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Condensation Polyesters

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5.1 Introduction

Polyesters can be referred to as macromolecules in which the main chain segments are repetitively linked by ester units. This excludes polymers that contain ester linkages within the side groups of the repeating unit such as poly(vinyl acetate) and poly(meth)acrylates [1]. As will be discussed later, the main chain ester linkages play a key role in the biodegradability of polyesters. Within the polyester chain, a great variety exists with respect to the repeating units that are used, which includes linear aliphatic polyesters with varying spacer length (e.g. poly(butylene succinate) [PBS]), semi-aromatic polyesters containing at least one aromatic and one aliphatic unit (e.g. poly(ethylene terephthalate) [PET]), or wholly aromatic polyesters (e.g. poly(4-hydroxybenzoic acid)).

The condensation polyesters are one of the oldest classes of synthetic polymers. The first group of synthetic polyesters was the alkyds, which were commercially developed between 1910 and 1915 by General Electric Company [2]. Notably, a resin was obtained from the condensation reaction between glycerol and phthalic anhydride. Later in the twentieth century, in 1928, W.H. Carothers started his research toward condensation polyesters at DuPont. For the first time, a linear polyester was obtained from octadecanedioic acid and 1,3-propanediol with a molecular weight of 12 000 g/mol, and at the time, it was called a "super polyester." [3] The improvement in molecular weight was significantly higher than the previously obtained molecular weights of between 400 and 5000 g/mol. The research group of Carothers continued the work on (mainly aliphatic) polyesters, but this did not lead to any commercial development at the time. Later, the incorporation of terephthalic acid for the production of semi-aromatic polyesters was further investigated, which led to the discovery of PET fibers [4]. At the same time, other polyesters containing terephthalic acid and glycols with various spacer lengths were developed. Since then, large developments were made in the field of polyesters, and they are a prevalent class of polymers in the current plastics market. Still, nowadays, polyesters are continuously

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studied by scientists because a significant fraction can be considered as biobased or biodegradable polymers. This is now relevant more than ever with the concerns regarding the net increase in CO_2 emissions and plastic waste management, which are accompanied by the consumption of plastics.

The history of biodegradable plastics is quite recent, but (condensation) polyesters have played a major role so far. The first commercial biodegradable condensation polyesters were launched in the beginning of the 1990s. These were PBS and copolymers thereof and were sold under the trade name Bionolle®. In the late 1990s, biodegradable aromatic condensation polyesters based on terephthalic acid copolymers with high melting temperature were developed and later sold under the trade names Ecoflex®, Eastar Bio®, Origo-Bi®, and Biomax®. Most of the developments in the discovery of biodegradable condensation polyesters have been made in the 1990s and since then has focused on introducing new biobased and/or functional monomers, polymer blends with other biodegradable polymers, composites, and the copolymer composition–property relationship to achieve the optimal balance between the physical performance and degradability.

Nowadays, commodity plastics such as poly(propylene) and poly(ethylene), which make up the majority of the market, persist for many years in nature after disposal because of their non-degradability. Biodegradable plastics only make up a small fraction, approximately 0.5% of the total plastic production [5]. They mainly find applications in products where biodegradability is one of the main desired features, such as biomedical, pharmaceutical, packaging, and agricultural industries. However, with the current surge in interest in the circular economy and waste management, the biodegradable plastic market is expected to grow steadily in the coming years. A recent report of the Nova Institute predicted that the total production of biodegradable plastics will grow from 1.17 mt in 2019 to 1.33 mt in 2024 [5].

Another reason for the growing interest in condensation polyesters is their renewable characteristic. Many monomers that make up polyesters can also be derived from renewable resources, especially the aliphatic ones. On the other hand, investigations toward obtaining bio-derived terephthalic acid from renewable resources are currently ongoing [6].

In this chapter, we will elaborate more on the most important types of biodegradable condensation polyesters that are currently available and their synthesis. Furthermore, the most important mechanism of their degradation is further explained. This is followed by a section that addresses the currently available applications for biodegradable condensation polyesters. A brief discussion regarding the recycling of polyesters together with the concluding remarks is provided at the end of the chapter.

5.2 Preparative Methods

Condensation polyesters are prepared by condensation polymerization, which is a type of step growth polymerization. This involves the reaction between two molecules to form dimers, which in term react with more molecules to form trimers, tetramers, and so forth, eventually forming large structures. This occurs under the release of small molecules as a by-product, also known as the condensate. Condensation polymerization requires a constant supply of heat and optionally a vacuum in order to evaporate and distill the low boiling condensate. Reaction completion is required because of the relationship between molecular weight and conversion in step growth polymers. This relationship was first described by Carothers (Eq. (5.1)) [7].

$$\overline{X}_n = \frac{1+r}{1+r-2rp} \tag{5.1}$$

The number-average degree of polymerization X_n is defined as the average number of structural units per polymer chain, r is the stoichiometric ratio of functional groups, and p is the conversion. Furthermore, in order to reach high molecular weights, the monomers should be present in stoichiometric balance. If one is added in excess, the theoretical attainable molecular weight decreases drastically.

The most common methods to produce aliphatic and semi-aromatic condensation polyesters are polycondensation and transesterification polycondensation. In a typical polyester synthesis, two bifunctional monomers containing functionalities AA and BB are reacted together in an AABB-type polycondensation. This usually involves a diacid and a diol releasing water as the condensate (Figure 5.1). Alternatively, it is also possible to obtain polyesters from AB-type monomers, which contain both an alcohol and a carboxylic acid group. Upon self-condensation, they form poly(hydroxy acids) of ABAB type. To speed up the reaction, homogeneous esterification catalysts such as antimony, titanium, tin, zirconium, and zinc are typically used [8–13].

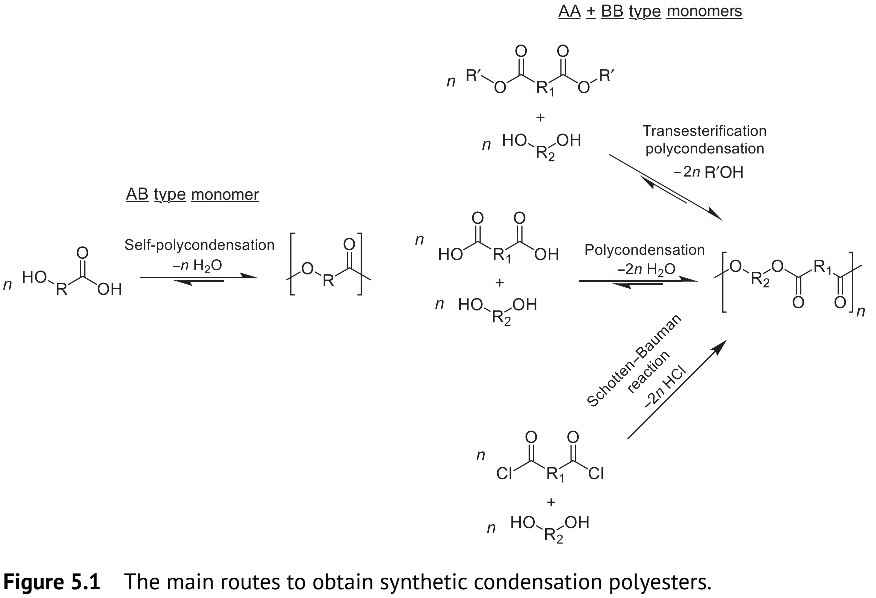


Figure 5.1 The main routes to obtain synthetic condensation polyesters.

The functionality of the monomers involved plays an important role in the outcome of the reaction. With the addition of a trifunctional or a higher functional monomer, a cross-linked network is obtained. When a monofunctional monomer is added, the molecular weight is reduced because the growing chain end is terminated. Therefore, the molecular weight and the cross-linking density depend on the functionality of the monomer and the ratio of each of the monomers in the polymerization.

Another polycondensation method is transesterification polycondensation. In this method, a diol is reacted with a diester. Usually, methyl or ethyl esters of the corresponding diacids are used (Figure 5.1). Transesterification polycondensation can have several advantages, for example, more facile removal of the condensate because of the higher volatility of methanol and ethanol compared to water, or instability of one of the monomers in the presence of carboxylic acid. The most prevalent example of transesterification polycondensation is the reaction between dimethyl terephthalate and ethylene glycol to produce PET.

Besides conventional metal-based catalysts, other catalytic methods can be employed, for example, enzyme-catalyzed polycondensation. In these methods, the reaction temperatures are low compared to melt polycondensation, but the reaction is generally performed in solvents. As catalysts, enzymes are used, which makes this procedure suitable for thermally or chemically unstable monomers. In the case of aromatic polyesters, usually, other types of polycondensation methods are employed. They are typically synthesized by reacting a diacylchloride with a diol releasing hydrogen chloride or by acetate exchange with aromatic diacids and phenyl esters. These reactions are performed in solutions and in bulk respectively and require modification of the monomer before polymerization [14, 15]. However, wholly aromatic polyesters are non-biodegradable and are therefore beyond the scope of this chapter [16].

5.3 Biodegradation of Polyesters

In general, biodegradation of polymers is achieved by scission of the main chain into progressively smaller segments and eventually undergoing decomposition into carbon dioxide, water, methane, and inorganic compounds. The latter could be as a result from the remaining catalysts or additives. In other words, long macromolecular chains are broken down to oligomers and then to monomers, which are then further metabolized by microbes. The whole process should be (at least partially) a result from the enzymatic action of microbes, such as bacteria or fungi. The most prevalent degradation mechanisms for polyesters are hydrolytic degradation and enzymatic degradation. This is because chain scission occurs at the ester bonds, which are susceptible to both hydrolysis and enzymatic attack. This results in the creation of a carboxylic acid and an alcohol and reduces the molecular weight, ultimately leading to the failure of the structural integrity of the plastic material.

The mobility of polyester chains is considered as one of the most important features that determines biodegradability [17]. This, in term, is correlated with a variety of polymer properties such as glass transition temperature (T_g), molecular weight, melting temperature, and degree of crystallinity. For example, most condensation polyesters are semicrystalline, which indicates that they are composed of crystals connected by amorphous segments. In degradation experiments, it was shown that first the amorphous segments are biodegraded because they possess higher mobility, especially above the T_g of the polymer [18]. For most aliphatic polyesters, the T_g value is low (typically well below the room temperature) and are thus susceptible for degradation under natural conditions. A prevalent example of an aliphatic polyester with a high T_g of around 59 °C is poly(lactic acid) (PLA). PLA is extremely slow to degrade under natural conditions but can degrade rapidly in composting facilities where elevated temperatures (up to 65 °C) and high humidity are used [19]. Another important factor is the hydrophilicity of the polyester, which is determined by monomer type and end group concentration. Hydrophilicity promotes biodegradability by increasing the interaction with the surrounding water molecules, which are essential in the most important modes of biodegradation [20]. The amount of end groups in the polymer is related to the molecular weight. Biodegradability can also be influenced by the synthesis procedure and processing method because these affect some polymer properties. For example, a relatively low molecular weight is obtained for condensation polyesters (typically 10^4–10^5 g/mol), whereas for polyesters obtained via ring opening polymerization (ROP), a higher molecular weight is typically obtained (10^5–10^6 g/mol). The molecular weight and the synthesis method influence properties such as crystallinity and end group concentration and monomer type.

As such, many commercial biodegradable polyesters are copolymers consisting of multiple types of monomers. The biodegradability of a copolyester can be tuned by incorporating monomers with various levels of rigidity and hydrophilicity. An additional concern that comes along is the degradability and toxicity of the liberated monomers. In general, aliphatic naturally occurring monomers, such as lactic acid, possess low toxicity for their environment [21]. On the other hand, aromatic monomers are typically more harmful than the aliphatic ones and persist for a longer time in the environment [22].

5.3.1 Hydrolytic Degradation

Hydrolytic degradation is the scission of macromolecular chains and accompanying lowering of the molecular weight because of the reaction with water molecules. In this process, H_2O is consumed, and as a result, chain scission occurs. The synthesis of a polyester is a reversible process. This indicates that in the presence of water, ester bonds can undergo reversible reaction into a carboxylic acid and an alcohol. This reversibility is a slow process at ambient temperatures. The susceptibility of ester bonds to undergo scission by hydrolysis is governed by the charge value of the reacting carbon [23]. Because strong aromatic compounds are able to delocalize the charge value on the involved carbon bonds, resistance to hydrolytic degradation is increased. This is one of the reasons that aromatic polyesters are less prone to undergo biodegradation than aliphatic polyesters.

Two main modes of hydrolytic degradation exist: bulk degradation and surface erosion. During bulk degradation, water is able to migrate into the polymer and cleave the ester bonds homogeneously throughout the material. However, in surface erosion, only macromolecular chains at the surface of the material are affected, indicating that the diffusion of water into the polymer is slower than the rate of bond hydrolysis [24]. This will have a heterogeneous breakdown of the macromolecular chains as a result. With the liberation and accumulation of carboxylic end groups upon bond cleavage, bulk autocatalytic hydrolysis occurs [25]. Several factors, such as the hydrophilicity, crystallinity, and geometry (thickness, surface area, porosity, and surface topology) of the polymer, are known to influence water diffusion [26].

5.3.2 Enzymatic Degradation

Enzymatic degradation of polyesters occurs in the presence of water, microorganisms, and their enzymes. Slightly stricter conditions are required for enzymatic degradation to take place in contrast to hydrolytic degradation, which is promoted in acidic or basic media and at high temperatures. Besides the presence of water, microbial degradation usually requires oxygen, nutrients, and mild temperatures. Furthermore, the process only occurs at the surface of the material because the large size of enzymes restricts them from diffusing in the polymer. For this, the enzyme needs to undergo an adsorptive binding to the substrate surface to start the degradation process [27]. Therefore, surface erosion is the only mechanism in the case of enzymatic degradation. Enzymatic hydrolysis of the polyester can proceed on the terminal ester bonds (exo-hydrolysis) resulting in monomers, or on the ester bonds within the macromolecular chain (endo-hydrolysis) resulting in oligomers and then monomers. The surface is continuously eroded, resulting in a linear mass loss [28]. Small macromolecular segments are expelled into the medium, which in term are further degraded and metabolized by other microbes present in the medium. With the slow decrease in mass because of degradation from the surface to the center of the material, other components present in the polyester are slowly expelled into the surrounding medium. That is why, these materials are particularly interesting for biomedical applications that require a controlled delivery process such as the release of drugs.

Similar to hydrolytic degradation, enzymatic degradation is affected by most of the features involving chain mobility and length. Furthermore, it is also influenced by the hydrophilic/hydrophobic balance in the main chain and molecular structure of the monomers [29]. A strong effect of the presence of aromatic groups exists. Aliphatic polyesters can be effectively degraded by lipases, but aromatic polyesters remain unaffected. Copolymers containing both aliphatic and aromatic monomers show biodegradability, which is mainly dictated by the amount of aliphatic units present. This is considered to be related to steric hindrance of the bulky aromatic units, which change the chain aspect ratio and limit the accessibility of the enzyme to the ester bond [30].

5.4 Aliphatic Polyesters

5.4.1 Poly(alkylene dicarboxylates)

Poly(alkylene dicarboxylates) are a family of aliphatic biodegradable polyesters. They are obtained from the polycondensation of diols such as ethylene glycol or butane diol with aliphatic dicarboxylic acids such as succinic acid and adipic acid. Typically, they exhibit low T_g because of the high conformational freedom of the aliphatic chains. However, they obtain their mechanical properties from their high crystallinity. The most prevalent examples are PBS and its copolyesters, and poly(ethylene adipate) (Figure 5.2).

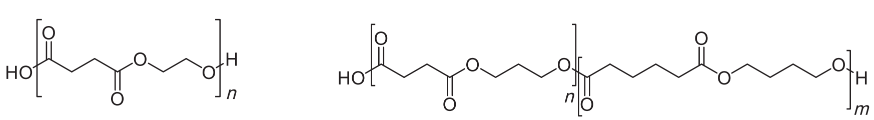
PBS is obtained from the polycondensation of butane diol with succinic acid (or dimethyl succinate) and usually results in a molecular weight below 100 000 g/mol. Because PBS with a molecular weight below 100 000 g/mol is fairly brittle, with a low strain at break, higher molecular weights are usually desired to improve the ductility for processing. In order to achieve high molecular weights, chain extenders such as diisocyanates [31] and bisoxazoline [32] can be used during the synthesis. The chain extenders couple the chains by reacting with the end groups. This reaction is performed in a finalizing step to reach the desired high molecular weight.

Variations in the spacer length of the monomers result in different polymers such as poly(ethylene succinate) (PES), poly(butylene adipate) (PBA), and copolymers of PBS, namely, poly(butylene succinate-*co*-adipate) (PBSA) [33]. The nature of the comonomers that are used influences the properties and biodegradation rate [34]. For example, biodegradability improves when more adipic acid is incorporated because of the lower crystallinity and melting point [35].

Added value of PBS is its renewable character because the monomers can be synthesized from renewable resources. Both butane diol and succinic acid can be obtained from the fermentation of sugars [36]. In 2004, succinic acid was appointed by the US department of Energy (DoE) as one of the major biobased platform molecules [37]. However, currently, succinic acid is obtained from the hydrogenation of maleic anhydride, which is produced by oxidation of butane.

Poly(butylene succinate) (PBS)

Poly(butylene adipate) (PBA)



Poly(ethylene succinate) (PES)

Poly(butylene succinate-*co*-adipate) (PBSA)

Figure 5.2 Chemical structures of some biodegradable poly(alkylene dicarboxylates).

PBS is a semicrystalline polymer with a melting temperature of around 90–120 °C and a T_g of between −45 and −10 °C [13, 34], fairly similar to those of poly(ethylene) and poly(propylene). Because of its high crystallinity, the biodegradation rate is relatively low, but PBS exhibits good mechanical properties. Furthermore, it has good processability, with film properties comparable to that of LDPE (low-density poly(ethylene)). The films of commercial PBS (Bionolle) have Young's modulus of about 0.5 GPa, tensile strength of 30 MPa, and strain at break of 710% [34]. The thermomechanical properties of PBS are superior to some other aliphatic polyesters, such as PLA. PLA has a higher Young's modulus and tensile strength than PBS but suffers in some applications because of its high brittleness, slow crystallization, and low heat distortion temperature [38].

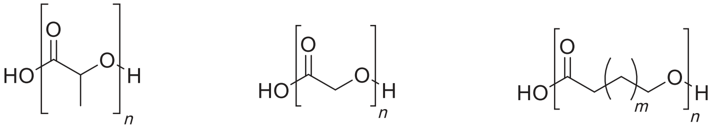
An important application for aliphatic polyesters is in starch blends. This is done in order to reduce costs and improve biodegradability. For example, PBSA blends with starch content up to 30 wt% retain sufficient mechanical performance to be processed into films via film blowing extrusion [39]. Blending can also be performed in the presence of a compatibilizer in order to increase the amount of starch in the blend without significant loss in the mechanical properties. Compatibilized polyester/starch blends have typically higher water uptake and lower strain at break [40], but the tensile strength remains largely unaffected even at high starch content (up to 70 wt%) [41].

Another interesting class of poly(alkylene dicarboxylates) are obtained from long-chain diols and dicarboxylates. These monomers can be obtained from fatty acids, which naturally occur in plant oils and exist as triglyceride esters. Their corresponding polymers are structurally similar to polyethylene (PE) and have similar physical and mechanical properties [42]. The difference is that long aliphatic segments containing up to 24 carbon atoms are separated by ester bonds. Therefore, they are proposed as a biodegradable and biobased alternative for PE [43].

5.4.2 Poly(hydroxy acids)

Hydroxy acids can undergo self-condensation because they contain both a hydroxyl group and a carboxylic acid in their chemical structure. Upon polycondensation, a poly(hydroxy acid) is formed. They can be classified into α-, β-, ω-, and aromatic hydroxy acids. A separate class exists for hydroxy acids containing more than one hydroxyl or carboxyl group, which can yield cross-linked or branched polyesters. Recently, hydroxy acids have gained increased interest because they can be obtained from renewable resources.

The most studied and industrially relevant hydroxy acids for polymers are the α-hydroxy acids, particularly lactic acid and glycolic acid. Upon polymerization, they form PLA, poly(glycolic acid) (PGA) (Figure 5.3), and the copolymer poly(lactic-*co*-glycolic acid) (PLGA). However, in the industry, these polymers are obtained from the ROP of lactide and glycolide. Therefore, it is more appropriate to refer to these polymers as poly(lactide) and poly(glycolide). Direct condensation of lactic acid omits the synthesis and isolation of lactide, but polycondensation



Poly(lactic acid)

Poly(glycolic acid)

m = 13, Poly(16-hydroxy palmitic acid)
m = 15, Poly(18-hydroxy stearic acid)

Figure 5.3 Chemical structures of some poly(hydroxy acids).

typically results in a much lower molecular weight. Polycondensation requires long reaction times and high temperature, in the presence of Brønsted acids, or tin or zinc based catalysts such as tin chloride and zinc oxide. In addition, this reaction generally suffers from racemization, transesterification, and discoloration compared to the polymers obtained in ROP [44].

The self-condensation of lactic acid results in an M_w of below 50 000 g/mol in most cases. To obtain high molecular weight PLA, binary catalysts comprising tin dichloride and *p*-toluenesulfonic acid have been proven to be effective [45]. Polycondensation is followed by solid-state polymerization to increase the molecular weight. Herein, the polymer is heated to above the T_g but below the melting point in a vacuum or nitrogen atmosphere. Through this way, PLA with an M_w of above 600 000 g/mol can be achieved [45]. Alternatively, water released during the condensation reaction can be azeotropically removed by means of a solvent. The reaction setup usually includes a Dean–Stark setup, which allows recovery of the dry solvent. Herein, the condensation polymerization occurs in solutions. In this process, high molecular weight PLA with an M_w of 230 000 g/mol can be reached [46, 47].

Other hydroxy acids that have attracted attention for the production of biodegradable polyesters are ω-hydroxy fatty acids (Figure 5.3), which have long aliphatic chains separating the carboxylic acid and the alcohol group. They in fact have similar properties as the long-chain poly(alkylene dicarboxylates), which were discussed in the previous section [48]. Similar to lactic acid, they can also undergo ROP from the corresponding lactone to yield the polyester. The most notable example is poly(pentadecalactone) [49, 50].

5.4.3 Cyclic Sugar-Based Monomers

Polyesters based on rigid cyclic monomers such as isosorbide and its isomers (diols) [51], as well as bicyclic diacetalized D-manno-, D-gluco-, galacto-alditols or aldirates (diols, diacids or diesters), are interesting because of their high T_g, non-toxicity, renewability, stereoselectivity, and biodegradability (Figure 5.4).

Incorporation of cyclic monomers in both aliphatic [8, 52–55] and aromatic [56, 57] polyesters has been reported. For isosorbide copolymers, generally, low molecular weight polymers are obtained because of the low reactivity of the sterically hindered secondary alcohols in isosorbide and its isomers. Nonetheless, they have received a considerable amount of attention from polymer scientists for the use in biobased and biodegradable polymers [51]. Acetalized alditols exhibit

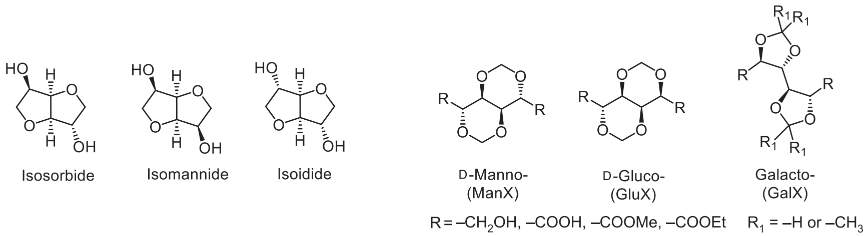


Figure 5.4 Chemical structure of some cyclic sugar-based monomers.

similar properties as isosorbide but with the benefit of being much more reactive in polycondensation, resulting in relatively higher molecular weights.

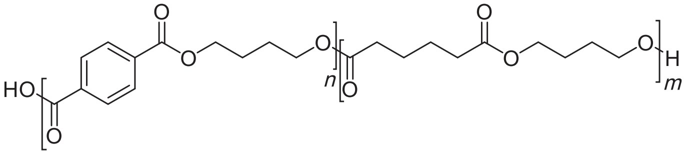
The group of Sebastian Muñoz-Guerra [53, 58] has shown that the hydrodegradability of polyesters is enhanced by the presence of bicyclic diacetalized D-manno, D-gluco, or galacto sugar derivatives. Moreover, not only the chemical hydrolysis was accelerated but also the sensitivity to enzymatic degradation with lipases was significantly increased when cycloaliphatic sugar-derived monomers were used instead of aromatic monomers.

With the incorporation of rigid sugar-based monomers in aliphatic biodegradable polyesters such as PBS, expansion of the performance window can be achieved without compromising the biodegradability, which is the case with aromatic monomers. Therefore, they are interesting for applications where good biodegradability and chain stiffness are required. For example, incorporation of isosorbide in PBS results in an increase in the T_g from −37 to 65 °C with 0 to 100 mol% isosorbide incorporation relative to succinic acid [59]. At the same time, the melting point and crystallinity decrease. Above 30 mol% incorporation relative to succinic acid, crystallization of the polyesters is troublesome. As a result, isosorbide PBS copolymers show a higher degree of weight loss than the pure PBS polymer in biodegradation studies [59]. Similar trends are observed for the incorporation of ManX-diol and GluX-diol in PBS with respect to biodegradability and thermal properties [60]. The tensile behavior showed that a higher Young's modulus and tensile strength were obtained for polymers containing more ManX-diol at the expense of the strain at break, which is typically very low for these type of polymers [54].

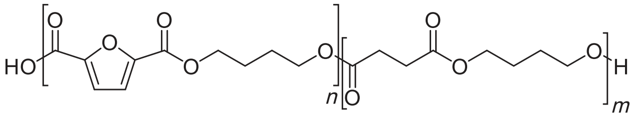
5.5 Semi-aromatic Polyesters

5.5.1 Poly(butylene adipate terephthalate) (PBAT)

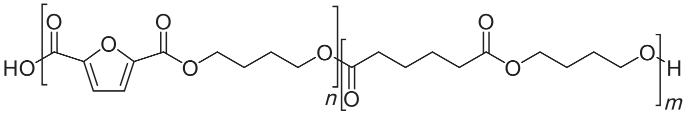
Incorporation of aromatic monomers in the polymer chain improves the mechanical properties such as Young's modulus and tensile strength. However, polymers with high aromatic content such as PET are non-biodegradable. This is related to the previously mentioned charge delocalization and steric hindrance of the aromatic units, which hinder chemical hydrolysis and enzymatic degradation. Therefore, a range of semi-aromatic copolyesters were developed to balance the mechanical



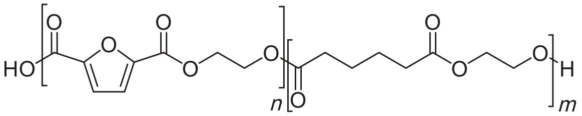
Poly(butylene adipate-*co*-terephthalate) (PBAT)



Poly(butylene succinate-*co*-furanoate) (PBSF)



Poly(butylene adipate-*co*-furanoate) (PBAF)



Poly(ethylene adipate-*co*-furanoate) (PEAF)

Figure 5.5 Chemical structures of some relevant biodegradable semi-aromatic polyesters.

and biodegradability properties. Typically, a mixture of aromatic and aliphatic diacids is copolymerized with an aliphatic diol. The resulting biodegradability is then a contribution from the incorporated aliphatic monomers, while the aromatic monomers improve the mechanical properties. The most prevalent biodegradable semi-aromatic polyester is poly(butylene adipate terephthalate) (PBAT) (Figure 5.5). It is prepared from the condensation copolymerization of terephthalic acid with adipic acid and butanediol.

The biodegradability of semi-aromatic copolyesters based on terephthalic acid, adipic acid, sebacic acid, and 1,3-propanediol was demonstrated for the first time in 1995 [62]. Since then, the development and biodegradation of semi-aromatic polyesters were well studied. In the case of PBAT, the biodegradation rate depends on the amount of terephthalic acid in the polymer. It was estimated that with a content ranging from 40 to 50 mol% terephthalic acid relative to adipic acid, the optimal balance between mechanical performance and biodegradation rate was reached [63]. Indeed, the typical terephthalic acid mole fractions in PBAT range from 35 to 60 mol% relative to adipic acid. In laboratory tests, it was shown that PBAT first degrades to oligomers and then to monomers. Furthermore, toxicological studies of the degradation products showed no adverse effects [64].

The mechanical properties of PBAT are similar to those of LDPE, but with a higher strain at break of around 800%. These properties make it a promising material for film applications. To reduce costs, the thickness of the film is reduced to improve cost competitiveness, which requires sufficient melt strength. In order to achieve the desired properties and stability during melt blowing, long-chain branching is introduced. This is achieved during the synthesis by introducing multifunctional branching agents such as polyhydric alcohols and multifunctional acids or epoxides [65].

Efforts in improving the mechanical performance have shown that increasing the terephthalic acid content improves Young's modulus but at the expense of the strain at break [66]. PBAT has a relatively low degree of crystallinity, which is caused by the copolymerization of terephthalate and adipate units. Because the monomers are randomly distributed, crystal formation is disrupted. Nucleating agents can be used during the synthesis to facilitate the crystallization. The melting points of PBAT range between 115 and 125 °C and the T_g between −9 and −33 °C for copolymers with a terephthalic acid content ranging between 40 and 60 mol% relative to adipic acid [66].

5.5.2 Furanoate Copolymers

With the continuing efforts in finding a route toward biobased terephthalic acid, the biobased alternative 2,5-furandicarboxylic acid (FDCA) has gained interest as well. Poly(ethylene furanoate) (PEF) has therefore been proposed as a PET replacement. Similar to PET, PEF is also considered non-biodegradable even though the enzymatic hydrolysis rate of its films is reported to be 1.7 times faster than PET [67]. Therefore, a range of (potentially) biobased semi-aromatic polyesters based on FDCA were developed recently (Figure 5.5) [61]. The monomers that are used for this polymerization are FDCA, 1,4-butanediol, ethylene glycol, succinic acid, and adipic acid. Polycondensation is performed by a two-step synthesis where first the monomers are heated together in an esterification step at 190 °C. Then, a polycondensation step is applied where the temperature is raised to around 230 °C [68]. Loos and coworkers prepared similar furan-based copolyesters via a two-step procedure using enzymatic transesterification polymerization in diphenyl ether at 95 °C [69].

The thermal properties of the copolymers largely depend on the amount of FDCA incorporation. Copolymers of poly(butylene succinate-*co*-furanoate) (PBSF) with different FDCA-to-succinic acid ratios yield a series of semicrystalline polyesters that crystallize slowly. Their melting points range between 93 and 170 °C and the T_g between −40 and 45 °C depending on the amount of FDCA incorporated. Similarly, the copolymers of poly(ethylene adipate-*co*-furanoate) (PEAF) show crystallinity only at low and high FDCA incorporation, which is the same for poly(butylene adipate-*co*-furanoate) (PBAF). The melting temperatures range between 50 and 190 °C and the T_g between −32 and 70 °C [70].

With respect to the mechanical properties, the incorporation of FDCA strongly influences the properties. Mechanical testing on semicrystalline PBAF with molar percentages of FDCA relative to adipic acid between 10 and 75% show a Young's modulus between 55 and 110 MPa. With 30, 40, and 50 mol% FDCA, the polymers are amorphous and therefore exhibit a lower Young's modulus but a high strain at break between 1040 and 1850% [71].

Semicrystalline polyesters based on FDCA and aliphatic diacids show a relatively good biodegradability. Depending on the FDCA content, PBAF shows a significant weight loss in the presence of a lipase at 37 °C in 28 days. Furthermore, the degradation rate is also influenced by the crystallinity and melting point [71]. The degradability of PEAF in enzymatic hydrolysis studies is complete within 30 days for copolymers with 10 mol% FDCA relative to adipic acid or less. The degradation rate is strongly decreased when the FDCA content is higher. The copolymers of PEAF containing more than 50 mol% FDCA relative to adipic acid are hardly susceptible to hydrolysis [70].

Recently, academic interest in biodegradable polyesters based of FDCA has surged. In these studies, the researchers aim to develop semi-aromatic polyesters with improved biodegradability or mechanical performance and study important parameters connected to these properties such as crystallinity (differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies) and morphology. In order to tune the degradability and mechanical properties, modification of poly(butylene furanoate) (PBF) and PEF with other biobased monomers is possible. In this way, modifications of semicrystalline polyesters with typical biodegradable and/or rigid monomers such as ε-caprolactone [72], lactic acid [73, 74], and isosorbide [75] were reported.

In summary, the combination of various aliphatic and aromatic monomers truly expands the possibilities for biodegradability and mechanical performance optimization. Related to the polymer structure, trends in biodegradability and mechanical performance based on monomer type and ratios can be observed. Besides chain rigidity, hydrophilicity is one of the important predictors for biodegradability [76]. This is related to the amount of polar (end) groups in the polymer structure such as esters, alcohols, and carboxylic acids. In aliphatic polyesters, usually, the presence of branches and the amount of methylene groups that separate the ester bonds negatively affect the hydrophilicity (Figure 5.6). Similarly, the presence and type of aromatic groups negatively affect the degradability as well. For example, the faster degradation of PBAF compared to PBAT originates from the disordered structure of FDCA in contrast to the symmetric terephthalic acid, which allows tight stacking of the polymer chains and thus retarding the degradation (Figure 5.6) [77].

As mentioned before, aromatic monomers can be incorporated to improve the rigidity and strength of the polymer. To obtain high-stiffness polyesters, incorporation of aromatic monomers must be high, but this is usually at the cost of ductility (Figure 5.7). Semi-aromatic polymers with alternating aromatic units such as PEF, PBT, and PET are considered non-biodegradable because of the high stiffness and aromatic content. This is represented in the high Young's modulus, unlike most of the biodegradable polyesters that typically exhibit a much lower Young's modulus but have high strain at break. This can be observed in Figure 5.7, which displays

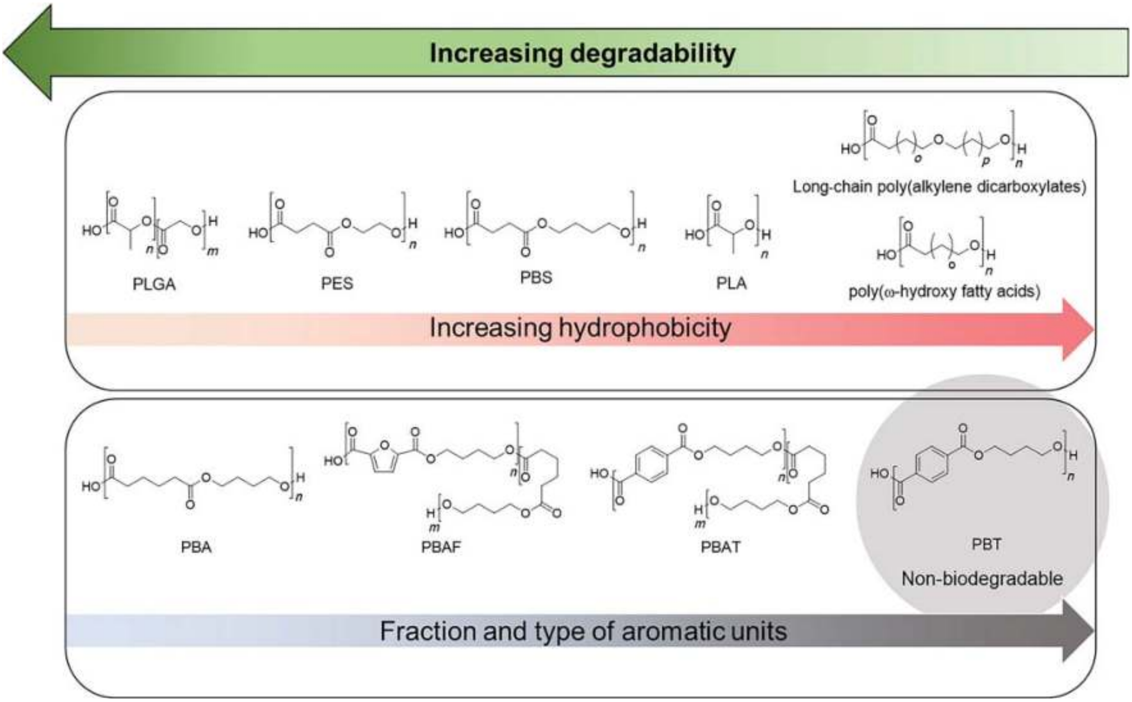


Figure 5.6 Schematic overview of the influence of hydrophobicity and aromatic units on the degradability of polyesters.

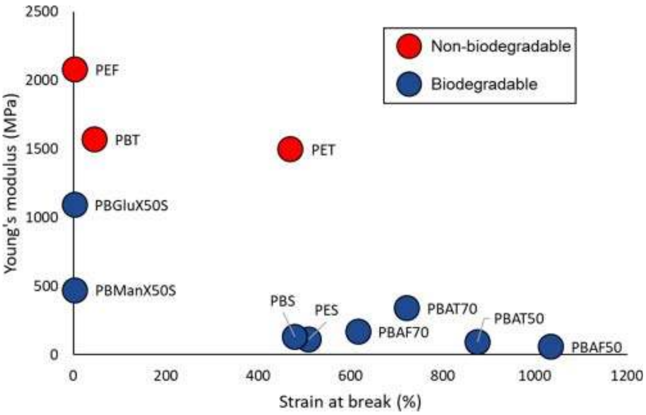


Figure 5.7 Young's modulus as a function of strain at break for several biodegradable (blue) and non-biodegradable (red) polyesters. Poly(ethylene furanoate) (PEF), poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET), poly(butylene GluX succinate) (PBGluXS), poly(butylene ManX succinate) (PBManXS), polybutylene succinate (PBS), poly(ethylene succinate) (PES), poly(butylene adipate furanoate) (PBAF), and poly(butylene adipate terephthalate) (PBAT) [78].

the Young's modulus as a function of strain at break for some biodegradable and non-biodegradable polymers. At the moment, it remains challenging to combine the properties of engineering plastics with good biodegradability.

5.6 Cross-linked Polyesters

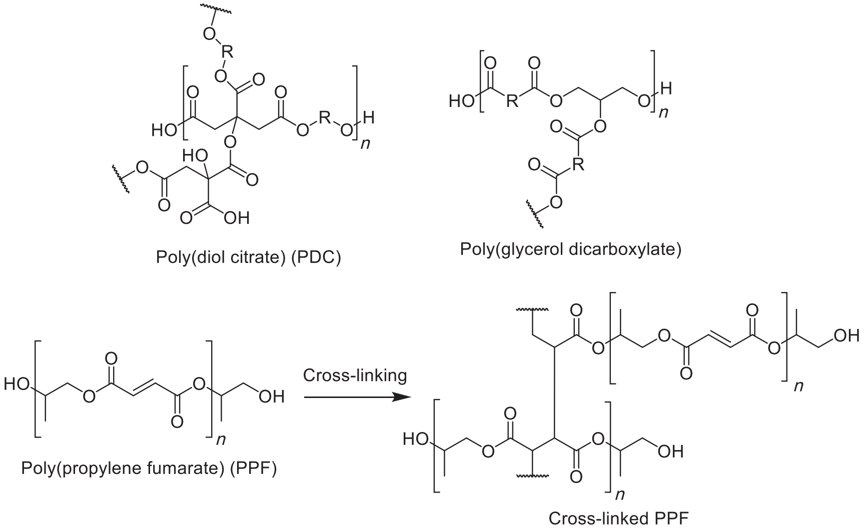
Condensation polyesters are usually semicrystalline, which is required for the mechanical performance. When polymer chains are connected with each other via covalent bonds, the material is cross-linked and unable to form crystals and therefore remains amorphous. These cross-linked polyesters gain their mechanical performance from the 3D network that they form. Several strategies exist in order to obtain cross-linked condensation polyesters, which include the following:

- Cross-linked condensation polyesters can be prepared by adding multifunctional (number of functional groups ≥3) monomers.
- Functional groups can be added to the polymer structure by means of functional monomers, which are capable of undergoing (self-)cross-linking at a later stage.
- Native polyesters can be directly employed for cross-linking via radical reactions with the use of peroxide initiators.

These strategies will be discussed in the next section.

5.6.1 Multifunctional Alcohols or Carboxylic Acids

The addition of multifunctional monomers during polycondensation is an effective and inexpensive strategy to obtain cross-linked polyesters. Often, the monomers


Poly(diol citrate) (PDC)

Poly(glycerol dicarboxylate)

Poly(propylene fumarate) (PPF)

Cross-linked PPF

Figure 5.8 Chemical structures of some important biodegradable cross-linked condensation polyesters.

exhibit a simple structure, which can be multifunctional alcohols such as glycerol or pentaerythritol or acids such citric acid. This strategy is straightforward from a biodegradability perspective because the cross-links consist of the same degradable ester linkages as the main chain backbone, thus preventing heterogeneous degradation. Another advantage is that the polymers are usually biocompatible and produce non-toxic decomposition products. In this way, a range of poly(diol citrates) and poly(glycerol dicarboxylates) have been developed (Figure 5.8), which are especially interesting for soft tissue engineering applications. For the fabrication of materials, usually, first a pre-polymer is synthesized. The pre-polymer is then solubilized and solvent-cast in a mold. After evaporation of the solvent, a post-polymerization step is applied to form the cross-linked network.

An interesting example is fully biodegradable, plant-based, and non-toxic cross-linked resin foams obtained from the condensation between glycerol and citric acid at moderate temperatures (80 °C). The hardness, brittleness, and toughness of this resin can be controlled by changing the alcohol-to-acid ratio, the temperature, and the presence of additives. The resin is fully biodegradable with a degradation period ranging from a few days to a few months, depending on the degree of polymerization. Upon biodegradation in water, the original molecular components are formed back [79].

Cross-linked polyesters based on polyhydric alcohols and aliphatic dicarboxylic acids with various spacer lengths have also been investigated. The alcohols that were investigated were glycerol, pentaerythritol, 1,1,1-trimethylolpropane, 1,2,3,4-butanetetrol, and D-glucitol [80–82]. The resulting materials show a particular degradation behavior. Networks based on short spacer diacids show low sensitivity to enzymatic degradation, but upon increasing the spacer length, the weight loss as a result of biodegradation increased rapidly. When the spacer length consists of more than 14 methylene units, the degradability decreases rapidly. This is proposed to be related to the network structure and the concentration of degradable ester bonds. Also, an effect of the amount of hydroxyl groups of the polyhydric alcohol was observed. The degradation decreased when the amount of hydroxyl groups increased, which could be related to the cross-linking density. This shows a clear window of operation with respect to the possible monomer structures.

Besides the use of polyhydric alcohols, the use of multifunctional carboxylic acids to produce cross-linked condensation polyesters has also been investigated. One of the most interesting multifunctional carboxylic acids is citric acid. Citric acid is inexpensive, non-toxic, and produced from renewable resources at large scale, which contributes to the concept of circular economy. A range of cross-linked aliphatic polyesters based on citric acid and various diols have been investigated [83, 84]. It was found that the biodegradability could be tuned with the amount of methylene units present in the diol that was used.

5.6.2 Incorporation of Functional Monomers

Incorporation of functional monomers during the synthesis of condensation polyesters is a versatile method to obtain cross-linked materials. Incorporation of different types of functional groups may allow for different curing methods, such as UV curing, thermal curing, or with the aid of a cross-linker. One prerequisite is that the functional groups remain intact during the high temperatures typically involved during polycondensation; therefore, the monomers used must be thermally stable.

Monomers containing double bonds in the backbone have been employed to produce biodegradable cross-linked polyesters. Even though undesired cross-linking of double bond containing monomers during the polymerization can occur at elevated temperatures, a radical scavenger such as hydroquinone can be added to prevent cross-linking reactions. In this way, polyesters were prepared based on fumaric acid and 1,2-propylene diol to produce poly(propylene fumarate) (PPF) (Figure 5.8) [85–87]. Cross-linked PPF shows remarkable retention of the mechanical properties during degradation, which make them exceptionally useful in load-bearing applications [88]. Therefore, it is an important material for bone tissue engineering applications. In the presence of radical initiators, PPF can cross-link via radical polymerization with itself or together with monomers such as methyl methacrylate or *N*-vinyl pyrrolidinone. Also, biocompatible cross-linkers such as acrylated poly(ethylene glycol) can be used in order to perform an in situ cross-linking step after injection with PPF [87].

With respect to biodegradation of cross-linked PPF, chain scission occurs via the ester bonds and biodegradability depends on molecular weight, type of cross-linker, and cross-linking density. Furthermore, the T_g of non-cross-linked PPF is around 32 °C, which is below the body temperature. This promotes the biodegradability of non-load bearing scaffolds in biomedical applications [85]. For load bearing applications, cross-linked PPF is required for the improvement of the mechanical properties.

Similar to fumaric acid, long-chain unsaturated dicarboxylic acids based on oleic acid or castor oil can be used for cross-linked polyesters. The double bonds present in the polymer backbone can be transformed to epoxide groups and subsequently cross-linked using UV light and a cross-linker. However, these polymers showed only limited biodegradability because of the high hydrophobicity of the fatty acid monomer [89]. This can be relieved by decreasing the amount of functional fatty acid monomer but is at the expense of cross-linking density [90].

Also, modification of the existing biodegradable polyesters such as PBS is reported. Upon incorporation of functional monomers such as itaconic acid and maleic acid, cross-linking is enabled. As a result of the cross-linking, the biodegradability decreased, but some of it is retained [91].

5.6.3 Cross-linking of Native Polyesters

Finally, self-cross-linking of native polyesters is also investigated for biodegradable condensation polyesters. This is one of the most straightforward methods in cross-linking polyesters because the existing polymers can be directly employed in this method. One reason for cross-linking the existing polyesters such as PBS is to improve the mechanical strength.

The use of peroxide radical initiators in order to cross-link polymers is currently well established. Notably, it can be applied in saturated rubbers consisting of ethylene copolymers. Similarly, aliphatic polyesters containing ethylene moieties can also be cross-linked using this procedure. It involves heating the polymer together with the peroxide initiator to produce radicals, which can abstract hydrogen atoms from the polymer chains. The polymer radicals are then able to combine and form covalent bonds. During the process, chain scission reactions also occur as a result of the radical formation. This should be prevented to avoid a large decrease in molecular weight and loss of mechanical properties. Careful selection of the type of radical initiator is important because an adequate formation of radicals is required at the processing temperatures while avoiding premature cross-linking. Dicumyl peroxide is one of the most versatile radical initiators because it has a suitable decomposition range for polymers melting between 100 and 120 °C and shows a high hydrogen abstraction efficiency [92]. Using the method of radical formation, cross-linking of aliphatic polycondensates such as PBS [93, 94] and PBSA [95] can be achieved while retaining the biodegradability behavior. Furthermore, with the use of peroxide initiators, the grafting of monomers on polyester backbone and blend compatibilization with other biodegradable polyesters is enabled [96, 97].

5.7 Applications for Biodegradable Condensation Polyesters

In the past few decades, products developed from biodegradable condensation polyesters have been receiving a lot of attention. Recently, more applications for the investigated materials are being developed. In general, the good processability and mechanical properties of condensation polyesters allow for a variety of applications, especially where tunable properties are required. Processing of biodegradable condensate polyesters is usually possible in conventional polymer processing equipment and can occur via cast film extrusion, blown film extrusion, injection molding, hot pressing, and fiber spinning.

5.7.1 Biomedical Applications

One of the large advantages of polyesters, next to their biodegradability, is their biocompatibility, which expands the potential to biomedical applications. In addition, because degradation products are generally non-toxic, they are excellent candidates for biomedical uses such as (micro)capsules, implants, or sutures, which benefit from the breakdown of the temporary polymeric structure that provides mechanical support or carriage of bioactive molecules. In this context, biodegradability can enable the controlled release of drugs or prevent surgical intervention to remove implants because the material is able to undergo biodegradation and subsequently absorption or secretion of the degradation products by the body. Quantitatively, biomedical applications are only a minute fraction of the total biodegradable polymer market, but the effects on public health with respect to medical procedures are major. This therefore allows the relatively high price of biodegradable polyesters (e.g. >$10/kg).

Aliphatic condensation polyesters generally show a good biocompatibility *in vitro* and *in vivo* [98]. The use of PBS for tissue engineering applications has been extensively researched. PBS-based blends, composites, and copolymers display the potential for bone tissue engineering [99] and cardiac tissue engineering [100]. Furthermore, controlled drug release has been realized using PBS-based micro- and nanocapsules [101] and scaffolds [99]. On the other hand, semi-aromatic polyesters (i.e. PBAT and copolymers thereof) can possess a tunable balance between mechanical and biodegradable properties with the incorporation of terephthalic acid. Although being less investigated than aliphatic polyesters, they have been reported for the use in vascular applications [102] and bone tissue engineering applications [103].

Biomedical materials that are implanted in the mechanically dynamic environment of the body must be able to recover from deformations. Ideally, the material is able to undergo large deformations without imposing damage to the surrounding tissues. Specifically, elastomers exhibit this property. Therefore, some implants are aimed to mimic the extracellular matrix, which is a soft and elastomeric material providing support to tissues such as cartilage, blood vessels, tendons, and ligaments. Condensation polyesters are of particular interest especially because common monomers such as glycerol and sebacic acid have been approved by the US Food and Drug Administration for medical applications. In this way, tough biodegradable cross-linked polyesters based on glycerol and succinic acid [104] or sebacic acid [105] have been developed. The material shows a desirable mechanical performance such as high elasticity and toughness. As such, tubular scaffolds based on poly(glycerol sebacate) were developed and can be applied in blood vessel tissue engineering [106, 107]. The degradation rate and biointeraction can be tuned by grafting hydrophobic or bioactive molecules on the backbone.

Another issue with biomedical polymeric materials is the presence of catalysts, originating from the condensation polymerization. Metal-based catalysts can lead to unfavorable effects with respect to toxicity in the body. The low limit for metals present in polyesters such as tin excludes the use in biomedical applications. Currently, in polyester synthesis for biomedical applications, catalysts based on zinc, titanium, and zirconium are used. Nonetheless, there is a continuous trend toward the use of alternative (metal-free) catalysts and catalytic systems such as enzymatic polycondensation [108].

5.7.2 Agricultural Applications

One of the main applications of biodegradable condensation polyesters is in mulch films. They are used for controlling the soil temperature, limiting the weed growth, protection against harsh weather and pests, and improving water retention and crop yield. Mulch films are generally made from non-biodegradable plastics such as PE, which are difficult to recover because of the loss of the structural integrity after use. As a result, PE residues remain and accumulate in the soil, which negatively affects the crop yield [109, 110]. EU regulations require adequate waste disposal of mulch film by incineration or recycling. Therefore, employing a biodegradable film can be more cost-effective in some cases, even though the biodegradable mulch film is about twice as expensive as the PE mulch film. However, the benefit is that the waste does not need to be collected and can be tilled into the soil [111, 112]. It was estimated that approximately 161 000 tonnes of bioplastics were produced for the agricultural and horticultural applications, of which more than half consisted of PBAT and PBS [5].

5.7.3 Packaging Material

Because of the low cost and good properties, conventional plastics are widely used in packaging and plastic bag industry, which is a high-volume application. However, despite the higher costs, a growing awareness and interest of the consumers in environment-friendly products supports the implementation of biodegradable plastic carrier bags in retailers. Similar to compost bags, they can be processed in organic waste disposal. Both require good mechanical properties such as puncture and tear resistance, and they need to be able to support loads of 100 times their own weight [64]. Films made from PBAT are highly suitable for these applications. Another potential packaging application where biodegradability could bring added value is the small-size food packaging because of the high litter risk.

5.8 Polyester Recycling

With the drastic increase in the consumption of plastics in the past decades, the problems related to waste disposal and conservation of petrochemical resources have become more critical. In the transition from a linear to a circular economy, much more of the plastic waste we produce must be recycled. Recycling even has the preference over biodegradation, which is rather a litter management strategy. Thermoplastic polyesters represent an important class of recyclable plastics. The most significant example is PET. PET is the third most widely diffused polymer exploited in the packaging industry, monopolizing the bottles market for beverages, and covering almost 16% of the European plastic consumption in the packaging industry [113]. As mentioned earlier, PET is not biodegradable, but advanced progress is made in recycling PET, which allows us to reduce PET waste in an economical and environmentally acceptable way [114].

Currently, the dominant form of PET waste recycling worldwide is mechanical recycling. The process requires sorting, decontamination, and treating by washing, drying, and grinding before new plastic products can be obtained via melting and extrusion [115]. Thus, it is very difficult to recycle complex and contaminated PET wastes mechanically [116] because this process in fact requires homogeneous plastics and relatively clean material. Mechanical recycling is often called a "downcycling" route because the obtained recycled polymers have inferior properties (lower molecular weight, discoloration, risk of more impurities, etc.) compared to polymers made from virgin feedstocks [117].

Strategies to counterbalance the loss in the properties of mechanically recycled polymers upon reprocessing include intensive drying, reprocessing with vacuum degassing, and the use of chain extenders [118]. A good example in this respect is the increase of molecular weight of PET via additional solid-state polycondensation (SSP) [119]. SSP is usually done at a high temperature (below the melting temperature of the polymer) in the absence of oxygen and water, by means of either vacuum or purging with an inert gas to drive off the by-products of reactions [116].

In cases where plastic waste is not suitable for mechanical recycling, e.g. because of the complexity of the mixture and contaminations, incinerating the waste and using the heat to generate electricity can be applied, particularly if the CO_2 this generates can be captured sustainably rather than releasing to the atmosphere [117].

Chemical recycling plays an increasingly crucial role in extracting more value from waste plastic and is essential in creating a circular economy for plastics [120]. Chemical recycling is carried out either by solvolysis or by pyrolysis [121]. Pyrolysis occurs through degradation by heat in the absence of oxygen or air or under vacuum. However, pyrolysis of PET is seldom used as a method to depolymerize PET into its monomeric units on an industrial scale because pyrolysis generally leads to other liquid and gaseous side products, reducing process efficiency and necessitating costly separation steps [114, 116].

Solvolysis occurs through polymer degradation by different solvents such as water (hydrolysis), methanol (methanolysis), or glycol (glycolysis). In the case of polycondensation polyesters such as PET, this type of chemical recycling is based on the reversibility of polycondensation chemistry. This indicates that the polymer in the presence of a low molecular weight component (typical water, methanol, or glycol) and the required reaction conditions (temperature and catalyst) can be depolymerized back into the starting monomers or oligomers, namely, ethylene glycol, terephthalic acid (hydrolysis), dimethyl terephthalate (methanolysis), bis(hydroxylethylene) terephthalate (glycolysis), or polyols (glycolysis) [121]. The main advantage of this chemical route is the possibility of purifying (through distillation/crystallization steps or surface/vacuum treatments) monomers/oligomers by removing possible post-consumer contaminants (decontamination process) and consequently directly re-using these monomers for the production of recycled PET again for high-end applications with similar high molecular weights as the virgin polymers [116, 122]. The polyol oligomers can be reused in other polycondensates such as polyurethanes and epoxy resins. However, chemically recycled PET is more expensive than virgin PET because of its raw material cost, capital investment, and scale of operation [116].

The most recent inventions with respect to chemical recycling allow even the reuse, reprocessing, or reshaping of thermoset polymers. Conventional thermosets, widely used in composites, coatings, electronic packing materials, foams, etc., cannot be reprocessed, recycled, or reshaped under mild conditions. Traditional recycling of cross-linked polymers via mechanical reprocessing is impractical because their structures preclude flow, even at elevated temperatures. Their insolubility also precludes solution reprocessing. Although some of these materials are down-cycled into lower value products, most thermosets are incinerated, landfilled, or otherwise unaccounted for (i.e. leakage). This causes serious resource and environmental problems. Developing strategies to recycle these materials without compromising their performance represents a formidable challenge. Covalent Adaptable Networks (CANs) [123–125] are an emerging class of materials that contain exchangeable chemical bonds in the polymer network, leading to reversible cross-links. CANs combine the easy processing of thermoplastics that can flow upon heating and the high durability and resistance of thermosets. A subclass of CANs, called "vitrimers," has been developed in 2011 by Leibler and coworkers [126]. Vitrimers undergo stress relaxation upon associative bond exchanges, which are triggered by temperature, pH, or light. During this process, the cross-linking density stays intact because a new covalent bond needs to be formed either simultaneously or before breaking an existing covalent bond [127]. Vitrimers are thus permanent networks characterized by a combination of insolubility and gradual thermal viscosity behavior, in analogy with the thermal behavior of traditional glass. A typical class of vitrimers is based on transesterification chemistry, e.g. between hydroxyl and ester groups in the network at high temperatures in the presence of the right catalysts [126, 128–131].

5.9 Concluding Remarks

In this chapter, the development of condensation polyesters, from the first pioneering work by Carothers to today's advancements in biodegradability, is briefly reviewed. The preparative methods of condensation polyesters and fundamentals of polycondensation, developed over 80 years ago, are still relevant today and are discussed with focus on the synthesis of biodegradable polyesters.

Currently, much research is devoted to the incorporation of novel monomers with added functionality or improved properties. A main challenge remains to combine good mechanical performance with biodegradation properties. This leads to a surge in different polymer structures with tuned properties. Some potential disadvantages are connected to these developments. From a recyclability standpoint, the simplicity of plastic types in waste streams is desired to achieve efficient separation and purification of the plastics for recycling. The inherent reversibility of the condensation polymerization may also allow for facile recovery of monomers from plastic waste when recycling is not possible. Nonetheless, with the widening scope of applications (such as in the medical field), and because of increasing environmental awareness and legislation, the interest toward biodegradable condensation polyesters has expanded greatly in the past decades.

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