11

Design of Recyclable Thermosets

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11.1 Introduction

11.1.1 Polymers and Plastics

Plastics have become an indispensable class of materials, fueling modern civilization on every imaginable level - from packaging to healthcare, to construction, to space exploration, and everything in between. However, some of the very attributes (e.g. longevity/durability) that make plastics so appealing have also caused one of the world's most pressing crises – plastic waste. Worldwide plastics manufacturing has experienced exponential growth since its inception in the 1950s and continues growing unabated today [1]. It has been estimated that 7800 million metric tons (Mt) of plastics were manufactured between 1950 and 2015 [2]. A further 359 Mt of plastics were produced worldwide in 2018 [1]. This is the equivalent to c. 40 kg per person per year. Tragically, much of this has found its way into the environment [3]. Enormous quantities of solid waste persisting in our oceans continue to wreak havoc on marine environments (see Chapters 3 and 12) [4]. Manufacturing practices, the fossil-fuel origins of the monomers used to make most plastics, and the end-of-life incineration of plastics are exacerbating climate change. Plastic use unquestionably delivers unprecedented convenience, on which we have come to depend. However, this dependence is contributing overwhelmingly to a series of global crises. Thankfully, there is a concerted effort to remedy the current predicament with multidisciplinary exploration seeking new scientific breakthroughs. The very ingenuity responsible for creating the "original" plastic revolution will also enable the next generation of materials to address concerns related to resource origins, carbon output, and environmental impact. More responsible use of current plastic waste-streams (see Chapter 3) in conjunction with design of smarter chemical scaffolds are necessary steps along the path toward a sustainable, circular plastics economy. All parts of the value chain are being scrutinized in an effort to improve the conventional plastic life cycle.

This chapter provides a brief overview of several strategies being employed in the last decades to re-design certain classes of plastics specifically for recyclability by purposefully incorporating degradable, reversible, or labile chemical bonds. This strategy enables reconfiguration of the chemical bonds responsible for imparting mechanical integrity in the original material, thereby rendering it degradable or reprocessable. In this manner, the reversibility in chemical bonding is utilized to rearrange the bonds, allowing the reshaping of polymer materials without substantial destruction of the underlying macromolecular scaffold. This strategy enables the original material to be directly transformed into an alternate product, thereby extending its useful lifetime substantially. This strategy has been applied predominantly to conventional thermoset-type constructs, which are typically considered un-recyclable and impossible to re-process. Ultimately, such a strategy may afford materials that are fully degradable at the end of their useful lifetime, or for materials that are disposed of irresponsibly (i.e. not collected for recycling).

11.1.2 Handling of Plastic Waste

Currently approximately 10% of global plastics are recycled, 14% incinerated, and 40% is disposed of in landfills (Figure 11.1) [5]. Landfilling is particularly concerning as it essentially represents a huge loss of potentially high-value chemical feedstocks and creates an enormous environmental burden, especially as most of this waste can essentially be considered non-degradable, except on a geological timescale. Worse, it has been estimated that 32% of polymers escape the waste collection process completely and pollute the general environment [2]. Plastics have been identified as efficient transporters of toxins for marine organisms as they travel through streams and rivers into the ocean [6].

Clearly, increasing the efficiency of waste collection will dramatically reduce the detrimental environmental impact of discarded plastics. Increased recycling must be pursued in conjunction. In part, recycling more plastic requires the intrinsic, structural redesign of certain plastic materials such that the recycling process can be conducted using manageable processes. The inherent recyclability of plastics can be influenced in several manners. The most convenient pre-requisite involves synthesizing polymers having functionality that is amenable to chemical transformations under mild conditions. On the other hand, volumes of recycled plastics can be increased by improving the processes that are already routinely used for recycling (see Chapter 12). This is often enabled by improved catalysis, which lowers the energy barriers responsible for the chemical transformations that occur during degradation [7]. In this chapter, we do not explicitly cover catalysis but instead focus on the design of polymer scaffolds and the chemical transformations responsible for polymerization and rearrangement in reconfigurable thermosets [5a, 8].

11.1.3 Chemical Nature of Plastics

Commercial plastics span an impressive range of physical properties, which is largely attributed to the chemical makeup (Chapter 04). While morphology,



Figure 11.1 Estimated global flow of plastic packaging materials from 2013. 1: Closed-loop recycling: Recycling of plastics into the same or similar-quality applications; 2: Cascaded recycling: Recycling of plastics into other, lower-value applications. Source: Reproduced with permission from Ellen MacArthur Foundation [5b]. Copyright 2017 Ellen MacArthur Foundation.

architecture, and stereochemistry are all key determinants for physical and mechanical properties, the nature of the backbone chemistry has an enormous influence on reactivity, and is thus key for enabling efficient recycling. The term plastic, from the Greek word "plastikos" meaning "moldable," applies to the subset of polymers used in engineering applications. Plastics may be further subdivided into three types, based on the synthetic mechanism employed during buildup of molar mass.

- 1) Thermoplastics strength provided by chain entanglement
- 2) Thermosets strength provided by permanent covalent bonds between chains to generate a network
- 3) Vitrimers a subset of thermosets wherein the covalent crosslinks are reversible, facilitating breaking and reforming of the network

Thermosets often exhibit superior mechanical properties and durability compared with thermoplastics due to their crosslinked network structure. The extensive interchain bonding provides improved durability and strength. The interconnected scaffold also enables swelling in solvents to make highly elastic gels. However, owing to the chemical bonding, thermosets essentially possess infinite molar mass and as such are not recyclable by conventional (i.e. mechanical or chemical) means. There are a few exceptions to this discussed below. End-of-life is typically landfill. In certain applications, the permanent structure afforded by crosslinking and the durability is welcome (e.g. tires). In that sense, thermosets fill several niche markets, in which thermoplastics are unsuitable.

The general reason for a material to be considered unrecyclable is the permanent, irreversible nature of the connections responsible for the mechanical integrity in thermoset polymers. An effort to introduce recyclability by using reversible chemistry has begun to bear fruit in a variety of contexts and employing various chemical moieties. This goes for both thermoplastics and thermosets. With the emergence of a subgroup known as vitrimers, the potential to have the mechanical properties of a thermoset, but the recyclability of a thermoplastic have been realized [9]. Currently there are no commercial products using these chemistries, but it is hoped that their introduction will be transformative, particularly for environmentally problematic segments like tires.

11.2 Design of Recyclable Thermosetting Polymers

Recycling has been an *ad hoc* matter; materials were developed and if they were found afterwards to be recyclable, then that was a bonus. Nowadays, we can do better; we can design thermoset materials that are specifically easily recoverable. This "closes the loop" allowing for reduction of the use of precious virgin, non-renewable resources. Furthermore, it is foreseen that by incorporating labile crosslinking into newly designed materials, the degradation can be promoted for materials that ultimately end up dispersed in the environment.

There are several complementary approaches to this, based primarily on differences in the nature of the crosslink (Figure 11.2). The crosslinks can be reversible (i.e. equilibrium reactions) and designed to be susceptible to various stimuli such as temperature, acids or bases, or light. These reversible or dynamic crosslinks are described under the collective term covalent adaptive networks (CANs), which can be further subdivided into two categories: dissociative CANs, where the dynamic crosslink concentration decreases above a critical threshold temperature, and associative CANs (aka vitrimers) where the bond concentration is constant and only the rate of exchange changes with changes in the external environment. The critical differences are shown in Figure 11.2 and elaborated further.

Along a parallel trajectory, recyclable thermosets can be achieved by incorporation of degradable (i.e. non-reversible dissociation) building blocks. This can be achieved in several manners, whereby every repeating unit is degradable (fully degradable in Figure 11.2), select units (i.e. comonomers) are degradable (partially degradable in Figure 11.2), or simply the crosslinking junctions are degradable (selectively degradable in Figure 11.2). Some select examples of these different classes of degradable thermosets will be discussed in the subsequent sections (Sections 11.2–11.4).

In essence, the premise behind CANs is to obtain a material with mechanical properties that are characteristic of traditional thermosets (e.g. creep resistance, durability) while retaining the appealing processing properties of thermoplastics (e.g. (re)moldability, recyclability). Marrying these two sets of properties leads to materials exhibiting the best of both worlds.



Figure 11.2 Strategies for introducing recyclability into thermosets. Top: two-stage trajectory via degradation and recovery of monomers/polymers; bottom: one-stage trajectory via reconfiguration of dynamic crosslinks. Source: Reproduced with permission from Post et al. [10]. Copyright 2019 Taylor Francis.

11.2.1 Recyclability by Triggered Degradation

Many conventional thermosets have a major issue with recycling due to the irreversibility of the crosslinks. Hence replacing these irreversible crosslinks with a crosslink capable of triggered degradation would in principle allow for easy recovery of the polymer. By focusing specifically on the reversibility of the network junctions and developing strategies for introducing dynamic behavior, in principle all thermosets, regardless of the chemical nature of the main chains, can be transformed into recyclable materials. A variety of chemistries are available [11], and chemical connections must be chosen so as to not open except when desired (i.e. at the recycling plant), to avoid compromising the material properties.

Chemistries, which rely on thermal decomposition of the linkers, result in thermally reprocessable polymers. Early examples of these materials were epoxy resins linked by acetals [12], carbonates [13], phosphoesters [13, 14], and sulfites [14a] which were stable up to 180-300 °C, depending on the chemistry and crosslink density. C—O—C bonds were more stable than those containing other heteroatoms. Investigation of the degradation of ester-crosslinked epoxies showed that the electron density in the ester was critically important, and there has been an effort to reduce the critical decomposition temperature (T_d) . This has been successfully reduced from c. 340 to 120 °C (Table 11.1). Tertiary esters can easily form alkenes and the carboxylic acid [19]. α -Terpinyl epoxides (i.e. with an additional methyl on the epoxide) have activation energies $(E_a's)$ typically 2 kJ/mol higher than epoxides [15]. With di(meth)acrylates crosslinked with a spacer of 1-4 carbons using tertiary esters, the networks were stable at 150 °C in all cases, but degraded at 180 °C with a rate dependent on the length of the spacer; increased spacer length leads to more rapid degradation [18]. There is an auto-acceleration effect, as the acidic products catalyze further reactions. Chemical triggers include acid-catalyzed hydrolysis of acetals and ketals [20], Schiff bases [21], and hexahydrotriazines [22], base-catalyzed hydrolysis of dilactones [23] and sugar-derived epoxies [24], and ozonolysis of alkene containing linkages [25].

11.2.2 Dissociative Covalent Adaptive Networks

In the CAN systems the crosslinks are reversible, leading to dissociation of the crosslinks responsible for network formation. This is often thermally induced. Above a certain critical temperature dissociation become predominant, and hence the network progressively undergoes a transition of material properties. Above a critical gelation temperature (T_{gel}), there are no crosslinks, and the material behaves as a conventional thermoplastic. Crosslinks re-form upon cooling below T_{gel} and the polymer behaves like a crosslinked material (i.e. thermoset), which contrasts with the materials discussed above that do not reform their crosslink when the external stimulus is stopped. Dissociative CANs are thereby potentially recyclable thermoset-like materials [26]. Their properties depend upon the crosslinking chemistry, crosslink density, and crosslink lifetime. Thus, they are rendered reprocessable and have in some cases been considered for design of recyclable thermosetting

Linker chemistry	Degradation temperature	References
Epoxies		
Primary ester	340 °C (202 °C with acid catalyst) $(E_a = 186 \text{ kJ/mol})$	[15c, 16]
Secondary ester	$320 ^{\circ}\text{C}$ ($E_{a} = 183 \text{kJ/mol}$)	[15a]
Tertiary ester Polymer ₁ O Polymer ₂	220 °C (reduced to 180–196 °C in presence of a strong acid) $(E_a = 104 \text{ kJ/mol})$	[15c, 16, 17]
<i>p</i> -cyclohexyl di- <i>tert</i> -ester $HO_{1_{n_1}}$ $Polymer_1$, $Polymer_2$ $HO_{1_{n_1}}$ $Polymer_1$, $Polymer_2$ $HO_{1_{n_1}}$ HO_{1_{n	120 °C (110 °C with strong acid)	[15c, 16]
<i>m</i> -phenyl di- <i>sec</i> -ester Polymer ₁ , h_{O} ,	262 °C	[15c, 16]
<i>m</i> -phenyl di- <i>tert</i> -ester (terp) Polymer _{1 n} $+ 0$	192 °C (165 °C with acid)	[15a, 16]
Cyclohexyl <i>tert</i> -ether (terp)	250 °C with acid	[17]
Polymer ₁ $-O$ OH Cyclohexyl <i>tert</i> -ester (terp) Polymer ₁ O OH	182 °C with acid	[17]

Table 11.1 Degradable ester, ether, and carbonate crosslink functions used withassociated degradation temperatures.

Table 11.1 (Continued)



The thermally induced decomposition temperatures are consistent with breakdown to acid and olefins (and CO₂ in the case of carbonates), as observed by several analytical tools.

materials [27]. Various dissociative CAN systems are known, which have been retroactively dubbed "vitrimer-like" despite preceding vitrimers chronologically (see Section 11.2.3) [28].

Various crosslink systems have been explored in this context (Table 11.2). The use of photocatalysts also allows light to be used as a trigger instead of heat [38]. These dissociative CANs are generally researched as potential healable materials, but they have drawbacks compared to conventional thermosets. As their moduli do vary significantly upon even moderate heating, they have a tendency to creep, especially as the crosslinks are often of similar strength to hydrogen bonds (ΔG c. -20 to -30 kJ/mol, where ΔG is the free energy of bond-formation). There are however two reported systems that are significantly stronger than hydrogen bonds, both from the collaboration of Winne and Du Prez. The indole-triazolinedione system (TAD) is a strong but reversible reverse Diels–Alder adduct (Figure 11.3) [27, 32].

Du Prez and coworkers have also reported a system using thiol-yne Michael addition [37]. The initial product of the first Michael addition is weak (c. -20 kJ/mol), but the π -system can react again to form a stable crosslink giving essentially complete creep resistance up to 80 °C. Catalytic quantities of an organic base (TBD) are necessary to facilitate exchange reactions, and if the material if heated too strongly it is degraded. The crosslink strength of these two systems is such that they may be useful in the creation of reprocessable/healable materials that resist creep in normal use.

11.2.3 Vitrimers (Associative CANs)

Vitrimer networks are a variety of covalent adaptable networks in which the crosslink density remains constant [39]; no free reactive groups exist on a long

System	T _{gel}	ΔG	Notes	References
Furan-maleimide $Polymer_1$ O_{2}	c. 90 °C	−8 to −15 kJ/mol	Requires heating to c. 40 °C to form network	[29]
Polymer, CN Polyme	c. 50 °C	−8 to −15 kJ/mol		[30]
Cyclopentadiene-thioester	c. 80 °C	-35 to -45 kJ/mol		[31]
Indole-triazolinedione Polymer1 2_{2} , N, N H Polymer2 2_{2} , N, N H	c. 90 °C	−60 to −70 kJ/mol		[27, 32]
Disulfides	c. 60 °C			[33]
Polymer ₁ S_{s}^{s} Polymer ₂ Alkoxyamines				[34]
Activated urea	c. 90 °C	−10 to −50 kJ/mol		[35]
Thiol-ene Michael				[36]
$\begin{array}{c} & \bigcirc \\ Polymer_1 & \bigcirc & \bigcirc \\ Polymer_2 & Folymer_2 \\ \textbf{Thiol-yne double Michael} \\ Polymer_1 & \bigcirc & $		-160 to -252 kJ/mol (double reacted) $(E_a = 120 \text{ to} 200 \text{ kJ/mol})$	Requires base (TBD) as catalyst. Creep resistant to 80 °C	[37]

Table 11.2 Functional groups utilized as crosslinkers in dissociative CANs.



Figure 11.3 Reversible TAD dissociation used to transfer a dye to an unsaturated polymer. Source: Reproduced with permission from Houck et al. [32]. Copyright 2017 Royal Society of Chemistry.

molecular timescale. Hence vitrimers are associative CANs. Vitrimers are polymers utilizing an alternate crosslinking to thermosets, in an effort to create thermoset-like materials that are "infinitely" recyclable by secondary recycling. Several types of dynamic crosslinks have been employed in this context. A mechanistic/thermodynamic comparison illustrating the contrast between associative and dissociative CANs provides some insight (Figure 11.4).

The mechanically distinct feature of these associative systems (i.e. vitrimers) is that the storage and loss moduli are practically invariant up to a critical temperature, which prevents creep [27]. Viscous flow is observed above a certain temperature threshold. This contrasts with the previously considered dissociative systems as a consequence of the different network topology.

There are two important transition temperatures in typical vitrimers. The first is the glass transition temperature (T_g) . The second is the vitrification transition temperature (T_v) – that is the temperature at which the topology of the network becomes unfrozen and transitions from a viscoelastic solid to a liquid. Diffusion limits the displacement of bonds between the T_g and T_v and the Williams–Landel–Ferry equation determines the viscosity; hence elastomeric behavior is observed [41]. Above the T_v , Arrhenial behavior is observed with the material being a viscoelastic liquid.

The T_v is conceptually similar to T_m in semicrystalline thermoplastic systems, but the vitrimer does not become a free-flowing liquid as the number of crosslinks is essentially constant. They are simply exchanging on a rapid timescale, enabling reconfiguration of the network topology across the entire material and rendering the system processable. These two numbers are governed by the following factors:



Figure 11.4 Difference between (a) associative CANs (vitrimers) and (b) dissociative CANs. (First line) The rate of exchange (*k*, black line) varies in the same manner for both, but the association equilibrium constant (K_a , orange line) decreases with increased temperature for associative CANs, while it is constant for vitrimers. (Second line) Pseudo-3D plot showing the evolution of storage moduli (*G*') against frequency (ω) and temperatures. (Third line) Pseudo-3D plot of relaxation time spectra showing temperature differences in transition to a viscoelastic liquid. (Fourth line) Evolution in zero sheer viscosity (black line) and crosslink density (orange/blue line) against temperature. Source: Reproduced with permission from Jourdain et al. [40]. 2020 American Chemical Society.

- 1) Chemical nature of the crosslinking moieties
- 2) Density of the crosslinks and crosslinkable groups (if one is in excess)
- 3) Catalyst concentration and nature (if applicable)
- 4) The underlying nature of the base polymer.

All these factors must be considered together for the properties of the final material. The crosslink density and nature of the base polymer is a matter of design. In addition to simple heating, thermal radiation can be used if an efficient acceptor is incorporated. If carbon nanotubes or graphene is embedded in the network as a filler, they heat the network when illuminated, bringing the temperature above the T_v [42].

11.3 Examples of Vitrimers

Vitrimers were conceptually pioneered by Liebler and coworkers utilizing ester crosslinks and a zinc transesterification catalyst (Figure 11.5; see Table 11.3) [43]. The strength of the network is dependent upon the ability of the network to conduct these transesterifications, with higher catalyst loading leading to more extensibility [43b]. Epoxides were used to drive the initial esterification, leading to essentially no free hydroxyl groups. During the transesterification, free acetic acid was produced from the catalyst, which may be a long-term problem, since the acid can leach from the vitrimer.

In 2014 Winne and Du Prez reported enaminone chemistry as a suitable vitrimer that avoided the use of a catalyst [27, 50]. In this system, the crosslinks are formed by the amidation of a conjugated 1,3-dicarbonyl with an amine to form a vinylogous ure thane; that is the crosslink is essentially a ure thane with a π -system inserted into it to resonate via the inductive effect (Figure 11.6a,b). These crosslinks are hydrolytically stable, and indeed the reaction can even be carried out in water. However, the system relies on an excess of free amines in the system, which are oxidatively unstable. Nevertheless, this chemical transformation has been successfully exploited to produce various vitrimeric systems. For example, vinyl-acrylate-based copolymers with beta-keto ester side groups was effectively transformed into a vitrimer by introducing branched primary amines in various amounts (Figure 11.6c) [52]. The proportion of functional groups was shown to be critical, as in nearly all vitrimers. Exchange kinetics can be fine-tuned by adjusting the relative building block concentrations (i.e. branched monomers vs. comonomer in the acrylate backbone). The diketoenamine moiety has recently also been incorporated into mixed plastic waste feeds, essentially converting plastic waste into useful thermosets, which are in turn themselves recyclable [53].

Since vitrimers are "silica like" the obvious chemistry to exploit was that of silica itself. The first report of such a system was by Guan and coworkers [46]. They used classical chemistry for the formation of silyl ethers; the reaction of either an alkyl silyl chloride or an activated aminoalkyl silyl methoxide with a hydroxyl group. They found that the alkyl crosslinks were very slow in their exchange, with a window



Figure 11.5 First report of a vitrimer exploiting thermally activated esters as the interchangeable groups (a and b). This leads to reprocessable thermoset materials (c) with shape memory behavior (d). Source: Reproduced with permission from Montarnal et al. [43a]. Copyright 2011 Science.



Figure 11.6 (a) Chemical exchange responsible for vinylogous urethane vitrimers, showing (b) the kinetic dependence on catalyst type (DBN = 1,5-Diazabicyclo[4.3.0]non-5-ene; DBTL = dibutyl tin laurate; pTsOH = toluene sulfonic acid). (c) schematic illustration of the reconfiguration of the junctions in a polymer network. Source: (a and b) Denissen et al. [51] / Springer Nature / CC BY 4.0. Reproduced with permission from Lessard et al. [52]. Copyright 2019 American Chemical Society.

between the T_v and T_g of only 6 °C and an activation energy of 174 kJ/mol. However, the amino-activated silyl crosslinks were much more dynamic, lowering the T_v to 47 °C (see Table 11.3).

Guan and coworkers purported that boronic acid esters would make excellent vitrimeric crosslinkers based on small-molecule studies [24]. However, it was

Chemistry	T _v	E _a	References
Carboxylate	68 °C (1% Zn ²⁺) 57 °C (5% Zn ²⁺) 53 °C (10% Zn ²⁺)	68 kJ/mol (7.5% Zn ²⁺)	[43a, 44]
Enaminone $HN^{Polymer_3}$ Polymer _{1 O} HN^{2} Polymer ₂	27 °C uncatalyzed, -1 °C with 0.5% TsOH or -63 °C with 0.95% DBTL	81 kJ/mol uncatalyzed (70 kJ/mol catalyzed with 0.5% TsOH or 30 kJ/mol with 0.95% DBTL)	[45]
Siloxane alkyl ether	117°C	174 kJ/mol	[46]
OMe Polymer₁≷Si OMe OMe			
Siloxane aminoalkyl ether	47 °C	81 kJ/mol	[46]
Polymer; \$\$;NNNSi {Polymer_2} OMe OMe			
(all MeO groups are labile)			
Boronic acid ester	60 °C	28 kJ/mol	[47, 48]
Polymer ₁ -B			
Thioesters		Δ ‡H = 143 kJ/mol (uncatalyzed)	[49]
1,2,3-Triazolium	Not a true		[40]
Polymer ₁ ∼N [×] ⊕N ⁵ ₂Polymer ₂	vitrimer		
$\langle \rangle$			

 Table 11.3
 Example chemistries used as vitrimeric linkers.

Leibler and coworkers who first reported the implementation of boronic acid esters as a crosslinking strategy [47]. This obviated the need for a catalyst with the T_v reduced to c. 60 °C. Since the boronic acid esters were incorporated into PMMA and high density polyethylene (HDPE), the properties of materials were similar to the mother polymer. At the T_v , PMMA was still glassy, and hence no change in properties occurred. However, the incorporation of boronic ester crosslinks improved the creep of HDPE significantly.

Bowman and coworkers reported the use of thioesters as vitrimeric crosslinks [49]. These required a basic catalyst, since the enthalpy of dissociation (ΔH^0) is estimated to be 143 kJ/mol without a catalyst, consistent with a very stable network.

In the presence of a base, which can deprotonate the thiol, the ΔH^0 is reduced to c. 17 kJ/mol, leading to a very dynamic system. The base can even be photoactivatable. However, doping the polymer with DBU or other strong bases was problematic. Bowman and coworkers have reported that in thiol-anhydride-based CANs with large excesses of thiol, there is some contribution of an associative thiol-thioester exchange [26].

Montarnal and Drockenmuller have reported 1,2,3-triazolium crosslinks produce a network which is mechanistically a dissociative CAN, but shows vitrimeric rheology [43a]. Essentially, the ΔH^0 for viscous flow is so high (232 kJ/mol) that the network can't enter that regime, and hence the material behaves as a vitrimer even though it is not one in the strictest sense.

11.4 Adaptable Cross-Linking of Conventional Polymers

While most of these chemistries are demonstrated with a "pure" vitrimer network, these materials are of very little use in engineering applications. Alternatively, the direct replacement of more conventional crosslinking chemistries employed in thermosets has also been considered. As seen above, the crosslinking of PMMA and HDPE with boron acid esters was very successful [47]. Caffy and Nicolaÿ reported an improvement wherein HDPE could be converted into a boronic-ester-crosslinked vitrimer using reactive extrusion at 170 °C that introduced the boronic esters using a TEMPO-based radical crosslinker [54]. The properties are essentially the same as HDPE vitrimer copolymerized from virgin feedstocks.

Unsaturated polyolefins are extensively used as precursors to thermosets and rubbers (i.e. polyisoprene), owing to the reactivity of the double bond, making it amenable to crosslinking. The cross-metathesis of double bonds is also widely used for introducing various functionalities. Therefore, metathesis offers an obvious opportunity in creating vitrimers. Guan and coworkers effectively used cross-metathesis to form reconfigurable thermosets, employing the Grubbs catalysts based on ruthenium (Figure 11.7) [55].

Essentially any polyester or polycarbonate can be converted into a vitrimer assuming it has crosslinking sites and is doped with an appropriate catalyst. Hillmyer and coworkers reported a vitrimer formed from star poly(L-lactide) (PLA) doped with dioctyl tin (which is also the polymerization catalyst) when crosslinked with diisocyanates (Figure 11.8) [56]. In the absence of catalyst the network was a conventional thermoset, and with it, it was a vitrimer for which the properties were tunable based on catalyst concentration. In another example of a polyester converted to a vitrimer by this strategy, PBT copolymerized with glycerol is vitrimeric with a zinc catalyst [22]. The $T_{\rm m}$ was slightly reduced, in line with the expected $T_{\rm m}$ decrease from the lowered $M_{\rm w}$ of the individual polymer chains, but above the $T_{\rm m}$ of the bulk polymer, vitrimeric activity was observed.

Ester interchange has also been applied to more complex architectures. Highly branched bottle-brush copolymers with pendant hydroxyl groups were combined with a bicyclic ester crosslinker [57]. The crosslinking reaction liberates additional



Figure 11.7 Reconfigurable unsaturated polyolefins using olefin metathesis. Source: Reproduced with permission from Lu et al. [55]. Copyright 2012 American Chemical Society.



Figure 11.8 PLA vitrimers based on transesterification. Source: Reproduced with permission from Brutman et al. [56]. Copyright 2014 American Chemical Society.

hydroxyl groups that participate in the interchange at elevated temperatures. This feature, as with many vitrimers, is amenable to self-healing, which is otherwise prohibitive in conventional thermosets having irreversible bonding (Figure 11.9).

A similar approach utilizing carbonyl exchange was taken by using a polycarbonate with excess branched polyol building blocks, whereby carbonate exchange was responsible for the transfiguration upon heating [58]. The same research group took this concept one step further and applied interchangeable groups to crosslinked polyurethane foams [59]. In a twin-screw extruder, the polyurethane materials were heated in the presence of added catalyst to promote rapid exchange of urethanes, thereby rendering the materials reprocessable (Figure 11.10).

To date, research into vitrimers has concentrated on finding various temperaturesensitive chemical transformations. Several innovative strategies have exquisitely



Figure 11.9 Crosslinked bottle-brush copolymers with ester-interchanged responsible for the vitrimeric behavior (N_{BB} = Backbone degree of polymerization). Source: Reproduced with permission from Self et al. [57]. Copyright 2020 American Chemical Society.



Figure 11.10 Polyurethane-based vitrimers shown to be reconfigurable in a twin-screw extruder. Source: Reproduced with permission from Sheppard et al. [59]. Copyright 2020 American Chemical Society.

been employed to various polymer backbones, effectively transforming thermosets into reprocessable materials to various extents. To move forward, these chemistries have to be incorporated in polymers with real-world applications.

11.5 Outlook and Summary

Thermoset polymers have historically been considered unrecyclable due to the permanent nature of the crosslinks. Initial efforts into degradable crosslinks may ultimately allow for some recyclability, but dynamic crosslinks offer a potentially appealing alternative, whereby the properties and reconfiguration conditions can be finely tuned via the molecular makeup. Dynamic, reversible crosslinking also provide other opportunities in addition to recycling/reprocessing. For example, dissociative CANs can self-heal upon heating. On the other hand, the crosslink strength and thermal properties have to date not proven strong enough to compare with traditional thermosets, and as such they have failed to provide the performance of true thermosets. Such disadvantages are a topic of active research, and this remains an area with some promise. Associative CANs or vitrimers retain a constant crosslink density and so their material properties fall off in a far more gradual

manner and hence are useful thermoset replacements which can in principle be mechanically recycled by remolding. Translating this to real applications and real markets still has many challenges. This remains firmly in an exploratory stage.

Nevertheless, vitrimers offer the opportunity for designing new materials from the ground-up, where the end-of-life is specifically built into the material constructs. This concept makes recycling a key feature in newly designed materials, instead of merely an afterthought, such as the case with conventional commodity plastics. The concept of vitrimers, whereby the materials comprise the remarkable properties associated with thermosets, offers new avenues for reconfiguration and reprocessing of plastics that have traditionally been exclusively reserved for a select subset of thermoplastics. Rapid progress has been made in the decade since the inception of vitrimers, and the coming decades surely offer many new exciting developments. Most exciting is the commercialization of the first vitrimer materials, which is certain to have an impact on the several important plastic and rubber segments.

With respect to the current situation, vitrimers and CANs in general still have a long way to go to gain a foothold in large volume markets. Of course, the challenges associated with recycling apply to any new material, regardless of how reprocessable it is from a technological standpoint. Some of these challenges include the loss of properties with each successive reprocessing cycle. Likewise, sorting and separation offer logistical challenges, which are naturally exacerbated by increasing the variety of chemical building blocks. This is currently seen in the essentially non-existent recycling of mixed plastic streams and multi-component constructs. Therefore, the development of recyclable thermosets will certainly encounter the same roadblocks that currently impede the widespread recycling of commodity thermoplastics. In the near future, at least, the reprocessing and reuse of reconfigurable thermosets will be limited to clean sources that are well separated. Furthermore, chemical recycling methods that rely on specific decomposition mechanisms (e.g. ester exchange for poly(ethylene terephthalate) (PET)) are challenging when a multitude of chemical moieties must be dealt with.

Parallel to opportunities in recycling technology lies the (bio)degradation pathways. If collecting, sorting, and chemical recycling is impractical or deemed unsustainable, ideally natural degradation pathways should be built into the material, leading to benign byproducts after breakdown. The use of hydrolysable links in the main polymer chain and their cross-link is a significant step toward that goal. Of course, biodegradation should be tuned/timed to start well after the expected usability/durability of the product. This very feature has made widespread use of bio-based plastics in engineering applications (see Chapter 7 on PLA). To date, the express focus on biodegradable vitrimers has received minimal attention. However, this remains an area that holds many opportunities for further investigation.

The next generation of polymer design provides great opportunities, wherein the end-of-life can specifically be taken into account along with the properties for various applications. Adaptive networks and vitrimers offer a particularly appealing avenue for attaining the superior physical/mechanical properties and durability often observed in thermosets, even if it is particularly suited for niche applications. At least the concept takes into consideration the need for rationally designed systems, where the full life cycle is accounted for. This chapter offers some insight into several strategies that have emerged with this circularity in mind, applied specifically to crosslinked networks. The research outlined may provide viable pathways toward making environmentally troublesome waste streams from ever escaping. Among the products ripe for investigation are of course rubber tires, polyurethanes, urea-formaldehyde, and others. There is great promise for designing new plastics that even contribute to sustainability without sacrificing the material after its (initial) useful lifetime.

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