 m,

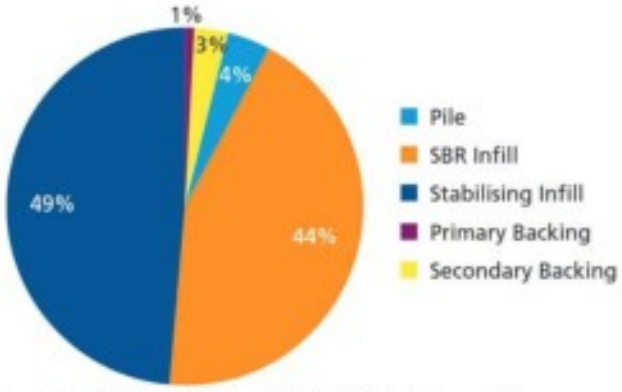


Figure 14.2 Components of a typical FIFA certified artificial turf field, by weight.

the share of the performance infill exceeds 100 tons per field [4]. Add to this thought that best estimates are that more than 80% of fields installed worldwide use some form of recycled tires as their performance infill. This number is based on historical data from a limited sample size and may be shifting but is a good benchmark.

While grasping the scale of the market is next to impossible as only very few official and reliable statistics exist on how many artificial turf fields are being installed around the world, some published statistics give a glimpse into the volumes that we are dealing with: in a response to the European Chemical Agency (ECHA) investigating the role of performance infill in the larger context of micro plastics, the Union of European Football Associations (UEFA) quantified its European member states to have around 42,000 artificial turf fields. Depending on the source, it is fair to estimate that advanced economies in Western Europe will by have more than 1000 fields in their territories, with larger countries like Germany or the UK well exceeding this [5]. Genan, in the same the International Association for Sport and Leisure Facilities (known as IAKS after its former German name Internationaler Arbeitskreis Sportstättenbau) report, estimated that 1500 new fields were installed in the EU every year with comparable numbers being rumored for other markets such as the United States and China. Whatever the magic number may be, it is clear that sports fields are capable of absorbing enormous amounts of recycled tires as performance infill. It therefore comes as no surprise that the application in sports leisure facilities is a popular and commonly used path for tire recyclers. For the manufacturers and installers of the fields, SBR has become the backbone for most systems for a large number of reasons with the two main ones being cost-effectiveness and the suitability of the material product due to its elastic yet resistant properties (and degradation resistance/longevity). The argument of being a recycled product with a low carbon footprint is also sometimes mentioned but has mostly been reflected in the rationale of the other two main arguments. Cost-effectiveness comes down to tires being waste under most legislations and therefore the reuse (or rather reprocessing for new application) are a win-win for both sides as it extends the life of a product that would otherwise typically be incinerated and offers sports a cheaper and readily available alternative to much more expensive virgin materials, while also reducing the impact on new material production. The nowadays prevalent and seemingly apparent argument of ecological meaning in reusing existing resources and reducing environmental impact has shown to bear some truth

and has seen a surge in comparison to virgin rubbers in some markets but was never the driver behind the growing success of this infill type in sport applications. While it will be discussed later, it does – in effect – only delay the issue of the end of life of the tire as the crumb rubber will eventually also no longer be suitable for sports and will need to be reingested into the circular economy, but this is rarely picked up in the debate around sports facilities. The material properties of the crumb rubber, on the other hand, answer many of the dilemmas faced by the R&D departments trying to mimic natural turf's properties of an elastic yet durable surface. The purpose of a tire as a very durable, slow-wearing product with energy absorption and restitution properties have proven one of the best ways to hit the sweet spot for a performing yet safe infill to a synthetic playing surface mimicking good natural turf. These two arguments combined with essentially endless supply explain why so many of the globally offered products for sports playing surfaces (except elite hockey fields that are mostly unfilled) include SBR or recycled tire products.

Irrespective of the exact volumes, it is clear to the governing bodies of most football codes that artificial turf plays a vital part in providing durable and heavily usable playing surfaces for its users. UEFA, the governing body for European association football, in a written statement to ECHA in 2019 estimated that artificial turf (with SBR infill) accounts for 92 million playing hours in any given calendar year and suggests that up to 21 million players use such surfaces regularly. The statement further postulates that many countries have been able to highlight that removing (or reducing) the number of artificial turf fields in their territories would have a noticeably detrimental effect on physical activity of their populations as a whole. SBR is therefore – currently – so central to this societal macroeconomic discussion due to the fact that it offers the most cost-effective solution: it was estimated by the BIR Tyre & Rubber Committee that additional costs for alternative infills would amount to around € 50,000 per field with concerns on the long-term sustainability and availability of these infills [5]. This is not to say that this additional cost may bring other benefits and that possibly some of the markets in question may be able to afford this surplus, but the number alone does suggest that many markets would struggle and possibly turn to alternatives that, on the whole, have more detrimental effects to either the environment or its society.

Taking into account this quick snapshot of the market – bearing the reservations on the validity of the numbers in mind – it seems

inevitable that alternative solutions to lessen the dependency on SBR are needed. Although an incredibly strong case can continue to be made in favor of the continued use of this material in sports facilities on a global scale, the growing challenges that sport and the artificial turf industry are facing from regulators and society will need to be taken into consideration. These will be addressed in more detail below.

14.2 Outlook and challenges: how will styrene butadiene rubber fit into sports systems down the line?

The portrayal of SBR-filled artificial turf thus far has been largely to quantify and explain why it is a relevant use case of tire recycling. In order to understand what the future of this resource holds, a number of current trends need to be taken into account. While the trends are universal, the dynamics of their impact change significantly depending on geography, society, and economic means. There is arguably a quasiglobal consensus that climate change is having an impact on the planet, but the effects and practical implications for the developed and developing world are different. The same logic applies to the trends seen across Europe discussed here in more detail and that can be summarized into four distinct but linked categories: (1) customer preferences, (2) environmental paradigm shifts, (3) legislation, and (4) product innovation.

14.2.1 Player preference: heat, smell, and years of question marks around health

As sports fields filled with crumb rubber grew in popularity and have been more widely experienced, a more informed set of preferences has developed around it. While there is no question of the value in having the playing fields and many will still wish for such a facility, trends have shown to have moved away from the old simplified stigma of "plastic pitches will injure you." A large study carried out between 2010 and 2012 surveyed in excess of 1000 professional or semiprofessional football players to understand their take on artificial surfaces and showed that 41% of players had played on the surface and were able to give more qualified feedback regarding ball speed, impact on playing style, or perception of what causes injuries [6]. As one of the consequences of this feedback, FIFA commissioned a large study on

some of the characteristics that were mentioned and known to have an impact. The build-up of heat due to the black rubber granule was one of the most alluded to problems with many synthetic surfaces heating up to 80°C in unfavorable conditions [7].

Heat is often seen as a contributor to a second major consumer complaint: the smell of the field, which is attributed to the rubber. This is prevalent in countries where more expensive alternatives exist and are generally available but has created a wave of resistance in a number of countries where health and well-being are being valued increasingly within a shift to a more environmentally aware policy.

Last, and without running the risk of a spoiler alert for the legislative challenges SBR is facing, there have been questions around health risks that artificial turf and its crumb rubber infill (turning into microplastics) cause to humans and nature. While there has been no outright conclusive evidence to support this, concerned citizens and activist groups are seeking limitations and bans for the infill due to their belief that it is not safe and that alternatives must exist and be developed. These initiatives to limit the use of SBR have focused on issues such a zinc leaching into the environment and polycyclic aromatic hydrocarbons (PAHs) in the material that are known carcinogens. Studies to date have therefore rather triggered legislative reaction that sets limits [8] rather than bans (most EU-derived tires have had low risks of breaching). Besides the direct human health considerations, the topic of microplastics has gained more momentum in recent years: there is currently a consultation with the European Union on the need to restrict the quantity of contamination caused by intentionally added microplastics, which includes infill of artificial turf pitches. At the time of writing this is ongoing and the final decision is not yet confirmed, but if a ban or a restriction is applied (as looks likely) in the EU, it could have significant impacts on the supply and use of SBR infill [9].

Notwithstanding the above, the end users of sports fields are rarely consumers, economically speaking. Due to the large amount of capital required for such an installation, it is often funded by the municipality or a larger entity (e.g., educational establishments/professional clubs) and not always in the interest of the players who end up playing on it so their considerations have not always played a role in decision-making. As the concerns of citizens grow, so do their responses to politics concerning their well-being and the well-being of their children

thus increasing pressure on the decision-makers and purchasers of such fields to take their wishes and concerns into account when procuring such facilities.

14.2.2 Reuse and recycling of existing fields as pressure mounts on being more efficient with resources

Technology to extract materials from used artificial turf fields has existed for quite a while as proof of concept but was only truly applied at scale to fully address the topic of reuse and recycling in recent years. As this technology has been made fit for purpose and consequentially matured to separate and recycle entire fields, it has become possible but also economically viable to extract the performance infill and indeed reuse it on the same or a new field. The inherent resilient qualities of the SBR crumbs mean that their lifecycle can exceed that of a carpet and thus can find a much longer application, significantly reducing the amount of new SBR required.

However, before going down the route of exploring viability of individual material reuse, the obvious downside needs to be addressed: today we can only recycle what is currently in place and, to a less immediate degree, influence future recycling by controlling today's installations. To the first point, large-scale sampling and feasibility studies have shown some major concerns with regard to reusing many of the materials used in artificial turf sports facilities in Europe, including sand and yarns but also the rubber infill. The outright lack of quality of some materials (in some cases not even compliant with their national legislation) mean a good percentage of currently installed fields are not viable for reuse. For those fields that do have sufficiently good materials, there is a lack of traceability that then in turn often leads to a lack of homogeneity (in material type, sizes, or properties) in the product itself making it next to impossible to reuse an entire batch without significant testing required to ensure that the performance infill will offer the properties required.

Taking this into consideration, the outlook and challenges in relation to reusing materials is clear: the entire value chain from producer to the purchaser and the end user must become more aware of the circular economy and start applying these principles rigorously in order for resource optimization via reuse to become more realistically applicable. This includes a better labeling and tracing process akin to some that we have started

to see. The second challenge about how to deal with existing fields that are coming to the end of use will require a more flexible approach since a higher percentage of these installations may not be suited for reuse and therefore need evaluation with regard to recycling for use in other industries or applications or disposal via means of incineration or landfill. While this may not be an overly satisfactory solution, the reality of forensically testing the composition of so many fields to identify what can and what cannot be reused may simply not be possible or economically viable.

As the market demand increases along with new recycling operations worldwide, this trend is likely to continue. Technologies for cleaning, sampling, and testing will improve allowing significantly better results when separating the good reusable materials from the bad materials. Currently the cost of doing this is higher than using new materials so a degree of specificities driving design via suitability will also be required. This is already occurring in several countries (e.g., the Netherlands) on a wide scale and will likely expand.

14.2.3 Legislative pressure on the industry around artificial turf ranging from product labeling, toxicity concerns, and microplastics

Debates on the potentially carcinogenic properties of the PAHs inside the SBR have been going on for well over 10 years. FIFA first responded to an article published in the United States in 2006 [10] quoting the known scientific papers on the effects of SBR on players exposed to the surfaces. While consequent studies have suggested links, there has never been any scientific evidence that could conclusively link playing on an artificial turf field with SBR to any particular illnesses. This was reiterated in a position paper in 2017 [11]. For the avoidance of doubt, FIFA is monitoring this market alongside many other government and sports stakeholders and would take immediate action if there was any concrete evidence that pointed to players being put at risk by any material components within such a system. Until such evidence exists, sports refer back to national (or European) law, which regulates the levels of acceptable substances in materials and products.

Further noise has been made with regard to the application of shredded tires on football fields when a pan-European consultation process was started by the European Commission potentially seeking to reclassify artificial turf. Understanding the

system approach outlined at the beginning of this chapter is critical here as the debate centered around whether a sports field was in essence its own product made of materials to which different thresholds apply than if each component was being treated as its own material. The essential difference comes down to whether SBR in a football field should be treated the same way or differently from the car tire it once was: if it was to be considered differently, different thresholds of toxicity levels or components would apply to this same product in its two different applications, which would cause difficulties for meeting standards in the application as infill on a football field.

European regulators have clearly set their sights on various aspects that will impact the use of recycled tires in artificial turf sports fields. Irrespective of which lobby you stand for or what interests various groups support, it is apparent that change is imminent: the European Chemical Agency has set a limit at 20 mg/kg for PAHs [12] – which is below acceptable risk – but it is the topic of microplastics that is hitting home hard with an outright transitional ban currently proposed. While the final verdict on these developments is outstanding, the latter decision will have a huge impact. It essentially means that no rubber product could be used as performance infill (at this stage even significant mitigating measures in place to avoid materials leaking into the groundwater and other surroundings would be of no use). Given any transitional ban or restriction will be in the range of 6 years and that the life expectancy of most artificial turf systems is in excess of 10 years, the transition could be almost immediate. This will change the current marketplace as we know it and will require the industry as a whole to rethink its products very quickly or find new applications for the materials used. Some innovations are explained in more detail below.

14.2.4 Innovation as a driver away from rubber-filled fields

The three previously listed trends all have in common that they are external pressure on the manufacturing and installing sectors of artificial turf. Consumers, lawmakers, and interest groups are pushing their agendas, which may have significant impacts on how artificial turf can be made and installed and, in particular, how crumb rubber could be used in them. The one party that has not yet been addressed is the producing party or the system manufacturer who is equally addressing this question: whatever the underlying reason for product innovation

may be – most likely a combination of the above – alternatives are emerging on the market and ways are being sought for these to be tested and implemented.

One area of innovation with particular relevance to this book is the development of the so-called "nonfilled systems," which differ from the previously mentioned third-generation artificial turf fields because they have no performance infill (but may or may not have stabilizing infill). Instead, the entire product consists of a carpet with a much larger density of yarns but therefore does not require any additional materials to add weight or elasticity. The three major hold-backs for the wider introduction of these systems, which appear to solve many problems that artificial turf has or is perceived to have, are the economics, the fine-tuning of the performance properties to meet regulations, and the first-mover problem. As of today, infilled systems are cheaper and have a proven track record, which is why many communities and clubs continue to opt for this solution. Pricing is difficult to assess generally but a premium would need to be paid for such a system (that does, however, arguably address the issues of excessive heat retention and smell and in fact make the product look and feel more like natural grass), and with no long-term figures available, the return on investment is still somewhat of an unknown. Add to that, that some tweaks will still be required to meet the last performance criteria that the systems are struggling with at the moment (including an outdated skin friction test), it does make it more apparent why there has not been a surge for this product yet but with an increased focus on intentionally added microplastics several regions and countries are already starting to specify and use these types of products (notably Germany).

A second area that has been promoted by a handful of industry actors for the last decade is what has been labeled as "natural infill." These are organic products such as cork, coconut fiber, and/or similar wood/food production by-products are being developed to offer a clean and natural alternative to the current rubber-based systems. Much can be said for the properties of these new infill types since they address the major concerns that are out in the open from the consumers, users, and regulators in that performance is guaranteed without the microplastics problem or the heat build-up within the synthetic particles. However, questions have been raised about the true durability of these alternative infills as well as the effective cost, availability, temperature sensitivity, and required maintenance and care (including regular watering). Much like the nonfilled systems outlined above, the natural infills have equally faced problems around

pricing and meeting regulations and performance specifications over a longer period of time. As such, they clearly offer a solution for some users in favorable geographic conditions and with the right incentive structure for clubs and municipalities to install such fields, but the sheer limitation of these natural resources and the possible rivalry with other agricultural uses have yet to be solved on a medium scale, let alone a global one.

Assuming, nevertheless, that it is more a case of when rather than whether such alternative nonrubber infill systems will enter the developed artificial turf markets, this does not necessarily mean the end of crumb rubber applications for sports fields. For one, bar a global ban on use of recycled tires as infill there will still be significant demand for this but there will equally be an enhanced use for this rubber as part of elastic layers below such nonfilled systems. As explained in Fig. 14.1, turf systems can get their elasticity from the rubber infill or from a shock pad installed below the carpet (this can include upwards of 20 kg/m^2 of SBR material on thicker e-layer constructions). Due to the comparatively high cost of the carpet, systems are likely to be designed to minimize the amount of carpet needed thus relying on the elasticity from a sublayer, for which SBR could still provide one of the major materials. Due to the construction under the field and the fact that it would need to be bound to create a fixed underlayer, most of the concerns around microplastics, performance, and health would be mitigated. In a sense, what could be considered the worst-case scenario for SBR could in fact give it a much accepted new role within the system where the traditional cost-effectiveness and resilient material properties continue to impact – albeit from below rather than on the surface.

14.3 What is the verdict on the status quo of tire waste application in sports installations?

This chapter has shown how sports, in particular the different codes of football, have been able to benefit from recycled tires as a cost-efficient and highly suitable infill material answering many of the technical and practical questions that were being asked of it. Its rise and spread on a global level is therefore easily explicable as the governing bodies of sports have promoted the use of artificial turf. Sports like field hockey were early movers in gaining buy-in from all its stakeholders for

games played on synthetic surfaces (albeit fields mostly did not have rubber infill) and as such enabled the pathway for other sports to consider these as credible alternatives too. When the football codes followed the example set by field hockey to allow the use of artificial turf fields (only now prevalently with rubber infill) the societal and economic reach and impact of this decision was much larger. It is clear that artificial turf filled with SBR has provided playing surfaces in an unprecedented scale to a growing base of players and is arguably one of the success factors for all sports in attracting new participants. This fate in itself, of young and old athletes actually being able to practice their team sport in a facility in their proximity within ever-densely urbanized cities, should not be underestimated in times where the additional attraction of individual sports and off-field entertainment is growing. A decline in such playing surfaces could therefore prove detrimental to some sports in that participation and membership could well be lost if new legislation and bans prohibit the installation of cost-effective fields.

That being said, the trends that were described will have an impact on the volumes of SBR used in developed countries due to a shift in preference of those societies that can afford alternatives on a larger scale and have adjusted environmental legislation accordingly. While Europe is leading the way, it is safe to assume that parts of North America, much of Oceania, and some selective countries in Asia will follow suit and seek alternatives. However, there is still an overwhelming amount of evidence that suggests that there will be a continued, and most likely growing, use for recycled tires as artificial turf infill on a global scale, the most obvious use being the projected increase of tires that will be produced and seek reuse or recycling. Furthermore, as large economies such as India, China, or many Asian and Latin American countries prosper and grow their sporting infrastructure, it is very likely that they will turn to SBR-filled fields if there is no conclusive evidence of health risks for its users. It is equally probable that this growth could offset the decline in the more developed countries at the start. While there is no way of verifying this projection, it is furthermore hard to quantify the rate at which the shift in environmental policy will start to impact a larger number of countries to follow the trends away from SBR infill, which will also depend, once more, on available alternatives based on what is permitted in that jurisdiction and what the market has to offer based on the demands of its respective clients.

For the time being this relationship, which can almost be seen as love-hate between many sports and SBR-filled artificial

turf, continues as the biggest benefit of providing access to large portions of the population at comparatively low cost still on the whole still outweighs the counterarguments although innovation from the industry and external stakeholder pressure are bringing viable alternatives to the foreground that could shift this balance in the near future.

References

[1] FIFA (2020). FIFA Quality Programme for Football Turf. Available on URL: https://football-technology.fifa.com/en/standards/football-turf/

[2] FIH (2020). FIH Quality Programme for Hockey Turf. Available on URL: http://www.fih.ch/inside-fih/fih-quality-programme-for-hockey-turf/

[3] World Rugby (2020). Regulation 22. Standard relating to the use of rugby turf. Available on URL: https://www.world.rugby/handbook/regulations/reg-22/reg-22?lang = en

[4] Eunomia Research & Consulting Ltd for FIFA (2017). Environmental Impact Study on Artificial Turf Pitches. Available on URL: https://football-technology.fifa.com/media/1230/artificial_turf_recycling.pdf

[5] IAKS (2019). BIR Tire & Rubber Committee Report from 17.05.2019. Found on URL: https://deutschland.iaks.sport/sites/default/files/downloads/Best%20practices/2019-07/BIR%20document%20microplastic%20restriction%20-%20BIR.pdf

[6] J. Roberts, P. Osei-Owusua, A. Harland, A. Owen, A. Smith, AssociationElite football players' perceptions of football turf and natural grass surface properties, Procedia Engineering 72 (2014) (2014) 907–912.

[7] FIFA (2015). Handbook of Test Methods. Available on URL: https://football-technology.fifa.com/media/1238/fqp-handbook-of-test-methods-2015-v31-w-cover.pdf

[8] European Chemical Agency (2020a). ECHA's completed activities on restriction. Available on URL: https://echa.europa.eu/completed-activities-on-restriction

[9] European Chemical Agency (2020b). Registry of restriction intentions until outcome: microplastics. Available on URL: https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e18244cd73

[10] FIFA (2006). An Open Letter concerning the potential cancer risk from certain granulate infills from artificial turf. Found online on URL: https://news.mondoiberica.com.es/wp-content/uploads/2016/10/INFORME-FIFA-let_13.07.06-open-letter-SBR-Cancer-issue.pdf

[11] FIFA (2017). A statement on potential cancer risks from exposure to SBR in artificial turf fields URL: https://aptwebassets1.s3.amazonaws.com/wp-content/uploads/sites/3/2017/06/20170330-statement-on-sbr-infill-v1.0.pdf

[12] European Chemical Agency (2020c). Registry of restriction intentions until outcome: Polycyclic-aromatic hydrocarbons (PAH). Available on URL: https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e181d5746d

This page intentionally left blank

15

Roads to opportunities

Serji Amirkhanian
Department of Civil, Environmental and Construction Engineering, The University of Alabama, Tuscaloosa, AL, United States

15.1 Brief history of roads

The paths of the first reported road in history were constructed several thousands of years ago (6000 BCE) by various animals, while the first constructed roads date to about 4000 BCE. These roads, located in modern-day Iraq, were made of stone. By 2000 BCE, the use of wheeled vehicles necessitated the construction of paved roads considering many technical issues such as the proper width (e.g., 12 feet or 3.7 m), road crown, and drainage. One of the oldest and longest (1500 miles) roads was constructed between the Persian Gulf and the Mediterranean Sea around 3500 BCE. It has been reported that the immense limestone blocks used in the construction of the Pyramids were moved on Egypt's first roads made with rocks.

Greeks, in about 800 BCE, built special roads for religious purposes and transport that were paved with shaped stone and contained wheel ruts about 55 inches (140 cm) apart. The Romans observed and gained road building knowledge from many sources, such as the Greeks, Phoenicians, and Egyptians. The Romans used one of the most widespread and oldest construction materials in the world (concrete). One of the oldest road systems (over 40,000 km) in the world was constructed and utilized in China by CE 700. The major trade route, from China to India (Silk Road), is one of the oldest and best known road systems in the world.

One of the best-known pavement engineers in the world is the Scot John McAdam, who is known as the "father" of advances in modern road building techniques. For instance, one of the most important factors that he considered in road design was the importance of providing drainage to all types of pavements. This concept is still true in all pavements constructed around the world. The first engineered and planned road in the United States was approximately 225 years ago (Lancaster Turnpike);

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00003-X
© 2021 Elsevier Inc. All rights reserved.

it was a 62-mile-long privately constructed toll road. However, there were some pavement failures around that time that caused an evaluation of the techniques used and the decision to follow more of the new European methods [1–11].

15.2 Introduction

Why discuss "roads" or "roads to (or of) of opportunities" in a book dedicated to scrap tires and recycling? There are many reasons for that, one being that the paving industry for many years has been one of the biggest users of the recycled materials that provide cost-effective materials with excellent performance. For example, the paving industry in the United States utilizes over 80 million tons of recycled asphalt pavement in new pavements each year. In addition, the industry has been utilizing many other recycling materials such as scrap tires in many applications (e.g., rubberized asphalt, molded goods, etc.). An important note must be made here: "we are not trying to create linear landfills!" The main reason for proposing the utilization of scrap tires in infrastructure is the enhancements made and better life cycle cost–benefits to the final product (e.g., rubberized asphalts; sound barrier walls containing crumb rubber, etc.). The abovementioned brief history of the road system indicates the importance of infrastructure systems in each era in the past.

One of the most important factors in the development of any country is proper transportation infrastructure and, in general, countries with excellent road systems are economically more competitive. Transport infrastructure connects and allows people to have jobs, to attend educational institution, and to provide better health services. Good roads, generally, will enable commerce to go around the world and also enable people to socialize and interact, attend school, and provide for the family. Rural roads provide timely access to medical care and therefore less deaths. Having good roads that are functional, durable, cost-effective, and environmentally susceptible (e.g., recyclable) is proven to be the key to a productive society. One of the most effective pavement types that has been proven to be durable and cost-effective is rubberized asphalt pavements. There are other chapters in this book that cover in detail the rubberized asphalt concept and other related materials; therefore in this chapter those topics will not be covered. The following is a series of statistics regarding the existing road infrastructure system, where are

we going from here, what do we need to get there, and where might the utilization of scrap tires fit in this system.

15.3 Roads around the world

These days, all over the world, approximately 65,000,000 km of roads are used by over 7.5 billion people. The countries with the most roads in the world include the following:

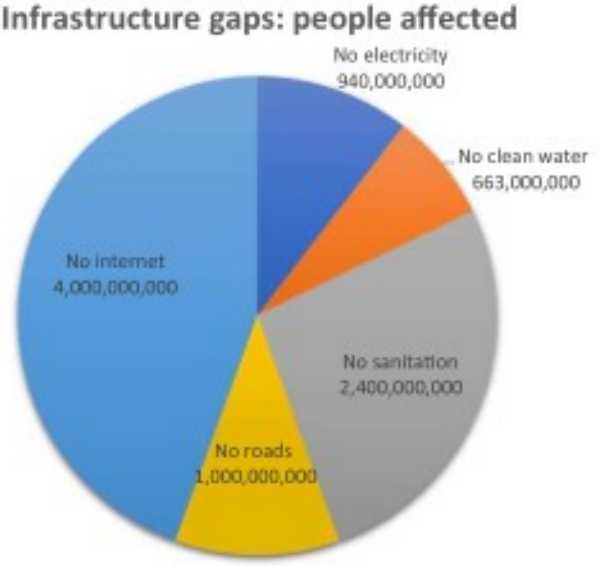
Country	km, × 1,000,000
United States	6.6
India	4.7
China	4.1
Brazil	1.6
Russia	1.3
Japan	1.2
Canada	1
France	1
Australia	0.8

Many of these roads are functional dirt or gravel roads and the rest are either flexible (asphalt) or rigid (concrete) pavements [12]. In many parts of the world, the majority of the hard-surfaced pavements are asphalt pavements. For instance, in Europe and the United States over 90% and 94% of paved roads and highways are surfaced with asphalt, respectively. In addition, approximately 85% of airport runways and parking areas in the United States are surfaced with asphalt [13]. In many other parts of the world, the same type of statistics applies. The asphalt and concrete paving industries play a major role in many countries' well-being, employing millions of people. The asphalt mixtures have been used all over the world for many purposes including the following:

1. motorways;
2. highways;
3. streets;
4. airport runways;
5. parking areas;
6. driveways;
7. coastal protection;
8. canal linings;
9. reservoirs;
10. footpaths and cycle paths; and
11. sport and play areas.

15.4 Impact of road infrastructure on society

However, there are major gaps within the infrastructure system that provide many opportunities for the engineering world and recyclers to tackle many problems for years to come. For instance the World Bank reports (https://www.worldbank.org/en/news/press-release/2019/02/19/price-tag-for-sustainable-infrastructure-spending-in-developing-countries-is-45-of-gdp) that the infrastructure gap includes many shortcomings, as shown below.



Due to lack of quality pavements, millions of people around the world are unable to access work and take advantage of educational opportunities. These future roads helping many people could and should include rubberized asphalt mixtures in many forms (emulsion, surface mix, etc.). Many of these roads, especially dirt roads, could be rehabilitated utilizing modified rubber binders creating durable pavements serving the community and increasing commerce. This major investment will enable millions of people in many parts of the world to have better access to commerce and other communities, and therefore to have a more productive life.

Many roads, around the world, are in poor condition, underfunded, and are becoming more crowded and dangerous to the traveling public. In many less developed countries, these issues cost many lives and many billions of dollars of economic

damage may be caused due to "bad" roads. In many developed countries, even though much positive work regarding the safety problems has been achieved, there are still major issues regarding managing an almost "accident-free" infrastructure due to "good" roads. For instance, it has been reported by the American Society of Civil Engineers (ASCE) that more than two out of every five miles of interstates in the United States are congested and each year traffic delays cost the public over $160 billion (e.g., wasted time and fuel). In addition, the report indicates that 20% of highway pavement system is in poor condition and this situation is getting worse since there are increasing backlogs of rehabilitation needs. After years of decline, traffic fatalities have been increasing and it is estimated that over 35,000 people are dying on roads each year in the United States. It has been reported that having good roads and minimizing surface distress (e.g., potholes and cracking) will address some of the issues discussed above. Good roads with less surface distress will save many lives and money. The concept of rubberized asphalt fits within this category that has the potential to provide to many municipalities a pavement system that will have less surface distress; therefore less maintenance is required, thus making an easy flow of traffic and decreasing the congestion.

In many developed countries, roads are among the most visible form of infrastructure. For instance, in the United States, the public utilizes the roads for almost 5 trillion km for various reasons. Obviously, there are some exceptions such as the 2008 recession and 2020 COVID-19 period that produced a slight dip in the travel schedule. More traffic on the roads produces major congestion problems and therefore more maintenance issues; this problem is just getting worse every year around the world. Over 40% of the US urban interstates are congested (6.9 billion hours delayed and 12 billion liters of wasted fuel); however, adding more traffic lanes or constructing new roads will not solve this situation on its own. The US Federal Highway Administration (FHWA) estimates that each dollar spent on highway improvements returns five times in the form of decreased delays, reduced fuel consumption, reduced emissions, and many other factors. A comprehensive program of providing less distressed pavements by utilizing rubberized asphalt will provide the public with a better ride, in addition to being an excellent cost-effective alternative to the existing system.

The World Bank (http://documents1.worldbank.org/curated/en/970571549037261080/pdf/WPS8730.pdf) estimates that between $0.8 trillion and $1.2 trillion dollars is needed across the low- and middle-income world to bring the infrastructure to an acceptable range, divided among various

regions: 54% to East Asia and the Pacific and 15% to Latin America and the Caribbean. Almost 90% of low- and middle-income countries' investment in infrastructure is undertaken by the public sector which will provide a major opportunity for tire recyclers to provide their services and save taxpayers money by providing quality and cost-effective materials to the governments and the general public.

With limited resources, countries will need to spend the infrastructure funds better. This could be accomplished by improving efficiency and building capacities. Therefore the governments can support high-quality infrastructure projects to achieve significant development results to meet the Sustainable Development Goals. One of the major goals of Global Infrastructure Forum 2016 was increasing coordination among development institutions to support planning and development of infrastructure projects. According to the President of the World Bank during these discussions, more efficient spending should be encouraged and more investment from the private sector, which, in many cases and countries, is seen as a key source of financing for infrastructure projects. This is where, the author believes, the scrap tire recyclers could contribute in many ways and generate many business opportunities in many parts of the world, utilizing millions of scrap tires to produce products that could be used in various infrastructure projects.

In recent years, many governmental agencies have been discussing the concept of investing in more resilient infrastructure. The World Bank has estimated that in low- and middle-income countries that investment will be approximately $4.2 trillion. One of the major concepts of resilient infrastructure is the ability of infrastructure systems, such as power, water and sanitation, transport, and telecommunications, to function and meet users' needs during and after a natural hazard. Rubberized asphalt pavements are an example of making a resilient infrastructure critical since it will not only avoid costly repairs but also will minimize many consequences of natural disasters for the public. Disruption to transportation will affect many aspects of life (e.g., income, quality of life). It has been estimated that disruption, in low- and middle-income countries caused by natural hazards and "bad roads" costs approximately $400 billion a year. By providing durable and lower maintenance roads (such as rubberized roads), these countries could save many lives and several billion dollars each year. In addition, the quality of life will be improved by proving a better infrastructure that requires a minimum amount of maintenance [14].

There are many benefits of having durable and "good" roads. One of the most important items is the safety of the public. As mentioned before, the infrastructure of any society is an important part of providing improved quality of life (e.g., reducing poverty) and transportation plays a major role in providing this critical development. However, there are many challenges overcoming this issue including the following [15]:

1. *Road safety*: each year, unfortunately, over 1.25 million people are killed and up to 50 million are injured on the roads around the world; this is the number one cause of death for children and young adults ages 5–19 years old and the eighth leading cause of death for all ages. Over 25,000 and 36,000 people are killed on roads in the European Union and the United States, respectively, each year. In addition, over 135,000 and 3 million people are injured in accidents in EU and the United States, respectively. In Europe, each year, it is estimated that the socioeconomic cost of accidents is approximately 120 billion Euros. Due to many reasons, approximately 90% of the deaths happen in the low- and middle-income countries, although they have just half of the world's vehicles. Pedestrians and the motorcyclists account for more than half of the deaths.
2. *Climate change*: approximately 64% of global oil consumption is related to the transport sector (27% of all energy use), accounting for 23% of the world's energy-related CO_2 emissions. This issue will get worst since more vehicles are being sold each year all over the world, especially in India and China, who have a combined population of over 2.75 billion people.
3. *Urbanization effect*: it is estimated that by 2050 cities around the world will be home to some 6.7 billion residents, which will be 67% of the projected global population, causing an increase in ownership of vehicles up to 2 billion.
4. *Accessibility and affordability*: as mentioned before, one billion still lack access to a proper road. In many cases, congestion and time loss due to "bad roads" affects the local population's prosperity. The "cost" of transportation cuts the disposable income of the poor people.
5. *Pollution*: air pollution from road transport has been associated with many health conditions, such as cardiovascular and pulmonary diseases. It is estimated that approximately 185,000 people die each year due to pollution from vehicles. Better quality pavements and longer lasting roads will produce less pollution and therefore a better quality of life for the users. Based on many research projects all over the world

regarding the rubberized asphalt mixtures, the utilization of these mixes will provide a much better environmentally sustainable product [16–21].

15.5 Impact of new innovations on roads

These days, there are many innovations that will impact the way that we travel and live for many years to come. There are many important issues to consider; however, one of the most important factors to be considered is highway and road transportation sustainability. There is also another aspect of transportation infrastructure that will impact the quality of life in the future and that is the construction materials used for the system either being Kevlar and nanofibers for reinforcement or crumb rubber modifier (CRM) products in many applications. The transport sector, for many years, has been transformed by smart connected infrastructure and the key to its success is multimodal mobility which is integrated transport—seamless connectivity between different modes of transportation (e.g., buses, trains, bikes, etc.).

Another issue that will impact the mode of transportation is the autonomous driving technology. Nowadays, the automakers are experiencing rapid changes as major technological advancements continue to change the industry. This system is expected to have a major and a profound impact on multiple industry sectors; however, its impact on the future of pavement design is not known. The question is will rubberized asphalt mixtures play a role in this case? The answer will be clear soon. It is estimated that by 2030, approximately 25% of all miles driven in the United States will be from autonomous vehicles (AVs). In addition, it is estimated that by 2030 around the world, over 11 million AVs will be on the road. This translates to about 5% of the world's traffic population. By 2040, the Center for Automotive Research estimates that AVs could account for 55% of new-vehicle sales. Another question that should be considered by the engineers is "should our roads be designed for AVs or should AVs be designed for our roads"?

The development of AV is directly related to a transformation of the structures on which these cars drive (e.g., road surfaces) which, in reality, must have a better quality and technology. These days, even though there might be distress, such as potholes, on the road surface, cars still drive and try to avoid the damage, while users complain. Repairs might take a while to complete and cause other issues (e.g., congestion), but all this will change. The concept of the self-driving vehicle works like

this: the car will inform the driver in detail of any problems with the road surface and then will advise the driver what to do (e.g., a visit to the garage). In general, car mobility has many challenges including:

1. reducing the potential of accidents;
2. improving environmental and sustainability impact; and
3. traffic pollution and jams.

It is hypothesized that the self-driving vehicles will help the abovementioned issues. For instance, many of the accidents will not occur; the carbon footprint of the vehicles will be reduced, and time savings will be achieved by improving the traffic conditions. However, there might be some issues, at least in the United States, regarding the funding issue unless some other new program is implemented. Every time someone buys gas at the pump in the United States, among many other countries, each gallon (or litter) of fuel purchased puts money into a variety of pockets (oil companies, refineries, distributers, and governmental agencies). In the United States the funds go to the Highway Trust Fund that finances most federal spending on highways and mass transit. Currently, 25% of traffic jams are caused by accidents caused by human error. It is assumed that this issue will completely disappear with self-driving vehicles. Since 2012 over 1 million plug-in vehicles have been sold. There are over 250 million vehicles currently registered and legally drivable on US highways. Sales of the electric cars are increasing dramatically these days [22–31].

15.6 A brief introduction: what is rubberized asphalt and why should you use it?

There is no easy answer to the abovementioned issues and problems with pavements around the world. However, due to the history of rubberized asphalt and its success in the field applications in many parts of the world and different environments (cold or hot), it is hypothesized by many researchers that this type of mix will be an ideal candidate to solve many of the issues discussed in this paper. Rubberized asphalt binder, in general, is a modified asphalt binder utilizing crumb rubber producing a product with improved temperature susceptibility and more flexibility. It is made by adding the crumb rubber obtained from processed scrap tires with asphalt binder at high temperatures for a certain period of time. There are many advantages in using these types of modifiers, including increased elasticity and also increased resistance to aging due to the antioxidants contained in tires. In

addition, it is an environmentally sustainable material which improves the performance of asphalt pavement.

There are many ways researchers and industry experts refer to these materials. One of them is CRM, which refers to a modifier used to enhance the properties of an asphalt binder. There are many techniques used to produce the modified binder including, but not limited to (1) wet process and (2) dry process. These modified binders may contain additional additives or modifiers (e.g., aromatic oils). These modified binders could be utilized in many aspects of the pavements such as surface and intermediate courses, crack and joint sealants, binders for chip seals, and many more.

CRMs have been used for over 50 years in asphalt mixtures either utilizing the wet or the dry process. Initially, the dry process was a patented process called PlusRide and at this point, it is not being used in the United States anymore. In other countries, the dry process, in many forms, is still being utilized. Different gradations of aggregates such as dense-, open-, and gap-graded are used in the rubberized modified mixtures all over the world.

In the United States, there are several states that use these types of mixtures every day including Arizona, California, Florida, and Texas. In some cases, for example, Arizona, the primary use of asphalt rubber binder is in a specific area of the pavement (open-graded and gap-graded hot-mixes). For instance, in Arizona, the open-graded friction course, containing CRM binders, is now the most popular use of modified binders. There are several states that initiated the use of these modified binders years ago and have expanded the programs in many ways. For instance, the first use of CRM binders in Arizona was in 1975. Nowadays, California DOT is utilizing the CRM binders in many layers of the pavements and several applications (e.g., dense-, gap-, and open-graded hot mix asphalt). Other states, such as Texas, use the CRM modified binders in gap-graded mixture with high binder content. In addition, Florida DOT uses up to 12% CRM, by weight of binder, in modified binders in dense- and open-graded asphalt mixtures. These binders are not referred to as "asphalt rubber," as defined by ASTM, since the definition indicates that the materials must contain a virgin binder and a minimum of 15% CRM.

In general, the production of tires consists mainly of utilizing many materials and chemicals, including, but not limited to, natural and synthetic rubber, carbon black, sulfur, zinc oxide, and coloring agents. Research has shown that the CRM absorbs asphalt binder and swells. The degree of swelling depends on

many factors such as the nature, temperature, and viscosity of the asphalt binder. This is a diffusion process and ultimately results in an increase in the dimension of the rubber network until the concentration of asphalt is uniform and equilibrium swelling is achieved. This process, in general, affects the performance grade of the binder, especially, as rubber size, type, and blending process are different.

There are several benefits of using rubberized asphalt mixtures including the following:

1. Improved resistance to surface cracking
2. Improved aging and oxidation resistance
3. Improved resistance to fatigue and reflection cracking
4. Improved resistance to rutting
5. Increased nighttime visibility
6. Reduced tire noise due to increased binder film thickness and open texture
7. Reduced splash and spray during rain storms
8. Reduced construction times
9. Lower pavement maintenance costs
10. Better chip retention due to thick films of asphalt (chip seal applications)
11. Lower life cycle costs
12. Savings in energy and natural resources

There are several limitations of this concept that should be considered and analyzed, and some of these are:

1. Compared to the conventional mixes, rubberized asphalt mixtures have, in general, higher initial unit cost. However, in many cases, this has been offset by using reduced thickness, resulting in lower life cycle costs. Because of this increase in cost, in many areas around the world, they are primarily used for surface courses only.
2. For many years and in many parts of the world, improper construction practices have resulted in reporting of poor performance of these mixtures; however, since then many new and improved specifications have corrected these deficiencies.
3. Since these materials, like many polymers, are more temperature sensitive, more attention should be made to the temperature requirements during the production and placement of these mixtures.
4. Potential odor and air quality problems.
5. Handwork of the rubberized mixtures is difficult.

ASTM D 6114 defines asphalt rubber as "a blend of asphalt cement, reclaimed tire rubber, and certain additives in which the rubber component is at least 15% by weight of the total blend and has reacted in hot asphalt cement sufficiently to cause

swelling of the rubber particles." The effects of the CRMs on the enhancements made to the modified binders are very similar to the effects of polymer modification. One of the major changes is the increase in the high temperature stiffness compared to other polymer modification. In addition, CRMs require a reduction of dependency on temperature and loading frequency. In general, the main function of crumb rubber is that of an interactive filler. Crumb rubber remains as particulates even after mixing, since the crumb rubber particles do not dissolve in the asphalt, and they have been shown to swell in the asphalt. This results in effective volumes that are larger than their initial volume.

For many years, all over the world, various polymers that have been used to modify asphalt, including styrene–butadiene–styrene (SBS), styrene–butadiene rubber (SBR), Elvaloy, rubber, ethylene vinyl acetate (EVA), polyethylene, and others. There are many desirable characteristics of polymer-modified binders that must be considered, since there is a major price difference between the modified and unmodified binders. These characteristics include greater elastic recovery, a higher softening point, greater viscosity, greater cohesive strength, and greater ductility.

For many governmental agencies, it is desirable to choose an asphalt modifier that resists multiple distresses. These distresses might include the following: rutting, fatigue cracking, thermal cracking, and water damage. Many researchers have indicated that the choice of polymer may have a major impact on fatigue properties. In addition, it has been reported that the mixtures boasting the highest fatigue life contained reactive styrene–butadiene cross-linked polymer. Other polymers tested were a chemically modified crumb rubber, SBR, linear block SBS, and other modified SBS products.

During the blending process of any polymer and asphalt binder, the low-molecular-weight oil fraction of the binder will be absorbed by the polymer and will become swollen, and they connect together to form a three-dimensional network. This network is the reason for the asphalt binder having physical properties such as elasticity, plasticity, and elongation. In general, most modified binders become more viscous and tend to improve the binder coating due to an increase in film thickness on aggregates. This increase in return helps to attain a better adhesion between the aggregate particles and asphalt binder; therefore resulting a better pavement performance. Shell Chemical Co. developed SBS, which is the most widely used polymer in the modified asphalt binder industry.

At ambient temperatures, SBS behaves like an elastic rubber. However, it can be processed like a plastic when heated

(thermoplastic elastomer). Since most types of rubber are cross-linked they are difficult to process. However, SBS and other thermoplastic elastomers can be rubbery without being cross-linked. Therefore they are easily processed into useful shapes. The SBS in its structural form has a backbone chain made up of three segments. Polystyrene is a hard plastic which provides durability at high temperatures, while butadiene is a rubber contributing to the elasticity of the binder at low temperatures. The SBS network is believed to interact with the asphaltene and resin parts of the typical asphalt binder.

In general, the research results have indicated that the flow values of both SBS and EVA asphalt mixtures are higher than the virgin mixtures; therefore they are more resistance to permanent deformation. In general, the polymer additives are contributing to a stronger adhesion of aggregates and binders, and therefore are playing an important role in the performance properties of the modified binder. Researchers concluded that binders modified with elastomeric modifiers produced better recoveries than those made with plastomeric modifiers (e.g., Elvaloy). Overall, the results also indicated that the CRM binders exhibited the least creep, while also demonstrating a very high recovery rate over the range of temperatures [32–49].

There are several hundred more research works and several thousand kilometers of pavements that have been in place for decades with most of them having excellent performance records and providing a very good cost-effective pavement to the taxpayers. In order to overcome some of the issues discussed above, I recommend that we utilize rubberized asphalt materials in many applications to provide safe and environmentally sustainable pavements to the public.

15.7 Conclusions

As the urbanization is rapidly increasing in the developing countries, there is an opportunity for the tire recycling industry to provide a product that will enable the engineers to build safer, cleaner, more efficient, and more accessible transport systems. This environmentally sustainable infrastructure results in less congestion, reduces the pollution, increases access to jobs and educational institutions, and, which many believe is the most important factor, lowers consumption of transport energy. In many emerging mid-size cities, the engineers have a great opportunity and obligation to design sustainable and inclusive transport systems that should include the utilization of CRM applications. In several larger

cities, better construction materials such as rubberized asphalt are being utilized for building roads and improving the quality and efficiency of transportation systems.

I believe that there must be organized and aggressive action from the tire recycling industry regarding the education of politicians, highway engineers, and the public. There have been several thousand kilometers of rubberized asphalt roads constructed all over the world. This is no longer an experimental product since it has been used all over the world regularly for the last 30 years. It is a proven and engineered product producing durable, safe, environmentally sustainable, and cost-effective pavements in many environmental conditions from the hot areas of Middle East (e.g., 45°C) to the cold weather of Alaska (−30°C).

References

[1] Roads, Encyclopaedia Britannica Online, 2016.
[2] John Noble Wildord (1994-05-08). World's Oldest Paved Road Found in Egypt. The New York Times.
[3] R.A. Gabriel, The Great Armies of Antiquity, Praeger, Westport, CT, 2002.
[4] M. Grant, History of Rome, Charles Scribner, New York, 1978.
[5] L. Boulnois, Silk Road: Monks, Warriors & Merchants, *Odyssey Books, Hong Kong*, 2005. ISBN 978-962-217-721-5.
[6] How the Inca Empire Engineered a Road Across Some of the World's Most Extreme Terrain, Smithsonianmag.com (2016).
[7] L. Xinru, The Silk Road in World History, Oxford University Press, New York, 2010.
[8] The Horses of the Steppe: The Mongolian Horse and the Blood-Sweating Stallions | Silk Road in Rare Books, Dsr.nii.ac.jp (2017).
[9] S. Bhandari, Dinner on the Grand Trunk Road, *Roads & Kingdoms*, 2016-01-05.
[10] P. Khanna How to Redraw the World Map. The New York Times. ISSN 0362-4331, 2016.
[11] M.G. Lay, Ways of the World: A History of the World's Roads and of the Vehicles that Used Them, Rutgers University Press, 1992. ISBN 978-0813526911.
[12] Available from: https://www.cia.gov/library/publications/the-world-factbook/rankorder/2085rank.html.
[13] Available from: <https://www.fhwa.dot.gov/infrastructure/history.cfm>. 2018.
[14] Available from: <https://sdgs.un.org/goals>. 2020.
[15] J.A. Epps Uses of Recycled Rubber Tyres in Highways. Washington, DC: Synthesis of Highway Practice No.198, TRB National Research Council. NCHRP Report; 1994.
[16] T. Kuennen, May Asphalt Rubber Makes a Quiet Comeback, Better Roads Magazine, 2004.
[17] R. Souza, Experiences With Use of Reclaimed Rubber in Asphalt Within Europe, s.n. Rubber in Roads, Birmingham, 2005.
[18] S. Mavridou, N. Oikonomou, A. Kalofotias Worldwide survey on best (and worse) practices concerning rubberised asphalt mixtures implementation

(number of different cases, extent of application. Thessaloniki EU-LIFE + Environ. Policy Govern. ROADTIRE D, 2, 2010 1.1.
[19] R.L. Terrel, J.L. Walter Modified asphalt materials – the European Experience, in: Proceedings of the Association of Asphalt Paving Technologists. vol. 55. 1986. p. 482–518.
[20] A.T. Visser, B. Verhaege Bitumen–Rubber: Lessons Learned in South Africa. Portugal: Asphalt Rubber. ISBN: 972-95240-9-2, 2000.
[21] I. Widyatmoko, R. Elliot, A Review of the Use of Crumb Rubber Modified Asphalt Worldwide, Waste & Resources Action Programme (WRAP), Banbury, 2007.
[22] A. Henao, Impacts of Ridesourcing – Lyft and Uber – on Transportation including VMT, Mode Replacement, Parking, and Travel Behavior, University of Colorado, Denver, CO, 2017. Available from: https://www.cpr.org/sites/default/files/cu-uber-lyft-study.pdf.
[23] F. Alemi, C. Rodier. Regional and Station Based Analysis of Shared Use First and Last Mile Transit Access: Ridership, Equity, Travel and Environmental Effects. National Center for Sustainable Transportation Report for the California Department of Transportation, Task Order 65A0528; 2016.
[24] E. Martin, S. Shaheen, Impacts of car2go on Vehicle Ownership, Modal Shift, Vehicle Miles Traveled, and Greenhouse Gas Emissions: An Analysis of Five North American Cities, Transportation Sustainability Research Center (TSRC), UC Berkeley, 2016. Available from: http://innovativemobility.org/wpcontent/uploads/2016/07/Impactsofcar2go_FiveCities_2016.pdf.
[25] (a) Rodier, C., Alemi, F., & Smith, D. (2015). Synergistic interactions of dynamic ridesharing and battery electric vehicles land use, transit, and auto pricing policies.
(b) C. Rodier, F. Alemi, D. Smith, Dynamic ridesharing: exploration of potential for reduction in vehicle miles traveled, Transp. Res. Rec. J. Transp. Res. Board (2542)(2016) 120–126. Available from: http://scholarworks.sjsu.edu/cgi/viewcontent.cgi?article = 1199&context = mtipublications.
[26] F. Alemi, C. Rodier. Simulation of Ridesourcing Using Agent-Based Demand and Supply Regional Models: Potential Market Demand for First-Mile Transit Travel and Reduction in Vehicle Miles Traveled in the San Francisco Bay Area (No. NCST20161200); 2016. Available from: < https://ncst.ucdavis.edu/wp-content/uploads/2015/09/NCST-Rodier-RidesourcingSimulation-Final-June-2017.pdf > .
[27] S. Feigon, C. Murphy, Center, S.U.M. Shared Mobility and the Transformation of Public Transit. Transit Cooperative Research Program (TCRP) Report, 188; 2016. Available from: < https://www.apta.com/resources/reportsandpublications/Documents/APTA-SharedMobility.pdf > .
[28] L. Rayle, D. Danielle, N. Chan, R. Cervero, S. Shaheen, Just a better taxi? A survey-based comparison of Taxis, transit, and ridesourcing services in San Francisco, Transp. Policy 45 (2016) 168–178. Available from: http://doi.org/10.1016/j.tranpol.2015.10.004.
[29] B. Schaller, Unsustainable: The Growth of App-Based Ride Services and Traffic, Travel and the Future of New York City, Schaller Consulting, 2017. Available from: http://www.schallerconsult.com/rideservices/unsustainable.pdf.
[30] R.R. Clewlow, G.S. Mishra, Disruptive Transportation: The Adoption, Utilization, and Impacts of Ride-Hailing in the United States. Institute of Transportation Studies, University of California, Davis, 2017. Research Report UCD-ITS-RR-17- 07. Available from: < https://itspubs.ucdavis.edu/wp-content/themes/ucdavis/pubs/download_pdf.php?id = 2752 > .
[31] E. Martin, S. Shaheen, J. Lidicker, Impact of carsharing on household vehicle holdings: results from North American shared-use vehicle survey,

Transp. Res. Rec. J. Transp. Res. Board (2143)(2010) 150–158. Available from: http://sfpark.org/wpcontent/uploads/carshare/Impact_of_Carsharing_on_Household_Vehicle_Holdings.pdf.
[32] J.R. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, et al., Plastic waste inputs from land into the ocean, Science 347 (6223) (2015) 768–771.
[33] Available from: <https://datacatalog.worldbank.org/dataset/world-development-indicators>.
[34] A.L. Brooks, S. Wang, J.R. Jambeck, The Chinese import ban and its impact on global plastic waste trade, Sci. Adv. 4 (6) (2018). eaat0131. Available from: <http://advances.sciencemag.org/content/4/6/eaat0131>.
[35] S. Angelone, M.C. Casaux, M. Borghi, F.O. Martinez, Green pavements: reuse of plastic waste in asphalt mixtures, Mater. Struct. 49 (2016) 1–11.
[36] M.E. Abdullah, N.A. Ahmad, R.P. Jaya, N.A. Hassan, H. Yaacob, M.R. Hainin, Effects of Waste Plastic on the Physical and Rheological Properties of Bitumen, IOP Conf. Ser. Mater. Sci. Eng., 204 (2017) 012016.
[37] C. Fuentes-Audén, J.A. Sandoval, A. Jerez, E.J. Navarro, F.J. Martínez-Boza, P. Partal, et al., Evaluation of thermal and mechanical properties of recycled polyethylene modified bitumen, Polym. Test. 27 (8) (2008) 1005–1012.
[38] Y. Becker, M.P. Méndez, Y. Rodríguez, Polymer modified asphalt, Vis. Tecnol. 9 (1) (2001) 39–50.
[39] A. Pérez-Lepe, F.J. Martınez-Boza, C. Gallegos, O. González, M.E. Muñoz, A. Santamaria, Influence of the processing conditions on the rheological behaviour of polymer-modified bitumen, Fuel 82 (11) (2003) 1339–1348.
[40] Z.N. Kalantar, M.R. Karim, A. Mahrez, A review of using waste and virgin polymer in pavement, Constr. Build. Mater. 33 (2012) 55–62.
[41] Y. Yildirim, Polymer modified asphalt binders, Constr. Build. Mater. 21 (1) (2007) 66–72.
[42] M. García-Morales, P. Partal, F.J. Navarro, C. Gallegos, Effect of waste polymer addition on the rheology of modified bitumen, Fuel 85 (7-8) (2006) 936–943.
[43] M. Garcia- Morales, P. Partal, F.J. Navarro, F. Martınez-Boza, C. Gallegos, N. González, et al., Viscous properties and microstructure of recycled eva modified bitumen, Fuel 83 (1) (2004) 31–38.
[44] S. Hınıslıoğlu, E. Ağar, Use of waste high density polyethylene as bitumen modifier in asphalt concrete mix, Mater. Lett. 58 (3-4) (2004) 267–271.
[45] D. Casey, C. McNally, A. Gibney, M.D. Gilchrist, Development of a recycled polymer modified binder for use in stone mastic asphalt, Resour. Conserv. Recycl. 52 (10) (2008) 1167–1174.
[46] U. Isacsson, X. Lu, Characterization of bitumens modified with SEBS, EVA and EBA polymers, J. Mater. Sci. 34 (1999) 3737–3745.
[47] P. Morgan, A. Mulder, The Shell Bitumen Industrial Handbook, Shell Bitumen Chertsey, Surrey, 1995.
[48] N. Ali, S. Zahran, J. Trogdon, A. Bergan, A mechanistic evaluation of modified asphalt paving mixtures, Can. J. Civ. Eng. 21 (6) (1994) 954–965.
[49] Available from: https://www.researchgate.net/publication/.

16

Construction: acoustic insulation in buildings and railway applications

Valentí Fontserè, Miquel Morata and Joan Peset
COMSA Corporación, Barcelona, Spain

16.1 Introduction

In the past, there were two acceptable ways to get rid of used tires: stockpiling or incinerating. The ban on landfilling of used tires due to national and European regulations expedited the search for reduction, reuse, recycling, and other forms of recovery. Recently, the technologies, products, and applications using end-of-life tires (ELTs) have completely altered the marketplace. In this chapter, an overview of the most relevant applications of recycled rubber from ELTs within the construction sector will be presented, describing the current state of the art and the huge potential for the near future.

16.2 Neoballast

One of the most difficult challenges within the railway industry yet to be solved is the degradation of ballast aggregates. Large cyclic loading, weathering, and also periodical tamping activities lead to a progressive deterioration of ballast aggregates resulting in a descent of track quality. In order to reinstate track geometry, more tamping operations need to be done, which cause further ballast deterioration. Then, this process is repeated until the ballast layer is contaminated with fines and aggregates are rounded, leading to noneffective maintenance and ballast cleaning or the need for track renewal. In general, most railway infrastructure administrations, due to the intrusive and costly operation of ballast cleaning, decide to renew the whole track superstructure without taking into consideration that the rest of the materials (rails, sleepers, etc.) have not reached the end of their service lives. Consequently, ballasts are considered to be critical to overall track service life [1].

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00005-3
© 2021 Elsevier Inc. All rights reserved.

Neoballast appears to be an innovative, cost-efficient, and sustainable solution to enhance both the economic and environmental performance of railway tracks. Neoballast is a ballast stone covered by a special coating made of recycled rubber powder and an advanced binder (see Fig. 16.1) [1].

Neoballast was developed under a project of the same name, under the Fast Track to Innovation program of Horizon 2020 of the European Commission. The project was led by Comsa and completed by Dynamics, Structures and Systems International (D2S), Talleres Felipe Verdés, Mapei, and Sorigué [2]. However, the work started in 2011 and was initially developed under the Neobalast project cofunded by the Spanish Government under the Innpacto 2012 program.

The main idea was to find a product that could combine the advantages of the ballast track and the slab track. The merge of the properties leads to a primary estimation of:

- Low initial cost
- Easy to laid out
- Allows geometry restoration (tamping)
- High permeability
- Low maintenance cost
- Longer life expectancy
- Higher speeds permitted
- Higher tonnage capacity

The use of recycled materials such as rubber from ELTs is considered a breakthrough in such a traditional sector where the

Figure 16.1 Neoballast.

use of recycled materials is nearly unthinkable due to the misguided belief that recycled materials mean low performance [1].

It should be noted that:

- Used tires are industrial waste products that are abundantly generated every year.
- Mining and transport of natural aggregates used for the construction of ballasted tracks have an extensive negative impact on the environment as well as elevated construction costs.
- Landfill disposal of used tires causes important impacts on the environment.

Another key factor of Neoballast is its property of insulation or reducing one of the most important and widespread environmental problems in the railway sector: noise and vibrations (N&V). According to the World Health Organization, rail noise has severe consequences for public health, increasing risk of high blood pressure and cardiovascular diseases [1].

Hence, the main goal of Neoballast is to improve ballast properties in order to increase the lifespan of ballast tracks and decrease the intervention level using a smart coating, which reduces N&V as well. The main technical upgrades introduced by Neoballast are [1]:

- Reduction of layer stiffness
- High abrasion resistance (less fines)
- More energy dissipated (rubber contact)
- Stress reduction under ballast layer

These upgrades achieve the following [1]:

- Extended lifespan of the ballast layer components
- Less maintenance needed
- Reduction of the material extraction from quarries
- Improvement of N&V performance
- Preserved high permeability
- Increase of load capacity
- Fit for tamping
- Compatibility: recycled/precast ballast

Los Angeles and Micro-Deval Test allow the measure of toughness, abrasion resistance, and durability of aggregates in order to determine the quality of the material.

The results obtained for the most common ballast test (Los Angeles) reflect a reduction of up to 13 times the fragmentation obtained by the coated ballast with respect to the natural ballast. A similar trend can also be seen in the Micro-Deval test and in the Magnesium Sulfate Resistance test (see Table 16.1) [3].

Regarding the behavior of the material against vibrations, the damping produced by the coating is substantial. The most

Table 16.1 Los Angeles and Micro-Deval test results.

	Conventional Ballast	Neoballast
L.A. Coef	16	1
MDE, RB	8	0

LA, Los Angeles; *MDE*, Micro-Deval.

Table 16.2 Fire response results.

	Results	Regulations
Critical flux (kW/m^2)	>11.0	≥8.0
Smoke production (% min)	3.56	≤750
Propagation of flames (mm/s)	Fs < 150 mm in 60 s	Fs < 150 mm in 20 s

interesting results have been recorded in the tests carried out at 2 Hz and in the measurements made with the external accelerometer, which has a measurement range of 0–200 Hz [3].

Also, it is important to point out that there were also tests conducted to understand how the product will respond to fire. The main fire tests carried out were:

- Measurement of smoke production and smoke toxicity in a horizontally mounted sample under exposure of nonflaming irradiance of 50 kN/m^2 (ISO 5659–2:2012)
- Assessment of the time for the front part of a flame to reach different reference marks in a horizontally mounted sample (ISO 9239–1:2010)
- Assessment of the ignitability by direct small flame impingement in a vertically oriented specimen (ISO 11925–2:2010)

The final results from the fire response are summarized in Table 16.2.

According to these results, the final classification is "BFL,s1 Non combustible substrate," fulfilling both national and European regulations.

In addition, the results of real-scale simulations that were undertaken showed that Neoballast could lead to:

- 20% global stiffness reduction
- 25% stress reduction under ballast layer
- 54% more energy dissipated
- 70% less degradation

Figure 16.2 Neoballast on railway track.

Once the prototype to produce Neoballast at a large scale (Neoballast plant) was constructed, it was possible to begin the field test. The field test section was designed and constructed in a railway track open to traffic, along with a traditional ballast section, in order to assess and compare the performance of Neoballast under real conditions and for an extended time period. The field test is located in a long straight section between Maçanet–Massanes and Caldes de Malavella (Girona, Spain) in the ADIF line 270 (Barcelona to Cerbère), which is a mixed traffic conventional track with Iberian gage. A 100 m long Neoballast section was built next to a 100 m section of conventional ballast, including the required transition zones.

Both the Neoballast and conventional ballast sections were instrumented to monitor track settlement, track deflection, N&V and, indirectly, track degradation. Those parameters were measured by means of accelerometers, total pressure cells, and microphones installed in both the Neoballast and conventional ballast sections. A camera detected the passage of trains and starts the registration. All the compiled data was centralized in a monitoring cabinet, which was contiguous to the field test site and remotely controlled by D2S. In addition, periodical topographical surveys were carried out by COMSA (see Fig. 16.2).

The performance of Neoballast is expressed in comparison to traditional ballasts in the following terms:

- Noise emission
- Vibration emission

- Track degradation
- Track settlement

The monitoring of the field test section has been up and running since June 2019. The preliminary results are summarized here.

The effect of the Neoballast is on average a reduction in overall noise level of about 0.6 dB.

The overall vibration reduction for Neoballast in comparison with conventional ballast is about 5–10 dB.

No final conclusions can be drawn from the total pressure measurements in the given monitoring timeframe. The monitoring will continue for a longer period in order to collect and analyze more data from the total pressure measurements to properly assess the track stress and track degradation behavior.

Track settlement measurements are being performed on a regular basis. The measurements show an initial important settlement of the Neoballast section, which was expected based on laboratory tests. After this initial settlement, the rate of track settlement decreases [4,5].

From the results obtained, a life cycle analysis (LCA) was performed for Neoballast in comparison with conventional ballast. Note that in the aggregate industry, the majority of the emissions of all greenhouse gases are carbon dioxide and methane, emissions that dominate the global warming potential (GWP). Fig. 16.3 shows the LCA results for the GWP.

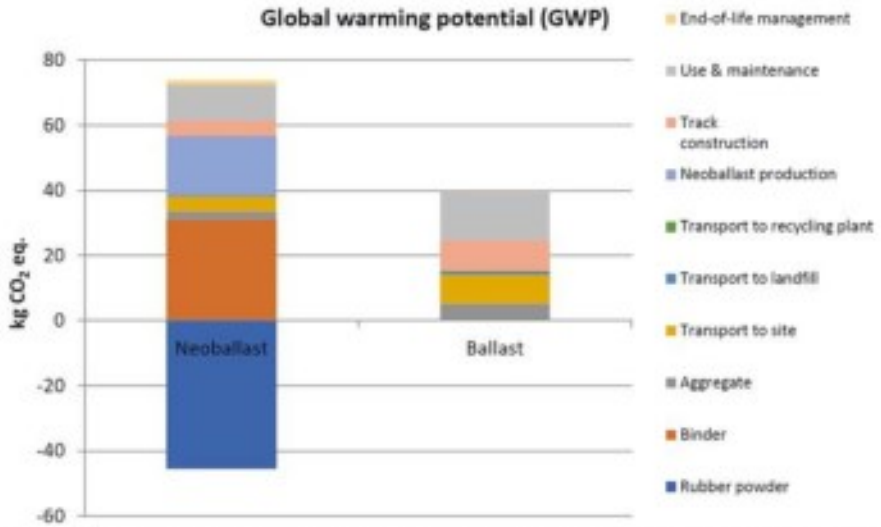


Figure 16.3 Contribution to global warming potential for 100 years of Neoballast and conventional aggregates for 1 ton (cradle-to-cradle).

Figure 16.4 Train on Neoballast.

At first glance, it may look as though Neoballast has a greater carbon footprint than conventional ballast. Nevertheless, since Neoballast elude the incineration of ELTs, this influence should be deducted. Therefore the results show a total impact for Neoballast nearly 30% less than conventional ballast (around 28.44 kg CO_2 eq. against 39.76 kg CO_2 eq.).

In the near future, and as it is currently being done in big scale industry, the commercialization of Neoballast will avoid the heating phases. So, Neoballast, when produced at a large scale, will have a reduction up to 20.68 kg CO_2 eq., counting to nearly 50% the impact of the conventional ballast. This gives the conclusion that Neoballast reduces significantly the footprint.

Note that Neoballast shows a better performance than conventional ballast in terms of GWP, as indicated above. Indeed, if the thickness of the Neoballast layer is reduced by 8 cm (i.e., by 27%) as a consequence of its higher elasticity and its better load distribution capacity, the GWP impact and the LCC would result in ever higher performances [6].

Regarding the sustainable development goals (SDGs) [7], the Neoballast project could be involved within the SDG 9: Industry, innovation, and infrastructure; SDG 11: Sustainable cities and communities; and SDG 12: Responsible consumption and production. Specifically (see Fig. 16.4):

- **9.4** By 2030, upgrade infrastructure and retrofit industries to make them sustainable

- **11.2** By 2030, provide access to safe, affordable, accessible, and sustainable transport systems for all
- **12.2** By 2030, achieve the sustainable management and efficient use of natural resources
- **12.4** By 2020, achieve the environmentally sound management of chemicals and all wastes throughout their life cycle
- **12.5** By 2030, substantially reduce waste generation through prevention, reduction, recycling, and reuse

As demonstrated above, the use of Neoballast could be used in several applications, such as for high track deterioration areas, heavy haul lines, noise and vibration reduction, enabling the use of low-quality aggregates, stiffness transitions, tunnels and bridges and Switches and crossings.

16.2.1 High track deterioration areas

Neoballast leads to reduction of maintenance activities, extends ballast life, and enhances reduction of N&V. It could be applied in areas of high wear and high traffic lines (urban areas). Note that the number of tamping operations is reduced in comparison with conventional ballast.

16.2.2 Heavy haul lines

Neoballast increases load capacity and reduces ballast fouling/breakage. This makes Neoballast the perfect solution for heavy haul lines where there is a need for more durable and stronger ballast as well as a need to reduce maintenance interventions (costs).

16.2.3 Noise and vibrations

Neoballast is compatible with under sleeper pads (USP) and under ballast mats (UBM), and it also does the function of USP and UBM. Thanks to that, there is a reduction of N&V, a common issue in urban areas (see Fig. 16.5).

16.2.4 Low-quality aggregates

With Neoballast, low-quality aggregates could be used, such as calcareous aggregates. This advance in the field sector is possible thanks to the improvement of the Los Angeles test, but also due to that coating avoids water aggression and distributes stress, as well as its high abrasion resistance (less fines).

Figure 16.5 Neoballast on railroad track.

16.2.5 Stiffness transitions

Neoballast can attenuate/improve stiffness transition areas. Controlling stiffness is a key advantage due to railway infrastructure goes through different stiffness conditions (e.g., transition areas in tunnels and bridges), but also because high stiffness changes accelerate infrastructure deterioration.

16.2.6 Tunnels and bridges

Neoballast layer thickness reduction avoids tunnel enlargement. Today, modern vehicles have bigger vertical gage, so this relevant improvement leads to a tunnel gage reduction, being the infrastructure a part of the solution. Note that this attribute could be applied to both road vehicles and rail coaches.

16.2.7 Switches and crossings

Neoballast reduces stiffness and increases energy dissipation. Switches and crossings are zones of high stiffness, high level of rail wear and high impact load in crossing areas, so Neoballast is an ideal solution to these areas in railway lines.

In summary, Neoballast has proven to be an ecofriendly and ecoefficient product that, in the long term, will be a better solution for the environment than conventional ballast thanks to its

durability. Moreover, it is a sustainable and cost-effective technology that gives solution to the most important shortcomings of European railways (e.g. high deterioration and high environmental impact) which will result in wide-ranging benefits for the whole European society.

Neoballast has a longer life, so it reduces the extraction of natural aggregates from quarries. Also, end-of-life tires can be shredded and have a second use, instead of being incinerated and releasing toxic and carcinogen emissions to the environment.

16.3 The Anagennisi project

The Anagennisi project was submitted to the Framework Program for Research, Technological Development and Innovation of the European Union, which was the main legal and economic tool to finance community research during the period 2007–13. The Seventh Framework Program (FP7) has funded research projects in transnational cooperation, selected in competitive calls, with the fundamental criteria of scientific excellence, and where there were no preestablished quotas for each country [8].

The project was developed by the University of Sheffield, the Imperial College, Twincon Limited, University of Zagreb, Arkada, Gradmont, Werkos, Dulex, GUMIIMPEX-GRP, TUIASI, Cyprus University of Technology (CUT), Zebra General Constr, ADRIA, ETRA, COMSA, Fhecor, and ZYP Ingeo.

The following sections are based on the ANAGENNISI final report [9].

16.3.1 Overview of the project

The aim of the project is to re-use end-of-life tyre fibres in concrete applications to increase its performance while reducing its environmental impact.

Concrete is composed, among others, by cement, sand, and aggregates, in which the former act as a binder and the latter as structural filler. Aggregates are normally used to improve durability and strength, but the use of small amounts of rubber in concrete can enhance ductility, and the use of high volume of fractions can lead to a less-stiff concrete and significant reduction in compressive strength. Concrete is inherently weak in tension and it is normally reinforced with steel rebars or fibers.

In this project, rubber, steel cord, and polymer textile from recycled tire were analyzed in order to understand the behavior

and possible applications in civil construction (e.g., bridges) rather than use discontinuities and expensive bearings.

Rubber is an ideal candidate as aggregate for concrete due to its strength, flexibility, and a remarkable ability to maintain its volume under stress, not to mention the fact that it is a highly durable material. The steel cord used for tire reinforcement is currently being discarded, while the same cord not used for tires is used for other applications such as high security applications. Something similar happens to the polymer fibers in tires: due to the way it is extracted, is mainly landfilled or incinerated because it is contaminated with rubber and too tangled to be easily introduced into concrete while the same new polymer fibers are used in concrete.

Taking everything into consideration, the consortium, aware of the environmental problems related to used tire disposal, considered it feasible to reuse them for civil construction, helping to mitigate climate change as well as to give a second use for the product that would otherwise be incinerated.

The aim of this proposal was to develop innovative solutions to reuse all tire components in high value innovative concrete applications with reduced environmental impact. The main objective of the project is to develop concrete, concrete mixes, and concrete elements using rubber, steel fibers and polymer fibers from ELTs to be used on slabs on grade, precast concrete, sprayed concrete, screeds and integral bridge elements, and base isolation systems.

The main achievements, features, and applications that Anagennisi project discovered are as follows. Before the three tire by-products [recycled rubber, recycled tire steel fibers (RTSF) and recycled tire polymer fibers (RTPF)] can be used in concrete, they had to be cleaned, sorted, characterized, and classified.

16.3.2 Rubberized concrete and confined rubberized concrete

16.3.2.1 Compressive behavior of unconfined and FRP-confined rubberized concrete

After several research works to estimate the compressive behavior, for plain rubberized concrete (RuC), a decrease of axial strain capacity and compressive strength as the rubber content increased was observed, while the lateral strain capacity raised considerably when the rubber content was increased.

Regarding CruC, lateral confinement with fiber-reinforced polymer (FRP) jackets was effective and mitigated the detrimental

effects of rubber on concrete performance. More importantly, RuC cylinders wrapped with four layers of Aramid Fiber-reinforced polymer (AFRP) achieved axial strains that have never seen before in conventional concrete: stress and strain capacities of around 90 MPa and 6%, respectively, despite the high rubber content (60% total aggregate replacement).

16.3.2.2 Medium- and large-scale tests using RuC and AFRP CRuC

These tests were performed in order to estimate the behavior of reinforced rubberized concrete (RRuC) and AFRP CRRuC columns reinforced with longitudinal and transverse reinforcement bars, focusing on structural members incorporating large proportions of rubber particles as a replacement for mineral aggregates (60% by volume).

The results showed that AFRP CRRuC is effective at enhancing the energy dissipation (up to 44%−169%) and deformation capacity (up to 33%−35%) of the columns in comparison to counterpart specimens cast with RRuC or RC (conventional reinforced concrete) columns, respectively. Also, it was observed that yielding of the longitudinal reinforcement controlled the behavior of the column specimens.

16.3.3 Steel fiber-reinforced concrete

16.3.3.1 Surface finishing of industrial flooring using RTS

The Anagennisi project developed a mitigation method to eliminate a common surface finishing issue in industrial Steel fiber-reinforced concrete (SFRC) floors using RTSF, in which a large number of fibers appears on the surface of a slab creating esthetic as well as health and safety concerns. Various types of surface hardeners were used to address this issue.

The study of a slab-on-grade concrete mix design (20 kg/m^3 of manufactured steel fibers plus 10 kg/m^3 of RTSF) concluded that a potential solution to the surface finishing problem, common in industrial concrete slabs with RTSF, could be addressed by using 10 kg/m^2 of surface hardener.

16.3.3.2 Flexural performance of SFRC prisms and circular slabs using manufactured fibers and sorted RTSF

This study was undertaken to examine the behavior of the SFRC mixes for slabs on grade and suspended slabs using typical concrete mix and fiber dosages. This investigation concluded that comparing the mix that contained only manufactured fibers or RTSF with the one compound of manufactured fibers and RTSF,

the synergetic effect of the latter seemed to improve the flexural concrete behavior.

16.3.3.3 A restrained shrinkage investigation on large-scale concrete SFRC strips using manufactured fibers and recycled tire steel fiber

Five SFRC mixes with various fiber dosages were used in order to provide visual evidence of how well different fiber blends resist the onset of restrained shrinkage cracking. To conduct this test, 40-m-long strips were monitored for both free and restrained shrinkage deformations.

The results showed that for free shrinkage, all mixes had similar behavior with a deformation of around 200 με. However, the results for restrained shrinkage were quite different as well as the crack formation:

- In mix UND 0.8/55 (30) no cracks were observed.
- Plain concrete (PC) mix developed a longitudinal crack of around 600 mm long with thicknesses of 0.33.
- Mix RTSF (30) developed a longitudinal crack of around 600 mm long with thicknesses of 0.1.
- Mix UND + 1/60 (35) + RTSF (10) developed a longitudinal crack of around 600 mm long with thicknesses of 0.46 mm.
- In hybrid mix UND 0.8/55 (20) + RTSF (10), four cracks were measured with dimensions of 500–600 mm length and with a thickness of 0.4–0.5 mm.

16.3.3.4 Compressive and flexural behavior of steel fiber-reinforced rubberized concrete

This experimental project focused on how the use of waste tire rubber affects steel fibers on both fresh and mechanical properties of RuC. Some of the results are summarized as follows:

- The increase of rubber content causes the reduction of the modulus of elasticity as well as the compressive and flexural strength.
- The reduction of workability and unit weight and the increase of air content of the fresh concrete mixes when replacing conventional aggregates with rubber particles.
- The addition of steel fibers in conventional concrete enhanced compressive strength and did not affect the modulus of elasticity.
- The diminution of workability and the increase of air content while marginally increased unit weight of steel fibers.

16.3.3.5 Wear of SFRC using RTSF

When concrete was exposed to abrasion, steel fibers had a beneficial effect on the mass loss. The increase of RTSF dosages led to a decrease of the mass loss from 13% to 30% compared to 30M0R mix (30 kg/m^3 of manufactured fibers).

16.3.3.6 Accelerated corrosion on SFRC using manufactured and/or RTSF

Three fiber-reinforced concrete (FRC) mixes with RTSF and/or manufactured steel fibers were evaluated to test corrosion, which was imposed by potentiostatic anodic polarization of specimens immersed in NaCl solution. The results obtained showed corrosion on both types of steel fibers whereas their presence reduced corrosion of steel reinforcement.

In addition, significant corrosion was evident in the case of RTSF mixes. The cause of this was thought to be due to the use of higher fiber dosages with smaller cross-section.

16.3.3.7 Performance of conventional and rubberized SFRC subjected to wet and dry cycles

The results of this study indicated that no sign of deterioration or cracks were noticed. However, after 5 months of wet-dry cycles, an increase of the compressive strength of all mixes was observed in comparison with the 28-day compressive strength. Moreover, when 30% and 60% of fine and coarse aggregates were replaced with rubber particles, the mean 28-day compressive strength of the control PC mix was reduced by 54% and 86%, respectively.

Also, the 28-day flexural strength could be improved by 28% if adding fibers to the conventional concrete mix. While the 28-day flexural strength decreased with higher rubber replacements, the inclusion of steel fibers alleviated the adverse effect of rubber. The 28-day flexural strength reduction of steel fiber-reinforced rubberised concrete (SFRRuC) mixes was 11.7% and 44% compared to control mix.

16.3.4 Fiber-reinforced concrete

16.3.4.1 Effect of RTPF on fresh and hardened concrete properties

In order to evaluate the effect effect of RTPF on fresh and hardened concrete properties, a PC mix, mixes with monofilament (PPm) and fibrillated (PPf) fibers, mixes with different dosages of

mixed RTPF (RTPFm), mixed RTPF type 1 (RTPFm1) and sorted RTPF (RTPFs) were tested. The results are summarized below:

- A decrease of workability and increase in air content in fresh concrete were observed when using fibers.
- Mechanical properties (compressive strength and modulus of elasticity), if compared to the reference mixes, were not deteriorate when adding sorted RTPF and both mixed types of RTPF fibers (at 5 kg/m^3).
- A decrease of the mechanical properties when adding both types of mixed RTPF types (at dosages >10 kg/m^3) was observed, which can be directly correlated to the air content in fresh mix.

16.3.4.2 Shrinkage behavior of RTPF-reinforced concrete

This study, which involved PC mix, mixes with monofilament (PPm) and fibrillated (PPf) fibers, and mixes with different dosages of mixed RTPF and sorted RTP, focused on early-age deformations. The results showed that both RTPF influenced the early-age concrete deformations and that mixed RTPF at dosages >5 kg/m^3 and sorted RTPF at dosages >1 kg/m^3 decreased autogenous deformation in comparison with PC mix.

16.3.4.3 Self-compacting concrete reinforced with RTPF

The results of the compressive strength showed that that the fiber addition did not affect the compressive strength of SCC at dosages ≤ 2 kg/m^3. Besides, RTPF decreased the autogenous shrinkage by more than 47%.

16.3.4.4 Sprayed concrete with RTPF

The autogenous shrinkage results showed that 1.8 kg/m^3 of RTPFm reduced autogenous shrinkage by 35% when compared to plain mix. In addition, concrete mixes, compared to PC, reinforced with RTPFm resist higher stresses induced from restrained shrinkage.

Results also showed the possibility of increasing tensile stresses that concrete can resist prior to cracking by substituting 0.9 kg/m^3 of PPm with 0.9 kg/m^3 of mixed RTPFm (up to 116% compared to PC, 36% compared to concrete at 0.9 kg/m^3 of PPm fibers, and 4% less than the concrete mix with 1.8 kg/m^3 of PP fibers).

16.3.4.5 Durability properties of concrete with RTPF

The main durability results for capillary absorption, performed on mixes reinforced with three types of RTPF and compared to

plain concrete (OC) and concrete with monofilament (PPm) and fibrillated PP fibers (PPf), are summarized as follows:

- Concrete resistance to penetration of fluids was ameliorated by adding all types of fibers.
- The positive effect on penetrability properties was reduced when higher dosages of RTPF were used.
- No relevant benefit of RTPF on the concrete properties was perceived in terms of water permeability, gas permeability, and chloride diffusion.

Concerning freezing and melting with deicing salts, an important influence on concrete resistance to scaling was seen. Meeting the criteria for XF2 and XF4 exposure classes without addition of air entraining admixture was possible for several mixes with mixed RTPF.

The test of freezing/melting resistance without the presence of chlorides performed in this study led to the conclusion that all tested mixes with RTPF without air entraining could be applied for concrete elements exposed to XF1 and XF3 exposure classes.

Note that for impact of freezing/melting with or without antiicing agent, if wet concrete is exposed to a considerable number of freezing/melting cycles, the exposure classes are [10]:

- XF1: Moderately saturated with water, without antiicing agent
- XF2: Moderately saturated with water, with antiicing agent
- XF3: Highly saturated with water, without antiicing agent
- XF4: Highly saturated with water, with antiicing agent or seawater

16.3.4.6 Durability of hybrid FRC mixes reinforced with RTSF and RTPF

When substituting manufactured fibers by RTSF and RTPFm in concrete, a positive effect could be achieved in terms of water permeability and wear resistance properties of FRC.

In addition, concerning freeze and thaw properties and in comparison with the mix reinforced with manufactured fibers, the cumulative mass loss for mixes reinforced with recycled fibers was two times lower after 28 cycles.

16.3.4.7 Screeds reinforced with RTPF on their own or blended with RTSF

Regarding abrasion resistance, the results of this project, in which sorted RTPF and sorted RTSF were used as reinforcement in the screed mixes, displayed a beneficial effect with the addition of RTSF or RTPF fibers to the screeds.

Tests on plastic and restrained shrinkage performed in this project concluded that 0.9 kg/m^3 of sorted RTPF could alleviate early-age plastic concrete cracking.

16.3.5 Hybrid steel fiber-reinforced concrete

16.3.5.1 Flexural performance of hybrid steel fiber-reinforced concrete elements after long-term free or restrained shrinkage deformations

During the investigation conducted on the effect of hybrid steel fibers on nonuniform free and restrained concrete shrinkage, it was noticed that, among several SFRC mixes using manufactured fibers on their own or blended with RTSF or RTPF, SFRC mixes showed higher free shrinkage strains than PC mix. On average, the restrained factor for all mixes (except mix 30:0.3) varied between 0.5 and 0.6.

16.3.5.2 Punching shear behavior of HSFRC

This research work focused on the punching shear behavior of hybrid steel fiber-reinforced concrete (HSFRC) flat slabs and footings using manufactured steel fibers (MF) on their own or blended with RTSF at various dosages.

For slabs, mix 20M20R (20 kg/m^3 of MF + 20 kg/m^3 of RTSF) was confirmed to be a good option in contrast with the concrete mix 40M0R (40 kg/m^3 of MF), which used only manufactured fibers. Meanwhile, for footings, all series performed equally well with minor variations. Compared to series F1 (no fibers + no punching shear reinforcement), punching shear load for series F2 (40 kg/m^3 of MF) decreased by 3% and increased by 2% for series F3 (20 kg/m^3 of MF + 20 kg/m^3 of RTSF) and F4 (10 kg/m^3 of MF + 45 kg/m^3 of RTSF). Based on the above results, it can be concluded that HSFRC footings can replace MF by 50% (F3) or even in higher dosages (F4) and achieve similar shear capacity and deformation with manufactured SFRC mixes (F2).

16.3.5.3 Fatigue performance of HSFRC

In order to assess the fatigue performance of HSFRC, two HSFRC mixes using MF on their own or blended with RTSF were needed. Series 40M0R (40 kg/m^3 of MF) showed the best fatigue resistance among all series since all specimens reached 2 million cycles even at stress level of $S = 0.7$. Series 20M20R (20 kg/m^3 of MF + 20 kg/m^3 of RTSF) also demonstrated good fatigue resistance since two out of three specimens survived at $S = 0.7$ stress level. Significant deterioration was noticed at stress level of

$S = 0.9$ for all series. Both series (20M20R and 40M0R) resisted much higher displacements than PC at higher stress levels. Taking everything into consideration, we can conclude that hybrid series 20M20R could be a good alternative of a concrete mix reinforced only with MF at the same total fiber dosage.

16.3.5.4 Flexural behavior of slab-like HSFRC

To understand the flexural performance of HSFRC slab-like beams using various ratios of conventional flexural reinforcement combined with either MF on their own or blended with RTSF, a study comparing different series to series PC (no fibers + 5F12−5 × 12 mm rebars) was necessary. Overall, the series H2 (20 kg/m^3 of MF + 20 kg/m^3 of RTSF + 4F12) showed improvement regarding cracking control regarding PC series, with relatively small decrease of yielding load. Thus series H2 with 20% less conventional reinforcement could be a great candidate to bridge decks when sustainability and durability are required.

16.3.6 Others

16.3.6.1 Shake table tests

The goal of this task was on one hand to study the performance of a new seismic isolation system comprising slender FRP confined rubberized concrete (CRuC) elements and on the other hand to assess the seismic behavior of vulnerable conventional concrete buildings as well as to improve their performance by using rubberized concrete at regions where enhanced deformability is needed.

The main achievement of this task was the replacement with FRP-CRuC elements in those places where high-deformability is required allowing the structure to survive earthquakes with at least 65% higher peak ground acceleration.

16.3.7 Pilot tests

Several pilot tests were carried out, as described here.

16.3.7.1 Suspended slab using RTSF

COMSA was in charge of the construction of a suspended slab using both recycled tire steel fibers and conventional ones, with dimensions of 0.15, 5.65, and 7.46 of thickness (width and length, respectively). The pilot test was located in Salou (Tarragona—Spain) and was the roof of a sanitary hut at a recreational summer camp (Camping La Siesta). In total, 8 m^3 of concrete were cast,

which contained 240 kg of sorted RTSF (fiber dosage: 30 kg/m^3) supplied by Twincon Ltd.

16.3.7.2 Slabs on grade using hybrid SFRC (MF + RTSF)

Two pilot tests were conducted in order to assess the technology developed within the project: HSFRC reinforced with manufactured and RTSF on slabs on grade. The slabs were monitored for shrinkage deformations.

Two demonstration sites were selected. The first one was in Bosnia and Herzegovina in which the company Dulex Ltd. casted the slab in a plant for prestressed concrete elements. Nearly 5 tons of MF and 2.5 tons of sorted RTSF were supplied by Dulex Ltd. and Twincon Ltd., respectively. And the second one was cast in Didam, Holland and, again, Twincon Ltd. undertook the construction of an indoor SFRC slab on grade that would be used as a general storage facility.

16.3.7.3 Tunnel lining using recycled steel fibers

Due to the high knowledge within the construction sector, COMSA was responsible of this project in which sprayed concrete with recycled tire steel cords was used on two tunnel lining sections with a dosage of 30 kg/m^3 in a motorway in Spain. Both tunnel segments were monitored during construction and both segments were completed successfully with no reported issues.

16.3.7.4 Precast concrete elements

CUT used SFRRuC reinforced with RTSF to create road safety poles. The SFRRuC road safety poles were confined with a steel tube on the lower end of the pole in order to support the pole connection to its foundation. Also, it was reinforced centrally with an 8 mm glass fiber-reinforced polymer rebar.

16.3.7.5 Repair screed using recycled steel filaments

Twincon Ltd. took over the reparation of a damage concrete floor at a farmhouse located in Sheffield (United Kingdom) in which tire cord filaments (TCF) were used as reinforcement in the screed mix to increase its toughness. TCF and RTSF are made of the same material with the difference that the fibers in TCF can be chopped in specific lengths since the extraction procedure uses a cryogenic method. The final fiber dosage for the existing slab reparation was of 20 kg/m^3 and included the 12 mm TCF.

16.3.7.6 Insulated concrete formwork walls using RTSF

Once again, Twincon Ltd. was responsible of the construction of insulating concrete form (ICFs) walls at a farmhouse located in Sheffield (United Kingdom), which contained recycled tire steel fibers (30 kg/m^3). Note that ICFs are hollow blocks made up of polystirene, which serves as a mold for cast-in-place concrete walls as well as insulating material, so forms do not contribute to the structural capacity of the wall, although they stay in place permanently after the concrete is cured and function as a thermal and acoustic insulator.

16.3.8 Environmental benefits

Regarding the environmental benefits, an LCA was needed to assess the environmental performance of a flexible suspended slab constructed with hybrid-reinforced concrete, a slab-on-grade constructed with HSFRC, and two sprayed SFRC tunnel linings.

An indicative analysis of the slab on grade, which was cast in the Netherlands, is presented below (constructed by TWINCON). The full results of the LCA and LCCA of all the Anagennisi projects are publicly accessible. The results of the LCA indicated that the Product stage (A1−3) had the highest impact, followed by the Construction stage (A4−5) (see Fig. 16.6).

First, recycled rubber can be used as aggregate resulting in more flexible elements and, in addition, new isolation systems; not to mention the huge potential to replace products that contain rubber such as bridge bearings and base isolation units, as well as to be used in structural applications utilizing confined concrete elements. To attain the same design criterion, CRuC elements would require less concrete volume and reinforcing materials than

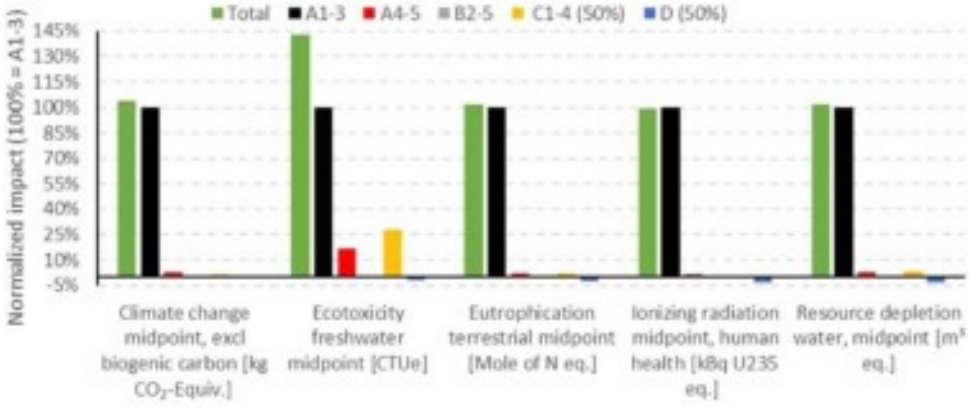


Figure 16.6 LCA Anagennisi.

conventional confined concrete elements. For instance, 40% less concrete and 70% less steel rebars and AFRP sheets are needed in a confined concrete column to attain a curvature ductility of 7. This results in a significant environmental benefit.

Second, RTSF can replace an equivalent amount of new steel fibers currently produced from wire rod. According to the project, it is estimated that each ton of RTSF eventually saves 1 ton of new steel fiber. The estimated overall reductions per ton of RTSF are 1.9 tons of CO_2, dust 1.39 kg/ton, hydrogen chloride 0.0534 kg/ton, hydrogen sulfite 0.0991 kg/ton, sulfur dioxide 3.59 kg/ton, nitrogen oxides 2.84 kg/ton, cadmium 0.00006 kg/ton, chromium 0.000338 kg/ton, lead 0.00265 kg/ton, mercury 0.000914 kg/ton, and so on.

Lastly, RTPF can replace an equivalent amount of new polymer fibers currently produced from new chemicals (petrochemicals). Again, the Anagennisi project determined that each ton of RTPF could eventually save one ton of new polymer fiber. The estimated overall reductions per ton of RTPF are 2.2 tons of CO_2, dust 0.285 kg/ton, hydrogen chloride 0.00157 kg/ton, hydrogen sulfite 0.0612 kg/ton, sulfur dioxide 2.67 kg/ton, nitrogen oxides 3.1 kg/ton, cadmium 0.00007 kg/ton, chromium 0.00052 kg/ton, lead 0.00203 kg/ton, mercury 0.00033 kg/ton, and so on.

In summary, the Anagennisi project investigated the possible reutilization of the materials extracted from tires (rubber, steel fiber, and polymer/textile fibers) in order to avoid the environmental hazards of incineration, stockpiling, and occasionally landfilling (despite the EU landfill directive).

Anagennisi explored how to integrate those high-quality materials into the civil construction sector for both structural and nonstructual uses (buildings, bridges, tunnels, pavements, etc.) reducing environmental impacts.

16.3.8.1 Recycled rubber particles

Recycled rubber particles, when used in the replacement of conventional aggregates in concrete and with confinement, create a new concrete that can dissipate more energy by increasing concrete deformability up to 6%.

Rubberized concrete can be used for base isolation of structures as an alternative to lead-rubber bearings in which FRP confinement to enhance compressive strength and deformability is required.

Moreover, rubberized concrete can reinforce concrete bridge piers and abutments leading to many advantages such as reduced restraining forces induced by the deck movements due to more flexible piers and abutments, reduced shear forces at the piers and abutment walls, and also the axial forces in the deck.

It is also important to mention the application of rubberized concrete as a full transition slab and its benefits to accommodate movement.

16.3.8.2 Recycled tire steel fibers

Structural applications for the steel fibers extracted from used tires can replace the well-established steel fiber manufactured industry.

One possible application for steel recycled tire fibers was presented before: tunnel linings. This application was demonstrated to be effective in both controlled and operational environments.

Another application for SFRC is the construction of suspended slabs, in which, in order to withstand the applied flexural and shear loads along with controlling shrinkage, fibers provide the necessary strength to enable the slab. But also this technology could be applied on nonstructural application. For instance, industrial flooring using ground slabs where the steel fibers are introduced into the concrete mix to control and even to eliminate shrinkage cracking. In these cases, traditional rebar mesh reinforcement could be substituted with steel fibers, which provide a cost-effective and environmentally friendly option and also permit the construction of "jointless" floors where relevant proportion of the construction joints normally used for shrinkage control could be eliminated.

16.3.8.3 Recycled tire polymer fibers

The Anagennisi project showed how tire polymer fibers can be used in nonstructural applications and how the addition of RTPF in concrete mix can help control autogenous shrinkage deformations and deterioration due to restrained concrete shrinkage. Also, the project showed how appropriate dosages of RTPF in the concrete mix can be used to prevent damage related to high temperatures and how sprayed concrete using RTSF and RTPF can also be used in applications comprising spraying concrete.

16.3.9 Insul-eco

Another application for the building sector is Insul-eco, panels with high-performing thermoacoustic properties obtained by mixing high-density synthetic textile fibers from recycling of ELTs, providing a sustainable solution to textile fiber disposal [11].

The Insul-eco panels were developed under the framework of a European project called INSUL–ECO under the competitiveness and innovation programme (CIP) Ecoinnovation Program in

2012. The consortium was led by European Tyre Recycling Association. (ETRA) and completed by Isol-Eco, AD.RI.A, and COMSA. The goal of the project was to produce insulating sheets that were able not only to protect buildings from noise and temperature, but also improve the environmental performance and make better use of natural resources, as well as meet sustainable development goals. A prototype was already produced and then, due to its good performance, the viability of product development and commercialization was considered [12].

The Insul-eco panels are made of up to 90%–95% recycled materials and are 100% recyclable.

Their main features are [11]:

- Self-supporting even with small thickness (2.5–3 cm) due to their high density and therefore mechanical or chemical unions between panels are unnecessary.
- High mechanical resistance, making the panels suitable for use in floors.
- No need for hollow spaces to prevent steam condensation due to its good steam permeability.
- Few scraps when used for the typical building applications thanks to its specifically studied dimensions.
- Usable both in building and mechanical environments.
- Environmentally sustainable thanks to its composition (up to 95% recycled materials) and recyclability.

Table 16.3 gives the main properties of INSUL–ECO panels, which they are an ecofriendly product with high-power insulation and sound absorption, thermal insulation, especially in

Table 16.3 Main features of the Insul-eco panels.

Panel size	60 cm × 40 cm × 3 cm
Panel weight	3.50 kg
Density ρ	490 kg/m^3
Sound absorption UNI EN 11654:1998 αw	0.6
Sound absorption at 500 Hz UNI EN ISO 354:2003 α	0.7
Dynamic stiffness UNI EN 29052-1:1993 s't	50 MN/m^3
Specific heat Cp	1650 J/kg K
Compressive strength UNI EN 1926:2007 Rc	0.46 N/mm^2
Resistance to water vapor diffusion m	5.5
Resistance to water vapor diffusion Sd	0.16
Thermal conductivity λ	0.063 W/m^2 K
Thermal capacity C	217 Wh/m^3
Flexural strength UNI EN 12372:2007 Rtf	1.1 N/mm^2

summer heat, good mechanical resistance to compression, and high transpiration (see Table 16.3) [11].

Another advantage of the Insul-eco panels is that their versatility makes them able to be placed in walls (external or internal); in light coverings, receives the welded bituminous sheaths; in double brick wall; in double sheet metal, drywall, or wood; under any type of flooring (civil, industrial, etc.); under the wall to eliminate thermal and acoustic bridging; on timber roofing (it is very breathable and tolerates humidity); and also in hoods of engines or noisy machinery [11].

Studies so far indicate that the panels can be done with more recycled materials to be added to the mixture, finding an optimum 15% by weight of rockwool scrap. This new panel, called INSUL−ECO 15, presents the same thermal characteristics of INSUL−ECO panels, and supposedly the same acoustic ones, although further research in this area is needed [12].

In order to give a better insight to the life cycle process, a flowchart related to the innovative solution is shown in Fig. 16.7.

Currently, the fibers from tire recycling go to landfills or are burned and, in the latter case, there are few authorized plants, so the process requires long distance transportation and hence more emissions are produced [12].

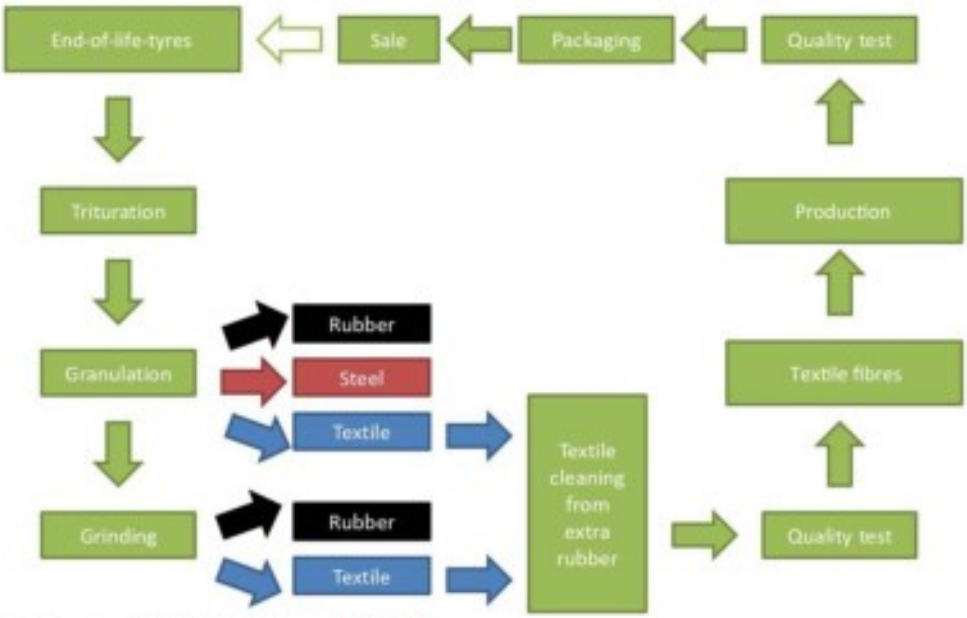


Figure 16.7 Flowchart of INSUL-ECO panels [11,12].

The use of the textile fibers in these new panel results in the following environmental benefits [11]:

- An estimated reduction of 3.6 tons CO_2 kg-eq emissions per ton of material not burned (Italian grid mix) by avoiding the burning of the textile–rubber residues.
- An estimated reduction of 4.9 tons CO_2 kg-eq per ton of recycled textile fiber used (Italian grid mix) by using a recycled material instead of virgin raw materials.
- Also, it has to be pointed out that the process to produce textile fibers panels is basically at ambient temperature and only for a short period of time does it require a temperature of 70°C, showing that an improvement in environmental performance related to the process itself is achieved. The consumption of energy could be estimated at 50 kWh/ton of textile fibers processed (including pretreatment). The CO_2-eq emissions are 27.5 kg/ton of fibers processed (considering the Italian grid mix) with an estimated chemical's CO_2-eq emission at 0.7 tons of textile fibers processed.

Comparing the INSUL–ECO emissions with the main conventional alternatives made of virgin materials such as rock wool or mineral wool panels and polystirene panels, gives a result of 1.1 ton CO_2-eq per ton (INSUL-ECO) and 3.2 ton CO_2-eq per ton (conventional alternatives), respectively, confirming the huge benefits of INSUL–ECO panels to the environment [11].

Once the panels were produced, they needed to be tested in real operational conditions to be able to demonstrate the results achieved in a controlled environment. The pilot test took place at NH Sants Hotel in the city center of Barcelona (Spain) [13].

Due to lack insulation between the rooms of the hotel, many guests complained about the noise problems. To solve this issue, and after several attempts to find a solution (e.g., asphalt fabric inside the walls), NH hotels agreed to carry out a test with INSUL-ECO panels [13].

In order to be able to make a fair assessment, acoustical measurements were taken before placing the panels, so a receiver was placed in the studied room as well as a transmitter in an adjacent room from which different frequencies were transmitted and collected [13] (see Figs. 16.8 and 16.9).

After that, the installation of the panels was carried out. It is important to mention the quick installation of the panels, which was done in less than 5 h [13] (see Fig. 16.10).

Once the installation was concluded, another acoustical measurement was taken to demonstrate the performance of the developed panels [13].

Figure 16.8 INSUL—ECO acoustical equipment.

Figure 16.9 INSUL—ECO acoustical apparatus.

Figure 16.10 INSUL–ECO on wall.

The results showed that the installation of Insul-eco panels led to a noise reduction, especially at a frequency range from 400 up to 2500 Hz, confirming the great performance of Insul-eco panels in a real operational environment [13].

16.3.10 Other applications

Currently, there are a great variety of steel fibers for SFRC that obtain optimal adhesion with concrete and, at the same time, have workability with fresh concrete. These features could also be obtained with recycled steel fibers from ELTs. Likewise, textile fibers are used for the manufacture of insulating panels for building since it is a material with low density, mechanical properties comparable to glass fibers, and porosity, which gives acoustic and thermal insulation properties. Thus the possible applications could be:

- Steel fibers as reinforcement for shotcrete (gunite)
- Thermal and acoustic insulation panels for textile fibers in buildings
- Cement-based composite materials reinforced with textile fibers

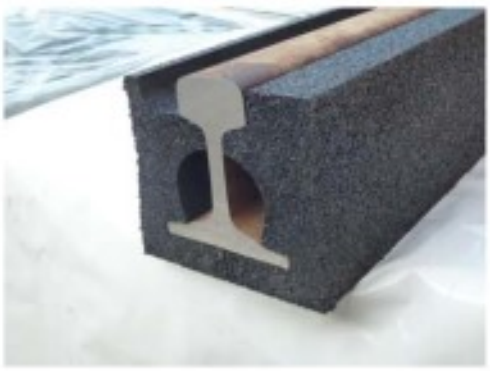


Figure 16.11 ECOTRACK profile.

Another application developed for the railway sector is Ecotrack, an isolation device for rails made from ELTs, which was designed by COMSA, GMN, and Isolgomma [14] (see Fig. 16.11).

Ecotrack was designed and tested under the framework of a European project with the same name with the goal of proving the ecoinnovative production process and the technical and market viability of a recycled rubber railway profile using end-of-life tires [15]. Finite element method simulations were carried out and a full-scale testing was implemented and monitored in a freight line at the Port of Barcelona (Spain) (see Figs. 16.12 and 16.13).

There are several environmental and economic benefits derived from the use of Ecotrack: innovative design of the profile, which reduces the production cost; reducing tons of CO_2 emissions coming from transportation costs; improvement of the environmental performance by using granulated rubber and avoiding the incineration, deposition in landfills, or spilling and their damaging impacts; better use of natural resources by saving trees since the product is made from wasted tires and by using solar energy from the photovoltaic plant, and so on [14].

Finally, another application developed is Powder-Road, which takes advantage of the use of asphalt mixtures with new binder formulations that include rubber extracted from used tires out of use. COMSA developed this project, which was aimed at obtaining road sections with more effective asphalt pavements and with better properties, reducing the thicknesses at the upper layers and thus material costs [16].

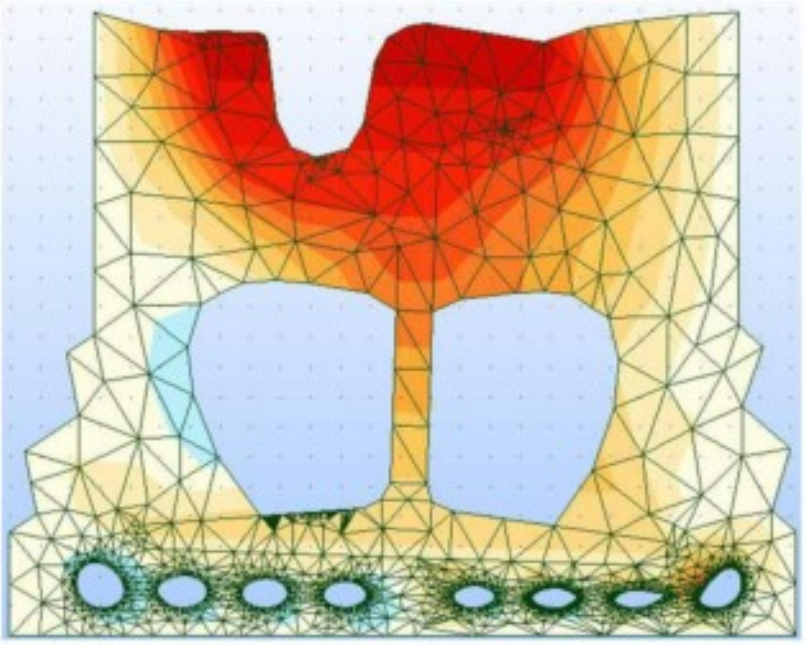


Figure 16.12 ECOTRACK FEM. *FEM*, Finite element method.

Figure 16.13 ECOTRACK rail.

16.4 Conclusions

The main purpose of this chapter was to illustrate the wide variety of possible applications in civil engineering and construction by using ELTs in ecofriendly products and hence reducing the large volume annually disposed in landfills. It has been shown that those by-product obtained from large-scale industrial waste enhance environmental benefits and mechanical properties.

Rubber particles, tire steel fibers, and tire polymer fibers from used tires can be recycled and turned into concrete, insulating sheets, ballast, asphalt mixtures, railway profiles, and so on, improving their mechanical properties (deformability, shrinkage, stiffness, abrasion resistance, stress dissipation, etc.) along with providing insulation of noise, vibrations, and temperature.

These innovative products have been tested in real operational conditions through pilot tests across Europe, refuting the myth that recycled materials mean a low-performance or a low-cost product. The resulting products are the consequence of long-term research projects in which the products were reengineered in order to optimize performance while reducing environmental impact.

There are multiples ways to reuse ELTs with great potential for even more products than those discussed here. However, further research needs to be aimed at reducing toxic and carcinogen emissions and at developing new solutions toward more sustainable urban environments.

References

[1] Neoballast Website. http://www.neoballast.eu/bbddcomun/GC/NeoBallastENG.nsf/.
[2] Neoballast Grant Agreement - 720491 - Executive Agency for Small&Medium Sized Enterprises - European Commission. https://cordis.europa.eu/project/id/720491.
[3] Via libre Técnica Website. https://www.tecnica-vialibre.es/documentos/Articulos/VLTecnica11_.
[4] Neoballast deliverable: D3.1 Design and construction of the field tests. http://www.neoballast.eu.
[5] Neoballast deliverable: D3.2. Monitoring of the field test. http://www.neoballast.eu.
[6] Neoballast deliverable: D3.3 LCCA and LCA of Neoballast. http://www.neoballast.eu.
[7] United Nation Sustainable Development Goals Website: https://sustainabledevelopment.un.org/sdgs.
[8] Horizon 2020 Spanish Website. https://eshorizonte2020.es/mas-europa/71-programa-marco.

[9] European Comssion Website. https://cordis.europa.eu/project/id/603722/reporting/es.
[10] Concrete Cover Exposure Classes. TMB Element report. www.tmbelement.ee.
[11] InsuL–eco Website. http://www.insuL–eco.eu/.
[12] INSUL-ECO Grant Agreement - ECO/13/630185. Executive Agency for Small&Medium Sized Enterprises - European Commission. https://ec.europa.eu/environment/eco-innovation/projects/en/projects/insul-eco.
[13] INSUL-ECO - ECO/13/630185. Executive Agency for Small&Medium Sized Enterprises - European Commission. Deliverable D2.2. Analysis of the pilot tests. http://www.insul-eco.eu/results/.
[14] ECO-TRACK - ECO/10/277299 - CIP Eco-innovation Programme. Final Report. https://ec.europa.eu/environment/eco-innovation/projects/en/projects/ecotrack.
[15] European Comssion Ecoinnovation Website. https://ec.europa.eu/.
[16] POWDER-ROAD. EUREKA-CDTI. Technical Report. https://www.itafec.com/downloads/ultima-generaci%C3%B3n-de-polvo-de-neum%C3%A1tico-fuera-de-uso-para-pavimentos-de-alto-rendimiento-proyecto-powder-road?lang = en.

This page intentionally left blank

17

Reuse of tire constituents in concrete

Kyriacos Neocleous[1,2], Thomaida Polydorou[1,2] and Kypros Pilakoutas[3]

[1]Department of Civil Engineering and Geomatics, Cyprus University of Technology, Limassol, Cyprus [2]ERATOSTHENES Centre of Excellence, Limassol, Cyprus [3]Department of Civil and Structural Engineering, The University of Sheffield, Sheffield, United Kingdom

17.1 Introduction

Following the successful use of recycled tire rubber particles in asphalt mixtures, researchers attempted their use in concrete in the early 1990s [1,2]. Research proceeds worldwide with a plethora of studies [3–13] on the properties, mix optimization, and applications of concrete that includes materials recycled from end-of-life tires (ELT). Initially an attempt to eliminate the health and environmental issues associated with tire accumulation, inclusion of recycled tire materials in concrete led to the development of innovative cementitious materials of unique properties. This chapter provides an overview of the developments on recycled tire material incorporation in concrete, presenting findings on the properties of the most investigated cementitious mixtures including recycled tire materials: Steel fiber-reinforced concrete, steel fiber-reinforced rubberized concrete, rubberized concrete, and textile polymer fiber-reinforced concrete.

17.2 Steel fiber-reinforced concrete

17.2.1 Tire-steel fiber properties

High-quality steel [14] is recovered from ELT in the form of short-discontinuous fibers, and this steel can be therefore used as fiber reinforcement in concrete. Steel fiber reinforcement increases concrete toughness, improves shrinkage behavior and durability of concrete, provides better crack control, enhanced surface characteristics, and lowers concrete permeability [14].

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00002-8
© 2021 Elsevier Inc. All rights reserved.

Recycled tire steel fibers (RTSF) have been proven to exhibit similar or even better performance as concrete reinforcement, compared to industrially manufactured steel fibers; the benefits include increasing concrete strength and ductility [14,15]. RTSF can be retrieved from tires through mechanical treatments (e.g., ambient temperature shredding, water jetting, and cryogenic degradation of tires) and also by anaerobic thermal degradation of tires (e.g., pyrolysis and microwave-induced pyrolysis) [15].

The properties [16] of several types of fibers retrieved from recycled tires are summarized in Table 17.1 including recycled tire cord filaments, which are made from the same material as RTSF but extracted using a cryogenic rather than mechanical treatment, and recycled tire steel cords, obtained from cutting the tire cord to lengths greater than 35 mm, thus keeping the cord intact and the individual cord filaments tangled together [16].

RTSF are an environmentally friendly alternative to industrially manufactured steel fibers; previous research [16] has shown that producing one ton of RTSF can ultimately save one ton of new steel fibers. Using RTSF instead of manufactured fibers therefore can reduce material costs of concrete mixtures and reduce CO_2 emissions resulting from steel fiber manufacturing [17]. The two main drawbacks [14] related to the use of RTSF as reinforcement in concrete are contamination and conglomeration. Steel fibers recovered from ELTs contain impurities, such as rubber and tire fluff or textile, which vary depending on the type of tire extracted from and method of extraction used, with fibers extracted through the cryogenic process having the benefit of no residual rubber and impurities [16], versus those extracted through mechanical reduction, which are highly contaminated. The second issue is encountered during mixing, as RTSF tend to conglomerate or ball together instead of spreading evenly throughout the mixture. Good concrete mix design is thus fundamental when including RTSF as reinforcement, since creating mixtures of adequate workability can be a challenge.

Table 17.1 Recycled tire steel fiber properties by type.

Fiber type	Length/(mm)	Diameter/(mm)	Tensile strength/(N/mm^2)	Shape
Unsorted RTSF	0–15 (85% of fibers)	0.1–0.4	~2500	Irregular (wavy)
Sorted RTSF, RTCF	15–40 (70% of fibers)	0.12–0.38	~2500	Irregular (wavy)
RTSC	Any	0.9	2800	Straight

RTCF, recycled tire cord filaments; *RTSC*, recycled tire steel cords; *RTSF*, recycled tire steel fibers.

Optimized fiber content is also vital, to offer adequate reinforcement without allowing too much air being entrapped in the concrete mix [15]. Fiber geometry, fiber quality, and contamination level as well as fiber distribution in a good amount of fine materials are some of the things to consider for successful mixtures [14]. RTSF geometry (length and thickness) varies depending on the process used for their extraction; for example, fibers obtained through ambient temperature mechanical tire shredding have larger diameter than those extracted from pyrolysis [15]. Classification of RTSF is now possible via photogrammetry, using specialized equipment and software, leading to CE Marking of cleaned and sorted RTSF aimed for concrete reinforcement [18]. Previous studies have assessed the mechanical performance of concrete reinforced with RTSF [15,17,19–22], validating the use of classified RTSF as concrete reinforcement.

17.2.2 Mix design process

Recycled tire steel fiber-reinforced concrete and mortar mixtures are designed for various applications, relying solely on steel fiber reinforcement from ELT tires, or partially reinforced with fibers from ELTs and partially reinforced by manufactured steel fibers or conventional reinforcement (rebars). Various mixture types can be designed, according to the final product specifications, offering conventional recycled tire steel fiber-reinforced concrete or mortar mixtures as well as self-compacting, roller-compacted, slurry-infiltrated, and sprayed fiber-reinforced concrete.

For successful mixtures with RTSF, recommendations [23,24] include fiber length-to-diameter ratio (L/d), fiber dosing, and mixing instructions.

Even though recommended mix designs are available [23], it is rather preferred that small-scale trial mixtures are developed using the particular constituents and concrete mixers, under the conditions that the final product will be made, since all these factors can affect the mixture properties. Steel fibers are added during the last phase of mixing, after the concrete mixture reaches constancy. To avoid conglomeration, steel fibers can be added using a steel fiber blowing machine to accelerate fiber integration into concrete mixtures [18].

17.2.3 Fresh concrete properties

In general, fresh concrete mixtures that include steel fiber reinforcement experience reduced workability compared to conventional concrete. In comparison to industrially manufactured

steel fibers, RTSF are of irregular geometries and thus tend to form conjunctions and also contain impurities such as rubber and textile polymer fiber or fluff, leading to further reductions in mixture workability. Their addition must be implemented carefully to avoid conglomeration and ensure even distribution of fibers throughout the concrete mixture. Providing additional cleaning and sorting of RTSF can reduce unfavorable effects on mixture workability; additional chemical admixtures, such as superplasticizer, should be added together with the RTSF to improve the reduced workability of the concrete mixture.

Another issue accompanying RTSF-reinforced concrete is surface finishing, since a large number of fibers tend to rise to the concrete surface, causing safety concerns (especially for slabs and pavements) and also ruining the material esthetic appearance. To mitigate this effect, researchers [16] recommend using 10 kg/m^2 of surface hardener, based on a comprehensive experimental study that included various types of surface hardeners.

In addition to its effects on workability and fresh concrete surface finishing, steel fiber reinforcement is shown to increase air content and unit weight of concrete [17].

17.2.4 Hardened concrete properties

Steel fiber reinforcement can enhance the hardened concrete properties of conventional concrete. An appropriate RTSF content of 40 kg/m^3 can increase the compressive strength of concrete up to 30%. A modest increase of the modulus of elasticity of concrete is also expected with the use of steel fiber reinforcement [17].

Compared to conventional concrete mixtures, concrete reinforced with RTSF is able to sustain higher stress levels and has greater endurance under the same stress. While RTSF are thinner and shorter than conventional manufactured steel fibers, they tend to have better control of microcracks. RTSF are also able to restrain micro- and mesocrack propagation, but are not as efficient as manufactured fibers in holding macrocracks together; thus, a blend of RTSF and manufactured steel fibers is ideal for hardened concrete property enhancement. It has been proven [16] that partial replacement of manufactured fibers by RTSF in concrete actually increases the flexural and tensile strength of the material, while concurrently saves new steel and reduces energy input requirements by 97%. Blends of RTSF (thinner fibers) and manufactured fibers (thicker fibers) are considered ideal in providing optimum flexural performance in steel fiber-reinforced concrete, bettering either type of fiber used alone, since the synergy provides both thin RTSF fibers,

which help control micro- and mesocracks, as well as thicker manufactured fibers that help when macrocracks appear [22]. Additionally, and considering RTSF lengths, previous research [16] has shown that to achieve satisfactory postcrack performance ($f_{R4} > 2$ MPa), a fiber length longer than 12 mm is required.

Similarly, to flexural performance, a blend of RTSF and manufactured fibers is also considered to be the optimum solution with regard to fatigue performance of fiber-reinforced concrete. The ideal RTSF content is 2% by mass of concrete [22].

Following an investigation of the punching shear behavior of steel fiber-reinforced flat slabs and footings reinforced with manufactured fibers only or blended with RTSF at various contents, it was reported [16] that by replacing 50% of manufactured fibers with RTSF, the shear capacity and deformation of flat slabs and footings is not notably affected.

Considering shrinkage, while there is no indication that RTSF have significant effects on free shrinkage, they are able to improve crack controlling or even prevent cracking under restrained conditions. Previous research [16] findings report that no cracking was observed during a 9-month period in specimens with 50% restraint.

Durability properties of concrete reinforced with RTSF are similar to those of concrete reinforced with manufactured steel fibers. Under freeze-thaw conditions, it was shown that concrete reinforced with RTSF is adequately resistant to environmental exposure class XF1 and with the addition of air entraining admixture will also have adequate resistance for environmental exposure class XF3. When tested under accelerated corrosion imposed using potentiostatic anodic polarization of specimens immersed in 3.5% NaCl, both RTSF and manufactured steel fibers showed evident corrosion [16].

17.3 Plain rubberized concrete and steel fiber-reinforced rubberized concrete

17.3.1 Rubber particle properties

Recycled tire rubber physical properties and composition vary depending on the type of tire they are extracted from as well as the method used for their extraction, while particles extracted from identical types of tires still vary between sources.

Fine rubber particles or rubber particles with size ranging between 75 μm and 4.75 mm, they are also referred to as "crumb rubber" and are used to replace fine aggregate in concrete and mortar mixtures. Similarly, coarse rubber particles replace equivalent-size coarse mineral aggregate in concrete.

17.3.2 Mix design process—plain rubberized, steel fiber-reinforced rubberized

When rubber particles are used in a concrete or mortar as aggregate replacement, the material volume is used to calculate the replacement amounts, since rubber has much lower specific gravity than mineral aggregates. Rubber particle specific gravities vary according to the type of tire they were retrieved from and the method used to recover them. It is thus advised that the specific gravity is determined [25] for a particular blend of rubber particles, intended to be used as aggregate replacement in concrete, as shown in Fig. 17.1. A suitable method for determining the specific gravity of rubber is the apparent particle density for lightweight aggregate procedure, included in EN 1097-6 [26] Standard.

Ideally, a combined replacement of fine and coarse aggregates is suggested [12,27,28] for optimized workability and strength in rubberized concrete mixtures, especially mixtures of high rubber content. For a successful mixture, a sample of the rubber particle blend to be used should be tested for both specific gravity and water absorption potential, before proceeding with mix design calculations.

Even though rubber particles are hydrophobic themselves, water is retained by a blend of rubber particles, due to the

Figure 17.1 Measuring the apparent particle density by EN 1097-6: 2013.

Figure 17.2 Water absorption of lightweight aggregate test by EN 1097-6: 2013.

impurities they might contain. To account for this effect, it is advised that a sample of the rubber particle blend intended for use as aggregate replacement in a concrete mix should be tested for water absorbability [25], as shown in Fig. 17.2. Since there are no testing methods approved for rubber particles, a suggested method for determining the water absorption potential of a sample of rubber particles is the European Standard method for water absorption of lightweight aggregate, as described by EN 1097-6 [26].

Following a successful mix design there is still one issue faced during mixing and casting rubberized concrete specimens. Specifically, rubber particles tend to rise to the surface of the fresh rubberized concrete mixture, while the mineral aggregates drop to the bottom, due to their dissimilar specific gravities. It is rather difficult to maintain a uniform distribution of the combined mineral and rubber aggregates in rubberized concrete specimens, thus alternative casting procedures or even consolidation techniques should be considered to alleviate this effect.

An example-mix design procedure for rubberized concrete with 60% combined fine and coarse aggregate replacement by equivalent-size rubber particles follows, based on given conventional concrete mix design.

Box 1.1 Aggregate replacement calculation example

Assume the conventional concrete mixture includes 1000 kg/m^3 of mineral aggregate, ρ_{water} = 997 kg/m^3, and the following aggregate specific gravities:

Rubber particle specific gravity = 0.955

Mineral aggregate specific gravity = 2.65

Equivalent volume of 1000 kg of mineral aggregate = (1000 kg)/2.65 × (997 kg/m^3) = 0.3785 m^3

Volume to be replaced = 0.6 × 0.3785 m^3 = 0.2271 m^3

Equivalent mass of rubber needed for replacing 0.2271 m^3 of mineral aggregate = 0.2271 m^3 × 0.955 × (997 kg/m^3) = 216.23 kg, therefore for a 60% replacement in this mix design, a rubber content of 216.23 kg/m^3 is required.

Mass of mineral aggregate to be used in rubberized concrete mixture (40% of mineral aggregate used in conventional concrete mixture) = 0.4 × 1000 = 400 kg/m^3

Water content adjustments (due to aggregate water absorption) should also be considered as a result of adjusting the aggregate content. The amount of water absorbed by the rubber particle sample tested by EN 1097-6: 2013 should be considered in addition to the absorption of mineral aggregates, to avoid resulting in an unworkable mixture.

17.3.3 Fresh concrete properties

In general, researchers [12,29–32] report reduction in workability of concrete mixtures when aggregate is replaced by rubber particles.

Only in a few cases it was reported that concrete workability improves with the inclusion of rubber particles; previous research findings [33] proclaim an increase in concrete workability in mixtures where up to 15% of the fine aggregate are replaced with fine rubber particles. Likewise, in dry mix roller compacted concrete, better consistency was observed with increasing fine aggregate replacement [34].

Findings have also led to the proposition [35] that a more appropriate procedure should be developed to evaluate rubberized concrete mixture workability, instead of using the traditional slump method, generated particularly for conventional concrete.

Fresh concrete unit weight decreases [33,36,37] with increasing rubber content, as expected, due to the much lower unit weight of rubber particles, compared to the unit weight of mineral aggregate they replace in a mixture. Rubberized concrete is therefore used as lightweight concrete.

Due to their hydrophobicity [38], rubber particles tend to repel water during concrete mixing and therefore entrap air on the surfaces [6,33]. Due to this effect, the air content of rubberized concrete mixtures is generally higher [33] compared to conventional concrete mixtures, resulting also in further reduction in unit weight [33,39,40].

It was also observed that inclusion of rubber particles has the ability to increase concrete setting time; the higher the rubber content percentage, the longer the setting time [41].

As far as rheological properties are concerned, previous research [42] results show that replacing mineral aggregate with rubber particles, which are not as spherical, results in higher applied torques, compared to conventional concrete being tested at identical rotational speed. Torque values increase with increasing rubber content, as well as with greater rubber particles sizes, indicating shear thickening [42], meaning that with increasing shear, the mix experiences an increase in apparent viscosity. To prepare workable rubberized concrete mixtures, the use of fly ash [41] as a binder is recommended. In addition, researchers [42] suggest that rubberized concrete mixing is performed under high shear rates.

When steel fibers are added, workability of rubberized concrete is further reduced.

Steel fibers are added to rubberized concrete mixtures during the last stage of mixing, just like in nonrubberized mixtures discussed in the preceding paragraphs. Addition of steel fibers results not only in decreased workability but also, as expected, increased air content and marginally increased unit weight of rubberized concrete [16].

17.3.4 Hardened concrete properties

Overall, rubberized concrete mixtures have lower hardened concrete densities compared to conventional concrete. As expected, hardened density of the material decreases with increasing rubber content.

In addition to hardened density, both static and dynamic moduli of elasticity of concrete decrease [43] with increasing rubber content. Research has also revealed that when coarser rubber particles are used, the elastic modulus is reduced to a greater extent compared to using equal volume of finer rubber particles [27].

Due to the low stiffness of the rubber aggregates, thus lower elastic modulus of rubberized concrete, the material attains the advantage of reduced thermal and shrinkage stresses [27],

increasing resistance to shrinkage cracking [44], while rubberized concrete was observed to experience drying shrinkage [45] to a higher extent, compared to conventional concrete. Creep strains, on the other hand, are much higher in rubberized concrete as expected due to lower aggregate stiffness [46,47].

Hardened concrete that includes rubber particles in replacement of the mixture's mineral aggregates exhibits different behavior compared to conventional concrete. Most interestingly, it is observed that when rubberized concrete is loaded to failure, cracks and discontinuities propagate gradually and uniformly in rubberized concrete specimens, in contrast to conventional concrete specimens, where failure is concentrated at one point and propagates suddenly. Similarly, hardened rubberized concrete specimens will undergo larger deformations compared to corresponding plain concrete specimens, which is explained by the ability of recycled tire rubber particles to decrease the internal friction among concrete elements due to their flexibility, thus allowing the recovery of extra strain [33].

The greatest drawback of the material is the decrease in compressive strength with increasing rubber content, observed throughout the years by researchers from around the world [27,38,48,49], not only due to the lower density of rubber compared to mineral aggregate, but also because of the weak interfacial transition zone (ITZ) [12] observed in rubberized concrete. The weak ITZ, which leads to great reduction in rubberized concrete compressive strength, is caused by the poor adhesion of rubber to cementitious paste, which is further justified by the hydrophobicity of rubber. The mechanism is explained by the tendency of hydrophobic material to repel water and liquids, thus in rubberized concrete, instead of rubber particles blending within in a fresh concrete mixture, air bubbles are formed on rubber surfaces, creating a weak zone, the ITZ. Recent findings [38] reveal that turning rubber particle surfaces into hydrophilic can improve mixing action, thus reducing the formation of air bubbles and therefore the air content throughout the mixture, but most importantly around the surface of rubber aggregate, thus significantly improving the compressive strength of rubberized concrete. Even though repeatability testing is recommended, the proof-of-concept study [38] achieved a compressive strength increase of over 200% by simply treating rubber particle surfaces with waste quarry dust paste. The pretreatment technique [38] is very promising in improving the compressive strength of rubberized concrete, which is actually the material property that suffers most by the inclusion of rubber particles.

In terms of tensile performance, rubberized concrete mixtures perform considerably worse than conventional concrete. The lower tensile strength performance is also explained by the weak ITZ [27]. To counteract this negative effect, researchers [50] suggest hybrid construction, providing a second layer beneath the rubberized concrete, made of conventional concrete.

Similarly, with compressive and tensile strength, flexural strength of rubberized concrete follows a reduction trend with increasing rubber content. On a positive note, it is observed that unlike conventional concrete, which tends to experience brittle failure under flexural loading, rubberized concrete failure does not happen suddenly [27]. To further improve the material behavior under flexure and increase its cracking resistance, researchers recommend the use of steel fibers [51,52].

Steel fiber reinforcement has similar effects on rubberized concrete as it does on conventional concrete. When rubberized concrete is reinforced with steel fibers, its mechanical properties are enhanced. The material compressive strength can be increased up to 12.5%, while the modulus of elasticity also increases by up to 28.4%. Most importantly, incorporation of fiber reinforcement (industrial fibres (IF), RTSF, or a blend of both) in rubberized concrete can considerably counterbalance the loss of flexural strength caused by the presence of rubber (i.e., a loss of 50% compared to conventional concrete can be reduced to a loss of 9.6% when steel fiber reinforcement is provided). In addition, rubberized concrete mixtures, significantly superior due to the presence of rubber particles in regards to these properties, can further enhance their strain capacities and postpeak energy absorption by incorporation of steel fibers.

As far as other hardened properties are concerned, remarks agree that with inclusion of rubber particles, ductility of concrete is increased and compressive strain control capacity is enhanced [39,53–55]. It was observed that greater enhancement of ductility and strain capacity was achieved by a combined replacement of both fine and coarse aggregate [28] by equivalent size rubber particles. Therefore with increasing rubber content concrete exhibits improved impact energy absorption capacity, greater damping ratios, and higher fracture energy values and thus increased toughness index. Rubberized concrete also performs better compared to conventional concrete under fatigue loading, with superior abrasion resistance, freeze-thaw resistance, resistance to chloride ion penetration, electrical resistivity, and sound absorption. In comparison to plain or conventional concrete mixtures, rubberized concretes experience greater water permeability and water absorption. In addition, with increasing rubber content, concrete exhibits lower

thermal conductivity and thus greater thermal insulation, but the material's fire resistance diminishes [27].

17.4 Textile fiber-reinforced rubberized concrete

17.4.1 Textile fiber properties

High-quality and strength textile fibers are obtained through the tire shredding process. Polymer textile fibers such as aramid, rayon, nylon, and polyester cords are used as reinforcement in tires. All these textile fibers break down and expand into fluff (gray colored fiber agglomerates) during the tire shredding process [16]. Recycled tire polymer fibers (RTPF) are too tangled to be used in concrete directly after they are extracted from tires, and as expected, they are also heavily contaminated with residual rubber particles, thus cleaning systems and equipment for successful integration and dispersal of the polymer fibers into fresh concrete are required. The process requires less than 2 kWh/ton of energy and can replace equivalent amounts of new polymer fibers, which are currently produced from petrochemicals [16]. RTPF are primarily used in concrete for controlling crack development due to plastic shrinkage, as well as explosive spalling caused by fire. RTPF cover a wide range of diameters ranging from 10.0 to 38.0 μm prior to cleaning, and 8.0 to 38.0 μm for cleaned RTPF, and as researchers [56] report, more than 80% of RTPF are found to be shorter than 12 mm.

17.4.2 Mixing procedure

Incorporation of RTPF into fresh concrete requires a vibrating machine to untangle the fibers and a blower to aid in carrying the fibers directly into the concrete mixer via pipes. Depending on the intended mixture application, RTPF content is adjusted; for example, 1 kg/m^3 of RTPF is suggested for controlling early-age cracking in concrete [56].

17.4.3 Fresh concrete properties

Concrete mixture workability was found to decrease with higher RTPF content, especially when RTPF are used without contamination removal [16]. In contrast, workability was observed not to be affected by RTPF contaminants [56], since the use of equivalent dosage of cleaned RTPF reflected similar reduction in workability

as that of contaminated RTPF. Low dosage of RTPF (e.g., 1 kg/m^3) did not have significant effects on mixture workability [56]. In addition to reducing workability, RTPF incorporation increases the air content of a concrete mix [16]. Fresh concrete air content increased up to 4.6% with the addition of various types of RTPF at various contents, while the corresponding conventional concrete mix had an air content of 1.7% [56]. Mixture air content increases further when rubber contamination is not removed from RTPF [56]; this is explained by the fact that residual rubber particles on RTPF entrap air during fresh concrete mixing due to their hydrophobic nature.

With regard to heat of hydration, previous research [56] has concluded that inclusion of RTPF in fresh concrete does not affect the liberated heat of hydration of concrete mixtures.

17.4.4 Hardened concrete properties

In general, addition of sorted RTPF at low dosage (e.g., 5 kg/m^3) was not found to affect compressive strength and modulus of elasticity of concrete, but at dosages greater than 10 kg/m^3 caused compressive strength and modulus of elasticity reduction, linked to the higher air content of the fresh mixtures [16]. The modulus of elasticity of concrete was reduced up to 7% when a dosage of 15 kg/m^3 RTPF was included in the mix. Similarly, a decrease in compressive strength of up to 25% was observed in concrete mixtures reinforced with noncleaned RTPF, attributed to both higher air contents and RTPF contamination by rubber particles [56].

With inclusion of high RTPF dosages, a decrease in density of concrete up to 5.5% was observed, while when added in lower dosages, ranging between 1 and 15 kg/m^3, or equivalent of 1% aggregate replacement by weight, RTPF incorporation did not affect concrete density [56].

The shrinkage behavior of concrete reinforced with mixed RTPF and sorted RTPF at different dosages was compared to that of conventional concrete in an experimental investigation, where early deformability properties such as autogenous deformations, total shrinkage, and retained shrinkage of concrete samples were measured. It was observed that both mixed and sorted RTPF were able to reduce early-age deformation of concrete significantly. The results indicated that both mixed and sorted RTPF added in either dosage (i.e., 1 and 5 kg/m^3) reduced autogenous deformation compared to conventional concrete, but no conclusions were made with regard to total shrinkage during the drying phase, since there was no observation of effects on the total shrinkage, even though significant effects on restrained shrinkage

were observed. Researchers concluded that substitution of monofilament fibers by mixed RTPF was able to increase the tensile stresses withstood by concrete prior to cracking [16].

In self-compacting concrete, an autogenous shrinkage reduction of more than 47% was observed with the inclusion of RTPF. Similarly, for sprayed concrete, addition of RTPF reduced autogenous shrinkage by 35%, increased the capacity of the material to withstand stresses induced by restrained shrinkage, and increased the tensile stresses withstood prior to cracking by up to 116% compared to conventional concrete. In RTSF-reinforced screeds tested for plastic and restrained shrinkage, it was shown that addition of 0.9 kg/m^3 of sorted RTPF is able to alleviate early-age plastic concrete cracking [16].

In agreement with these findings, researchers [56] have indicated the decreased early-age shrinkage in concrete mixtures reinforced with RTPF, is explained by the ability of RTPF to positively influence stress distribution in young concrete and thus lower shrinkage strains, due to the fact that RTPF and young concrete share similar moduli of elasticity. In addition, the presence of higher dosages of RTPF in concrete, by absorbing water during mixing, allows for water to be available during later stages of curing, instead of being released during initial swelling of concrete, a mechanism known to dictate autogenous shrinkage [56]. Based on experimental testing [56], RTPF can certainly reduce early-age deformations, while a content of 1–2 kg/m^3 of cleaned RTPF is suggested as optimum in term of this property.

With regard to durability properties, RTPF at low dosages have been proven to enhance concrete resistance to fluid penetration, but no significant effect was observed in terms of water permeability, gas permeability, and chloride diffusion. Another significant finding was the fact that concrete including RTPF met the criteria for both XF2 and XF4 exposure classes for resistance to freeze-thaw with deicing salts, without air entraining admixtures. In addition, concrete with RTPF without air entraining is able to withstand environmental conditions described by exposure classes XF1 and XF3 regarding freeze-thaw resistance with no chlorides [16]. Reinforcement with RTPF contaminated with rubber particles has proven to be better than cleaned RTPF with regard to increasing concrete freeze-thaw resistance [56].

In addition to its excellent durability, concrete reinforced with RTPF has shown exceptional performance under fire-induced loads. In previous research [16], the fire-spalling behavior of conventional concrete and RTPF-reinforced concrete slabs was assessed, by exposing the samples to the ISO fire curve. Severe spalling was observed in all three conventional concrete samples, with

spalling time recorded for each specimen, ranging between 9 and 11 minutes for the three samples. Interestingly, the samples reinforced with 2 kg/m^3 RTPF did not experience spalling, indicating the strong potential of RTPF to prevent fire-induced spalling in concrete [16]. In general, RTPF are an ecofriendly alternative to monofilament polypropylene fibers, providing equal or greater property enhancement with regard to concrete early-age behavior, freeze-thaw resistance, and performance under fire-induced loading.

References

[1] M. Heitzman, Design and Construction of Asphalt Paving Materials with Crumb Rubber Modifier, 1992.

[2] İ. Topçu, Y. Özçelikörs, Lastik Agregalı Beton, in: Proceedings of the Akdeniz Üniversitesi, Mühendislik Fakültesi, VII. Mühendislik Haftası, At Isparta, Turkey, 1992.

[3] N.N. Eldin, A.B. Senouci, Rubber-tire particles as concrete aggregate, J. Mater. Civ. Eng. (1993).

[4] D. Raghavan, H. Huynh, C.F. Ferraris, Workability, mechanical properties, and chemical stability of a recycled tire rubber-filled cementitious composite, J. Mater. Sci. 33 (1998) 1745–1752.

[5] R. Garcia, I. Hajirasouliha, K. Pilakoutas, Novel applications of rubberised concrete in RC structures located in seismic regions, in: Proceedings of the Second European Conference on Earthquake Engineering and Seismology, Istanbul. Aug. (2014) 25–29.

[6] Z.K. Khatib, F.M. Bayomy, Rubberized Portland cement concrete, J. Mater. Civ. Eng. (1999).

[7] R. Siddique, T.R. Naik, Properties of concrete containing scrap-tire rubber—an overview, Waste Manage. (2004).

[8] A. Turatsinze, S. Bonnet, J.L. Granju, Potential of rubber aggregates to modify properties of cement based-mortars: improvement in cracking shrinkage resistance, Constr. Build. Mater. 21 (2007) 176–181.

[9] M. Turki, E. Bretagne, M.J. Rouis, M. Quéneudec, Microstructure, physical and mechanical properties of mortar-rubber aggregates mixtures, Constr. Build. Mater. (2009).

[10] B.S. Thomas, R.C. Gupta, P. Kalla, L. Cseteneyi, Strength, abrasion and permeation characteristics of cement concrete containing discarded rubber fine aggregates, Constr. Build. Mater. (2014).

[11] B.S. Thomas, R.C. Gupta, A comprehensive review on the applications of waste tire rubber in cement concrete, Renew. Sustain. Energy Rev. (2016).

[12] E.O. Momoh, M. Emmanuel Owoichoechi, K. Pilakoutas, Highly deformable reinforced concrete elements for sesmic design of reinforced concrete structures, Int. J. Eng. Res. Appl. 7 (2017) 14–20. Available from: http://www.ijera.com.

[13] S. Raffoul, R. Garcia, K. Pilakoutas, M. Guadagnini, N.F. Medina, Optimisation of rubberised concrete with high rubber content: an experimental investigation, Constr. Build. Mater. 124 (2016).

[14] K. Pilakoutas, R. Strube, Re-use of tyres fibres in concrete, Recycling and Reuse of Used Tyres, Thomas Telford Publishing, 2001, pp. 225–236. ISBN 978-0-7277-4899-7.

[15] K. Pilakoutas, K. Neocleous, H. Tlemat, Reuse of tyre steel fibres as concrete reinforcement, Eng. Sustain. 157 (2004) 131–138.
[16] K. Pilakoutas, Anagennisi—Innovative Reuse of all Tyre Components in Concrete, 2017.
[17] A. Alsaif, L. Koutas, S.A. Bernal, M. Guadagnini, K. Pilakoutas, Mechanical performance of steel fibre reinforced rubberised concrete for flexible concrete pavements, Constr. Build. Mater. (2018).
[18] H. Angelakopoulos. No Title, 2020.
[19] K. Neocleous, H. Angelakopoulos, K. Pilakoutas, M. Guadagnini, Fibre-reinforced roller-compacted concrete transport pavements, ICE Proc. Transp. 164 (2011) 97–109.
[20] H. Tlemat, K. Pilakoutas, K. Neocleous, Stress-strain characteristic of SFRC using recycled fibres, Mater. Struct. 39 (2006) 365–377.
[21] M.A. Aiello, F. Leuzzi, Waste tyre rubberized concrete: properties at fresh and hardened state, Waste Manage. (2010).
[22] A.G. Graeff, K. Pilakoutas, K. Neocleous, M.V.N.N. Peres, Fatigue resistance and cracking mechanism of concrete pavements reinforced with recycled steel fibres recovered from post-consumer tyres, Eng. Struct. (2012).
[23] Pilakoutas et al., US7267873B2.
[24] TWINCON LTD Technical Data Sheet Product: Reused Tyre Steel Fibre (RTSF).
[25] T. Polydorou, K. Neocleous, R. Illampas, N. Kyriakides, A. Alsaif, C. Chrysostomou, K. Pilakoutas, D. Hadjimitsis, Steel fibre-reinforced rubberised concrete barriers as forgiving infrastructure. The International Federation for Structural Concrete 5th International fib Congress, Issue 7-11 (2018), (Accessed October 2018).
[26] CEN (European Commitee for Standardization) EN 1097-6: 2013. Tests for mechanical and physical properties of aggregates—Part 6: Determination of particle density and water absorption, 2013.
[27] A. Siddika, M.A.A. Mamun, R. Alyousef, Y.H.M. Amran, F. Aslani, H. Alabduljabbar, Properties and utilizations of waste tire rubber in concrete: a review, Constr. Build. Mater. (2019).
[28] M. Gesoglu, E. Güneyisi, O. Hansu, S. Ipek, D.S. Asaad, Influence of waste rubber utilization on the fracture and steel-concrete bond strength properties of concrete, Constr. Build. Mater. 101 (2015) 1113–1121.
[29] M.K. Batayneh, I. Marie, I. Asi, Promoting the use of crumb rubber concrete in developing countries, Waste Manage. 28 (2008) 2171–2176.
[30] H. Su, J. Yang, T.C. Ling, G.S. Ghataora, S. Dirar, Properties of concrete prepared with waste tyre rubber particles of uniform and varying sizes, J. Clean. Prod. 91 (2015) 288–296.
[31] A.A. Gheni, J.J. Myers, M.A.E. Mechanical Characterization of Concrete Masonry Units Manufactured with Crumb Rubber Aggregate. ACI Mater. J. 114.
[32] V. Corinaldesi, J. Donnini, 4-Waste rubber aggregates, in: Woodhead Publishing Series in Civil and Structural Engineering; de Brito, J., Agrela, F.B.T.-N.T. in E. and R.C. (Eds.), Woodhead Publishing, 2019, pp. 87–119. ISBN 978-0-08-102480-5.
[33] A.R. Khaloo, M. Dehestani, P. Rahmatabadi, Mechanical properties of concrete containing a high volume of tire-rubber particles, Waste Manage. (2008).
[34] A. Meddah, M. Beddar, A. Bali, Use of shredded rubber tire aggregates for roller compacted concrete pavement, J. Clean. Prod. 72 (2014) 187–192.
[35] N.N. Eldin, A.B. Senouci, Measurement and prediction of the strength of rubberized concrete, Cem. Concr. Compos. 16 (1994) 287–298.

[36] R. Hassanli, O. Youssf, J.E. Mills, Experimental investigations of reinforced rubberized concrete structural members, J. Build. Eng. (2017).
[37] M. Gesoğlu, E. Güneyisi, Strength development and chloride penetration in rubberized concretes with and without silica fume, Mater. Struct. 40 (2007) 953–964.
[38] T. Polydorou, G. Constantinides, K. Neocleous, N. Kyriakides, L. Koutsokeras, C. Chrysostomou, et al., Effects of pre-treatment using waste quarry dust on the adherence of recycled tyre rubber particles to cementitious paste in rubberised concrete, Constr. Build. Mater. 254 (2020) 119325.
[39] L. Li, S. Ruan, L. Zeng, Mechanical properties and constitutive equations of concrete containing a low volume of tire rubber particles, Constr. Build. Mater. (2014).
[40] B.S. Thomas, R.C. Gupta, P. Mehra, S. Kumar, Performance of high strength rubberized concrete in aggressive environment, Constr. Build. Mater. (2015).
[41] E. Güneyisi, Fresh properties of self-compacting rubberized concrete incorporated with fly ash, Mater. Struct. 43 (2010) 1037–1048.
[42] E. Güneyisi, M. Gesoglu, N. Naji, S. Ipek, Evaluation of the rheological behavior of fresh self-compacting rubberized concrete by using the Herschel-Bulkley and modified Bingham models, Arch. Civ. Mech. Eng. (2016).
[43] L. Zheng, X. Sharon Huo, Y. Yuan, Strength, modulus of elasticity, and brittleness index of rubberized concrete, J. Mater. Civ. Eng. 20 (2008) 692–699.
[44] J. Kang, Y. Jiang, Improvement of cracking-resistance and flexural behavior of cement-based materials by addition of rubber particles, J. Wuhan Univ. Technol. Mater. Sci. Ed. 23 (2008) 579–583.
[45] I. Mohammadi, H. Khabbaz, Shrinkage performance of crumb rubber concrete (CRC) prepared by water-soaking treatment method for rigid pavements, Cem. Concr. Compos., 62, 2015, pp. 106–116.
[46] M. Adamu, B.S. Mohammed, M.S. Liew, Effect of crumb rubber and nano silica on the creep and drying shrinkage of roller compacted concrete pavement, Int. J. GEOMATE 15 (2018) 58–65.
[47] D.V. Bompa, A.Y. Elghazouli, Creep properties of recycled tyre rubber concrete, Constr. Build. Mater. 209 (2019) 126–134.
[48] E. Güneyisi, M. Gesoğlu, T. Özturan, Properties of rubberized concretes containing silica fume, Cem. Concr. Res. 34 (2004).
[49] M.M. Reda Taha, A.S. El-Dieb, M.A. Abd El-Wahab, M.E. Abdel-Hameed, Mechanical, fracture, and microstructural investigations of rubber concrete, J. Mater. Civ. Eng. 20 (2008) 640–649.
[50] M.M. Al-Tayeb, B.H. Abu Bakar, H.M. Akil, H. Ismail, Performance of Rubberized and hybrid rubberized concrete structures under static and impact load conditions, Exp. Mech. (2013).
[51] A. Turatsinze, J.L. Granju, S. Bonnet, Positive synergy between steel-fibres and rubber aggregates: effect on the resistance of cement-based mortars to shrinkage cracking, Cem. Concr. Res. 36 (2006).
[52] Y. Park, A. Abolmaali, M. Mohammadagha, S. Lee, Flexural characteristic of rubberized hybrid concrete reinforced with steel and synthetic fibers, Adv. Civ. Eng. Mater. 3 (2014) 495–508.
[53] A.M. Rashad, A comprehensive overview about recycling rubber as fine aggregate replacement in traditional cementitious materials, Int. J. Sustain. Built Environ. (2016).
[54] K.B. Najim, M.R. Hall, Mechanical and dynamic properties of self-compacting crumb rubber modified concrete, Constr. Build. Mater. (2012).

[55] A.T. Noaman, B.H. Abu Bakar, H.M. Akil, Experimental investigation on compression toughness of rubberized steel fibre concrete, Constr. Build. Mater. (2016).
[56] A. Baričević, M. Jelčić Rukavina, M. Pezer, N. Štirmer, Influence of recycled tire polymer fibers on concrete properties, Cem. Concr. Compos. 91 (2018) 29–41.

18

Tire-derived aggregate applications in civil engineering

Armen Amirkhanian and Eleanor Skelton
The University of Alabama, Tuscaloosa, AL, United States

18.1 Introduction

As resources become more and more scarce and waste becomes a more and more pervasive problem, the reality of how the cradle-to-grave system can be destructive to society becomes more and more glaring. One example of such a problem is in the disposal of waste tires. In the United States alone, between 200 million and 300 million waste tires are generated each year and disposing of these tires is becoming an increasingly great burden on society. Whole tires when disposed of in dump sites or dumped illegally provide a breeding ground for harmful mosquito populations, present a highly volatile fire risk, and contain many harmful chemicals that can be released by uncontrolled burning. This has brought about incentives, both moral and monetary, for the shredding and processing of whole tires to produce a more manageable and safe form for this waste material. Tire-derived aggregate (TDA) has been used in a variety of civil engineering projects. In general, TDA is scrap tire that has been processed to a size between 12 and 305 mm. Such sizes are typically generated in one to two passes through the shredding process, and often the creation of TDA does not require removal of the belts. This differs significantly from granulated rubber derived from tires and used in other civil engineering applications, such as rubber modification of asphalt binders, mainly due to the size of particles used. Additionally, other requirements for TDA, such as exposed steel, are governed by ASTM D6270.

Some of the common applications of TDA include retaining wall backfill, engineered fill for embankments, vibration reduction for rail lines, and cover and drainage for landfills, among others. The vast majority of TDA usage is in backfill and embankment

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00016-8
© 2021 Elsevier Inc. All rights reserved.

applications. These applications benefit the most from the unique lightweight properties of TDA, and the large volumes required make the environmental impact substantial.

In the construction of a retaining wall, the backfill material has a great impact on the behavior and proper functioning of the structure. In some areas, seismic loading may complicate the normal behavioral expectations of such structures, and the structure and backfill must be designed to handle seismic loading without compromising safety and performance. Typically, a coarse-grained sand or gravel is used because these materials have high permeability even when compacted, which alleviates excess pore water pressure behind the wall. TDA has been shown as an alternative to these fills that offers similar permeability characteristics and shear strength properties alongside lower costs for materials and construction and lower demands on wall structures (period). However, the use of TDA as a backfill material does require some scrutiny of their suitability in this application based on material properties, material quality and variability, environmental compatibility, and other factors.

The usage of TDA for embankment fill, retaining wall backfill, and subgrades has been driven primarily by the lower unit weight of the TDA as compared to traditional soil fill. When poor quality soils are encountered, the overburden pressure exerted by the additional fill can lead to intolerable levels of settlement. TDA is cheaper than other lightweight fills (e.g., expanded polystyrene geofoam). Additionally, when TDA is used, standard construction equipment can be used to grade the site with little modification to standard construction processes. Some of the pertinent material properties for retaining wall designs are shown in Table 18.1.

18.2 Retaining walls and bridge abutments

When the backfill for retaining walls and bridge abutments consists of a lower unit weight material such as TDA, the risks of overturning, sliding, and strength failures are reduced and a less intense design is required for the same criteria and application. The lower overall mass also results in lower seismic loads when compared with traditional soil fill. In addition, the reduced unit weight of TDA is helpful in working with sensitive bearing soil which are soft or demonstrate excessive settlement. In one study, the use of TDA reduced the volume of backfill required and reduced the dimensions of the retaining structures required to meet structural and geotechnical standards [1].

Table 18.1 Review of geotechnical properties of shredded tires from literature.

Ref.	Nominal size (mm)	Unit weight (kN/m^3)	Friction angle (°)	Cohesion (kPa)	Elastic modulus (MPa)	Poisson's Ratio
[1]	12.5	5.5–5.9	27	7.0	–	–
[2]	16	6.7–7.4	30	–	–	0.33
[3]	50	6.3	21	17.5	3.4	–
[4]	50	6.3	15	0.4	–	–
[4]	50–100	7.3	32	0.4	–	–
[4]	100–200	6.5	27	0.4	–	–
[4]	200–300	6.3	29	0.3	–	–
[5]	50–300	5.9–6.9	19–25	8–11	1.1	0.30
[6]	38	6.1	25	8.6	0.8	0.32
[6]	51	6.3	21	7.7	1.1	0.28
[6]	76	6.1	19	11.5	1.1	0.20
[7]	10	5.7	32	0	1.1	0.28
[8]	152–305	7.9	27	9.3	–	–

In another study, researchers investigated the use of TDA as a replacement for conventional road embankment fill in an area with boggy soil [5]. The type of soil present in the area was expected to experience excessive settlement if conventional backfill were used. Measures typically required to improve the soil structure for road construction include applying a thick layer of base material capable of reducing stress on underlying soil, but the weight of this layer would be sufficient to produce undesirable settlement [5].

The unique particle shape and density of TDA also requires a modification of the active earth pressure coefficient used in retaining wall design calculations.

Retaining walls without sloping wall faces or sloping backfill have active earth pressure coefficients ranging from 0.49 to 0.27 with friction angles between 20 and 35 degrees, respectively. Following this Rankine model for TDA with a friction angle of 19° would yield an active earth pressure coefficient of 0.51. However, when tested, it was found that a TDA aggregate will have a much lower active earth pressure coefficient than calculated. In the aforementioned example, the measured active earth pressure coefficient was found to be around 0.23 instead of 0.51 [9]. Others have shown similar results with laboratory-scale and full-scale instrumented walls [10–12]. This can present a problem for the

design engineer as standard methods to calculate sliding forces and overturning moments will be overly conservative.

There have been several studies examining the earthquake resilience of TDA backfilled retaining walls. In one study, a large-scale test was conducted on retaining walls with and without TDA backfill [13]. Generally, the TDA backfilled walls experienced more lateral displacement but lower dynamic pressures (Fig. 18.1).

Another study examined the factors that affect the earthquake resilience of a TDA backfilled retaining walls using a series of finite element models [14]. A single cantilevered wall design was developed based on mean TDA properties from the literature and a project location in El Centro, California (Fig. 18.2). This

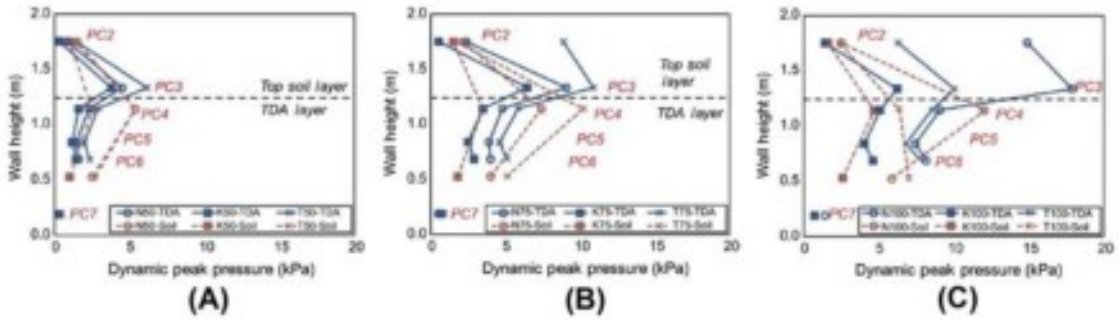


Figure 18.1 Comparison of peak dynamic pressures on the retaining wall under three different earthquake profiles (N: Northridge, K: Kocaeli, T: Takatori) at three levels of intensity shown: (A) 50%, (B) 75%, and (C) 100%. From I.S. Ahn, L. Cheng, Tire derived aggregate for retaining wall backfill under earthquake loading, Constr. Build. Mater. 57 (2014), 105–116. doi:10.1016/j.conbuildmat.2014.01.091.

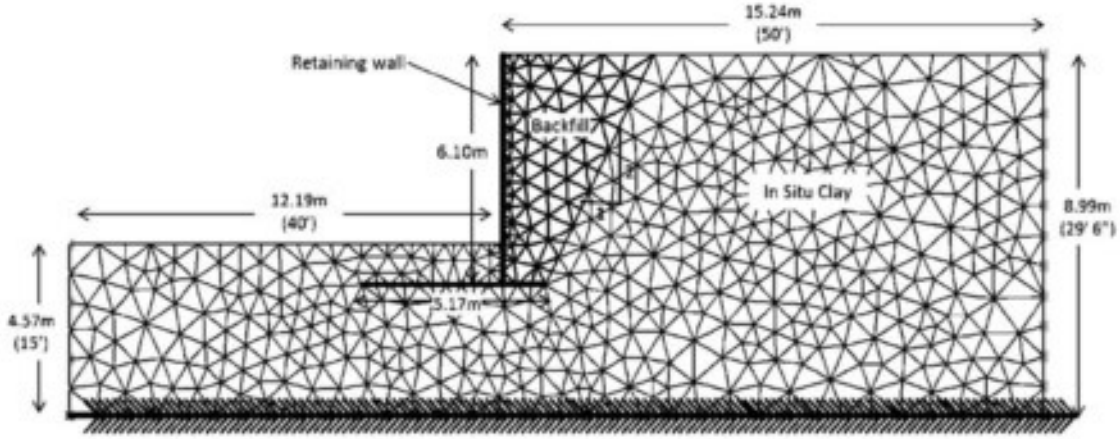
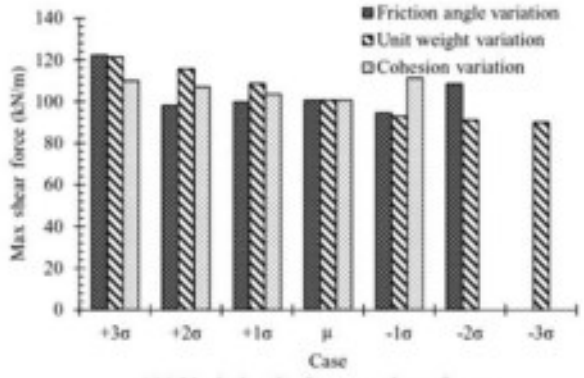


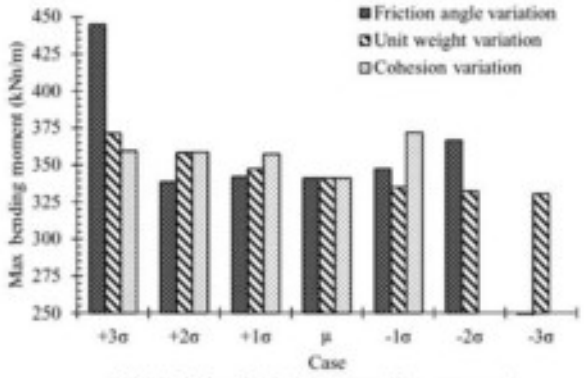
Figure 18.2 Finite element mesh used for all modeling analyses. From E. Huggins, Numerical and Reliability Analysis of Gravity Cantilever Re- taining Walls Backfilled with Shredded Tires Subjected to Seismic Loads (M.S. thesis), Clemson University, 2012.

model was subjected to an applied acceleration time history from the 1940 El Centro Earthquake. The friction angle, unit weight, and cohesion of the TDA backfill were all varied. The baseline case represented the average, μ, of the properties as reported in the literature (Table 18.1). The properties were changed up to three standard deviations, σ, away from the average to examine the sensitivity of each property (Fig. 18.3).

The friction angle when at three standard deviations above the mean showed the most dramatic increase in the shear force and bending moments. An absence of cohesion also showed a more marked increase in both shear force and bending moments in the wall. Otherwise, all shear force and bending



(A) Variation in the max shear force



(B) Variation in the max bending moment

Figure 18.3 Variation in the maximum shear force (A) and bending moments (B) as a function of material property changes. From E. Huggins, Numerical and Reliability Analysis of Gravity Cantilever Re- taining Walls Backfilled with Shredded Tires Subjected to Seismic Loads (M.S. thesis), Clemson University, 2012.

moments hover around the same value for both the friction angle and cohesion variations.

Generally, increases in unit weight induced greater forces and moments in the wall as was to be expected.

18.3 Embankments and engineered fill

The primary advantage of using TDA for embankments or engineered fill is to reduce the overburden pressure on the native soil due to the low unit weight of the material. This is especially important when the native soil is weak and/or prone to consolidation. Due to a small risk of self-combustion (see the Safety section 18.4), embankments using TDA are constructed using cells or layers (Fig. 18.4). The maximum recommended height of a TDA layer is 3 m among other criteria such as surrounding each TDA with geotextiles to prevent soil infiltration [10,15,16].

In one Canadian field study, an embankment failed during construction of a new four-lane highway and the reconstruction process employed TDA to address the weak marine clay soil [17]. The overall height of the embankment was approximately 15 m and two 3-m thick layers of TDA were used to reduce the overburden pressure on the weak underlying soil. Numerous sensors were installed during the reconstruction to provide the opportunity to monitor the behavior over a long-term period. Two years after construction, the embankment was still performing as designed. Other benefits of using TDA in this project were that the estimated costs were reduced by 30% and the project utilized over 1.6 million scrap tires. Another project in Canada demonstrated a 50% cost reduction in raw materials with the use of TDA [18]. The results of falling weight deflectometery (FWD) on highway road surfaces overlaying TDA embankments have demonstrated sufficient performance [19].

In the United States, over 42,000 m^3 of TDA was used in a project in Virginia [20]. A 6-m thick section of a TDA/soil blend

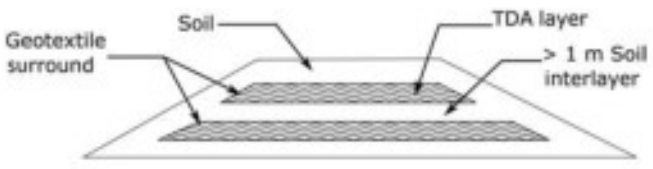


Figure 18.4 Example cross-section of an embankment with two TDA layers. The TDA must be separated from the surrounding soil with a geotextile and the thickness of any single TDA layer must not exceed 3 m.

was constructed alongside an identical thickness embankment of just soil. This allowed engineers to compare the settlements and vertical stresses for equivalent designs on the same site. It was observed that the TDA/soil portion of the site had measured vertical stresses 50% lower than expected, even when the reduced unit weight of the mixture was considered. It was thought that the TDA particles provided a substantial stress transfer mechanism between particles that reduced the vertical component of stress.

Another US project in Maine utilized TDA to better accommodate the weak underlying soil on the site [16]. The project utilized over 1 million equivalent passenger tires. A similar use of TDA to reduce the vertical stress on a weak underlying layer took place in California [16]. This project utilized over 600,000 equivalent passenger tires.

A project in Texas was conducted to directly compare TDA embankments with soil embankments with respect to settlements [21]. While the TDA sections did experience more settlement during construction, the postconstruction settlement was acceptable for all the sections. When accounted for in the design and construction phase, the additional settlement of TDA can be accommodated without sacrificing the performance of the structure.

18.4 Safety and environmental concerns

Tire piles are known to be a hazard to the environment and the health of individuals in the area. First, whole tires collect water and produce a warm, moist environment that is an ideal breeding ground for disease-carrying mosquito populations. Whole tire piles also pose a fire hazard in that they are readily ignited by the slightest source and trap air making them nearly impossible to extinguish. In addition, as tires burn they produce liquid oil and toxic smoke that are damaging to the environment and individuals living in the area. The shredding of whole tires and use of shreds in civil engineering applications is one method for reducing tire stock piles and the risks associated with that disposal technique. In order to implement this new disposal method, it is important to evaluate the environmental and safety concerns and make design adjustments as necessary. Because sand and gravel backfills are natural soil materials, they are not considered harmful to the environment when in use. Tires contain a complex mix of chemicals, some of which may negatively impact the environment if released into the soil

or water, thus this concern must be addressed before they can be widely used. These same chemicals also make it possible for tire shreds to catch fire and burn much like whole tires if conditions are right, so preventing chemical release and combustion is an important consideration. Another consideration is the safety and health concerns associated with the production and handling of shredded tires as opposed to sand or gravel backfill. Sand and gravel are produced by mining or collected by digging whereas the production of tire shreds is an industrial manufacturing process. Each production and handling process has inherent risks that must be evaluated before either backfill material can be supported. As such, some potential concerns about using shredded tires as a backfill material include possibility for combustion, water quality after drainage through tire layers, and human effects of the tire shredding process.

Because tire shreds retain the chemical makeup of whole tires, their combustibility is still a concern when tire shreds are used in civil engineering applications. In the event that sufficient heat is generated in a tire pile, combustion of the tires has been observed. Several decades ago, there were two fires in shredded tire road embankments in the state of Washington [22]. These unusual but prominent cases of combustion in shredded tires used as fill had a strong negative impact on the use of shredded tires in civil engineering applications. Samples of gases collected at these sites were consistent with controlled pyrolytic reactions in which tire compounds are broken down by the application of very high heat with no oxygen [22]. Such a reaction appeared possible based on unique conditions at these sites. Based on temperature readings taken from water before and after passing through one of the tire embankments, heat generation and retention in the tire layer was shown by a marked increase in water temperature [22]. The heating and resulting pyrolysis was believed to be due to heat generation from the combination of oxidation of steel belts, microbial digestion of carbon, chemical breakdown of any crumb rubber, and heating due to layer thickness [22]. The oxidation of steel belts and microbial digestion were both aided by the unusually high rainfall at both sites and the trapped heat in the thick tire layers. This was believed to cause a cycle where these reactions increased the temperature in the tire layer while the increased temperature increased the reaction rate particularly in the oxidation of steel belts. Other factors conducive to microbial decomposition included the presence of tire shreds with large surface area-to-volume ratio and the presence of some agricultural runoff [22].

In a review of the Washington state fires, the self-combustion behavior of the fill was modeled [23]. It was suggested that if the internal temperature rose above 185°C, there would be a high risk of self-combustion. The modeling of the temperature rise over time (Fig. 18.5) shows that the internal temperature of the fill likely exceeded the 185°C threshold by a significant amount and led to the fires. It was suggested that the rise of temperature was more due to the oxidation of the steel reinforcement left-over in the tire shreds as that reaction is highly exothermic. To reduce the opportunity for exothermic reactions and excessive heat generation and trapping, ASTM D6270 provides guidelines for gradation of the tires to eliminate crumb rubber, the elimination of any foreign matter such as organic materials or fuels, and the limiting of exposed steel belts.

Other studies confirm the thermal insulation abilities of scrap tire layers [21,24]. One study showed that though the temperature of the tire layers in these cases remained only slightly higher than ambient temperatures, temperatures in the embankment fluctuated less than that of surrounding air suggesting that the tires acted as an insulator [21]. No significant self-heating was noted in this study, likely due to the fact these embankments were located in the arid climate of El Paso, TX and contained a thinner layer of tires.

Groundwater contamination and the effect on aquatic life can be a serious concern for many TDA applications. Because

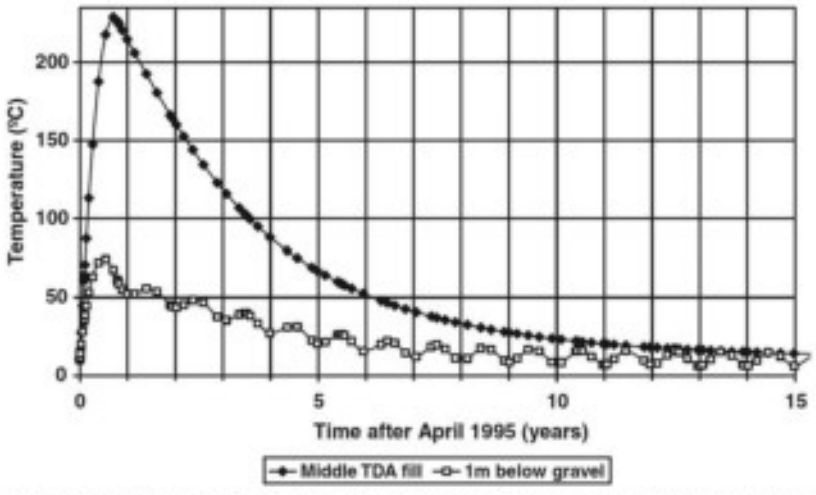


Figure 18.5 Results from modeling one of the Washington state tire fill fires. From M. Arroyo, I. San Martin, S. Olivella, M.W. Saaltink, Evaluation of self-combustion risk in tire derived aggregate fills, Waste Manage. 31 (9–10) (2011) 2133–2141, doi:10.1016/j.wasman.2011.04.014.

tires contain potentially hazardous metals and organic compounds, the risk is that these materials will enter groundwater in levels significant enough to impact the environment and water quality. In one study, water samples were taken from road embankments that utilized large tire shreds as a fill material [5]. These samples were tested for harmful organic materials as well as for inorganic metals over a short-term test period. It was determined that based on guidelines set by the Canadian Council of Ministers of the Environment any contaminants present in the water were below the mandatory limits for harm to humans. Levels of aluminum, iron, and manganese were above secondary levels set to control water esthetics, but these secondary limits are based on factors such as taste, odor, and color and are not an indication of health hazards. In addition, levels of organic compounds in the test samples were below the detection limit for the methods used, and thus of no concern based on this test. These results demonstrate that though water quality may be affected somewhat by drainage through a tire shred layer, the effects are not harmful to humans.

In another study, flow column tests were performed to assess the effects on water quality both in flowing and pause flow conditions [4]. In the flowing condition, tire shreds placed above the water table were simulated by pumping water through a column of shredded tires without ponding or extended exposure. The pause flow condition simulated a condition where tire shreds are placed at or below the water table without drainage by stopping the flow of water through the column and only opening flow valves for the collection of samples. The results from the flowing test showed that tires placed above the water table would not significantly impact the environment. It was even shown that with time the water quality could be expected to improve as the tires are cleaned by the water and the tires remove some of the water contaminants through filtration. In contrast, when drainage was inhibited and ponding occurred as in the pause flow test, a potential for negative environmental impacts were observed primarily due to the oxidation of steel belts.

To further understand the environmental impact of shredded tires on water quality, a study examined the effects of leachate from tire shred fills on aquatic life [25]. Rather than focusing on parameters for human consumption, this study investigated the effects of known leachates on aquatic life as well as how groundwater systems disperse and remediate contaminants. This study included detailed chemical analyses of tire shred leachate, a test of the toxicity effects of leachate on freshwater minnows and crustaceans, and groundwater modeling of chemical transport

and removal. In agreement with previous studies [26–29], it was found that no toxic effects were associated with the leachate from tire shreds placed above the water table. On the other hand, tire shreds below the water table produced leachates that were significantly toxic to the crustaceans, primarily hindering reproduction [25]. Based on chemical analyses, iron from exposed belts at the cut ends is primarily to blame for the toxicity. Because geochemical modeling in this study showed that iron quickly forms a precipitate in groundwater, it was determined that under normal conditions, the increase in concentration of iron in the water would be a local effect only. This means that though leachates are toxic to some freshwater crustaceans, the effects are diminished by natural chemical reactions in the groundwater system and will only negatively affect aquatic life in direct proximity to the tire shred layer. Based on groundwater modeling, the buffer distances necessary to remove iron to safe levels ranged between 3 and 11 m for almost all cases, with only a specific case requiring a buffer distance of 32 m [25].

This conclusion, coupled with information from other water studies, indicates that tire shreds above the water table are safe, and even tire shreds below the water table cause only localized toxicity in groundwater and aquatic systems. Aside from environmental impacts, the human effects in the production and utilization of shredded tires must be compared to that of sand and gravel. Tires are known to be made with chemicals that could be harmful to workers if released and contacted, and most contain steel or fiberglass belts that could pose a risk to those manufacturing or handling tire shreds. These risks must be evaluated before tire shreds can be recommended as a backfill replacement for sand. In one comprehensive study of the work environments in two tire shredding facilities in Taiwan, several parameters were measured where workers tend to spend the most time and included noise, volatile organic compounds, and production of particulate matter [30]. Although noise was the primary health hazard observed, some airborne particles were also noted particularly in the production of crumbs and belt removal. These particles were found to contain some mutagenic ingredients which may be carcinogenic. Though measures were in place to help remove the respirable particles and keep levels below nuisance standards, the potentially carcinogenic nature of some tire particulates suggests they should be more strictly regulated than a nuisance material. More broadly in a large German study, it was found there was an increased mortality rate for workers dealing with raw material and recycling operations

[31]. The authors hypothesized that the talc used in the tire filler was contaminated with asbestos and the processing and grinding operations led to it becoming airborne.

18.5 Summary

Waste tires are a persistent and pervasive issue in many countries. There is a risk of fire that can release toxic chemicals into the air and the interior portions of tires are ideal breeding grounds for mosquitoes that can transmit various diseases. Among the varied commercial uses for waste tires, TDA represents the biggest use case due to the inherent size of civil engineering projects. Additionally, the minimal processing and lower quality requirements, as compared to other recycled rubber products, makes TDA an attractive option for recycling waste tires.

Applications for TDA include lightweight backfill for retaining walls and embankments. In these applications, the use of TDA does not represent an equivalent replacement of current processes, but in fact represents an enhancement. For retaining wall applications, the use of TDA can reduce the wall size and provide additional stability during dynamic loading (i.e., earthquakes). For embankments, TDA can significantly reduce the overburden stress on weak underlying soils. Due to the size of embankments, these projects can easily utilize over 1 million passenger tire equivalents in a single project.

While TDA is generally a safe product to use for civil engineering projects, there are some important considerations to account for. There have been a few self-heating events in embankments due to the insulative properties of the material. Based on extensive studies of these events, guidelines have been developed that significantly reduce the risk and are present in the governing standard for TDA (i.e., ASTM D6720). Leaching toxicity testing on TDA has shown that minimal danger exists for groundwater contamination. However, there does exist some occupational danger in the actual processing of recycled rubber when generally recognized safety measures are not observed.

References

[1] V. Cecich, L. Gonzales, A. Hoisaeter, J. Williams, K. Reddy, Use of shredded tires as lightweight backfill material for retaining structures, Waste Manage. Res. 14 (5) (1996) 433–451. Available from: https://doi.org/10.1006/wmre.1996.0043.

[2] S. Youwai, D.T. Bergado, Strength and deformation characteristics of shredded rubber tire - sand mixtures, Can. Geotech. J. 40 (2) (2003) 254–264. Available from: https://doi.org/10.1139/t02-104.

[3] J. Lee, R. Salgado, A. Bernal, C. Lovell, Shredded tires and rubber-sand as lightweight backfill, J. Geotech. Geoenviron. Eng. 125 (2) (1999) 132–141.
[4] H. Moo-Young, K. Sellasie, D. Zeroka, G. Sabnis, Physical and chemical properties of recycled tire shreds for use in construction, J. Environ. Eng. 129 (10) (2003) 921–929. Available from: https://doi.org/10.1061/(ASCE)0733-9372(2003)129:10(921).
[5] A. Shalaby, R.A. Khan, Design of unsurfaced roads constructed with large-size shredded rubber tires: a case study, Resources Conserv. Recycl. 44 (4) (2005) 318–332. Available from: https://doi.org/10.1016/j.resconrec.2004.12.004.
[6] D.N. Humphrey, T.C. Sandford, M.M. Cribbs, W.P. Manion, Shear strength and compressibility of tire chips for use as retaining wall backfill, Transp. Res. Rec. (1422)(1993) 29–35.
[7] S. Yang, R. Lohnes, B. Kjartanson, Mechanical properties of shredded tires, Geotech. Test. J. 25 (1) (2002) 44. Available from: https://doi.org/10.1520/GTJ11078J.
[8] P.M. Strenk, J. Wartman, D.G. Grubb, D.N. Humphrey, M.F. Natale, Variability and scale-dependency of tire-derived aggregate, J. Mater. Civ. Eng. 19 (3) (2007) 233–241. Available from: https://doi.org/10.1061/(ASCE)0899-1561(2007)19:3(233).
[9] M. Garcia, M.A. Pando, B. Tempest, Tire derived aggregates as a sustainable recycled material for retaining wall backfills, in: ICSDC 2011, American Society of Civil Engineers, Reston, VA, 2012, pp. 542–552. doi:10.1061/41204(426)67.
[10] D.N. Humphrey, Tire derived aggregate as lightweight fill for embankments and retaining walls, in: Proceedings International Workshops on Scrap Tire Derived Geomoaterials, Yokosuka, Japan, 2007, pp. 59–81.
[11] M. Garcia-Theran, M.A. Pando, H. Celis, T. Abdoun, Estimation challenges of lateral pressures in retaining structures using granular recycled tire aggregates as backfill, in: Geo-Congress 2014 Technical Papers, American Society of Civil Engineers, Reston, VA, 2014, pp. 3666–3675. doi:10.1061/9780784413272.355. URL http://ascelibrary.org/doi/10.1061/9780784413272.355.
[12] S.B. Reddy, A.M. Krishna, Tyre chips as compressible inclusions in earth-retaining walls, Proc. Inst. Civ. Eng. Ground Improv. 170 (3) (2017) 137–148. Available from: https://doi.org/10.1680/jgrim.16.00034.
[13] I.S. Ahn, L. Cheng, Tire derived aggregate for retaining wall backfill under earthquake loading, Constr. Build. Mater. 57 (2014) 105–116. Available from: https://doi.org/10.1016/j.conbuildmat.2014.01.091.
[14] E. Huggins, Numerical and Reliability Analysis of Gravity Cantilever Re- taining Walls Backfilled with Shredded Tires Subjected to Seismic Loads (M.S. thesis), Clemson University, 2012.
[15] T.H. Dickson, D.F. Dwyer, D.N. Humphrey, Prototype tire-shred embankment construction, Transp. Res. Rec. (1755)(2001) 160–167. Available from: https://doi.org/10.3141/1755-17URL. Available from: http://journals.sagepub.com/doi/10.3141/1755-17.
[16] D.N. Humphrey, Effectiveness of design guidelines for use of tire derived aggregate as lightweight embankment fill, in: Recycled Materials in Geotechnics, American Society of Civil Engineers, Reston, VA, 2004, pp. 61–74. doi:10.1061/40756(149)4.
[17] B. Mills, J. McGinn, Design, construction, and performance of a highway embankment failure repaired with tire-derived aggregate, Transp. Res. Rec. (2170)(2010) 90–99. Available from: https://doi.org/10.3141/2170-11.

[18] H. El Naggar, A. Marlin, D. Dennis, Lessons learned from the construction of Kelly Lake TDA embankment, in: World Congress on Civil, Structural, and Environmental Engineering, no. April, 2019, pp. 1–8. doi:10.11159/icgre19.193.
[19] D. Meles, A. Bayat, M.H. Shafiee, S. Nassiri, M. Gul, Investigation of tire derived aggregate as a fill material for highway embankment, Int. J. Geotech. Eng. 8 (2) (2014) 182–190. Available from: https://doi.org/10.1179/1939787913Y.0000000015.
[20] E.J. Hoppe, Field Study of Shredded-Tire Embankment, Tech. Rep., 6, 1994.
[21] V. Tandon, D.A. Velazco, S. Nazarian, M. Picornell, Performance monitoring of embankments containing tire chips: case study, J. Perform. Constr. Facil. 21 (3) (2007) 207–214. Available from: https://doi.org/10.1061/(ASCE)0887-3828(2007)21:3(207).
[22] D. Nightingale, W. Green, An unresolved riddle: tire chips, two roadbeds, and spontaneous reactions, Testing Soil Mixed with Waste or Recycled Materials. (1997) 265–285. Available from: https://doi.org/10.1520/STP15657S.
[23] M. Arroyo, I. San Martin, S. Olivella, M.W. Saaltink, Evaluation of self-combustion risk in tire derived aggregate fills, Waste Manage. 31 (9–10) (2011) 2133–2141. Available from: https://doi.org/10.1016/j.wasman.2011.04.014.
[24] A. Shalaby, R. Ahmed Khan, Temperature monitoring and compressibility measurement of a tire shred embankment: Winnipeg, Manitoba, Canada, Transp. Res. Rec. (1808)(2002) 67–75. Available from: https://doi.org/10.3141/1808-08.
[25] P.J. Sheehan, J.M. Warmerdam, S. Ogle, D.N. Humphrey, S.M. Pate- naude, Evaluating the risk to aquatic ecosystems posed by leachate from tire shred fill in roads using toxicity tests, toxicity identification evaluations, and groundwater modeling, Environ. Toxicol. Chem. 25 (2) (2006) 400–411. Available from: https://doi.org/10.1897/04-532R2.1.
[26] K. Day, K. Holtze, J. Metcalfe-Smith, C. Bishop, B. Dutka, Toxicity of leachate from automobile tires to aquatic biota, Chemosphere 27 (4) (1993) 665–675. Available from: https://doi.org/10.1016/0045-6535(93)90100-J.
[27] L.A. Downs, D.N. Humphrey, L.E. Katz, C.A. Rock, Water Quality Effects Using Tire Chips Below the Groundwater Table, Tech. Rep., 1996.
[28] D. Humphrey, L. Katz, M. Blumenthal, Water quality effects of tire chip fills placed above the groundwater table, Testing Soil Mixed with Waste or Recycled Materials 53 (9) (1997) 299–313. Available from: https://doi.org/10.1520/STP15659S.
[29] D.N. Humphrey, L.E. Katz, Water-quality effects of tire shreds placed above the water table: five-year field study, Transp. Res. Rec. (1714)(2000) 18–24. Available from: https://doi.org/10.3141/1714-03.
[30] Y.C. Chien, S. Ton, M.H. Lee, T. Chia, H.Y. Shu, Y.S. Wu, Assessment of occupational health hazards in scrap-tire shredding facilities, Sci. Total Environ. 309 (1–3) (2003) 35–46. Available from: https://doi.org/10.1016/S0048-9697(03)00009-3.
[31] K. Straif, S.K. Weiland, B. Werner, L. Chambless, K.A. Mundt, U. Keil, Workplace risk factors for cancer in the German rubber industry: Part 1. Mortality from respiratory cancers, Occup. Environ. Med. 55 (5) (1998) 317–324. Available from: https://doi.org/10.1136/oem.55.5.325.

PART

V

The future

This page intentionally left blank

19

Green public procurement

Ettore Musacchi
President, ETRA, Brussels, Belgium

19.1 General information on green public procurement

Green public procurement (GPP) is "a process whereby public authorities seek to procure goods, services and works with a reduced environmental impact throughout their life cycle when compared to goods, services and works with the same primary function that would otherwise be procured."

By using environmental criteria, public authorities can buy electricity, transport services, office IT equipment, food and catering services and many other goods and services that contribute to the reduction of environmental impacts. Recycled tire materials (RTMs) are used in a wide array of products and applications and many of them are compatible with GPP. Examples include buildings, transport infrastructure, and sport and leisure facilities.

The scope of GPP is often misconceived. It is a tool that was designed to stimulate public authorities to use their budget in a more sustainable way, or in a "greener" way. It does not only mean the use of recycled material instead of virgin material, as there are many other ways for the public administration to become greener.

GPP could be an excellent tool, if properly implemented to support the use of RTMs. The concept of GPP has been widely recognized in recent years as a useful tool for driving the market for greener products and services and reducing the environmental impacts of public authorities' activities. GPP concerns:

- Contracting authorities include national, regional, or local authorities and so-called bodies "governed by public law." These are bodies established for the specific purpose of meeting needs in the general interest of the public, but without an industrial or commercial character and for the most part are financed, administered, or supervised by public authorities.

Contracting entities include all entities operating in so-called "special sectors," namely water, energy, transport, and postal

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00020-X
© 2021 Elsevier Inc. All rights reserved.

services. Even if the operating entities in those sectors are not necessarily any longer public authorities or bodies governed by public law, they provide public services and remain fairly dependent on public money. They are therefore often subject to similar, albeit less restrictive, rules. The increase consumption of resources in the EU is producing environmental damage that is not sustainable. Concerns have been raised on consumption and production models, either internationally or at the European level. Global resource use could quadruple within 20 years if the whole world's population followed the EU's model of consumption.

Apart from the resulting environmental and health problems, this trend could threaten economic growth due to decreasing natural resources and the cost of addressing these issues.

- In the EU, the share of GDP devoted by governments to the provision of public goods varies greatly. The public sector is the largest consumer in the economy. Government expenditure on works, goods, and services represent around 14% of the EU's gross domestic product (GDP), accounting for roughly €1.8 trillion annually.

Public finance expenditure amounted to 46.7% of EU27 GDP in 2018, unchanged compared to 2017. The *average public finance expenditures per EU citizen amounted to 14,078* €. For a citizen living in the *Euro area, the amount was 15,846* €.

The EU average composition of public expenditures as a percentage of GDP and expenditure per capita in 2018 is:

- Social protection 19.2% – €5799
- Health 7.0% – €2114
- General public services 6.0% – €1821
- Environment and housing 1.4% – €412
- Economic affairs 4.4% – €1322
- Defense and safety 2.9% – €868
- Culture and education 5.7% – €1700

Member States have been encouraged to draw up publicly available National Action Plans (NAPs) for greening their public procurement. The NAPs should contain an assessment of the existing situation and ambitious targets for the next 3 years, specifying what measures should be taken to achieve them. While the NAPs are not legally binding, they do provide political impetus to the process of implementing and raising awareness of greener public procurement and allow the Member States to choose the options that best suit their political framework and needs, and the level they have reached.

The EU GPP criteria are not mandatory. They were developed as part of a voluntary approach to GPP endorsed in the communication *Public procurement for a better environment*

(COM (2008) 400), which describes a number of measures to be taken by the European Commission to support the implementation of GPP by Member States and individual contracting authorities.

The purpose of the EU GPP criteria is to identify the main environmental impacts of each of the products and services covered, and propose clear, verifiable, and ambitious criteria to address these in the procurement process. They are not legally binding and encompass two separate levels – core and comprehensive (see the following on the GPP Criteria). Member States are invited to include the criteria into their national GPP policies and individual contracting authorities to use them when procuring.

In practice, a number of Member States have either referenced the EU GPP criteria in their national action plans, or adopted criteria that reflect these quite closely. Variations in the adopted criteria tend to reflect national differences in the needs and interests, as well as market availability of products/services, in addition to the approach to procurement, the environment, and other priorities. Individual contracting authorities can choose which criteria to apply, and how, in the absence of specific national regulatory laws.

The EU GPP criteria are developed based on consultation with stakeholders and reflect the scientific and market knowledge available at the time of their publication. The EU GPP criteria are designed to be flexible, and do not remove the responsibility of the individual authority to act fairly, transparently, and proportionately in determining which criteria to apply.

It is considered that by providing a common reference point-based comprehensive assessment of environmental impacts, the EU GPP criteria contribute to the alignment of procurement practices in the absence of mandatory common criteria. A number of studies have been undertaken to determine the extent of GPP implementation by EU contracting authorities.

19.2 Economic aspects

The most common idea about GPP is that green products are expensive. However, depending on how costs are considered, this may not necessarily hold true. Green products can have a lower purchasing price as they have reduced impacts on the environment with often less energy and raw materials consumed and/or less waste generated so lower associated production costs, as in the case of RTMs.

For example, the European Commission study on the "Costs and Benefits of Green Public Procurement in Europe" found that the purchasing costs for public authorities of green (including 100% recycled and eco-certified copying paper) and nongreen copying paper are very similar. In Germany, "green" versions of copying paper appeared to be significantly cheaper (23%). In Sweden, the same study showed that environmentally friendly floor care, sanitary, and window cleaning products were all less expensive than their conventional counterparts (74%, 82%, and 9%, respectively).

In addition, where a life cycle costing (LCC) approach is taken to competing products or services, greener alternatives may be less expensive even where the initial purchase price is higher. It is even more likely to be true where an environmental LCC approach is applied. LCC is being applied by an increasing number of public authorities across the EU and in a range of sectors.

A number of different approaches are available under this general heading, some of which may be considered appropriate for GPP. Cost or price will form part of the assessment of any procedure, and is usually one of the most influential factors. Costs may be calculated on the basis of a product's life cycle. But how do you define the cost?

When you purchase a product, service, or work, there is always a price to pay – at some point. The purchase price, however, is just one of the cost elements in the whole process of purchasing, owning, and disposing. LCC means considering all the costs that will be incurred during the lifetime of the product, work, or service:

- Purchase price and all associated costs (delivery, installation, insurance, etc.)
- Operating costs, including energy, fuel and water use, spares, and maintenance
- End-of-life (EOL) costs (such as decommissioning or disposal) or residual value (i.e., revenue from sale of product)

LCC may also include the cost of externalities (such as greenhouse gas emissions) under specific conditions laid out in the directives. The current (2014) directives require that where LCC is used, the calculation method and the data to be provided by tenderers are set out in the procurement documents. Specific rules also apply regarding methods for assigning costs to environmental externalities, which aim to ensure that these methods are fair and transparent.

LCC makes good sense regardless of a public authority's environmental objectives. By applying LCC public purchasers

take into account the costs of resource use, maintenance, and disposal, which are not reflected in the purchase price. Often this will lead to "win-win" situations whereby a greener product, work, or service is also cheaper overall.

19.3 Green public procurement policy

Under the Sustainable Consumption and Production and Sustainable Industrial Policy (SCP/SIP) Action Plan, the Commission undertook to further strengthen GPP and published the Communication on GPP. The objective of the Communication "*Public procurement for a better environment*" (COM (2008) 400, published on July 16, 2008), is to provide guidance on how to reduce the environmental impact caused by public sector consumption and how to use GPP to stimulate innovation in environmental technologies, products and services. At the EU level the European Commission set an indicative target that, by 2010, 50% of all public tendering procedures should be green, where "green" means compliant with endorsed common core EU GPP criteria.

More specifically, the Communication proposes tools that should enable the main obstacles to increased take-up of GPP to be addressed. The Commission was entrusted with the following:

- setting common GPP criteria;
- encouraging publication of information on LCC of products;
- increasing certainty about legal possibilities to include environmental criteria in tender documents; and
- establishing support for the promotion and implementation of GPP through a political target linked to indicators and monitoring.

In order to monitor GPP, the Commission proposes to establish two types of indicators: quantitative indicators to assess the progress of the policy and its impact on the supply side, and impact-oriented indicators allowing assessment of the environmental and financial gains made. This monitoring methodology was tested in the 2009 study undertaken on behalf of the Commission *Collection of statistical information on GPP in the EU*. To assess if the set 2010 target had been met, in 2011, the Commission commissioned a study in which over 850 public authorities from 26 Member States participated. A number of EU policies and strategies refer to GPP or regulated areas that are linked to its implementation.

On March 3, 2010, the Commission launched the Europe 2020 strategy: A European strategy for smart, sustainable, and

inclusive growth. The EU's new strategy for sustainable growth and jobs in some of its flagship initiatives also mentions GPP.

The Resource-efficient Europe flagship initiative is part of the Europe 2020 Strategy. The **Roadmap to a resource efficient Europe** (published in 2011) is one of the main building blocks of this flagship initiative setting the framework for the design and implementation of future actions. It outlines the structural and technological changes needed by 2050, including milestones to be reached by 2020. The Roadmap mentions the need for encouraging wider use of GPP.

EU leaders adopted a voluntary target for GPP under the renewed Sustainable Development Strategy in 2006, stating that, by 2010, the average level of GPP should be the same as the level of the best performing Member States at the time (2006). In its 2008 Communication, the Commission proposed that, by 2010, 50% of all public tendering procedures should be "green." "Green" means tendering procedures must comply with endorsed common "core" GPP criteria. The baseline for this target was a study "Green public procurement in Europe" (2005–2006) on GPP performance across EU Member States, which indicated the current levels of GPP in the seven best performing Member States (Austria, Denmark, Finland, Germany, the Netherlands, Sweden, and United Kingdom). This study also identified the most suitable product groups for immediate greening [2].

The target was confirmed as realistic by a 2009 study on the *Collection of Statistical Information on GPP in the EU* [3]. It showed that in the seven best performing Member States on average 45% of the total procurement value and 55% of the total number of procurement contracts included environmental considerations for the years 2006/07 in ten GPP priority sectors -, Green Public Procurement in Europe: Conclusions and Recommendations (2006).

In order to foster the GPP the Commission has:

- Set up a Helpdesk service (in January 2010) to answer any questions on GPP. Enquiries can be made in English, French, or German. Part of the GPP Helpdesk service is to provide regular information of interest to the broader GPP community via regular newsletters. Past editions of the newsletters (GPP News Alerts) are available here. The newsletters also feature the details of a number of examples of GPP in practice.
- Set clear political voluntary targets for GPP. By 2010, 50% of all tenders should be compliant with endorsed common "core" GPP criteria.
- Produced "Buying Green! a Handbook on environmental public procurement," which explains how best to integrate

environmental considerations into public procurement procedures based on the provisions of the 2014 Procurement Directives. The first edition of the Handbook was published in 2004, the second edition in 2011, and the third and current edition was published in spring 2016.
- Developed a set of GPP criteria. EU GPP criteria are available for over 20 priority sectors/product areas. The criteria are developed following intense exchanges with the relevant stakeholders.
- Provided a web-based training toolkit on GPP.

The Commission launched a program to train GPP experts and raise awareness about GPP in EU Member States, which took place between 2006 and 2010. The first round of events took place in 2006 and were held in Greece, Ireland, Italy, Portugal, and Spain. The second round of events (2009–10) served to train 40 national experts from 19 countries (Bulgaria, Cyprus, Estonia, Hungary, Latvia, Lithuania, Poland, Romania, Slovakia, Slovenia, Belgium, Czech Republic, France, Greece, Ireland, Italy, Malta, Portugal, and Spain) through train the trainer programs.

GPP depends on clear, justifiable, and ambitious environmental criteria for products and services. A number of national criteria and approaches to GPP have been developed. However, as the use of GPP increases, the criteria used by Member States should be compatible to avoid a distortion of the single market and a reduction of EU-wide competition. Establishing a single set of criteria could considerably reduce the administrative burden for economic operators and for public administrations implementing GPP. Common GPP criteria are of particular benefit to companies operating in more than one Member State, as well as to SMEs (small- and medium-sized enterprises) whose capacity to adapt and manage different procurement procedures is limited.

19.4 Legal framework for green public procurement

Public procurement in the European Union is subject to a number of sources of EU Community law including:
- The Procurement Directives (2014/24/EU and 2014/25/EU)
- The Treaties (Treaty on the Functioning of the EU and its predecessors)
- Case law of the Court of Justice of the European Communities
- Law applying to related areas such as State Aid and Competition

In addition there are a number of sources of interpretation of the relevant laws and principles, such as the "Buying Green" handbook and European Commission's Interpretative Communications.

19.5 Environmental management systems and green public procurement

Any organization (public or private) wishing to improve its overall environmental performance can decide to run an environmental management system (EMS). EMSs are organization-related tools aimed at improving overall environmental performance of the committing organization. With regard to GPP, they are typically relevant when it comes to the use of natural resources (e.g., water and energy), staff training, using greener production methods, and purchasing greener office materials. In terms of public procurement procedures, under the EU public procurement directives (2014), EMS can be used to formulate requirements in various phases of a purchasing process, in particular to screen the technical ability (in the "selection" phase) of a bidding company/supplier and/or during the "award" phase. An organization running an EMS may request certification under one of the two main environmental management systems in use in the EU: the "Eco-management and audit scheme" (EMAS) or the European/international standard on environmental management systems (EN/ISO 14001). The EMAS scheme is primarily used by organizations with a site in the EU or in the European Economic Area, although it can also be used by organizations and sites located elsewhere (but is always verified under the control of a European Accreditation Body). The ISO scheme is open to organizations across the globe. More information on the use of an EMS for GPP is available in sections 4.3.2 and 5.2.4 of the "Buying Green" handbook (third edition).

19.6 Clean vehicles directive and green public procurement

The Clean Vehicles Directive requires that contracting authorities take into account the lifetime emissions of carbon dioxide, nitrogen oxides, nonmethane hydrocarbons, particulate matter, and energy consumption in any purchase of road transport vehicles above the EU thresholds. This can be done through setting maximum values in the technical specifications and/or awarding higher marks to vehicles with lower lifetime emissions/energy

consumption. Ensuring equal treatment and the comparability of tenders is paramount – so contracting authorities must clearly describe the approach they will apply in the tender documents. Different Member States have implemented the Directive in different ways, so contracting authorities should check their national regulations.

It should be recalled that RTMs can play an important role in the automotive industry to produce various types of components, but again it is not automatic. Vehicle producers at the moment seem more under pressure for engine emissions. On the other hand, public authorities are more sensitive to air pollution and are concentrating their efforts to adopt zero or low emission vehicles or to look for a way to organize mobility through various alternative transport methods that could also be combined. For public authorities there is not much difference if the vehicle has more or less content of recycled materials, unless it impacts the price.

However, public authorities have understood the advantages of using retreaded tires for their vehicles, primarily on buses for urban transport. The benefit is not just economic but also of image, that is, the ability to communicate their "green" mentality to the public. The use of RTMs in the automotive sector will probably be more stimulated by private choices, either on the side of the producers or the consumer, both for economic reasons.

19.7 Green public procurement criteria

Common EU GPP criteria are those that can be incorporated into a public procurement procedure for goods, services, or works in order to reduce the environmental impact of the purchase. GPP criteria have been developed for priority products and services that have been identified as most suitable for "greening" through public procurement. The criteria were designed with public bodies operating in the EU with the European public procurement requirements and directives in mind. It is anticipated that additional sectors will be added in the near future. Criteria sets offer two types of criteria for each sector covered:

- The Core criteria are designed to allow for easy application of GPP, focusing on the key area(s) of environmental performance of a product and aimed at keeping administrative costs for companies to a minimum.
- The Comprehensive criteria take into account more aspects or higher levels of environmental performance, for use by authorities that want to go further in supporting environmental and innovation goals.

The priority sectors for implementing GPP were selected through a multicriteria analysis conducted in 2006. The criteria included scope for environmental improvement; public expenditure; potential impact on suppliers; potential for setting an example to private or corporate consumers; political sensitivity; existence of relevant and easy-to-use criteria; market availability; and economic efficiency.

A newer procedure for GPP criteria development established in 2010 aims to make the process more transparent and participatory and to enhance synergies among different product-related policy instruments such as GPP, Ecodesign, EU Ecolabel, and Energy label.

The GPP process will follow the key aspects of the structure for the EU Ecolabel criteria-setting procedure. It will provide stakeholders with the possibility to comment on the background studies and draft GPP criteria at several stages of the process.

19.8 Postconsumer tires and recycled tire materials in green public procurement

Public bodies are important purchasers of many different types of goods and services. The key point is how one tire can be greener than another. The criteria should be fixed by the Public Purchaser who probably has in mind other aspects than the content of recycled material. In fact, the technology now permits the use of a certain amount of recycled rubber in the production of new tires. This technology is not yet as widely circulated as it could raise competition issues in pushing these kinds of tires for public procurement, because it could give unrestricted freedom of choice to the contracting authority. On the other hand, tire retreading is an affirmed technology well spread all over Europe and perfectly in line with GPP legislation.

As explained above, GPP criteria must be designed and implemented in order to match the green efficiency objective of the purchaser and the green characteristics of the product. If these criteria are not fixed, even a well-known product could have trouble being acknowledged by a GPP system. This is the reason GPP criteria must be prepared in cooperation between public authorities and the stakeholders.

Transport efficiency can be achieved through various ways. The reduction of emissions can be achieved either by the purchase of electric vehicles or the adoption of a more efficient plan to coordinate public transport in a city, without focusing only on tire purchases. Retreading is the most obvious case. Equally significant are many other cases that include RTMs,

which are excellent materials that can be used in a wide array of products and applications.

Transport does not mean only tires or emission reduction but also roads and infrastructure. RTMs are valuable materials for road construction. In this case the benefit is not just the fact that they are recycled materials, but also by the fact they increase the performance of the road: durability, safety, etc. Again, the success of this application depends on how the GPP criteria are designed.

19.9 What are the opportunities for tire recycling sector critical and crucial point?

The crucial point in order to expand the use of RTMs is that more and more public authorities, with the support of stakeholders, apply environmental criteria in public tenders. RTMs are excellent materials that can be used in many products and applications, allowing cost savings and even better performance.

The goals of the public authority however compatible with those of tire recycling can be achieved through various criteria that have nothing to do with the use of recycled materials. For instance, in the building sector they could be more interested in buildings with a lower CO_2 emission thanks to a low energy consumption rather than the use of a low CO_2 material derived from recycling. The issue of recycling is often taken into consideration by taking into account the recycling option for the EOL of the building together with various decommissioning commitments. Low CO_2 emission buildings and recycled building materials are not in conflict, but are synergic to make buildings more sustainable. So not just RTMs but also recycled materials that could be used in construction sector require more support in order to enter into the logic of GPP: Over the years, ETRA working groups have prepared an inventory of a broad range of materials and products that are produced from RTMs, and will work with municipal authorities to prepare the appropriate criteria for use in GPP.

19.10 Some successful good practices as opportunities to use recycled tire materials

Since January 2010, the European Commission has promoted good practice experiences on GPP to illustrate how public

authorities in Europe have successfully "greened" a public tender or procurement process. These include the use of life cycle costing (LCC), circular economy principles, and approaches to fostering sustainable innovation.

In addition, the Interreg Europe program has implemented a web portal as well as a newsletter called GGP4Growth that describe and promote good practice and projects on GPP. National governments are also working to spread awareness and visibility of good practices. Indeed, many national and local public bodies are also partners in many EU projects. These good practice cases are published on the EU website with the aim of providing tips for replicating experiences under the "lessons learned" sections. We have selected two cases that are of interest and could be applied to RTMs:

- Concrete and buildings
- Asphalt and roads

19.10.1 Concrete and buildings

The European aggregates industry (concrete production, roads, and railways) produces 3 billion tons per year of concrete aggregate, from more than 28,000 extraction sites across Europe. The sites relate to small- and medium-sized enterprises. Due to the growing concerns over the environmental impact of natural aggregate extraction and the continued rise in aggregate demand, the construction industry and the civil engineering sector are working to develop a more sustainable approach, mainly related to the use of recycled and secondary aggregates to replace mineral aggregates, although they have also begun to work with other high-performance recyclates to replace some of the bulk material such as RTMs.

The building sector has vast potential for the use of RTMs. Recent research has demonstrated that RTMs in concrete increase performance, making the concrete more resistant and more flexible. The environmental benefits are also remarkable. We must remember that after water concrete is the most widely consumed substance on Earth.

19.10.1.1 Case study: using recycled concrete in the construction of a new building, State of Berlin (Germany)

The construction industry is heavily dependent on resources, in particular concrete. The extraction of primary resources used in concrete production, such as open pit mining for sand and gravel, can lead to environmental damage including soil loss,

habitat loss, and water, air, and noise pollution. In addition, the energy used to transport aggregates and process them into concrete can contribute to greenhouse gas emissions and air pollution.

It is possible, however, to reduce the environmental impact of concrete by replacing some of these primary materials with recycled materials, without impacting the performance of the end product. In 2013, Berlin was using more than 1 million tons of recycled concrete per year in road construction. However, demand for recycled concrete was still lower than its potential, and uptake in building construction was particularly slow.

19.10.1.1.1 Results

While recycled concrete is currently more expensive than virgin aggregate, the State of Berlin assumed that cost neutrality would be achieved in the future as demand becomes more regular and the retrieval of aggregate for reuse is improved.

The total cost of a particular building project was around €33.5 million. Tenders were submitted at the end of 2014 and construction began in 2015. The second phase of construction, which included the concrete structure, was completed in December 2016. Twelve bids were received, and all bidders were able to meet the technical requirements for recycled concrete. During the works, no difficulties in the use of recycled concrete were reported by the contractors.

19.10.1.1.2 Environmental impacts

Recycled concrete is an opportunity to close the loop in building materials, and create a more circular life cycle for buildings. It provides a means to avoid environmental impacts associated with gravel mining. In addition, it reduces the environmental impact associated with the transportation and production of recycled aggregates – particularly when construction rubble, which is located close to or on the same site that a new construction will take place, is used.

In comparison with traditional concrete using primary aggregates, using recycled concrete in the pilot project at Humboldt University saved 880 m^2 of virgin gravel, 66% of the energy required for production and transport (or 225 megajoule (MJ) per ton of recycled concrete), and 7% of the associated CO_2 (0.6 kg CO_2 per ton of recycled concrete). Thus the scientific monitoring of the pilot project proved that recycling firms are able to produce concrete at a high enough quality to meet all the requirements of building works (i.e., strength class

and consistency) without requiring any additional or special treatment during installation. This was also confirmed in the subsequent building of the Berlin Institute for Medical Systems.

19.10.1.1.3 Lessons learned

"This procurement and the earlier pilot (from 2013) demonstrates that recyclers are able to produce high quality aggregates which can be used in concrete, and are not of inferior quality compared to virgin aggregate. Moreover, this aggregate can be easily used to make concrete which meets all the necessary standards (such as strength, class and consistency), and requires no special or additional handling during installation in comparison to primary aggregate concrete."

19.10.1.2 Other opportunities for recycled tire materials in the building industry

RTMs can also be used in concrete for different purposes: more elasticity, higher resistance, altogether higher performance, reducing the use of virgin materials. The building sector already absorbs 18% of RTMs mainly for insulation and flooring but has vast potential to use more RTMs but has high increase potential. Recent research has shown that RTMs in concrete increase performance, making the concrete more resistant, more flexible, etc. The use of 10 kg of recycled steel fibers for concrete reinforcement corresponds to the emission of 1 kg of CO_2 eq. compared to 21 kg of CO_2 of virgin fibers.

It is possible to achieve significant replacements of recycled materials into concrete, depending on the type of product, application, and combination of the various recycled materials. We targeted the following:

- Recycled aggregates, at least 5%; but in some cases it will be possible to achieve 25%
- Recycled steel fibers, between 1% and 4%
- Recycled rubber powder, between 15% and 30%

19.10.2 Asphalt and roads

Asphalt is one of the most versatile construction materials, and is used in areas such as roads, railway beds, airport runways, taxiways, bicycle paths, playgrounds, running tracks, tennis courts, barn floors, greenhouse floors, ports, bridges, tunnels, and landfill caps.

There is more knowledge and science involved in this material than most people realize. This has resulted in the production of

many different types of asphalt, each having specific characteristics. For example, some are designed to be porous and very silent, and others to be impermeable.

The following list gives some idea of the importance that asphalt and roads have achieved over the past 50 years:

- The European road network consists of national roads (motorways), regional roads, and local roads. The total length of this network sums up around 5.5 million kilometers, from which more than 80,000 km are classified as motorways. Today more than 80% of motorized inland passenger transport depends on roads – this does not take into account cycling and walking.
- More than 70% of all inland freight transport in the European Union is transported by road; for part or all of each journey.
- More than 90% of the European Road network is surfaced with asphalt.

19.10.2.1 Case study: recycled asphalt used for road resurfacing, City of Hamburg (Germany)

In Hamburg there has been a long tradition of road construction methods that use materials such as factory-made mineral aggregates from demolished buildings or incineration ash. Since the 1980s, Hamburg authorities have worked toward increasing the use of granulated asphalt recycled from existing roads. Reclaimed asphalt pavement (RAP) consists of approximately 95% mineral aggregates and 5% bitumen.

The use of RAP began with the deeper, base courses of roads. After proof of performance was asserted and sound experience was gained from these applications, granulated asphalt made its way to the more sophisticated and technically critical binder and surface courses. The City's final goal is to proceed from using less than 50% RAP in these layers to recycling of 100% of the original construction materials when refurbishing and resurfacing roads. Using RAP is especially significant for surface layers (wearing courses).

Hamburg prescribes the use of a minimum 35% white aggregates in order to brighten road surfaces and to have a colder, deformation-resistant road surface in summer. The high cost of these aggregate materials increased the incentive to recycle more than just base courses. A more careful consideration of the whole process of asphalt production was also triggered by recent dramatic increases in bitumen prices. The City allowed a group of private companies, who originally came up with the full recycling technology, to test its use on public roads owned by the City. After the quality was tested by Hamburg's road

construction authority, the City was reassured of the use of the 100% recycling process. Having renovated two other roads using this technique, a restricted tender procedure was conducted, with five companies invited to bid.

19.10.2.1.1 Results

This is the third project to demonstrate that Hamburg's goal to minimize the environmental impact of road construction by reusing reclaimed asphalt can be successfully achieved. Moreover, the construction method is economically viable. While bitumen only constitutes approximately 5%–6% by weight of the materials used in asphalt, it can contribute to over half of the total cost and this price tends to rise further according to increasing world oil prices.

All five of the companies invited to tender made a bid and the company that quoted the lowest price was awarded the contract. Under this project alone, Hamburg saved 30% compared to the costs for conventional road resurfacing, which in this case equates to approximately €20,000.

Although significantly cheaper to produce, the recycled asphalt has the same properties and durability as new asphalt. Also, the costly replacement of stones with a color compatible with the architecture of Hamburg's Möncke-bergstrasse was avoided, as all existing materials were reused. Traffic disruptions and local air pollution associated with congestion was kept to a minimum, as the work was carried out in a period of only 36 hours over a weekend.

19.10.2.1.2 Environmental impacts

Road construction has significant environmental impacts. Combustion of fossil fuels during manufacturing causes the emission of carbon dioxide (CO_2) and nitrogen dioxides (NO_2). This contributes to greenhouse gas emissions and global warming, atmospheric pollution (ground-level ozone creation and acidification) as well as nutrient enrichment. Also, the traditionally very high temperatures associated with heating bitumen consumes a large amount of energy.

Meeting Hamburg's objective of recycling 100% of all material when resurfacing roads implied significant environmental benefits. Use of recycled asphalt along with warm-mix technology greatly reduces such emissions, as mineral aggregates do not have to be quarried and transported over long distances. Also, bitumen does not need to be manufactured from mineral oil. The rejuvenating additives have their own carbon footprint,

but this is far smaller than the benefits of avoiding quarrying and the use of fresh bitumen. Finally, the recycled mix is manufactured at lower than conventional temperatures, which reduces energy consumption for manufacturing and paving.

19.10.2.1.3 Lessons learned

The process described in this example is considered to be very innovative and other German cities have already voiced interest in doing the same or have already built similar roads.

In the future, the City of Hamburg intends to issue open tenders, rather than use restricted tenders for similar works. Now that suitable products are on the market, it is theoretically possible for any road construction company to carry out these works, but they will need to acquire additional skills to use them correctly. The process requires a great deal of expertise. Not only is the right manufacturing equipment needed, but also pretesting of asphalt needs to be conducted to determine the chemical composition and physical state of the aged bitumen in a surface prior to it being recycled.

In this specific case, recycled asphalt was used on the same road it was originally taken from. However, a more efficient overall process needs to be developed to carry such procedures out on a wider scale, using recycled asphalt on other roads in the same city or region according to need.

19.10.2.2 Other opportunities for recycled tire materials in asphalt and roads

RTMs have been used in asphalt since the late 1950s. There have been incredible developments and many success stories. Their use is compatible with others recycled materials and different techniques.

Rubberized asphalt has a longer life; is more resistant to weather, dynamic load, and aging; is more adherent; and dampens road noise. Using rubberized asphalt in up to 1% of the annual paving works would increase tire recycling by 10% in the EU, providing in exchange more sustainable, safer and quieter roads, with reduced maintenance costs and longer performance.

The advantages of using recycled rubber in asphalt compared to conventional asphalt can be summed up as:

- Improvement of the resistance to plastic deformations, because of the overall higher resilience of the material.
- Improvement of fatigue behavior, because of the elastic rubber granules and of the partial modification of the bitumen.

- Improved resistance to reflecting and thermal cracks, because of the stress-absorbing capacity of rubber grains.
- Reduction of thermal susceptibility, because of the partial modification of the bitumen.
- Reduction of rolling noise (in wearing courses), because of the "softening" of the surface.
- Reduction of transmitted vibrations, because of the softening and of the damping properties of the rubberized asphalt.
- Deicing effect (in wearing courses), because of the large deformation of the exposed rubber grains loaded by vehicles tires, which breaks the ice layer and starts the deicing process.

These advantages do depend on the relative amount of rubber used, and the characteristics of the final product (hot mix asphalt) can be, in comparison to conventional mixes, very different, and engineers have the chance to obtain a wide range of different products suitable to be used for specific tasks.

From an environmental point of view, the large amount of rubber normally required in granulate/asphalt technology offers great potential for waste rubber recycling; it has been calculated that the rubber used in each square meter of road surface comes from one passenger tire.

19.11 Circular procurement

A frequent misunderstanding is the belief that GPP should be focused on the use of recycled materials by public authorities. Public bodies buy many different products and services. Buying green could have many different meanings. GPP criteria could be extremely green and innovative and nonetheless does not involve recycled materials.

Circular procurement sets out an approach to GPP, which pays special attention to "the purchase of works, goods or services that seek to contribute to the closed energy and material loops within supply chains, whilst minimizing, and in the best case avoiding, negative environmental impacts and waste creation across the whole life cycle."

Circular procurement approaches have the potential to deliver multiple benefits. For example, as well as allowing purchasers to focus on need fulfilment and consider lifetime costs with potential for savings, circular procurement also provides a framework for more holistic consideration of environmental impacts and waste creation across the whole life cycle of goods and services.

In order to support public purchasers to leverage support for a transition to a circular economy, in October 2017 the European Commission published "Public Procurement for a Circular Economy." This brochure contains a range of good practice case studies as well as guidance on integrating circular economy principles into procurement.

19.11.1 CIRCPRO – an Interreg project on circular Economy and some good practices for recycled tire materials

CircPro in an Interreg project promoting the transition to a more circular economy related to national and regional decision making by increasing the implementation of the circular procurement. CircPro's main objective is to increase the implementation of circular procurement under the targeted policy instruments so that the circular economy principles and criteria are incorporated or taken into account as a horizontal principle. CircPro targets the circular procurement from different approaches that have different complexity: all of which facilitate closed loops, but where the focus shifts from better-quality products to new and innovative products and new business concepts. The ultimate goal after the project is to get circular procurement as an established practice of the procurement procedures within the partnership regions' municipalities and towns.

The objectives are pursued by increasing partner regions' know-how on circular procurement and recycled materials. Identifying, assessing, exchanging, and disseminating the existing national/regional initiatives, good practices, supporting measures, pilots and initiatives, main actors, organizations, and networks that could boost the implementation of the circular procurement in the regions. Identifying the procedural and legal barriers experienced by procurers and suppliers when implementing procurements with circular elements. Providing a meeting place and enhancing dialog between procurers and suppliers (both groups are represented in the partnership and stakeholders' group).

ETRA joined the project as an accredited stakeholder, with the aim of participating in the stakeholder group meetings in order to work with the public and private institutions, representing local authorities, innovation clusters, education and research bodies, business implementing agencies and associations, as well as a purchasing company.

As part of the activities ETRA promoted three good practices:

– ***Use of recycled tire powder in road asphalt***

The rubber powder may be used in hot-mix asphalt in partial substitution of aggregates, in order to increase the performance of the road paving. The use of bituminous mixes modified with powder from EOL tires allows to:

- improve the mechanical characteristics of the road paving (extension of useful life and maintenance intervals);
- improve the adhesion between the tire and the flooring, even in wet conditions; and
- contribute to the reduction of the noise produced by the rolling of the tire on the asphalt.

This practice is rarely used for various reasons:

– They are initially more expensive than traditional asphalt, but in the long run are cheaper due to a longer life span.

– Similar performances are normally obtained by bitumen modification through chemical additives. This method is even more expensive than rubber powder modification but more familiar to technician and paving companies.

In the period 2011–14 the Metropolitan City of Turin coordinated a life project (tyrec4life) for the development and implementation of innovative technologies to expand the use of rubberized asphalt in road paving and ensure an optimal balance between technical, environmental, and economic aspects.

During the project 7 km of roads were paved, equal to 48,800 square meters, contributing to recycle 9200 tires of medium-sized cars. This practice recycled about 1300 tires per kilometer of paved road.

– ***Use and reuse of recycled tire granulate as infill material for artificial turfs***

The rubber granulate used as infill material of artificial turf gives elasticity and improves shock absorption. Artificial turfs are replacing natural ones because the artificial turf can be played on at all times, equivalent to 2500 hours per season compared to 250 hours for natural grass. In addition, artificial turf retains its characteristics while its composition combines durability with long-lasting resilience and "soft touch" developed for intensive use. It is maintenance-friendly and environmentally friendly. There is no need to irrigate, meaning there is no water wastage and no mowing or weed removal is required; moreover, there are no CO_2 emissions or the presence of pesticides.

In Turin from 2003 and 2008 24 fields were transformed from natural to artificial surfaces; 20 of which were recycled

with rubber as infill; 2500 ton of rubber granulate were used, corresponding to 500,000 recycled tires.

The Turin experience was parallel in other countries in Europe but it was a first in Italy; anticipating a solution that has since been adopted everywhere in the country. Unjustified concerns about environmental and health impact were raised and still are in order to discourage the use of recycled materials and support the use of virgin materials. Today, after an average use of 15 years it is time to dismantle old fields and install new ones. It is also possible to replace just the green carpet and reuse most of the on-site materials, namely sand and rubber in particular.

– ***Use of Rubber granulate from tire recycling for draining paving in flowerbeds around tree bases***

Normally flowerbeds at the base of trees have a natural turf surround that requires high maintenance and costs. Unfortunately, in most cases these installations are in a state of perpetual abandonment as public administrations suffer from a chronic lack of funds, resources, and personnel. We often witness situations of neglect and degradation clearly visible in many cities. The rubber granulate, suitably agglomerated with synthetic binders and water-based pigments, and casted on site, can be used to make a walkable, draining, and transpiring flooring to cover the flowerbeds around trees. The result is a safe, comfortable surface for pedestrians compatible with the needs of air and water for the plants.

This page intentionally left blank

20

Roads to the future

Valerie L. Shulman[1] **and Serji Amirkhanian**[2]

[1]*The European Tyre Recycling Association (ETRA), Brussels, Belgium*
[2]*Department of Civil, Environmental and Construction Engineering, The University of Alabama, Tuscaloosa, AL, United States*

20.1 Introduction

Recycled tire materials come in many shapes and sizes, both large and small and everything in between, as well as steel and textile. What is currently being done with these materials could not have been imagined when the industry began to proliferate about 30 years ago in North America, the European Union, and other regions including South Africa and Australia, among others. The production of new tires was certainly not on the agenda – or even in the long-term planning, which was a critical concern to many recycling bodies.

The most common recycling schemes at the time were based upon the "what comes out is reproduced" model. In other words, to use the recycled materials to produce the same range of products as the original (e.g., steel for steel, glass into glass). Tires were among the first to stray from that model.

In the beginning tire "recycling" produced inexpensive replacement materials – the majority for products that had not been made of rubber but a broad array of other compressive/durable materials. But tire recyclers began to investigate the characteristics of the recyclate – and other materials, products, or even applications that could benefit from similar performance characteristics – virtually opening the entire elastomeric repertoire to investigation and even replication. And then they went beyond that!

A brief review of some of the products and applications that are included in this book will demonstrate how far the tire recycling industry has come. The biggest concern was whether or not there would continue to be a consistent flow of tires to recycle to allow companies to succeed. The concern was not an issue as we learned early on, that tire availability will not be an issue in the foreseeable future. In fact, the tire market has expanded in

Tire Waste and Recycling. DOI: https://doi.org/10.1016/B978-0-12-820685-0.00013-2
© 2021 Elsevier Inc. All rights reserved.

unexpected ways – partly due to the increased weight of newer vehicle models – notably with electric cars taking precedence, are heavier and tires have to be replaced more frequently. Thus one of the first relevant issues has been resolved.

This chapter explores where tire recycling is today, as an industry – its current context – followed by a preview of the future and the new roads on which it will embark with exciting new options. We have begun with a glimpse of the past and how we arrived at the present – with 2020 as our starting point.

20.2 The context for tire recycling

The year 2020 commemorates the 75th Anniversary of the United Nations as "UN75 – 2020 and Beyond." It celebrates the successful implementation of a new approach to resolving the world's conflicts and major issues of concern – including those impacting human health and the environment. It provides an opportunity to take a moment to reflect, review, and evaluate the progress that has been made in terms of changing the ways in which we as nations respond to global issues that impact our citizens, whether in relation to disagreements and hostilities, considerations of endurance and survival, or health and the well-being of the environment. It is the next step to preparing for the future.

The UN has had special meaning for recyclers and even more so for the tire recycling industry for a number of reasons – including the acknowledgment of tire recycling as a valuable participant and contributor to sustainable development. The impact of the Basel Convention has been important and far-reaching for 20 years in terms of the safe movement and treatment of waste tires. But the Basel Convention is not alone in impacting on tire recycling. To some extent the roots of the modern tire industry and hence the tire recycling industry are firmly planted in the WWII era.

Many actions undertaken by the Organisation for Economic Co-operation and Development (OECD) and other related bodies including the UNEP (UN Environment Program) and UNDP (UN Development Programme) have been instrumental in stimulating interest in the development of social actions that inadvertently impacted tire recycling. These bodies work directly with national and international sports and leisure infrastructure management federations that have directly and indirectly expanded the use of year-round sports programming, playgrounds, and playing fields. They have supported a variety of developmental programs focused on urban, rural, and isolated areas around the world by

supporting the construction of facilities that rely on this type of investment to encourage socialization of all age groups from toddlers to seniors.

These investments will continue in the future on the worldwide stage particularly with the advent of UNCTAD's Global Green Deal – which is projected to increase green investment considerably, at national levels, stimulating employment growth in related actions – including increased government support of improved infrastructure, which could have the potential to improve green public procurement programs at the local level. The EU, North and parts of South America, Australia, and parts of Africa and Asia have all followed up to some extent and expanded on the concept by implementing legislation that supports national programs for funding Green Public Procurement (GPP) designed to improve and expand their rail and road transport infrastructures. Uniquely, some of the most innovative of GPP programs also provide lobbying and training activities for engineers, politicians, etc., to understand the potential benefits and follow-up activities for the public. Measures are also included to contain some of the negative impacts as well, frequently focusing on the abatement and limitation of noise and vibrations from various forms of urban transport. Ironically, many of the products and applications supported in these offers include those produced from recycled tire materials!

The year 2020 also celebrates a second related and equally important major milestone – with the acknowledgment of the evolution of the tire recycling industry playing a singular role as provider of waste management services to a multifunctional role in which tire recycling is a fundamental contributor to the accomplishments of sustainable development and to the realization of the global circular economy. In other words, waste management has become a parallel responsibility (but not subsidiary), a preparatory tool for developing sustainable materials, products, and applications to fulfill the emerging needs of tire recycling and related industries – and through this aspect provide the raw materials for the development of other sectors as well. An essential role today that has been evidenced by many of the works discussed in this book illustrating the great intrinsic value of this valuable economic stream.

To summarize, today, tire recycling can be said to be comprised of several specific functions:

1. The identification and removal of no-longer-functional tires from the public marketplace (identification and management of nonroadworthy tires into the wastestream) (***waste management function***).

2. Participation and oversight of relevant legislation concerning tire road-worthiness, including monitoring and enforcement responsibilities and requirements for permitting and penalties.
3. The definition of the larger "tire marketplace," which includes both historic and future market movements identifying new potential sources of postconsumer tires from around the world (***chronicling and forecasting function***).
4. The identification and development of sustainable materials and products to replace those less sustainable and/or more costly to produce (***research function***).
5. Organization of research on ingredients, materials, products, structures, and applications – to resolve issues arising in the elastomer and related sectors as concerns wear, performance, durability, compatibilities, etc., to meet current and potential needs.
6. The preparation and production of the raw materials that will improve performance, cost-effectiveness, and sustainability of the output ingredients, products, and applications under defined conditions (***production function***).
7. The enlargement of the sector through outreach and demonstration of the benefits of the materials, products, and applications, etc. ***(development function)***.

In recent years, tire recycling has become an example of an alternative for other nonconforming sectors that do not follow the typical model of "circular development" (i.e., what goes in comes out) – by recycling the new product into the same as the original. It is, however, ironic that today, several recycled tire materials are being sought after for exactly that purpose due to the high-performance, durability, and cost-effectiveness of the materials produced. Among those selected are different types of devulcanizates discussed in several chapters, as well as pyrolytic outputs – including recovered carbon blacks – and tire-derived silicon carbide materials, which are also discussed herein.

Together these five actions complete the sequence of "tire recycling" – preparing the way for future elaboration and collaboration with other industries and increasing the avenues for increasing the valorization opportunities for this valuable resource. Notwithstanding, a crucial question remains to be addressed – will current markets provide sufficient feedstock material consistently enough to provide a consistent input flow for the expansion necessary to meet the capacity needs for future production? Needless to say, several chapters also address these issues and help to define how effectively these needs will be met.

Thus during the past more than three decades tire recycling has evolved from a series of waste management treatments that

process waste tires mechanically to a focused, global recycling industry that transforms those raw materials into valuable materials, products, and applications that can be used under, on, and in and around the road – as well as many other environments.

It is also interesting to note that the initiation of what has become "the tire recycling industry" can also be found during the WWII era – performing the same kinds of activities as we see today – with the creation of alternative materials and products to meet existing needs. In fact, when 95% of the rubber plantations in Southeast Asia were captured and no longer available as a source to Allied troops, there was concern that Jeeps and supply trucks would no longer be available and tanks could no longer roll because of the lack of this vital raw material – rubber. After much research natural rubber was substituted with synthetic rubber – and many of those synthetic rubbers first created to fill the gap are still in production today.

The quest for new, performant materials, processes, and products to replace earlier ones is not new. Many of the materials presented in this book have evolved because they fulfill an important need. Pyrolysis is an excellent example of a process that was imagined almost a century ago (1925) but that has attained only exemplary success within the past decade! At times, science must catch up with imagination. All of the elements were available – theoretically – but it took almost a century for the technology to catch up. Today, continuing the search, pyrolysis has moved to an even higher level – in which it is possible to produce a form of silicon carbide (SiC) from tire pyrolysis. SiC provides a totally new level of product sophistication with a range of costly applications in refractory linings, heating elements for industrial furnaces, wear-resistant parts for pumps and rocket engines, semiconducting substrates for light-emitting diodes, and a range of ceramics. The product output is continuing to expand.

Our goal in preparing this book is to offer an overview, a series of "the roads less taken," toward the future and the circular economy with an array of green opportunities using recycled tire materials. As noted in earlier chapters, one of the reasons this book is unique is because of the authors. Each chapter was written by one or more authors each of whom is an expert currently working in the field either in a commercial or municipal setting. Each has vast experience using these materials, products, and or applications as they have evolved throughout the years. Many have built their careers along with the materials and applications, and are pleased to share their experiences with you. We have included their contacts and they all are

willing to respond to your comments and requests. The outcomes are available for view and for additional support through a variety of related activities.

This book illustrates many of the practical ways in which tire recycling can and does contribute to the circular economy by recycling tires in commercially viable ways – either by reusing the tires themselves – or the three principal parts (i.e., the rubbers, the metals, and even the textiles) in a variety of formats. The opportunities for further exploration are included.

While much of the research on which these materials, products, and applications as well as the treatments and technologies used to produce them may have begun under research or laboratory conditions each was actually tested and later became widely known through actual use in the field. As you will notice, many of the terms used have become common parlance in various industries and even in construction and community development.

20.3 Market focus—thoughts for the future

Until recently, tire recycling markets were initiated and expanded in what appeared to be a rather haphazard manner – without a common focus. The products did not appear to be related – each was representative of a different industry (e.g., urban transport, sports fields, shoe soles). Tires were not the focus – but a variety of diverse, unrelated materials and products grew to prominence for apparently disparate reasons resulting in a hodge-podge roster. A glance at today's seven principal and several niche markets confirms that point.

Until now, production and use have maintained a relatively uneven pace, with some products or applications growing (e.g., automotive), and others beginning to wane as new materials come to the fore (sports field surfaces). There is some expansion into new realms, and there are strong indications that this pattern could continue into the future. There appear to be four common elements that drive each of these markets: sustainability (greenness), enhanced performance, resilience, and cost-effectiveness/economics.

The seven traditional large markets coupled with smaller niche markets consistently consume more that 80% of the materials produced. Newer niche markets, many of which have the capacity to use increasingly sophisticated technologies, are beginning to evolve. Recovered carbon black, silicon carbide from pyrolysis, recyclates from off the road (OTR) tires, compression molding without additives, among others – each innovative and produced

for high performance, at low cost. And, among the newest products being developed are automotive tires!

20.3.1 Planning for next steps

A number of areas have great potential for increasing the tire recycling rate in the future including roads, roofing, hermoplastics, and devulcanization. The following includes short descriptions of the processes that could have a major impact on the future of the tire recycling industry.

20.3.1.1 Roads

There are approximately 65,000,000 km of roads in the world. It is also estimated that there are over 1,000,000,000 tires discarded each year around the world. Many of the roads are dirt roads and the remaining are either concrete or asphalt roads. Most of these roads contribute in many ways to the society's well-being by providing safe and maintenance-free pavements and a better way of life for citizens. It is believed that success of any society depends heavily on having a proper functional infrastructure system. There are many applications of rubberized asphalt projects that will help in providing this type of system, as have been presented in this book.

Most interstate systems around the world utilize polymer binders in asphalt mixtures. One of the best polymerized asphalt binders is crumb rubber-modified (CRM) binders that usually contain from 10% to over 20% of crumb rubber by the total weight of the binder. This type of binder has been used in many applications of road construction, all over the world, including in surface paving, emulsion applications, and maintenance applications (e.g., crack fillers). Fig. 20.1 shows an example of the application of the CRM binder used to construct a field project. This pavement lasted approximately 20 years before some maintenance had to be done to the structure.

One of the applications that will have a major impact on people's lives will be improvements of dirt roads. There are many ways that this could be accomplished. One of the most effective methods is the utilization of CRM binders to pave these roads. This will result in a road that will last much longer, since the surface has been waterproofed, while providing a cost-effective alternative to the traditional techniques used for decades. There are several million kilometers of dirt roads in developing and underdeveloped countries. It is proposed to use a modified binder containing 20% CRM mixed at elevated

Figure 20.1 An example of crumb rubber-modified (CRM) asphalt binder field project (paving operation and the finished product).

temperature. This binder then can be sprayed on top of the dirt road enabling drivers to use a waterproofed and durable road. These dirt roads are costing governments much limited funds since they have to maintain them each year due to environmental issues (e.g., rain, etc.) and traffic. In many cases, these treated roads have lasted several years before they needed any maintenance saving governments money. In addition, the lack of disruptions when maintaining the roads will enable drivers to be more productive and have lower car expenses (e.g., costs of suspension damage due to potholes). It is estimated that each kilometer of dirt road (3 m wide) can utilize over 250 passenger tires (2.2 kg/m^2 rate of application). It is estimated that several million tires a year could be used for this application.

One of the most effective methods used in the construction industry to mitigate highway traffic noise is building noise barriers. There are many types of materials, including CRM as shown in Fig. 20.2, used in constructing these walls; however, in many cases, there might not be a need for a wall at all. One of the chapters of this book is dedicated to this topic, so we will not cover it in detail here, but it is important to note that many neighborhoods around the world are constructed around heavily traveled highways and noise, as it has been defined by many governmental agencies and the UN as a health issue, has been and will be a major concern. One of the most effective methods to overcome this issue is the utilization of open graded friction course (OGFC) on top of the existing highways.

Figure 20.2 Highway noise barriers containing crumb rubber-modified (CRM) binder.

An OGFC mix is a rubberized mix with approximately 18% air voids and 7% to 9% binder content, which consists of gap-graded aggregate and modified binder containing very high percentage of CRM (e.g., 20%). This allows a very thick film thickness around the aggregates, without any run-off of the binder even with the high percentage of the binder, and with the high air voids, the sound of vehicles in many cases is dropped by 5 to 7 dBa. This type of pavement also is known to make the pavements safer, compared to typical asphalt or concrete pavements, since by having very high air voids, the rainwater goes into the OGFC voids and is transferred out of the pavement system by providing a sloped surface beneath the OGFC (Fig. 20.3). We believe that many locations around the world could benefit from this type of structure since it provides two major benefits: reducing noise and a safer pavement during rainy seasons. The reported advantages are many including significant improvement in pavement permeability, enhancement in pavement friction, and reduction of tire/pavement noise. Each kilometer of pavement surfaced with OGFC (5 cm thick and 3.3 m wide) utilizes over 3000 tires. The OGFC is suitable for any heavily traveled asphalt or concrete road. For instance, for a motorway or an interstate system (three lanes each side, six total, and 10 km long), approximately 200,000 tires are needed to construct the pavement. The M25 motorway is one of the heaviest traveled highway in England with a length 185 km and in many areas eight lanes. Several million tires could be utilized if officials decided to implement an OGFC program. So, why don't they?

The answer to this question is complex, but at the same time very simple. There are political issues, lack of technical know-how and equipment in some cases, environmental issues, public

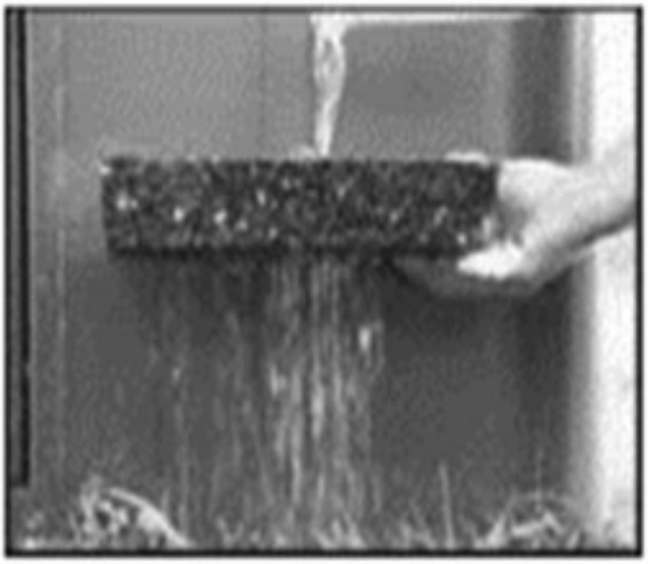


Figure 20.3 An example of a typical open graded friction course (OGFC) structure.

perception, and initial cost issues that impact the decision-maker views. The implementation should be based on scientific and technical facts and information; however, many times other factors govern the decisions made by officials. Therefore the recycling industry must be proactive and have an aggressive long-term program to educate everyone including engineers, the public, and politicians providing technical information and facts from the hundreds of available research projects and field projects all over the world. If only 0.1% of all pavements in the world used some form of rubberized asphalt mixtures in their various layers, over 50,000,000 scrap tires would be utilized. It is obvious that there are tremendous opportunities in this area and we must educate, train, implement, and lobby (using technical experts) all over the world. It is important to note again that rubber-modified asphalt binder is not an experimental binder but an engineered material that is helping enhance the properties of typical asphalt pavement.

20.3.1.2 Roofing

Many roofing systems, commercial and residential, are now utilizing CRM in products. The final products must satisfy established performance and technical standards set forth by various local and national governmental standards. Many of these roof systems, for instance, must satisfy some requirements regarding the flammability and moisture/vapor transfer. Both commercial

Figure 20.4 Residential rubber-made roofing system.

and residential roofing applications utilize a binder, such as an asphalt, as an adhesive. Asphalt is an excellent waterproofing material and a very good adhesive. In order to enhance the roofing system's flexibility, flow characteristics, and fatigue resistance, CRM is added to the matrix at a specified amount. There are other roofing products, such as water-based acrylic roofing systems, that utilize CRM to create a durable and flexible product that is compatible to any conventional membrane. These types of systems are also referred to as infrastructural coating systems. In order to produce a durable and waterproof rubber matrix for sealing and insulating the surface, the nontoxic, noncarcinogenic acrylic coating will be infusing the recycled rubber. In addition, there is another roofing product made from compression-molded CRM, called shake rubber roofing tiles, that is keeping houses cooler in the summer and warmer in the winter (Fig. 20.4). In addition, they are low maintenance, safe (fire resistant), immune to insects, and resistant to many other elements such as rot, mildew, and moss.

Polymer-modified roofing materials have been utilized in residential roofing shingle production (e.g., granules, asphalt, fiberglass) for over 30 years. In many cases, the warranties are 20 years or more and thus the product is expected to last a long time. In general, the recycling content is not important if it cannot improve the performance of the product. There are many advantages of utilizing CRM in the production of roofing shingles including the following:

1. Increasing the granule adhesion
2. improving scuff resistance

3. Improving shingle life
4. Retarding the aging and oxidation of the resulting binder
5. Lowering the carbon footprint due to many reasons such as less oxidation, utilizing less asphalt binder, plus using CRM instead of virgin materials
6. Improving the tear and tensile strengths and therefore less roof cracking

It is estimated that the asphalt shingles market will surpass the $9.5 billion by 2025, with residential applications showing a gain of at over 3% by 2025. This growth is attributed to a number of factors such as rapid urbanization, combined with builders continuing to develop advanced roofing systems (e.g., utilization of CRM in the production of the shingles). Many customers and homeowners are desiring more environmentally friendly materials and these types of products fit that narrative. For example, in the United States the residential roofing sector will be a major contributor to this multibillion-dollar market when, by 2025, the population is expected to hit 345 million. Obviously, in many cases, the population growth alone will result in replacing older, worn-out roofs around the country. We believe that this market must be explored by the tire recycling industry since there is huge potential for success and implementation.

The commercial roofing market encompasses many roofing solutions applied on a building's exterior structure. The solutions are different depending on many factors (e.g., geography, cost, etc.) and are made of diverse materials such as rubber, asphalt, stone slabs, and woods. These solutions are used in hotels, malls, offices, and hospitals. In recent years, the use of roofing products in the construction of green buildings has increased many folds and holds immense opportunities for the market and tire recyclers. Advanced commercial roofing products, including the ones utilizing high percentages of CRM, are in great need because they are considered to have lower environmental impact. In many cases, architects are demanding the utilization of these materials in the construction of buildings. These new products will have a profound impact on the global commercial roofing market. Considering global market, the North America's market is expected to see the highest demand for commercial roofing, and Europe is a close second in addition to the expanding construction market (e.g., India and China), which has resulted into a higher market share in Asia Pacific (Fig. 20.5), with a total market value, 2017, being as high as 113,381.1 million USD.

Due to the market size and the increased popularity of using CRM in the roofing industry, recyclers have a major opportunity to market their products. For example, one of the authors

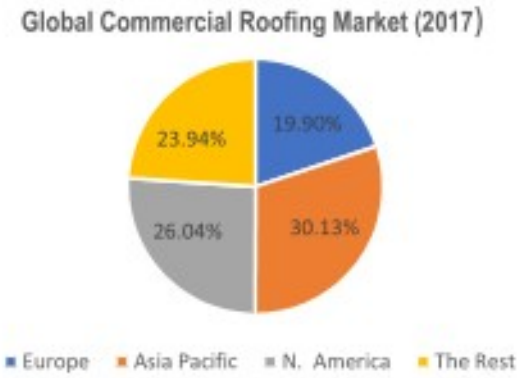


Figure 20.5 Global commercial roofing market for 2017: US $113,381.1 million.

has been working with a major commercial roofing company that uses approximately 45,000 tons of CRM each year. It is important to note that this is only one company and there are many others in need of alternative materials for production of commercial roofing products.

20.3.1.3 Thermoplastic elastomers

There are several areas of the utilization of CRM that will have a major impact on tire recycling industry. One of these areas is the use of CRM in the production of thermoplastic elastomers (TPEs). A brief introduction to this topic and its importance to the entire recycling industry is presented in the following.

Polyethylene (PE) is a common polymer used in a variety of consumer applications ranging from beverage containers to garbage bags. There are several types of PE with LLDPE (linear low-density polyethylene), LDPE (low-density polyethylene), and HDPE (high-density polyethylene) being among the most common. Regardless of the type, nearly all PE base material is in the form of pellets. In general, elastomers are commonly grouped into two major categories:

- Thermoplastics
- Thermosets

TPEs are materials that repeatedly soften/melt when heated and harden when cooled. Most thermoplastics are soluble in specific solvents and can burn to some degree. Softening/melt temperatures (some people refer this as the viscosity of materials) vary with polymer type and grade. They are very sensitive to heat/shear and therefore care must be taken to avoid degrading, decomposing, or igniting the material.

Most thermoplastic molecular chains can be thought of as independent, intertwined strings resembling noodles. When heated (e.g., for molding), the individual chains slip, causing plastic flow. When cooled, the chains of atoms and molecules are once again held firmly. When heated again, the chains slip again. Obviously, there are practical limitations to the number of heating/cooling cycles to which thermoplastics can be subjected before appearance and mechanical properties are affected. TPEs undergo a chemical change during processing and become permanently insoluble and infusible. It is this chemical cross-linking that is the principal difference between thermoset and thermoplastic systems. Natural and synthetic rubbers such as latex, silicone, butyl, and neoprene, which keep their properties through a process known as vulcanization, are typical TPEs.

When thermosets are cured or hardened, cross-links are formed between adjacent molecules, resulting in a complex, interconnected network. These cross bonds prevent the individual chains from slipping, thus preventing plastic flow when heat is added. If excessive heat is added to the TPE after the cross-linking is complete, the polymer is degraded rather than melted. A simple example is the frying of an egg. When it is cooked further heating does not return the egg to its liquid state, it only burns. There are many benefits of using TPEs compared to thermoset rubbers including:

1. Design flexibility
2. Lower fabrication costs
3. Shorter processing times
4. Scrap is fully recyclable
5. Simpler processing
6. Better control of product quality
7. Broader range in product density
8. Lower per-piece finished part cost
9. More environmentally friendly

TPEs are generally low modulus, flexible materials and are used in many industries (e.g., from household applications to the auto industry). TPEs can be stretched repeatedly to at least twice their original length, in many cases, at room temperature with an ability to return to their approximate original length when stress is released. One of the oldest materials with this property are thermoset rubbers, but many families of injection-moldable TPEs are replacing traditional rubbers. In addition to use in their basic form, TPEs are widely used to modify the properties of rigid thermoplastics, usually improving impact strength, which is necessary for sheet goods and general molding TPEs. In most cases, plastic is added to rubber to obtain these properties.

In some cases, the rubber (various sizes of crumb rubber) is added with recycled HDPE and some other chemicals to make the materials to foam (lighter weight), flow better, and cause better bonding capabilities. Then, this matrix is pelletized for ease of use. There are many pelletizing techniques used in the industry including underwater pelletizing.

Most plastics manufacturing companies, including those processes utilizing PE, follow the same general procedure. The base pellets are heated to form a melt. The melt is then extruded, blown, rolled, or injected to form the final product. The key factor in a proper manufacturing setting is ensuring that the pellets are completely melted so that the final product will be uniformly produced. There are many pellet types on the market. Some are designed and made for injection molding and some are used for rolled molding. In most cases, if the pellets are designed for a specific system (e.g., injection molding), they cannot be used effectively for other systems (e.g., blown or rolled). Unlike a stock material of 100% ground rubber, the TPE pellets have the ability to form a proper melt for various types of manufacturing processes. The chemical agents in the pellets, which includes Kraton or similar, aid in the processing by reducing the amount of foaming that occurs during the mixing and homogenization of the melt. While the ground rubber within the pellets does not melt, it is dispersed within the melted PE, which in a sense acts as the binder for the particles.

Unlike processing 100% ground rubber, the provided pellets do not require any binder to form manufactured goods. Typical processing of unmeltable materials generally involves heating the material with a binder under pressure to form a composite matrix. However, the pellets cannot be processed in this manner since excessive temperature and pressure, in general, will cause the PE to degrade into a variety of different compounds that will make processing extremely difficult. To properly utilize the pellets, they must be first heated to form a melt that can then be utilized in a variety of processing applications.

Each year, globally approximately 270 million tons of plastic is produced while 275 million tons are recycled. The U.S Environmental Protection Agency (EPA) estimates that Americans producing over 260 million tons of waste and recycle or compost more than 89 million tons for a recycling rate of approximately 35%. Some of the recyclable materials (e.g., plastics, rubber, etc.) from the United States and the EU have been exported to many countries around the world (e.g., India, China, etc.). For example, China at one time had been taking about 40% of US paper, plastics, and other recyclables.

However, recently, the Chinese government has stopped this practice with the implementation of the National Sword policy at the beginning of 2018 to protect their environment and develop their own domestic recycling capacity by restricting imports of waste. For example, recycled plastics from the United States to China dropped by 92% over the first five months of the year when the restrictions took in effect. All types of exported scrap, from plastics and paper to aluminum, cooper, and stainless steel, also fell 36%. The Chinese recycling market was greater than the next 15 markets combined; therefore leaving the US market, among others around the world, without any backup. Some of these materials that would have been recycled are now going into landfills instead. In some cases, municipalities have stopped collecting items that used to be recycled and others have been stockpiling them. This is a great opportunity for tire recycling groups around the world to investigate possible TPE applications in many industries.

Global demand for TPEs is forecast to be approximately 6 million metric tons and valued at around $20 billion. There have been many advancements in the area of product development with the aim of replacing the virgin materials in a typical TPE manufacturing production process. One reason for the tire recycling industry to concentrate in this area is that TPE demand will increase since there is much ongoing push in reducing motor vehicle weight. Some examples of TPEs used in various industries are shown in Fig. 20.6. The Asia/Pacific region have been, and it is estimated to be, the largest market for TPEs, making up nearly half of world demand. For example, China, in terms of the volume, is the world's largest consumer of TPEs. Other regions such as India and Southeast Asia are also benefitting from robust utilization of TPEs.

Figure 20.6 Examples of thermoplastic elastomer (TPE) applications for various materials.

20.3.1.4 Devulcanization process

Another area of the increase rate of utilization of CRM in many applications is the use of the devulcanized rubber, as it has been described in detail in another chapter. Goodyear invented vulcanization where sulfur can form bonds between unsaturated polymer chains found in latex to yield natural rubber. The process is also used for synthetic rubber where elevated temperatures are employed and accelerators can be added in the process. Depending on accelerator/sulfur ratio (A/S) between 0.1 and 12, accelerated sulfur vulcanizations are classified into three different types: conventional (CV), semiefficient (semi-EV), and efficient vulcanization (EV). Vulcanization process gives the properties to the synthetic or natural rubber, it renders the material into an elastomer. ASTM STP183A defines devulcanization as "a combination of depolymerization, oxidation and increased plasticity."

As has been mentioned in other chapters, there are several methods to produce CRM from ELTs. There are many applications for this product including its utilization, as a filler, in the production of new tires with only a little added at a time since there are some compatibility issues (Fig. 20.7). Therefore the ELTs must be devulcanized by breaking the three-dimensional cross-linking network, or they must be modified on the surface, as has been discussed in detail in other chapters of this book.

The devulcanization process aims at selectively splitting the C–S bonds while leaving the C–C bonds intact. A three-dimensional network is formed during vulcanization, the devulcanization of waste rubber applies energy to the material in order to

Figure 20.7 One example of new (future) tires.

break up, totally or partially, of these bonds. In general, selectivity is difficult to achieve, since the energies that are needed to break the SS and C–S bonds are rather close to the energy required to break the C–C bonds. The mechanical properties of these materials will be improved by achieving a higher level of selectively in the devulcanization process. Many research studies show that a high percentage (e.g., 65%) of devulcanized rubber could be utilized in many applications. This could enable a large percentage of ELTs to be utilized in the devulcanization process. Obviously, there are many technical issues and difficulties that must be addressed such as the quality and the consistency of the devulcanized materials. The process of the devulcanization should:

1. Be safe and environmentally sustainable
2. Provide a quality product to the industry
3. Be a cost-effective and financially viable business opportunity for the tire recycling industry

There are many benefits that recycling rubber scraps using devulcanization process could lead to, including the following:

1. Providing a quality and a cost-effective raw material to the industry.
2. A lower carbon footprint (energy savings when recycling vs. making rubber) while providing a quality product with less price fluctuation.
3. Creating TPEs with the devulcanized rubber that will enable the creation of many molded goods all over the world.

It has been estimated that the world's annual consumption of natural rubber is more than 15 million tons while the output of rubber products is more than 31 million tons. Around the world the demand for rubber is increasing for various reasons and the tire recycling industry is in a good position to address this issue by resolving some technical concepts and helping the rubber production industry by providing more devulcanized materials. The consumption of vulcanized elastomer is 17.2 million tons each year globally, of which 39% is natural rubber and the remaining 61% consists of other synthetic rubbers. This market has major potential for tire recyclers since there are many opportunities to make a profitable business around this concept as long as the devulcanized system is capable of producing a uniform and consistent product.

20.4 The future: getting started

Today, as we plan for the future, we realize that we have actually complied with our original mission – to identify

materials, products, and applications – and even treatments and technologies that would most benefit from the performance characteristics of recycled tire materials. The range of recycled tire materials has increased exponentially – but each output meets those three criteria as well as the four market considerations: greenness (sustainability), enhanced performance, resilience, and cost-effectiveness/economics. In other words, we have adopted and continue to adapt a model that works for tire recycling.

Each of the four vast potential markets introduced herein – roads, roofing, thermoplastics, and devulcanization – has the potential to create, develop, and maintain a range of new tire recycling activities into the future. Ironically, the roads segment links into the burgeoning infrastructure segment – potentially increasing exposure to the urban transport sequence, which currently integrates urban rails, trams, and roads. Indirectly, this component also meshes with certain aspects of the environmental products line – which focuses on noise and vibration abatement, as well as tremor containment in earthquake-prone regions.

Roofing, on the other hand, has the potential to vastly expand the construction sector particularly in older communities in Europe, North and South America, parts of Asia, and elsewhere. Roofing is also a major consideration in areas that appear to be more prone to climate change – particularly those with increased weather variances including hurricane and storm activity.

Thermoplastics and devulcanization are two technologies that open many new doors for recyclers by introducing broad ranges of new products and applications. Thermoplastics has the added value of contributing to the solutions to ongoing environmental problems with plastic waste – by defining new products and applications that require vast amounts of these materials. For instance, many products that had once been produced from glass or plastic are now transitioning to more durable and recyclable raw materials – including thermoplastics.

Devulcanizates are in a class of their own – and the entire global annual production could be absorbed by one industry – tire manufacturing.

This page intentionally left blank

Index

Note: Page numbers followed by "*f*" and "*t*" refer to figures and tables, respectively.

A

Acheson process, 204, 206–207, 213
Aggregate gradation, 376–379
Aggregate performance, 375–376
Agricultural tires, 146
Alpha Technologies Rubber Process Analyzer (RPA), 153–154
Ambient grinding, 51
Ambient process, 81
American Society of Civil Engineers (ASCE), 502–503
Anagennisi project
  applications, 541–543
  environmental benefits
    recycled rubber particles, 535–536
    recycled tire polymer fibers, 536
    recycled tire steel fibers, 536
  fiber-reinforced concrete, 528–531
  hybrid steel fiber-reinforced concrete, 531–532
  INSUL-ECO, 536–541
  pilot tests, 532–534
  rubberized concrete and confined rubberized concrete, 525–526
  shake table tests, 532
  steel fiber-reinforced concrete, 526–528
Annual tire sales, 43–44
Artificial reefs. *See* Tire artificial reefs
Artificial turf system
  biomechanical and psychological experimental research, 484–486
  components of, 484
  engineered synthetic surface, 484–486
  innovation, 493–495
  legislative pressure on industry, 492–493
  market potential for, 486–489
  player preference, 489–491
  reuse and recycling, of existing fields, 491–492
Asphalt, 501–502
Asphalt binder, 341–343
Asphalt emulsion binder modifier, 439–445
Asphalt emulsion chip seals, 448–449
Asphalt emulsions, 434–439
Asphalt grade and type, 345–346
Asphalt matrix, 298–300
Asphalt modifier, 432–434
Asphalt morphology, 346–349
ASTM D6270, 573
Automotive products (AU), 60–61

B

Balling, 50–51
Basel Convention, 9–10
Bead removal, 50
Biological devulcanization, 110
Biological treatment, 244–245
Biowaste, 206–207
Blending process, 96*f*
Butadiene rubber (BR), 111
Butyl rubber (IIR), 111

C

Carbon black (CB), 117–118
  acidic functional groups, 179
  advantage of, 177
  aglomerates, 178–179
  amorphous carbon core, 179
  and characteristics, 181*t*
  covalent bonds, 177–178
  iodine number (ASTM D1510), 179–180
  market price of, 191
  morphological features, 177–178
  nanostructured material, 177–178
  particle size and surface area, 178*f*
  primary particles, 177–178
  quasicrystalline shell, 179
  rCB. *See* Recovered carbon black (rCB)
  standard ASTM D6556, 179–180
  van der Waals interactions, 178–179
Carbon-containing waste, 206–207
Car sharing, 38–39
Chemical modification
  polyurethanes, 230
  trans-polyoctenamer
    binary rubber blends, 231
    binder system for molded goods, 235–236
    bitumen and asphalt, rubber modification of, 239–242
    bladders and innerliners, 231

Chemical modification (*Continued*)
coalescence, 231
coating process, 233–235
GTR, 232–233
partially macrocyclic polymer structure, 230–231
specification and properties, 231*t*
thermal stability, 230–231
in virgin rubber compounds, 236–239
Chipping, 51
Circular economy
producer responsibility
recycling limitation, 74
tires and circularity, 73
Circular Economy Action Plan, 206
Clean vehicles directive, 588–589
Coating/paints, 196
Cold plasma surface treatment, 300–301
Commercial roofing market, 614
Commercial technology, 158–159
Connected car, 41–42
Covid-19 pandemic, 27
CR-modified asphalt emulsions (E − CRMA), 439–445
characterization and performance, 442–445
Crumb rubber (CR), 226
asphalt emulsion binder modifier, 439–445
asphalt emulsion chip seals, 448–449
asphalt emulsions, 434–439
asphalt matrix, 298–300
asphalt modifier, 432–434
in Babbitt, Minnesota, 359
characterization of, 446–448
cold plasma surface treatment, 300–301
composition and content, 349–351
elastic bulk properties, 297
elasticity of, 354
in Flagstaff, Arizona, United States, 358
mixing process, 354–356
New Jersey DOT (NJDOT), 359–360
in Ontario, Canada, 357
plasma surface treatment, 298–299
plasma-treated rubberized asphalts. *See* Rubberized asphalt/asphalt rubber (AR)
plasma treatment, 299–300
production process, 353
replacement filler, 445–449
rubberized asphalt
performance evaluation, 303–306
preparation of, 301
SBR2 rubber surface, 298–299
surface characterization of, 301–303
surface chemistry, 309–312
surface hydrophilicity, 306–308
surface lipophilicity, 308–309
surface morphology, 312–315
surface treatment technologies, 298
type and particle size, 351–352
waste tire rubber (WTR), 299
Crumb rubber-modified binders (CRMB), 338–340, 609
Cryogenic processing, 51–52
Cryogenics, 75
Cryogenic tire recycling
ambient process, 81
cryorubber crumbs, 94–96
fine mesh cryogenic system, 91–94
freeze chamber, 84–85
hammermills, 85–91
liquid nitrogen (LN2), 81–82
shredder, 83–84
Cryorubber crumbs, 94–96

D

Devulcanization, 53, 95
of butadiene rubber, 113
of chlorobutyl rubber (CIIR), 114
defined, 152–153
and end-of-life tires (ELTs)
criteria and limitation, 131–132
ground tire rubber. *See* Ground tire rubber
mechanical characteristics of, 132–133
homogeneous breakdown, of polymer networks, 101–102
of natural rubber, 113–114
process parameters, 120–125
process technology, 110
rubber composition, influence of, 117–120
selective crosslink scission *vs.* random network breakdown
crosslink density, 100
Flory–Rehner equation, 101
gel fraction, 100
Horikx theory, 100–101
Horikx Verbruggen analysis, 98
of styrene butadiene rubber, 112
vs. regeneration
biological devulcanization, 110
chemical devulcanization, 107–110
mechanisms, 103–106
physical devulcanization, 108–110
of whole-tire rubber, 115–117
Devulcanized rubber
advantages of, 154
market opportunities
polymer-modified asphalt roads, 156–157
polymer-modified asphalt roofing, 157
thermoplastic polyolefins, 156

2-2'-dibenzamidodi phenyldisulfide, 119–120
Disulfides, 106
Disulfidic crosslink, 112
Double-deck screen, 89
Drying process, 90
Dynamic properties, 154

E
Electric vehicles, 40–41
Embankment stabilization, 76
End-of-life (EOL), 584
End-of-life tires (ELTs), 14, 77, 201–202
  circular and sustainable economy, 165
  postconsumer tires, 46–47
  raw material for recycling, 45–46
  of steel-free-basis, 166*f*
Energy consumption, 56
Energy, definition, 64
Energy recovery, 62–63
Environment, definition, 11
Equipment manufacturers, 58–59
EU Landfill Directive, 71
European Union (EU) waste streams, 44*t*
European Union recycling capacity, 59*f*
"Extended Producer Responsibility" scheme, 46

F
Field noise measurement studies, 427–428
Filler–polymer network, 119
Fine mesh cryogenic system, 91–94
Fleets, 27
Flory–Rehner equation, 101
Forklift tires, 146
Fourier transform infrared spectroscopy analysis, 330–333
Freeze chamber, 84–85
Fuel source, 74

G
Gel permeation chromatography analysis, 327–330
Global Infrastructure Forum 2016, 504
Globalization, 4–6
Global mobility
  in China, 30–31
  connected car, 41–42
  Covid-19 pandemic, 27, 31–32
  demand of
    demographic factor, 29
    economic and demographic trends, 29
    economies, 28
    global light vehicle parc, 29
    global population, 27–28
    per capita demand, 28
    population growth, 29
    vehicle density, 29
  economic growth, 30–31
  electric vehicles, 40–41
  GDP per capita and vehicle density, 30*f*
  global light vehicle parc (VIO), 31*f*
  global passenger car and light truck (PCLT) original equipment (OE) tire market, 31–32
  global PCLT replacement tire market, 32
  light vehicle production, 31–32
  mobility as a Service (MaaS), 27
  regional analysis
    in Asia Pacific, 32–34
    in Europe, 34–35
    in Middle East and Africa, 36
    in North America, 30, 35
    in South and Central America, 35–36
  shared and autonomous vehicles
    car sharing, 38–39
    ride-hailing, 39–40
  trends in, 28*f*
Global tire production, 43–44
Gradation optimization, 378–379
Granulate, 51–52, 54, 60
Granulation, 75
Green public procurement (GPP), 605
  asphalt and roads, 594–598
  circular procurement, 598–601
  clean vehicles directive, 588–589
  communication proposes tools, 585
  Comprehensive criteria, 589
  concrete and buildings, 592–594
  Core criteria, 589
  environmental management systems and, 588
  legal framework for, 587–588
  opportunities, for tire recycling sector, 591
  postconsumer tires and recycled tire materials, 590–591
  purchase price, 584
Ground rubbers
  particle size, 226
  source of rubber material, 226
  surface properties, 226–227
Ground tire rubber
  alternative processing systems, 149
  feedstock heterogeneity
    mechanical properties, 141–143
    viscosity measurements, 140–141
  ground tire rubber heterogeneities, 136–139
  incoming material analysis, 139–140
  samples, 133–136
  scrap tire recycling dysfunctions and inefficiencies, 149–150
  scrap tire recycling technologies, 149

H

Hammermills, 85–91
Heavy equipment tires, 146
Heavy haul lines
  low-quality aggregates, 522
  noise and vibrations, 522
  stiffness transitions, 523
  switches and crossings, 523–524
  tunnels and bridges, 523
High-temperature rutting resistance, 316–319
Horikx theory, 100–101
Horikx Verbruggen analysis, 98
Hybrid steel fiber-reinforced concrete
  fatigue performance of, 531–532
  flexural behavior of slab-like HSFRC, 532
  flexural performance of, 531
  punching shear behavior of, 531
Hydrogen transfer reaction, 103–105

I

Interfacial transition zone (ITZ), 556
Interim treatment, 48
Inverse pyramid, 73

L

Leaching, 285–286
Life cycle costing (LCC) approach, 584
Liquid nitrogen (LN2), 81–82
Long-term storage, 49

M

Making recycling work, 77
Manufactured products (MFR), 60
Marine construction
  coastal protection with tires, 286–292
  freshwater and marine organisms, 275
  microplastics, 292–293
  tire artificial reefs
    in Australia, 280
    in Hong Kong, 279–280
    in Israel, 280
    in Malaysia, 279
    Poole Bay artificial reef, 280–286
    in United States, 277–279
Market focus
  devulcanization process, 619–620
  on roads, 609–612
  roofing system, 612–615
  thermoplastic elastomers, 615–618
Market impacts, 56–58
Market opportunities, 154–158
Material composition, 45
Material outputs, 55–56
Measurement approaches, 153–154
Microwave pyrolysis, 173–174
Microwave technology, 75
Mining tires, 146
Mobility. *See* Global mobility
Mobility as a Service (MaaS), 27
Moderate-temperature fatigue resistance, 323–324
Monosulfidic bonds, 118
Monosulfidic crosslink, 118

N

Natural aberrations, 4
Natural rubber (NR), 106
Neoballast
  conventional ballast, 520
  factors of, 517
  fire response results, 518*t*
  goal of, 517
  heavy haul lines
    low-quality aggregates, 522
    noise and vibrations, 522
    stiffness transitions, 523
    switches and crossings, 523–524
    tunnels and bridges, 523
  high track deterioration areas, 522
  Los Angeles and Micro-Deval test results, 518*t*
  noise emission, 519
  properties of, 516
  technical upgrades, 517
  track settlement measurements, 520
  vibration emission, 519
Noise and vibrations (N&V), 517
Nonretreadable tires, 49
Nontire automotive products, 43

O

Octadecyl-3-(3,5-di-tert-butyl-4- hydroxyphenyl)propionate, 107–108
Omits aircraft tires, 146
Optimum asphalt content, 379–380
Organisation for Economic Co-operation and Development (OECD), 604–605

P

Pavement material damping, 425–427
Pavement performance, 391
Pevensey trial, 287–292
Physical devulcanization, 108–110
Physical modification
  free-flowing agents, 228–229
  swelling, 229–230
Planetary roller extruders, 110
Plasma surface treatment, 298–299
Plasma torch plant, 213–215
Plasma treatment, 299–300
Plastics industry, 196
PlusRide, 508
Pneumatic tire, 45
Polyethylene (PE), 615
Polymer-modified asphalts, 162
Polymer scission reaction, 103–105
Polyolefin component, 243–244
Polysulfidic crosslink, 112
Postconsumer tires, 46–47

Printing inks and toners, 196
Producer responsibility, 78
Public commentaries, 3
Pyrolysis, 52–53, 75, 607
  advantages and disadvantages, 168
  batch processes, 168–171
  carrier gas, 168
  catalysts, 168
  characteristics of technology, 170*t*
  commercial and semicommercial scale pyrolyzers, 168–171
  continuous operation, 171
  continuous pyrolysis, 171
  definition, 165–166
  indirect heating, 165–166, 169*f*
  industrial-scale pyrolyzers, 168
  microwave pyrolysis, 173–174
  positive/negative pressure, 168
  recovered carbon black (rCB), 166
  thermal pyrolysis, 172–173
  tire pyrolysis gas (TPG), 166
  tire pyrolysis oil (TPO), 166
  whole tires, chips, or granulate, 168
Pyrolysis gas, 220
Pyrolysis oil, 218–220

R

Raw material
  automotive products (AU), 60–61
  civil engineering and environmental management, 59–60
  construction, 60
  manufactured products (MFR), 60
  material categories, 45*t*
  material composition, 45
  material outputs, 55–56
  pneumatic tire, 45
  production and use patterns, 61–62
  sports and leisure infrastructure management (SLIM), 60
  treatments and technologies
    ambient grinding, 51
    balling, 50–51
    bead removal, 50
    cryogenic processing, 51–52
    devulcanization, 53
    interim treatment, 48
    long-term storage, 49
    nonhazardous waste, 49
    nonretreadable tires, 49
    posttreatments of pyrolytic char, 53–54
    pyrolysis, 52–53
    reclaim, 52
    road-worthy part-worn tires, 49
    shredding and chipping, 51
    sidewall removal, 50
    surface modification/activation, 53
    thermoplastic elastomers (TPE), 54
    thermoset rubbers, 49
  urban transport (UT), 61
Reclaim industry, 150–152
Recovered carbon black (rCB), 166
  active carbon, 197–198
  advantages, 202–203
  asphalt pavement-road fillers, 197
  ASTM D8178 standard, 183–185
  carbonaceous residues, 182–183
  coating/paints, 196
  colloidal properties, 182–183
  concrete and cement, 197
  hybrid particles *vs.* virgin carbon black/recovered carbon black, 197
  impurities, 185–186
  inorganics compounds, 181–182
  lithium-ion batteries, 198
  market price and projections, 198
  PAH, 182
  particle size distribution, 181–182
  plastics industry, 196
  printing inks and toners, 196
  rubber formulations, 182–183
  rubber industry
    nontire products, 194–196
    tire parts, 193–194
  standards in development, 185*t*
  sustainable and attractive market, 181
  upgrading of, 186–187
Recycled rubber powders, economic considerations of, 245–247
Recycled tire materials (RTMs), 44
  applications, 62*t*
  construction, 60
  principal uses of, 61*t*
  urban transport (UT), 61
Recycled tire polymer fibers (RTPF)
  durability properties of concrete, 529–530
  fresh and hardened concrete properties, 528–529
  hybrid FRC mixes, 530
  screeds reinforced, 530–531
  self-compacting concrete reinforced, 529
  shrinkage behavior of, 529
  sprayed concrete with, 529
Recycling industry, 64
Regulator, role of, 77
Replacement filler, 445–449
Resource-efficient Europe flagship initiative, 586
Retreading, 75
Ride-hailing, 39–40

Roads
accessibility and affordability, 505
around the world, 501
climate change, 505
COVID-19 period, 503
history of, 499–500
impact of infrastructure on society, 502–506
impact of new innovations on, 506–507
infrastructure gaps, 502
opportunities, 500–501
pollution, 505–506
road safety, 505
rubberized asphalt concept, 500–501, 507–511
Scot John McAdam, 499–500
urbanization effect, 505
Road-worthy part-worn tires, 49
Roofing system, 612–615
Rotational viscosity, 315–316
Rubber crumb, 91
Rubber industry
nontire products, 194–196
tire parts, 193–194
Rubberized asphalt/asphalt rubber (AR)
aggregate gradation, 376–379
aggregate performance, 375–376
asphalt binder, 341–343
asphalt grade and type, 345–346
asphalt morphology, 346–349
base asphalt, influence of, 374
bridge deck and tunnel paving, 396–398
chip seal, 398–402
construction of, 387–389
development of technologies
in Europe, 455–458
in Italy, 469–473
in Portugal, 464–469
in Spain, 459–464
in Switzerland, 473–476
economic benefits, 406–407
environmental benefits, 402–406
field noise measurement studies, 427–428
Fourier transform infrared spectroscopy analysis, 330–333
gel permeation chromatography analysis, 327–330
gradation optimization, 378–379
high-temperature rutting resistance, 316–319
low-temperature anticracking of, 343–345
low-temperature cracking resistance, 319–323
moderate-temperature fatigue resistance, 323–324
optimum asphalt content, 379–380
pavement material damping, 425–427
pavement performance, 391
performance evaluation, 303–306
preparation of, 301, 374–375
production of, 382–385
properties of, 380–381
rotational viscosity, 315–316
rubberized asphalt thin overlay, 391–393
rubber powder, influence of, 372–373
standard development of, 389
storage stability, 324–327
thermal tensile stress, 338–339
transportation and storage technologies, 386–387
typical overlay application, 389–391
viscoelastic properties of, 423–425
Rubberized asphalt thin overlay, 391–393
Rubber powder, 226
influence of, 372–373
Rubber waste
nature of, 147–148

S

Scot John McAdam, 499–500
Screw speed, 124
Secondary filler–polymer network, 118
Shear stress, 122
Shredder, 83–84
Shredding, 51
Silane, bis-(3-triethoxysilylpropyl) disulfide, 118
Silanes, 243
Silica–silane filler system, 118
Silicon carbide (SiC), 607
abrasive material, 203–204
Acheson process, 204
advantages, 203
attractive properties, 203
biomass/agriculture wastes, 207
biomass gasification residues, 207
carbon monoxide (CO), 204
carbothermal reduction, 209–210
from char, 217–218
circular economy approach, 205
conventional metallic silicon, 203
crystalline phases, 204
environment and climate changes, 205
e-waste- and ELTderived powder, 211*f*
Fourier-transform infrared (FT-IR) spectroscopy, 208
gas-phase reaction, 210–211
gas-phase reaction of, 208
glass- and ELT-derived powders, 210
high abrasion resistance, 203–204
high-tech applications, 203
mesoporous SiC nanofiber/particle composite, 209
milling and purification processes, 204

plasma processing methods, 205
production of, 206–211
from pyrolysis gas, 220
from pyrolysis oil, 218–220
RF thermal plasma technology, 208–209
thermal gravimetric analysis, 208
thermal plasma, 205
transmission electron microscopy, 208
TyGRe project
method and results, 215
plasma torch plant, 213–215
ultrafine nanometric or submicronic SiC powder, 205
X-ray diffraction, 208
Sol fraction, 122
Solid wheels, 146
Sports and leisure infrastructure management (SLIM), 60
Sports and tire wastes
artificial turf system
biomechanical and psychological experimental research, 484–486
components of, 484
engineered synthetic surface, 484–486
market potential for, 486–489
styrene butadiene rubber
innovation, 493–495
legislative pressure on industry, 492–493
player preference, 489–491
reuse and recycling, of existing fields, 491–492
waste application, 495–497
Steel, 89
Steel fiber-reinforced concrete
fresh concrete properties, 549–550
hardened concrete properties, 550–551
mix design process, 549
plain rubberized concrete and
fresh concrete properties, 554–555
hardened concrete properties, 555–558
mix design process, 552–553
rubber particle properties, 551
tire-steel fiber properties, 547–549
Steel fiber-reinforced concrete (SFRC)
compressive and flexural behavior of, 527
flexural performance of, 526–527
manufactured fibers and recycled tire steel fiber, 527
performance of conventional and rubberized SFRC, 528
RTS, 526
RTSF, 528
Steel fiber reinforcement, 557
Steel fibers, 555
Styrene butadiene rubber (SBR), 112, 124*f*
SBR-filled artificial turf
innovation, 493–495
legislative pressure on industry, 492–493
player preference, 489–491
reuse and recycling, of existing fields, 491–492
Surface-modified materials
surface treatment, 225
vulcanized rubber polymer, 225
Sustainable Consumption and Production and Sustainable Industrial Policy (SCP/SIP) Action Plan, 585
Synthetic rubbers, 44

T

Textile fiber-reinforced rubberized concrete
fresh concrete properties, 558–559
hardened concrete properties, 559–561
mixing procedure, 558
properties, 558
The European Union Landfill Directive
producer responsibility, 72
waste hierarchy, 73
Thermal pyrolysis, 172–173
Thermal stress – restrained specimen test (TSRST), 339–340
Thermal tensile stress, 338–339
Thermoplastic elastomer (TPE), 54, 91, 615–618
Thermoset rubber, 49
balance of properties, 160–161
Thermoset rubber market, 154
Tire and tire market
delivery chain, 22–23
design of, 20
domestic and export markets, 22
durability, 20
early days of, 15
evolution, 16–17
fuel economy, 20–21
global players and national roots, 15–17
manufacturing of, 17
product choice, 21
product design and manufacturing, 23–24
purchase challenge, 25
retailing and distribution, 24–25
Tire artificial reefs
in Australia, 280
in Hong Kong, 279–280
in Israel, 280
in Malaysia, 279
Poole Bay artificial reef
artificial reef, 282
benzothiazoles, 286
benzthiazoles, 282
cement-stabilized coal ash, 282–283
cluster analysis, 283–284

Tire artificial reefs (*Continued*)
epibiotic species, 284
fouling organisms, 283–284
hydroids and bryozoa, 283–284
2-(4-morpholinyl)-benzthiazole, 282
multidimensional scaling ordination, 283–284
natural reef organisms, 286
zinc concentration, 285–286
zinc oxide, 282
in United States, 277–279
Tire bales, 286–287
Tire-derived aggregate (TDA)
embankment fill, 566
embankments and engineered fill, 570–571
Rankine model for, 567–568
retaining walls and bridge abutments, 566–570
safety and environmental concerns, 571–576
Tire ground rubber
analysis of scientific database, 253–259
composites, 253–258
compression-molded thermosets, 252
digital scientific databases, 252–253
direct molding, 259
grinding technology, 266–268
rubber typology, 263–266
end-of-life tires (ELTs), 252–253
molding devulcanized rubber, 258
molding of
compression molded parts, 251–252
devulcanization, 251–252
material softening and pressure, 251
plastic recycling processes, 251–252
recycled materials, 251–252
thermosetting precursor, 251
vulcanization, 251
molding operations, 258–259
scientific papers, 253*t*
Tire pyrolysis gas (TPG), 166
Tire pyrolysis oil (TPO), 166
Tire recycling, 604–608
catalyst for change, 6–7
implementation and progress, 11–13
interpretations, 13–14
sustainable development
period of globalization, 9–10
postwar period, 8–9
Trans-polyoctenamer
binary rubber blends, 231
binder system for molded goods, 235–236
bitumen and asphalt, rubber modification of, 239–242
bladders and innerliners, 231
coalescence, 231
coating process, 233–235
GTR, 232–233
partially macrocyclic polymer structure, 230–231
specification and properties, 231*t*
thermal stability, 230–231
in virgin rubber compounds, 236–239
Treated distillate aromatic oil (TDAE), 121–122
Truck tread, 132
Twin screw extruders (TSE), 110, 124*f*
TyGRe project
method and results, 215
plasma torch plant, 213–215

U

United Nations Conference on Trade and Development (UNCTAD), 9
United Nations Environment Programme (UNEP), 9–10
Urban transport (UT), 61

V

Value-added products, 167
Vehicle parc, 31*f*
Virgin rubber, 146
VL tires, 132–133

W

Waste and Resource Action Program (WRAP), 286–287
Waste hierarchy, 72
Waste management, 3
Waste tire rubber (WTR), 299
White rubber test (WRA), 102
Whole truck tire, 132

TIRE WASTE AND RECYCLING

Edited by
Trevor M. Letcher, Valerie L. Shulman, Serji Amirkhanian

Tire Waste and Recycling uses a thorough and methodical approach to provide the reader with a detailed understanding of how to manage and process used tires, and how to turn waste tires into valuable materials and industrial applications.

- Offers systematic coverage of tire recycling, covering composition, life cycle, processing options, material developments, and latest technologies.
- Explains end-of-life-options in detail, considering approaches and methods for reduction, reuse, recycling, and recovery.
- Explores key application and product areas for recycled tire materials, from civil engineering, sports and leisure to roads and transport, construction, automotive, and many more.

This is an essential resource for scientists, R&D professionals, engineers, and manufacturers working in the tire, rubber, waste, recycling, automotive, and aerospace industries. In academia, the book is of interest to researchers and advanced scientists across rubber science, polymer science, materials engineering, environmental science, chemistry, and chemical engineering.

About the Editors

Trevor M. Letcher is an Emeritus Professor at the University of KwaZulu-Natal, Durban, a Fellow of the Royal Society of Chemistry, and a Director of the International Association of Chemical Thermodynamics. He has received the South African Chemical Institute's Gold medal and the South African Gold medal. He has published 300 papers in peer-reviewed journals and edited 26 books, including *Waste* 2nd edition (2019), *Future Energy* 3rd edition (2020), and *Plastic Waste* (2020).

Valerie L. Shulman is the Secretary General of the European Tire Recycling Association (ETRA). The research she initiated in 1989 formed the nucleus of ETRA, which was founded 5 years later. She contributed to the Basel Convention Guidelines on Use Tires (1999) and represented the recycling industry at the European Parliament. She has published over 100 articles in peer-reviewed journals and several books on tire recycling technologies, materials, and applications.

Serji Amirkhanian is a Professor of Civil Engineering at the University of Alabama, Tuscaloosa, United States. He was the Civil Engineering Mays Professor of Transportation and Director of the Asphalt Rubber Technology Services at Clemson University, United States. He has written over 250 peer-reviewed journal papers and research reports, and conducted more than 200 presentations.

ELSEVIER
ACADEMIC PRESS
An imprint of Elsevier
elsevier.com/books-and-journals

ISBN 978-0-12-820685-0
9 780128 206850