Chapter 23

Bioplastics: New Routes, New Products

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23.1 INTRODUCTION: DEFINITIONS AND CLASSIFICATION

There are two main drivers for the growing interest in bioplastics: the first is the production of plastics materials and the second is their disposal. The current global consumption of plastics exceeds 200 million tonnes, with an annual growth of approximately 5% (Siracusa et al., 2008). The plastics industry is said to be the largest field of application for crude oil, and the economic dependence of this important area is thus critically dependent on the price and availability of crude oil and natural gas. For this reason, routes to plastics materials involving alternative raw materials are becoming of increasing importance (See Section 1.8). The term bio-based eco-products has been used to describe products of this type, which have potential commercial and environmental acceptability; are derived from renewable resources; and have either recycling capabilities or biodegradability (Mohanty et al., 2002).

The question of terminology is important. In the context of this chapter, the term bioplastics is used to describe a plastic derived from a biological source. The short carbon cycle associated with this route contrasts with the much longer carbon cycle of fossil-based materials. The term biodegradable conventionally refers to a material that can be degraded relatively rapidly by biological agents in a bioactive environment. In practice, materials that degrade predominantly by direct hydrolysis are also regarded as biodegradable. In contrast, most conventional plastics materials degrade at such slow rates in these environments that they are considered to be nonbiodegradable. Biodegradable and compostable polymers such as starch; cellulose; and lignin, which are processed naturally derived carbon-based polymers have been known for many years. Similarly, some natural precursors are converted into either biodegradable or nonbiodegradable bioplastics as a matter of synthetic choice. Thus, dibasic acids can be used for either polyester or polyamide synthesis; repeat unit structure and crystallinity of the final polymer rather than the inherent properties of a specific intermediate are the determining factors.

It is convenient to schematically represent the different subsets or families of bio-based and fossil-based materials and the origin of biodegradable and nonbiodegradable bioplastics. Figure 23.1 illustrates the origin of four families—ranging from conventional nondegradable plastics from fossil-based raw materials to biodegradable bio-based plastics.

Three of the groups in Figure 23.1 can be classified as bioplastics:

1. Nonbiodegradable plastics such as polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), or poly(trimethylene terephthalate) (PTT) derived wholly or partly from bio-based intermediates (upper left quadrant).
2. Plastics that are both bio-based and biodegradable, such as polylactide (PLA) and poly(hydroxyalkanoate) (PHA) or poly(butylene succinate) (PBS) (upper right quadrant). This quadrant also contains processed or modified naturally occurring carbohydrate-based macromolecules such as starch and cellulose derivatives frequently used in biodegradable bioplastics blends.
3. Biodegradable plastics derived from fossil-based intermediates resources, such as poly (ε-caprolactone) (PCL) or poly(butylene adipate-co-terephthalate) (PBAT) (lower right quadrant).

23.2 BIOPLASTICS DEVELOPMENT: GENERIC CONSIDERATIONS

23.2.1 Recycling and Life-Cycle Analysis

The issue of plastic waste is a growing concern and the drivers behind it look set to continue with the growth in new products and applications of plastics materials. The political considerations associated with these issues, particularly the
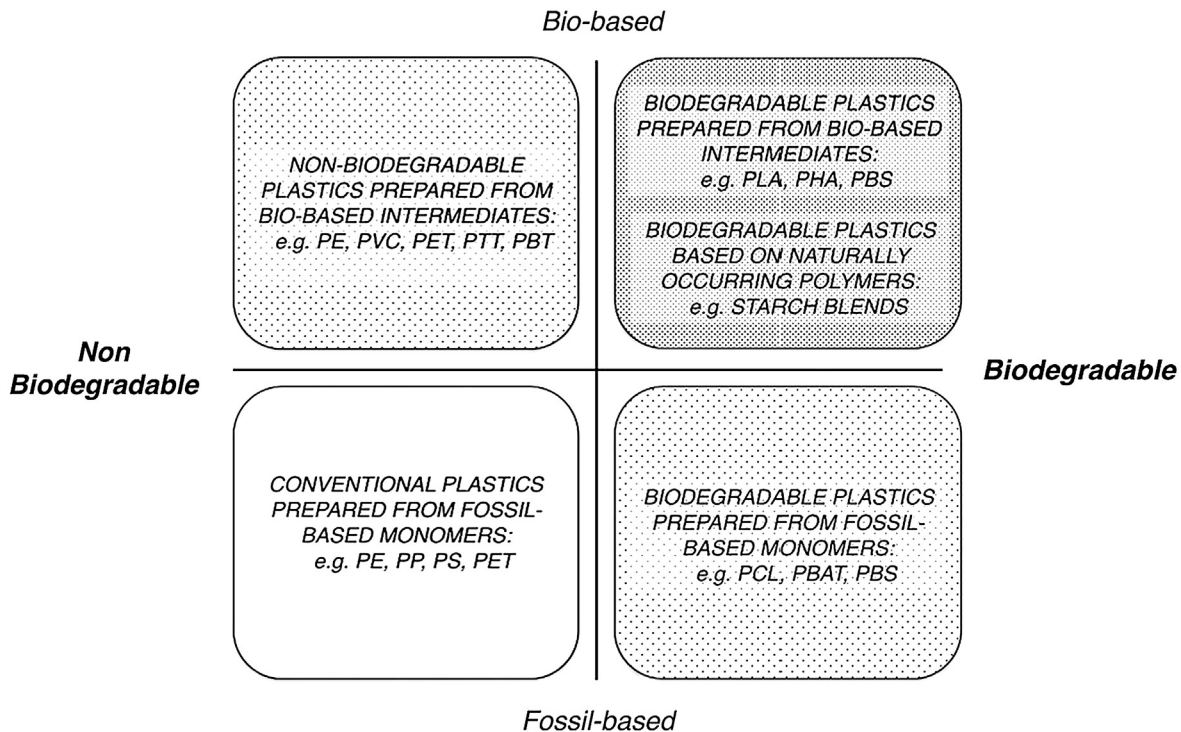
Bio-based

FIGURE 23.1   Four quadrant representation of plastics material types: PE, polyethylene; PVC, poly(vinyl chloride); PET, poly(ethylene terephthalate); PTT, poly(trimethylene terephthalate); PBT, poly(butylene terephthalate); PLA, polylactide; PHA, poly(hydroxyalkanoate); PBS, poly(butylene succinate); PP, polypropylene; PS, polystyrene; PCL, poly (ε-caprolactone); PBAT, poly(butylene adipate-co-terephthalate).

longstanding importance of recycling, have been referred to elsewhere (Section 1.10.2). Interest and activity in the management of waste has grown in recent years, and recycling has played a large part in this. The durability of conventional plastics materials, coupled with their widespread use, is the underlying issue, and food packaging applications together with the culture of disposability have been major contributory factors. Although biodegradable plastics appear to offer a logical way to reduce the adverse effects of increased landfill, complete life-cycle analysis, incorporating costs, benefits, and limitations of recycling, is necessary in order to obtain a complete picture of environmental impact and the consequent socioeconomic benefit (Soroudi and Jakubowicz, 2013).

LCA provides the critically important information that is necessary to assess the environmental impact of a specific material/product combination (Curran Ann Mary, 1996). In the context of bioplastics, the twin aspects of biodegradability and recyclability are the influential factors. The sustainability benefits of using a renewable precursor base does not in itself provide sufficient evidence unless the material can also be recycled. Recyclability of plastics materials is frequently assessed by carrying out repeated processing steps to determine the effects on simulated service life or accelerated aging studies. Biodegradability and compostability are particularly important in the bioplastics arena because recycling is expensive in terms of labor and energy, whereas composting is much less so. Compostable materials have the added advantage that they can potentially act as fertilizers and soil conditioners.

In addition, however, noncompostable plastics derived from renewable resources are growing in importance and are predicted to increase their market share progressively. Composite materials are particularly important in this respect. One reason for this is the fact that the technical aspects and cost-effectiveness associated with the recycling and reuse of conventional plastics both present significant problems.

23.2.2 Blends and Composites: The Importance of Polysaccharides

This chapter concentrates on the increasing versatility of bio-based sources in the development of biodegradable and compostable polymer systems and especially the way in which two- and three-component polymer blends have been investigated as a means of increasing the technical attractiveness and cost-effectiveness of this important class of plastics materials.

Plastics are compounded with several types of additives such as stabilizers, colorants, and processing aids, which influence and optimize the processability and properties of the final products. For these reasons, the manufacture of products entirely from renewable resources can present significant complications. The aim is to utilize the highest proportion of renewable resources possible, particularly in relation to fillers and blending agents.

The most commonly used biodegradable plastics materials over a period of several years have been starch blends—particularly those involving thermoplastic starch (TPS). It has been successfully used in blends with a range of biodegradable polymers that have also become established in their own right (Yua et al., 2006). These include aliphatic polyesters, such as polyhydroxybutyrate (PHB), PCL, PBAT, and PLA. TPS blends are widely used as cost-effective commodity plastics, especially in the food packaging industry (Shibata et al., 2003; Meinander et al., 1997). The applications of bioplastics depend upon processability, and common thermoplastics processing techniques such as injection molding, blow molding, and extrusion are used to convert bioplastics such as PLA into a range of forms including fibers, films and sheets, and commonly used articles such as bottles. The property range covered by the field of bioplastics is now considerable (Kabasci, 2014; Van de Velde and Kiekens, 2002). Despite this they are rarely able to meet the required property and price criteria as unmodified materials; as a consequence, blends and composites are commonly employed. Natural bio-fiber composites based on combinations of natural fibers such as flax, wood, jute, and hemp are emerging as a viable alternative to glass-fiber-reinforced plastics. Biocomposites are currently used mainly in the automotive, construction, furniture, and packaging industries, where renewable products are attracting great attention because of the driving force of increasing environmental awareness and depletion of fossil resources.

The use of native starch as filler in traditional plastics such as polyolefins has been used to promote environmental disintegration for over 30 years, but is now a much less popular way of approaching the plastics waste problem. Similarly, the use of chemically modified forms of cellulose as plastics materials dates back to the nineteenth century. Before the widespread availability of crude oil, the work of Staudinger, and the development of fossil-based plastics in the 1920 and 1930s, raw materials for preparation of early plastics materials had emerged over a period of more than 100 years. The well-recognized position of cellulose derivatives in this history lies outside the context of this chapter; here it is important to acknowledge the place that different polysaccharides (e.g., starch, cellulose, and recently chitin and their derivatives) occupy in the developing field of bioplastics. Since coverage elsewhere is vast, this brief section will simply acknowledge the importance of this longstanding topic and point to external sources of more detailed information (Kabasci, 2014; Halley, 2014).

Starch is produced during photosynthesis as a food reserve for plants and vegetables, such as corn, wheat, potato, tapioca, and rice. A range of refining and extraction processes (e.g., milling, slurrying, and centrifugation) is used to isolate the starch fraction which consists of two major components: amylose and amylopectin. The linear amylose molecules have a much lower molar mass (c. 200−2000 kg mol^{-1}) and make up a lower weight fraction (c. 15−35%) than the branched amylopectin molecules (c. 100,000−400,000 kg mol^{-1}).

It has been known for many years that starch-filled PE films deteriorate on exposure to a soil environment via microbial consumption of the starch which leads to increased porosity, loss of integrity, and fragmentation of the matrix (Griffin, 1973). The overall disintegration is accelerated by incorporation of transition metal-based pro-oxidants that catalyze photo- and thermo-oxidative degradation of the polyolefin (Scott, 1990, 2000). In recent years, various structural modification processes including mechanical, thermal, and hydrothermal treatments have been used in order to convert starch into less crystalline thermoplastic forms that are more amenable to conventional polymer blending techniques (Halley, 2014).

Cellulose esters prepared from the esterification of cellulose have been significant for many years as commodity plastics. Thermoplastic cellulose acetate is the most widely used derivative (see Section 22.2.2). Despite the fact that cellulose acetate is biodegradable, most of the waste polymer has been simply sent to landfill. There is some disadvantage in the fact that both rate of degradation and processability are linked to degree of substitution. As the degree of substitution increases, the biodegradation rate of cellulose acetate decreases and the melt processability improves (Quintana et al., 2012).

The prospects for future applications of cellulose acetate are viewed as being related to the ability to add new performance features, particularly thermal processability, water-dispersibility, and the ability to interact with other polymers on the molecular level. This can be achieved by such secondary modifications as the introduction of plasticizing (mixed) ester substituents, carboxyl groups, and the formation of block copolymers (Glasser, 2004). Blending is an important aspect of bioplastics development and is discussed in later sections.

23.3 BIODEGRADABLE AND COMPOSTABLE PLASTICS

23.3.1 Polylactic Acid (PLA)

23.3.1.1 Introduction

PLA is a poly(α-ester), well-known in terms of its disposable and hydrolytically degradable nature that stems from its labile ester bonds in its backbone (Figure 23.2). The abbreviation is taken to represent either poly(lactic acid)—if the material is obtained by step (condensation) polymerization of lactic acid—or polylactide, when obtained by the more usual ring-opening polymerization (ROP) of cyclic lactide. The polymer has a repeating ester unit of $(C_3H_4O_2)_n$, as shown in Figure 23.2, where R_1 is hydrogen and R_2 is methyl group.

PLA was first synthesized by condensation of lactic acid by Théophile-Jules Pelouze in early 1845, and then in 1932, when Carothers et al. reported the use of lactide as a monomer. Initially, however, PLA was limited in use due to its low molar mass and high cost. Cargill Inc. established a commercial ring opening process for lactide to high molar mass PLA, and it is now more widely used (Grossman and Nwabunma, 2010). Since 2010, Nature Works LLC in the United States, Evonik Industries (Germany), PURAC Biomaterials (The Netherlands), Synbra Technology BV (The Netherlands), and several other manufacturers produce PLA. PLA is now used in many fields, such as biodegradable packaging, woven and nonwoven textiles, together with biomedical devices and electronics. The environmental concern over conventional plastic packaging has increased worldwide demand for biodegradable materials such as PLA.

23.3.1.2 PLA Production

The key PLA building block is lactic acid, which is derived from both a petrochemical route and fermentation of sugars from sources such as sugarcane, cassava, corn, and tapioca. The stereo-regular forms of lactic acid are L-lactic acid and D-lactic acid (Figure 23.3). The petrochemical route produces D,L-lactic acid, while fermentation of starch from different renewable resources exists almost exclusively as L-lactic acid. These building blocks can be used to produce PLA via polycondensation, azeotropic dehydration condensation, and ring-opening polymerization (see Figure 23.4).

The direct condensation polymerization of lactic acid yields low molar mass and brittle polymers, which, for the most part are unusable, unless external coupling agents are employed to increase chain length. The equilibrium associated with
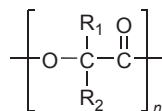

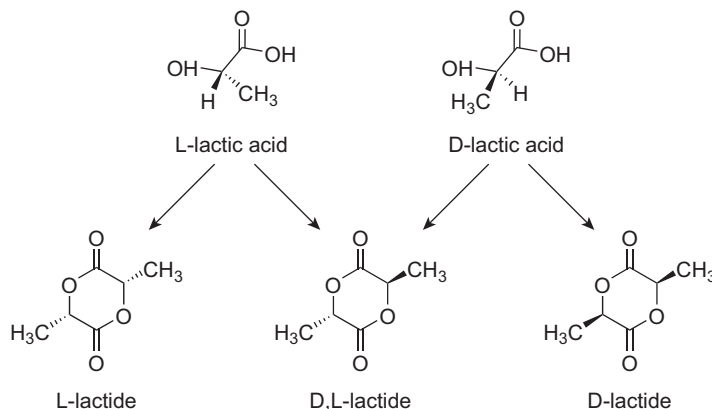**FIGURE 23.2** Poly(α-ester) repeat unit.

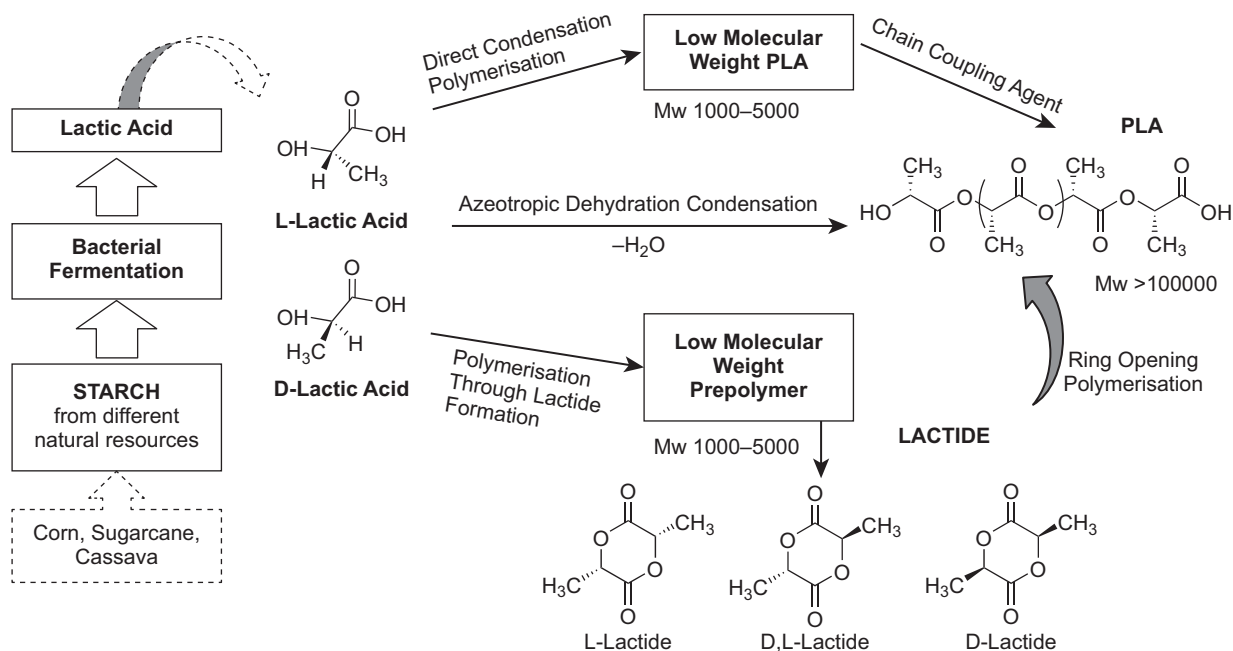**FIGURE 23.3** Stereochemical forms of lactides.

FIGURE 23.4 Synthetic routes to PLA (Lunt, 1998).

direct condensation does not produce high molar mass polymer because other side reactions, such as trans-esterification, can occur (Grossman and Nwabunma, 2010). The direct condensation of lactic acid to form PLA involves reaction of the hydroxyl and carboxylic acid groups of lactic acid and removal of water formed during this reaction (see Figure 23.5).

A variation of this reaction is the azeotropic dehydration condensation of lactic acid, which can yield high molar mass PLA. However, the most effective route to high molar mass PLA is the ROP of lactide, the cyclic dimer of lactic acid (Grossman and Nwabunma, 2010). The two asymmetric carbons of L-lactic acid and D-lactic acid, and the racemic or meso forms of the 50/50 mixture of L- and D-lactic acids, produce L-lactide, D-lactide, and D,L-lactide, respectively (see Figure 23.3). ROP is suitable for large-scale production and is generally used commercially due to the control of chemistry and consequent properties that it allows. In addition, it can be used in melt, bulk, solution, and suspension polymerization techniques.

Several catalysts have been utilized in the production of PLA by ROP, most are alkoxides of stannous tin (Sn), but aluminum (Al), copper (Cu), and zinc (Zn) are also used. Among these types of catalysts, stannous octanoate $(Sn(Oct)_2)$—that is tin (II) 2-ethylhexanoate—is the most widely used due to various reasons, for example: ready solubility in organic solvents and the molten bulk lactide, good stability during storage, and excellence in catalytic activity. It has good biological safety allowing use in medical and food applications, and is approved by the US Food and Drug Administration (FDA).

The classical "coordination—insertion mechanism" of lactide ROP using $Sn(Oct)_2$ and alcohol co-initiator is shown in Figure 23.6 (Bourissou et al., 2005; Masutani et al., 2014). At the first stage, $Sn(Oct)_2$ is reacted with alcohol to generate a
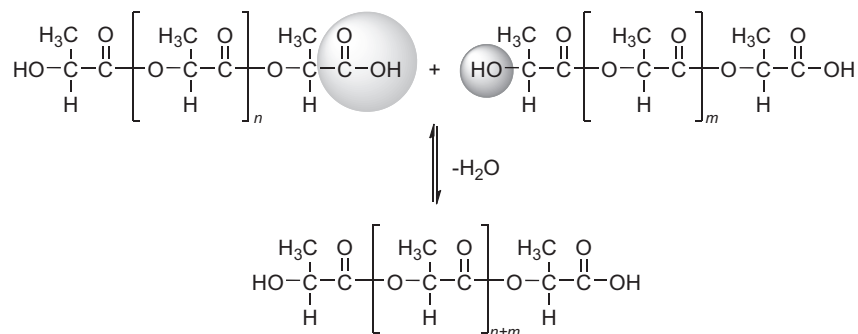

FIGURE 23.5 Direct condensation of lactic acid to produce poly(lactic acid).
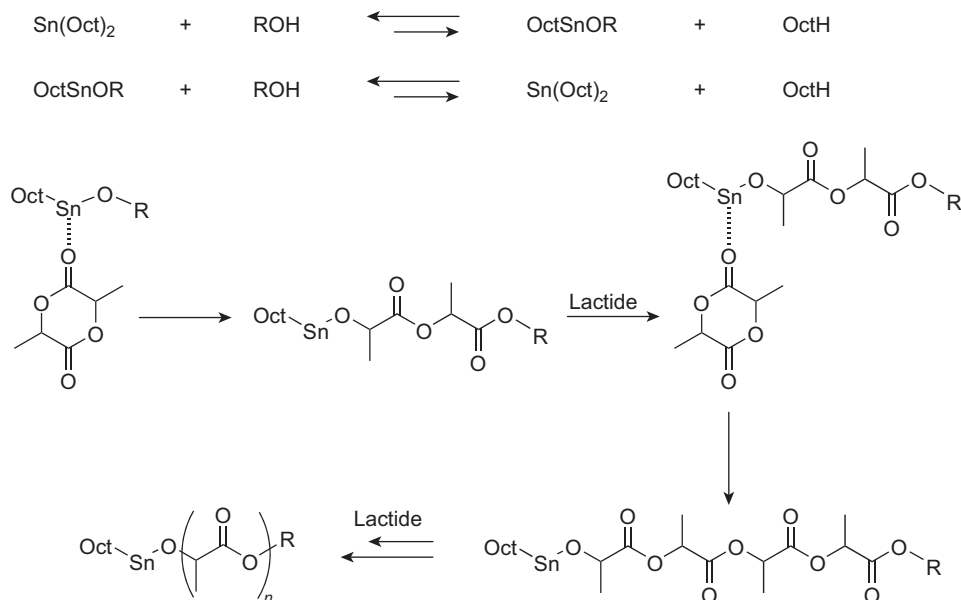
FIGURE 23.6 ROP of lactide with tin (II) octoate by coordination−insertion mechanism (Masutani et al., 2014).

stannous alkoxide. In the second step, one of the carbonyl oxygen atoms of the lactide coordinates with the stannous atom of the stannous alkoxide, which enhances the nucleophilicity of the alkoxide and the electrophilicity of the lactide carbonyl group. In the third step, the acyl−oxygen bond—the bond between the carbonyl group and the endocyclic oxygen of lactide—is opened to insert into the stannous oxygen bond. Finally, insertion of lactides continues to produce high molar mass PLA (Masutani et al., 2014; Bero et al., 1999; Ryner et al., 2001).

Polymerization of the pure enantiomeric L-lactide yields poly(L-lactide) (PLLA), and that of D-lactide yields poly(D-lactide) (PDLA); both of which are semicrystalline polymers. On the other hand, polymerization of the diestereoisomer (D,L-lactide) or a racemic mixture of D,D-lactide/L,L-lactide, produces amorphous poly(D,L-lactide) (PDLLA). PLLA is one of the most useful biodegradable materials among all these PLA stereotypes, in part because its building block L-lactide is produced from fermentation of starch from agricultural plants. PLLA is more expensive than many petroleum-based polymers, but PLLA produced from corn is becoming cheaper as the scale of production is increasing due to the higher demand. In general commercial literature, the abbreviation PLA is used to represent PLLA.

23.3.1.3 PLA Properties and Usefulness

The properties of PLA depend on the component isomer, processing temperature, annealing time, and molar mass. PLLA is semicrystalline with a crystallinity of around 37%, a crystalline melting temperature (T_m) between 170 and 180 °C, and a glass transition temperature (T_g) between 60 and 67 °C. PLLA can be normally dissolved in halogenated hydrocarbons such as chloroform, methylene chloride, 1,1,2-trichloroethane, and dichloroacetic acid, and is partially soluble in ethyl benzene, toluene, acetone, and tetrahydrofuran. PDLLA is an amorphous polymer and has a T_g in the region of 50−60 °C.

Because of its crystallinity, PLLA is a more slowly degrading polymer than PDLLA. High molar mass PLLA can take from two to five and half years for total resorption in vivo (Middleton and Tipton, 2002; Bergsma et al., 1995), while PDLLA is hydrolyzed and loses its chain length within 1−2 months and completely loses its mass within 12−16 months (Maurus and Kaeding, 2004). Because of this slow degradation rate and good tensile strength and modulus, PLLA is favored for use in load-bearing applications in the body. The range of marketed products for orthopedic fixation devices include the Phantom Soft Thread Soft Tissue Fixation Screw[®], Phantom Suture Anchor[®] (DePuy), Full Thread Bio Interference Screw[®] (Arthrex), BioScrew[®] (Linvatec), and the Clearfix Meniscal Dart[®] (Innovasive Devices) (Nair et al., 2007). In addition, PLLA is used for high strength scaffold fibers as placement or augmentation devices together with nondegradable fibers, such as Dacron (Lu et al., 2005; Cooper et al., 2005), in long-term blood vessel conduits (Zilberman et al., 2005), and in the form of injectable PLLA particles (Sculptra[®]), which have all been approved by the FDA (Nair et al., 2007).

PLA is widely used as a packaging material for food, as it is produced from lactide, which in turn is derived from lactic acid—a nontoxic substance found in the human body. Therefore, food contamination can be neglected when PLA is used as a packaging material. The crystallinity of PLA is very similar to that of polyethylene terephthalate (PET), which is frequently used for beverage containers because of its good strength, good gas barrier properties (O_2, CO_2), and relatively low cost. The gas permeability of PET and PLA are about 1000 times lower than low-density polyethylene (LDPE), while that of LDPE is about 100 times less than the silicones. Therefore, PLA can provide an adequate barrier against water vapor and gases, enabling it to prevent food degradation and oxidation while preserving the aromas and the flavors of the food. However, the limitations of PLA for packaging are because of properties such as flexural strength and impact strength that make PLA brittle, and its narrow processing window.

23.3.1.4 PLA Modification

With the limitations of thermal properties and brittleness, PLA is frequently modified to improve its properties by copolymerization and blending with other polymers. These two strategies for improving PLA properties have been extensively investigated as useful routes to vary the structure of the copolymer over a wide range, yielding products with particular combinations of desirable properties.

PLA Modification: **Copolymerization**. PLA copolymers with other polyesters, such as poly(glycolide) (PGA), PCL, poly(beta-hydroxybutyrate) (PHB), poly(beta-hydroxyvalerate) (PHV), poly(trimethylene carbonate), have been prepared via either polycondensation of lactic acid or ROP of lactide with other monomers. Lactides in L- and DL-forms are frequently copolymerized with glycolide to produce poly(lactide-co-glycolide) (PLGA) in various compositional ranges to adjust mechanical properties, crystallinity, and hydrolytic degradation. PLGA is used in the form of mesh, micro-, and nano-fibers for a wide range of biomedical applications including tissue-engineering scaffolds and drug delivery. There are many commercial PLGA products, for example, PuraSorb® PLG (80 L-lactide: 20 glycolide) (Tiainen et al., 2002), Vicryl® (10 L-lactide: 90 glycolide) (Nair et al., 2007), Vicryl Rapid®, PANACRYL®, Vicryl Mesh®, Dermagraft®, CYTOPLAST Resorb®, LUPRON DEPOT®.

PLA has also been extensively copolymerized with poly(ethylene glycol) (PEG), which is a biocompatible and hydrophilic polymer, to improve the hydrophilicity of PLA and its usefulness as a drug delivery system (Rasal et al., 2010). Starch, a hydrophilic water-sensitive polymer, is used to produce PLA-grafted polysaccharides by controlling the lengths and numbers of graft chains (Ohya et al., 1998). This grafted copolymer exhibits a lower glass transition temperature, melting temperature, and crystallinity and higher viscosity properties when compared to PLA. Biodegradable multiblock poly(L-lactide)-*block*-poly(butylene succinate) (PLLA-b-PBS) was also studied (Zeng et al., 2009). It was observed that PLLA and PBS segments were compatible in the amorphous phase, and that increasing the PBS block size significantly increased the crystallization of PLLA-b-PBS.

PLA Modification: **Blends**. As discussed earlier, the main objective of blending PLA is to improve its mechanical properties—especially the brittleness—to decrease the price and to help improve processability, optical properties, and degradation. Many polymers, both petrochemical-based and bio-based, including nondegradable and degradable plasticizers, are blended with PLA for different applications. However, the biodegradable polyesters (Figure 23.7) seems to be the most useful for blending with PLA as they can produce fully biodegradable materials.

PLA Modification: **Biodegradable Blends**. PLA has been blended both with plasticizers and with a number of candidate petroleum-based polymers. In this section, biodegradable or renewable resource polymers are reviewed. To obtain completely degradable blends, biodegradable polyesters represent a logical choice. Examples include: PCL, PHB, PBS, PBSA, and copolymers of PLA−PCL−PLA together with naturally derived polymers such as thermoplastic starch, chitosan, dextran, and collagen.

PCL has been extensively used to blend with PLA to increase impact strength and solve the brittleness problem, as it is a flexible polymer with low glass transition temperature and is also hydrolytically or enzymatically degradable. However, PLA/PCL blends are limited by the problem of immiscibility. Therefore, researchers have studied the addition of other components to improve blend miscibility and compatibility. Examples include: isocyanate-lysine triisocyanate (LTI), lysine diisocyanate (LDI) (Harada et al., 2008), triblock PLLA−PCL−PLLA (Dell'Erba et al., 2001), and poly(D, L-lactide-co-ε-caprolactone) (PLCA) (Wang et al., 2010). The PLLA−PCL−PLLA copolymer acts at the phase boundary as an interfacial agent and produces a more homogeneous distribution of particle size and a lowering of the fraction of large domains. Adding an amorphous PDLLA can affect the PLLA crystallization, as PDLLA is believed to disturb the diffusion of PLLA chains to the growth sites of PLLA crystallites, acting to reduce the brittleness of the semicrystalline PLLA (Bouapao et al., 2009).
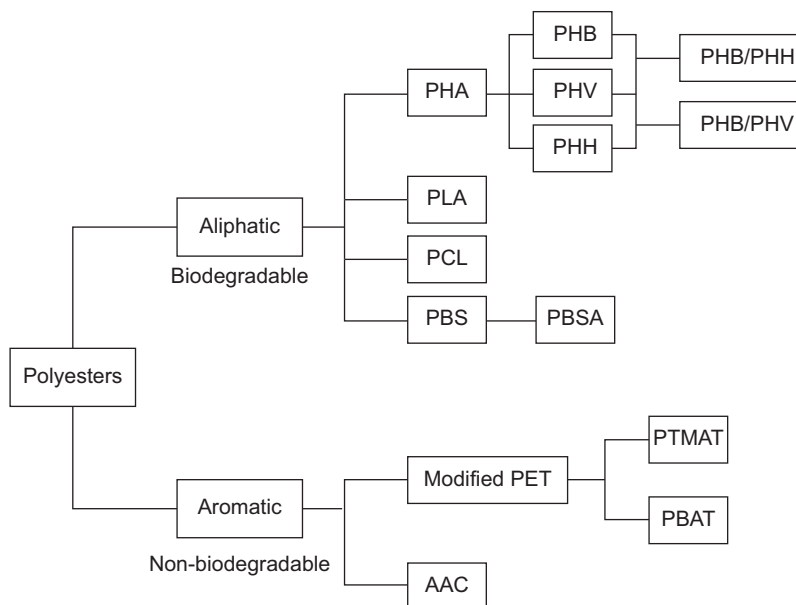
FIGURE 23.7   The classification of biodegradable polyesters: PHA, polyhydroxyalkanoates; PHB, polyhydroxybutyrate; PHV, polyhydroxyvalerate; PHHex, polyhydroxy hexanoate; PLA, polylactide; PCL, poly ε-caprolactone; PBS, polybutylene succinate; PBSA, polybutylene succinate adipate; PET, polyethylene terephthalate; PBAT, polybutylene adipate/terephthalate; PTMAT, poly(tetramethylene adipate-co-terephthalate); AAC, aliphatic—aromatic copolyesters.

Polymers related to PBS also blend effectively with PLA showing improved properties. For example, PBSA, a commercially available aliphatic polyester with high flexibility; excellent impact strength; melt processability; chemical resistance; and low melting temperature, that is more readily biodegraded than PLA, is found to show partial miscibility with PLA due to active interaction between PLA and PBSA chains (Lee and Lee, 2005). However, a group of PHA polymers (PHB, PHBHV) were observed to blend poorly with PLA, partially because of high crystallinity, resulting in hard and brittle materials (Iannace et al., 1994; Takagi et al., 2004). There is obviously considerable scope in this area of work especially as the range of bio-based polymers is increasing.

Starch is an attractive polysaccharide to blend with PLA because it offers advantages in terms of cost and biodegradability, but it is thermodynamically immiscible with PLA. Therefore, a third type of component—a compatibilizer, plasticizer, or block copolymer—is often added into PLA/starch blends to reduce the interfacial energy. This improves dispersion and consequently enhances adhesion between binary polymer phases. The presence of potato starch alone decreases the mechanical properties of PLA blends unless a plasticizer such as PEG is also added (Kozlowski et al., 2007). Similarly, addition of gluten reduced the number of processing cycles needed to change PLA crystalline structure to a predominantly amorphous form (Mohamed et al., 2006).

In order to induce better interaction between PLA and other biodegradable polymers, the blends are prepared through reactive blends, which can promote chemical reactions between the two polymers by adding a reactive third component with appropriate functional groups or a catalyst. Methylenediphenyl diisocyanate (MDI), maleic anhydride, poly(ethylene oxide) (PEO), and poly(propylene oxide) (PPO) are widely used as third components for reactive blends of PLA. Examples include using MDI and maleic anhydride for PLA/starch blends, which promotes a strong chemical linkage between the carboxyl groups of PLA and hydroxyl groups of starch (Zhang and Sun, 2004).

It is clear that blending PLA with other polymers and compatibilizers via solvent and reactive blending processes has been designed to improve the mechanical properties of PLA and to make it suitable for different applications. Therefore, the most important strategy for success is to find polymer pairs miscible with each other and then to promote the compatibility in their blends. The work of screening the types of polymer pairs, which have the potential for blending, has been studied and reported using a rapid screening method. This used the Coleman and Painter approach for first predicting the miscibility of polymer pairs, and then using a combination of microplate-reader and solvent mediated blend on a very small (microliter) scale to identify optical clarity by using ternary phase diagram. The method is quick and easy to measure the potential of polymer blend compositions and apparent miscibility. It is particularly useful for three-component blends (Ross et al., 2013, 2015a,b).

PLA Modification: **Petroleum-Based and Nonbiodegradable Polymer Blends**. In terms of petroleum-based and nonbiodegradable polymers used to blend with PLA, PE; polyurethane (PU); poly(ethylene terephthalate) (PET); poly(vinyl acetate) (PVAC); and acrylonitrile−butadiene−styrene copolymer (ABS) have been used, aiming to improve the physical and mechanical properties of PLA. For example, a blend of PLA and linear low-density polyethylene (LLDPE) in the presence of PLA−PE block copolymer as a compatibilizer for solution and melt blending has been used(Wang and Hillmyer, 2001; Anderson et al., 2003). The toughness of amorphous PLA (PDLLA) was improved by adding a compatibilizer, but this was not the case for semicrystalline PLA (PLLA). In contrast, PLLA showed significantly better adhesion to LLDPE than PDLLA. This was explained by tacticity effects on the entanglement molar mass or miscibility of PLLA, which allows for the improved adhesion between PLLA and LLDPE. Poly(ether) urethane elastomer, which is a flexible; compatible; durable; and toughening polymer, was successful in improving the toughness of PLA (Li and Shimizu, 2007). Other blended polymers include PCL diol- and triol-based PU network, acrylonitrile−butadiene−styrene copolymer (ABS), and poly(methyl methacrylate) (PMMA). In addition, organic or inorganic fillers, such as clay; beta-Ca(PO$_3$)$_2$; metal oxides (alumina and titania); carbon fiber; and calcium carbonate, have also been incorporated in PLA. Commercially available products of modified PLA include Biomax$^®$ Strong (PLA additives improve toughness without significant transparency loss), BlendexTM 338 (PLA toughness enhanced with an acrylonitrile−butadiene−styrene terpolymer containing 70% butadiene rubber), and PellethaneTM 2102-75A (polyurethane-modified PLA) (Rasal et al., 2010).

PLA Modification: **Plasticizer-Based Blends**. Plasticizers have been used to modify properties of PLA such as glass transition temperature, toughness, and processability. However, the problem of using plasticizers in PLA blends is normally the slow migration of plasticizers into the surface of materials and phase separation during storage. Bulk properties, crystallinity, and miscibility of PLA are all influenced by the plasticizer end groups. Examples of plasticizers include glycerol, citrate esters, PEG, PEG monolaurate, triacetine, tributyl citrate, acetyltri-n-butyl citrate, poly(propylene glycol) (PPG), and copolymers of PLA-b-PEG. PEG is widely used for PLA blends, but it can migrate into the surface of the blend, and its water sensitivity can lead to unstable materials. Incorporation of dual plasticizers such as tributyl citrate (to enhance elongation at break) and PLA-b-PEG (to increase tensile strength and interaction between PLA and copolymer phase through their ester groups) can reduce the volatiles and degradation products of the blends more than single plasticizers (Lemmouchi et al., 2009). PPG is another useful plasticizer for PLA blends as it has a low glass transition temperature, is miscible with PLA, and is noncrystalline. PPG consequently influences the crystallization behavior less that PEG (Kulinski et al., 2006). Even though extensive blending studies of PLA with plasticizers such as tributyl citrate (TBC) (Lemmouchi et al., 2009), ethylene oxide polymers (Lemmouchi et al., 2009; Lai and Liau, 2003; Bechtold et al., 2001), and citrate esters (Labrecque et al., 1997) have been carried out, there is still considerable need and opportunity to improve PLA properties for specific applications.

23.3.1.5 PLA Degradation

Polyesters are one of the most important families of biodegradable plastics being used in industry, due to their potentially hydrolyzable ester bonds. Aliphatic polyesters (PHA, PLA, PCL, and PBS) are completely biodegradable by both microbial and hydrolytic processes, while aromatic polyesters are almost resistant to microbial attack. It is believed that biodegradation of polyesters proceeds by attack on the ester groups by nonspecific esterases produced by ground microflora combined with hydrolytic attack, and then gradual hydrolytic degradation at the ester linkages (Fried, 1995). Low-molar mass polyester is the initial degradation product and carbon dioxide and water are the final products. The hydrolytic degradation of PLLA is shown in Figure 23.8. Intramolecular degradation occurs by base attack on the carbonyl
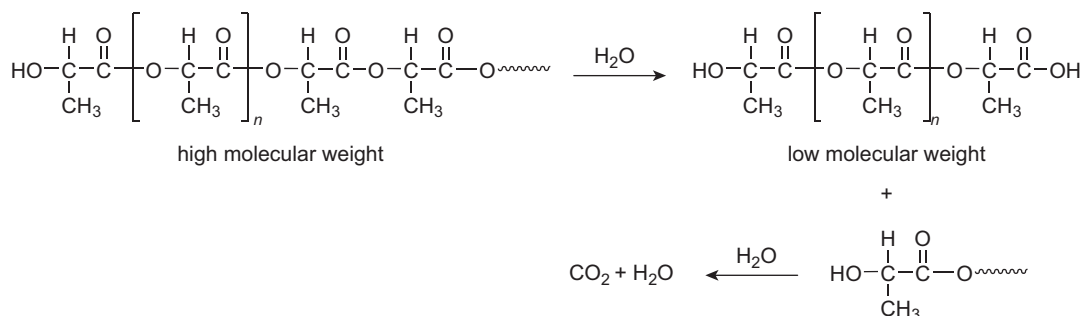

FIGURE 23.8 Hydrolysis of poly L-lactide.

carbon of ester group, followed by hydrolysis of the ester link, leading to low-molar mass polyester fragments. Finally, PLA is decomposed into carbon dioxide (CO_2) and water (H_2O).

Aliphatic polyesters, especially homo- and copolymers derived from glycolic acid or glycolide, lactic acid or lactide, ε-caprolactone, and 3-hydroxybutyrate, have been known for a long time as useful materials in degradable drug delivery systems. As discussed, aliphatic polyesters degrade chemically by hydrolytic cleavage of the backbone ester bonds, catalyzed by either acids or bases, or enzymatically. Carboxylic end groups are formed during chain scission, and this may enhance the rate of further hydrolysis. The human body can reabsorb the products from biodegradation with minimal reaction of the tissues (Albertsson, 2002).

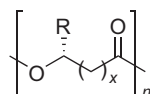## 23.3.2 Polyhydroxyalkanoates

23.3.2.1 Introduction

Polyhydroxyalkanoates or PHAs are aliphatic biodegradable polyesters (see Figure 23.7) that have different pendent groups at the beta-position of the repeat unit; their basic structure is shown in Figure 23.9. They are a family of bacterially synthesized polymers that exist either as homo- or copolymers. The first polymer within the PHA family is poly(3-hydroxybutyrate) (PHB), sometimes abbreviated as P(3HB), which has a pendant methyl group. It is produced by bacteria and algae, with a high degree of crystallinity (Moore and Saunders, 2013). PHB has brittleness and stiffness that are unsuitable for many applications. The mechanical and physical properties of PHB are in some ways similar to PP, except that it is biodegradable. The next member of the PHA family, having a pendant ethyl group, is poly(3-hydroxyvalerate) or PHV. Having an ethyl group (HV unit) instead of the methyl group of PHB gives PHV more flexibility and less crystallinity than PHB.

Incorporation of HV units into the PHB backbone leads to a range of PHBV copolymers, consequently improving the processing window of PHB, because desirable properties such as flexibility, tensile strength, elongation at fracture, and thermal stability vary according to the HV content. These copolymers are produced by Monsanto under the commercial name Biopol. Figure 23.10 shows the chemical structure of PHB, PHV, and PHBV. Other polymers in the PHA family include polyhydroxyhexanoate (PHHex), polyhydroxyoctanoate (PHO), polyhydroxydecanoate (PHD), polyhydroxy-5-phenylvalerate (PHPV), and their blends.

23.3.2.2 Production of PHAs

Production of PHAs is still on a small to medium scale compared to fossil-based polymers and also to that of some bio-based polymers such as PLA and PBS. The complicated bacterial synthetic route and purification process limits the production giving a low efficiency, resulting in high production costs. Various companies throughout the world produce

Polyhydroxyalkanoates (PHAs)

	R Groups	Polymers	Abbreviations
X = 1	Hydrogen	Poly(3-hydroxypropionate)	PHP
	Methyl [-CH$_3$]	Poly(3-hydroxybutanoates)	PHB
	Ethyl [-CH$_2$CH$_3$]	Poly(3-hydroxyvalerate)	PHV
	Propyl [-(CH$_2$)$_2$CH$_3$]	Poly(3-hydroxyhexanoate)	PHHex
	Pentyl [-(CH$_2$)$_4$CH$_3$]	Poly(3-hydroxyoctanoate)	PHO
	Heptyl [-(CH$_2$)$_6$CH$_3$]	Poly(3-hydroxydecanoate)	PHD
X = 2	Hydrogen	Poly(4-hydroxybutyrate)	P(4HB)
X = 3	Hydrogen	Poly(5-hydroxyvalerate)	P(5HV)

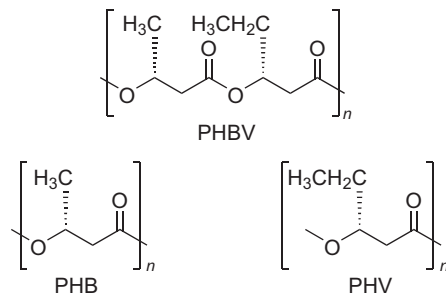**FIGURE 23.9** Polyhydroxyalkanoate family.

FIGURE 23.10   Chemical structures of PHB, PHV, and PHBV.

polymers from the PHA family, for example, P&G (USA), Biomer Inc. (Germany), Tianan Biologic (China), and PHB Industrial (Brazil) (Chanprateep, 2010). Life-cycle assessment (LCA) indicates that the energy requirement for the production of PHB is more environmentally favorable than that of conventional high-density polyethylene (HDPE) and propylene (Harding et al., 2007).

PHAs are synthesized and stored by Gram-negative and Gram-positive bacteria under limitation of nutrients. This occurs through the fermentation of a wide range of substrates, especially sugars (e.g., glucose, sucrose, and xylose), fatty acids, alkanes, alkenes, and alkanoic acid (Urtuvia et al., 2014). All polymers in the PHA family are completely biosynthetic and biologically polymerized, which is different from other bio-based polymers (Wang et al., 2014). Of the various members of the PHA family, only PHB, PHBV, and poly(3-hydroxyhexanoate-co-3-hydroxyoctanoate) (P(HH-co-HO)) have been produced at relatively high concentrations with high productivity (Lee, 1996).

Poly(3-hydroxybutyrate) (PHB) was first discovered in 1926 by Lemoige in the bacterium *Bacillus megaterium* (Urtuvia et al., 2014). There are three steps in the metabolic pathway by which PHB is produced (Figure 23.11) (Verlinden et al., 2007). Firstly, two molecules of acetyl-CoA are combined using 3-ketothiolase (PhaA) to form acetoacetyl-CoA. Secondly, 3-hydroxybutyryl-CoA is produced via the reduction of acetoacetyl-CoA by NADH using the enzyme acetoacetyl-CoA reductase (PhaB). Finally, PHB is polymerized from 3-hydroxybutyryl-CoA using PHB synthase (PhaC), coenzyme-A being liberated. During normal bacterial growth, 3-ketothiolase will be inhibited by free coenzyme-A released from the Krebs cycle. However, if entry of acetyl-CoA into the Krebs cycle is restricted, such as during noncarbon nutrient limitation, the excess acetyl-CoA is channeled into PHB biosynthesis (Ratledge and Kristiansen, 2001).

23.3.2.3 Properties, Degradation and Applications

The range of properties of the polymers in the PHA family depends on the individual building block units; the single most important property of all PHAs, however, is their complete biodegradability. PHAs are susceptible to degradation under both aerobic and anaerobic conditions, as well as by thermal or enzymatic hydrolysis routes. In the biological system of animal tissues, PHAs can be degraded using microbial depolymerases and by nonenzymatic and enzymatic hydrolysis (Gogolewski et al., 1990). Degradation by depolymerases initially produces oligomers that further break down into monomers (Philip et al., 2007). However, the biodegradation rate of PHAs depends on the environmental conditions such as temperature, moisture, pH, and nutrient supply, as well as the monomer composition, additives, surface area, and crystallinity of materials (Abe and Doi, 2002). In human tissue, PHAs are immunologically inert, and having slow degradation, they are usable as devices inside the body (Verlinden et al., 2007).

PHB has a melting temperature above $130\,^\circ C$ and its processing temperature is quite close to its decomposition temperature (c. $200\,^\circ C$) (de Koning et al., 1992). The mechanical properties of PHB are similar to those of PP, excluding the elongation at break which is lower than PP. Incorporation of HV units into the PHB backbone to form PHBV
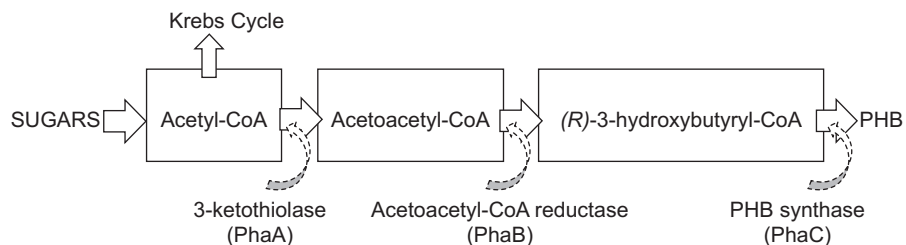

FIGURE 23.11   Biosynthesis pathway to produce PHB.

copolymers changes the properties of PHB, depending on the relative percentage of HV units. At low levels of HV (<10%), PHBV is hard and brittle resembling unmodified PVC; mid-range HV content (10−25%) gives PHBV a toughness similar to PP, while high HV content (25−40%) produces PHBV copolymers that are softer and tougher—similar to PE (Moore and Saunders, 2013). Poly(4-hydroxybutyrate) (P(4HB)) has a higher elongation at break than PHB, comparable to that of PE. P(4HB) is therefore a strong, malleable, and elastic thermoplastic material whose properties can be changed by incorporation of other hydroxy acid units into its backbone.

PHAs are fully biodegradable and exhibit a wide range of properties. The range of available structures is attractive, but they are however expensive to be produced on a large scale. PHAs have been used in a range of medical applications such as sutures, wound dressings, bone replacements and plates, and several others. Outside medicine, PHAs have potential uses as films, coatings, and fibers.

23.3.2.4 PHA Blends

As blending is one of the most useful techniques to improve the properties of polymer matrixes and lower material costs, it is not surprising that this area has been well studied. Many polymers, compatibilizers, and other additives have been used to form blends with PHAs, especially PHB and PHBV. Examples include PLA, chitin, poly(vinyl alcohol), PCL, PBS, poly(butylene adipate-co-terephthalate), poly(vinyl acetate), poly(ethylene oxide), cellulose esters, rubber, and starch. A large number of PHA blends have involved PLA.

Among all PHA blends, PHBV/PLA blends have been identified as particularly attractive to be studied in terms of morphology, rheology, and mechanical properties (Zembouai et al., 2013; Gerard and Budtova, 2012). For example, a 20−50% loading of PLA in PHBV was observed to increase the flexural strength and elastic modulus of the blends (but not tensile strength and elongation at break) when compared with unblended PHBV (Modi et al., 2013). In another work, the addition of PLA to the blend results in a remarkable increase in the complex viscosity of PHBV, and the barrier properties were found to be markedly dependent on blend ratio (Zembouai et al., 2013). Taken together, these results suggest significant molecular interaction between the blend components.

PHB has also attracted attention, particularly for medical applications, and blends with chitin (Khasanah et al., 2015), poly(3-hydroxyoctanoate) (PHO) (Basnett et al., 2013), and poly(ethylene-co-vinyl acetate)/starch (Ma et al., 2014) all show interesting behavior. It was reported that the crystallinity of PHB is reduced in chitin blends, probably due to the hydrogen bonding interaction between carbonyl groups of PHB and secondary amine and hydroxyl groups of chitin in the amorphous region of the blend (Khasanah et al., 2015). The behavior of poly(ethylene-co-vinyl acetate) was more straightforward and, as expected, produced blends having enhanced toughness (Ma et al., 2014).

23.3.3 Poly(Butylene Succinate)

In Figure 23.1 there is one polymer that appears in both fossil and bio-based biodegradable quadrants. This polymer is PBS, which can be produced from both petrochemical and natural raw materials. PBS is an aliphatic polyester produced from the polymerization of succinic acid (1,4-butanediacid) and 1,4-butanediol (BDO). It is biodegradable and can be composted, but is not transparent. PBS resembles PP in terms of mechanical properties, and when compared with many other bioplastics (e.g., poly(lactic acid)), it has a higher heat deflection temperature and is much tougher. Table 23.1 shows the properties of commercially available PBS (trade name, Bionolle).

The production of bio-based PBS is possible by a number of routes; Figure 23.12 summarizes either current or predicted routes to manufacture the bio-based intermediates for PBS synthesis. At present, both succinic acid and BDO are normally produced from maleic anhydride derived from petrochemical sources. However, petrochemical succinic acid (hydrolysis of maleic anhydride) is expensive and is used predominantly in niche markets. It is predicted, therefore, that the bio-based succinic acid, which is more cost efficient, will lead to a higher demand. BDO can be produced from succinic acid via a hydrogenation reaction, thus linking the production of bio-based PBS directly to the formation of bio-succinic acid. There are two very promising routes for the large-scale production of bio-succinic acid. First, fermentation of glucose to directly produce succinic acid and second, from other bio-based intermediates sourced from sucrose. Sucrose can be hydrated to glucose and fructose, which can then be dehydrated to 5-hydroxymethyl furfural (HMF). HMF is then hydrated to levulinic acid, which is converted to succinic acid by an oxidation reaction (Vasudevan and Mushrif, 2015; Assary et al., 2012).

The blends of PBS fall into two categories: fully biodegradable blends and blends with non-degradable polymers. PBS polymers are good components to blend with other bio-based polymers, such as poly(lactic acid) (PLA), polyhydroxyalkanoates (PHAs), or thermoplastic starch (TPS). PBS has also been blended with other nondegradable

TABLE 23.1 Properties of Commercial PBS (Bionolle) (Fujimaki, 1998)

	Units	PBS		
Density	Kg m^{-3}	1.260		
Heat of combustion	kJ g^{-1}	23.6		
Heat deflection temperature (at 0.45 MPa)	°C	97		
Crystallinity	%	33−45		
Melting point (T_m)	°C	114−115		
Glass transition	°C	−32		
Grade		1001MD	1020MD	#1903
MFR (190 °C, 2.16 kg)	g/10 min	1.5	2.5	4.5
Crystallization temperature	°C	75	76	88
Flexural modulus	MPa	660	640	690
Tensile yield strength	MPa	32	34	39
Tensile break strength	MPa	57	21	35
Tensile elongation	%	700	320	50
Structure	−	Linear		Long chain branch

polymers such as PS and polycarbonate (PC). In a collaboration between NatureWorks and BioAmber, in a joint venture called AmberWorks, the companies have announced that they will work together on the production of bio-based PLA/PBS blends. Metabolix recently licensed technology ("Polylactic Acid-based Blends") to NatureWorks for the production and sale of PLA/PBS blends. Bioamber has predicted a rapidly growing market for PBS, PBS blends, and PBS composites.
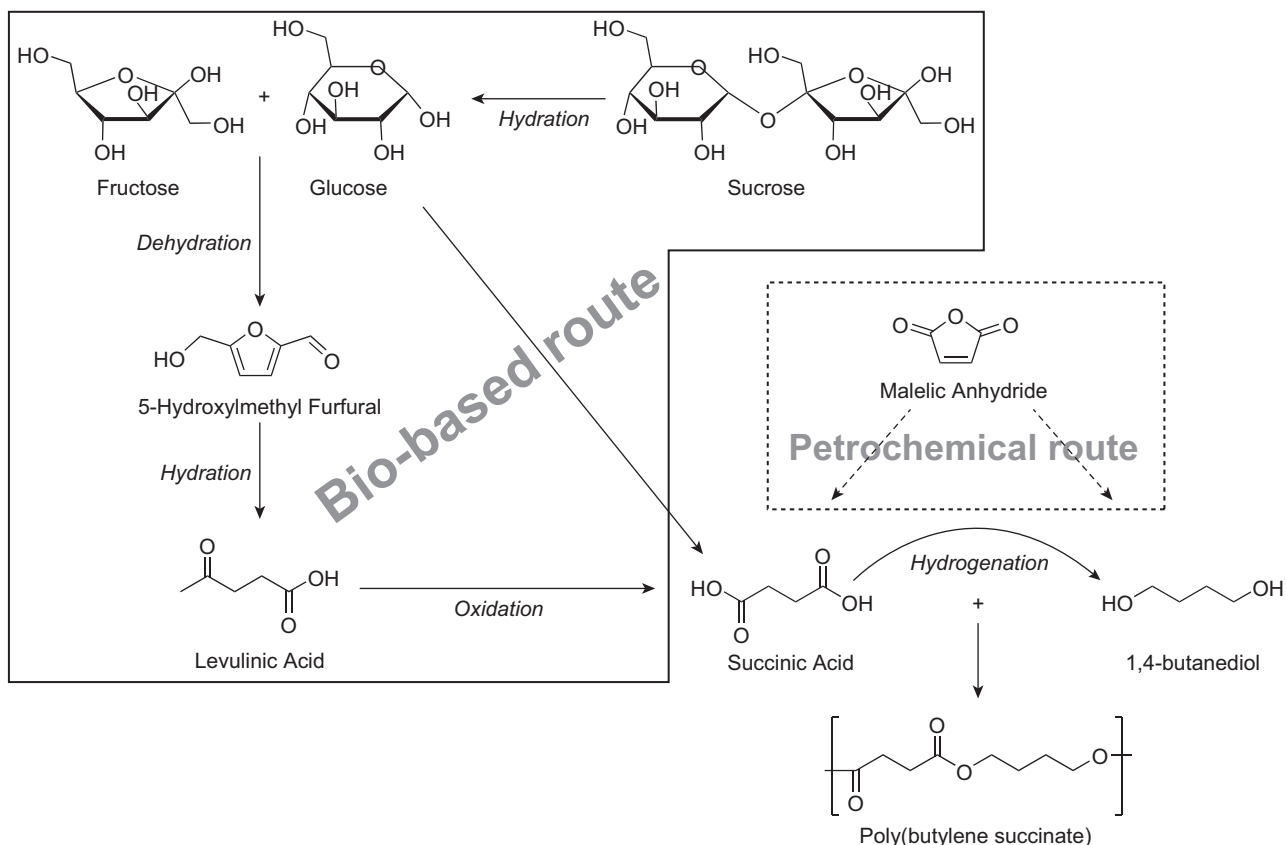
FIGURE 23.12 Poly(butylene succinate) production routes.

23.4 BIO-BASED INTERMEDIATES IN CONVENTIONAL PLASTICS PRODUCTION

To replace petroleum-based or conventional plastics, bioplastics will need to have either equivalent performance or much reduced cost. As most plastic processing/production is already established using conventional plastics, a "drop-in" approach for producing bio-based plastics is a logical progression to convert the current production to be more environment friendly. In fact, this process is already underway and is discussed in this section by highlighting the conversion of bio-based intermediates to conventional plastics together with examples of novel bio-based plastics that are related to their conventional cousins.

A useful starting point is to examine some of the most commercially successful polymers to see if their intermediates can be produced by bio-based processes, thus, classifying the resulting polymer as a bioplastic. Figure 23.13 lists the most common plastics used worldwide at the time of writing.

Figure 23.13 indicates that vinyl polymers (or polyolefins) are the predominant group of polymers used in the world today. One of the most important monomers for these materials is ethylene, with PE being the most basic and commonly used example of a vinyl polymer, followed by PP, PVC, and PS. PE in its various forms has a production volume of 88,000 kton year^{-1} and a market share of nearly 30%. The monomer ethylene is a versatile starting point for bio-based intermediates. The bio-ethanol production is currently (2016) around about 88,000 kton year^{-1}, most of which goes to the fuel industry. This is probably the most important bio-based intermediate because it can be dehydrated to form ethylene.

Ethylene acts as the precursor to most vinyl polymers. It can be polymerized directly to form PE, and with some further synthesis, it can provide precursor monomers for production of PP, PVC, and even ethylene glycol for PET.

After ethylene, the next mono-substituted monomer is propylene, which can be produced by numerous bio-based processes. From ethylene, there are two common routes, first, the direct ethylene metathesis, and second, the dimerization of ethylene to 1-butene, followed by isomerization to 2-butene, and then metathesis to propylene. Propylene can also be obtained by the dehydrogenation of propane (a by-product of the conversion of oil crops to biodiesel).

Vinyl chloride monomer can be obtained from ethylene by a two-step process. Ethylene is first converted to 1,2-dichloroethane, followed by dehydrochlorination to vinyl chloride. From ethanol, it is therefore possible to produce bio-based versions of three very common and very important vinyl polymers. Figure 23.14 summarizes the precursor monomers together with the processes used. The figure also shows the intermediate ethylene glycol; this is one of the monomers, together with terephthalic acid, used in the bio-based production of poly(ethylene terephthalate) (PET).
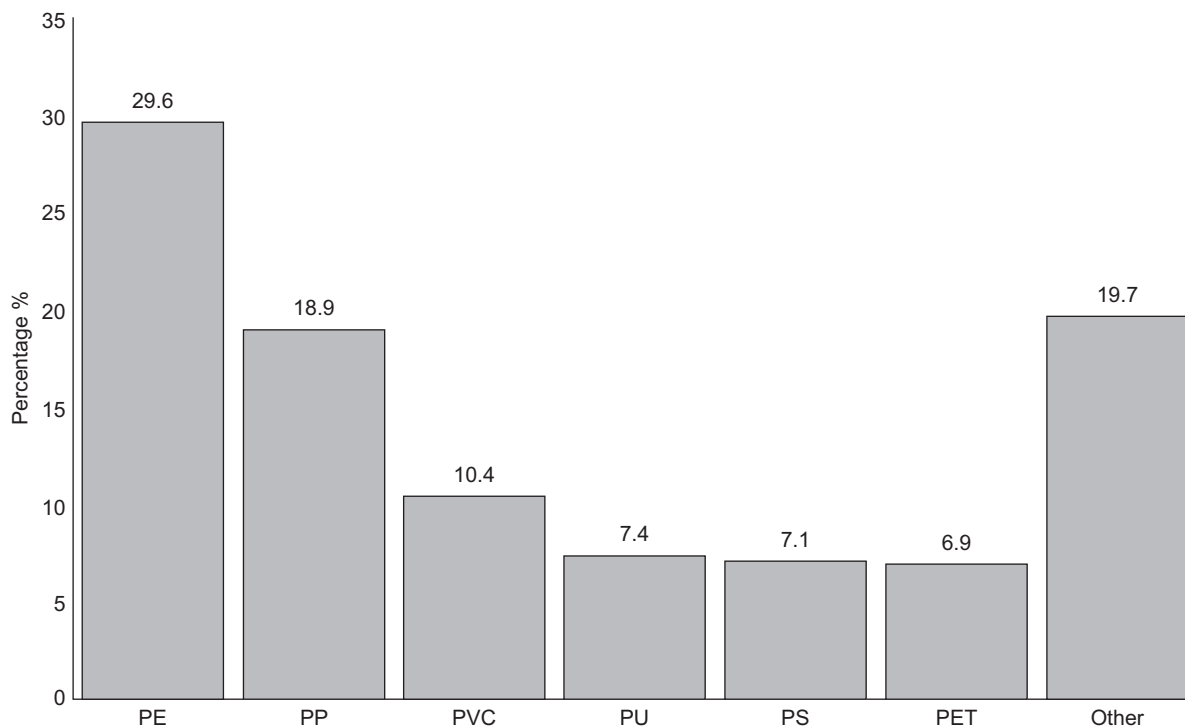

FIGURE 23.13   Relative plastic demand in Europe (percentage) (PlasticsEurope, 2015).
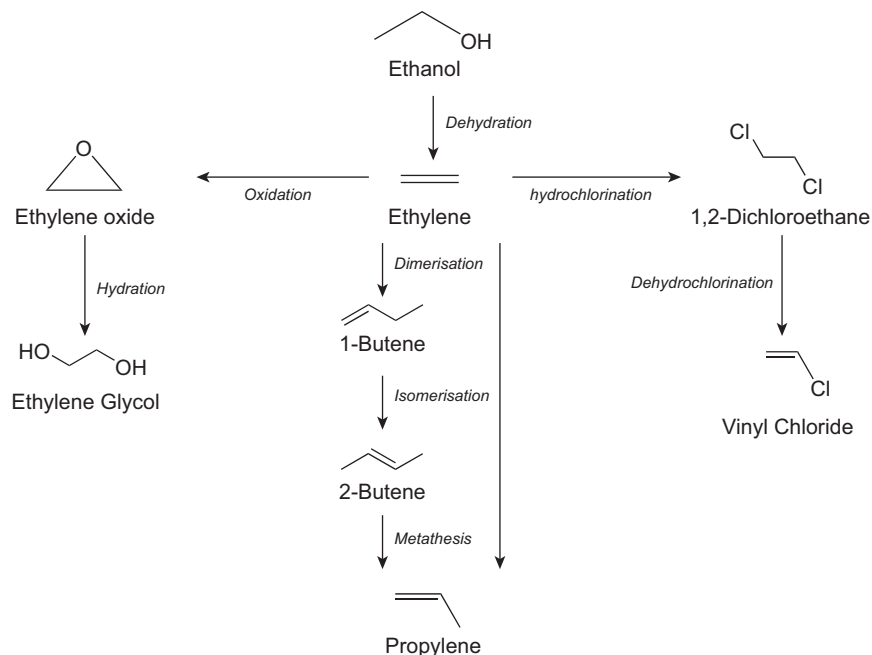
FIGURE 23.14   Vinyl intermediates from bio-ethanol.

Two further carbon-backbone polymers, PS and PMMA, are accessible by bio-based routes although the processes are more complex. For PMMA, the key intermediate is methacrylic acid, which is then esterified to methyl methacrylate. Bio-methacrylic acid can be produced by fermentation to itaconic acid followed by decarboxylation over a Pd, Pt, or Ru catalyst (Le Nôtre et al., 2014).

The most commonly used polyester is the aromatic polyester, poly(ethylene terephthalate) or PET, which currently makes up approximately 7% of total European polymer demand, and worldwide is the fourth-most-produced polymer after PE, PP, and PVC, all of which can be synthesized via bio-ethanol. PET is a nondegradable polyester produced from two precursor building blocks—ethylene glycol and terephthalic acid.

Ethylene glycol is conventionally produced from petroleum by oxidation of ethylene to ethylene oxide followed by hydration to produce ethylene glycol. Bio-based ethylene glycol is produced by the same route (Figure 23.14). In 2009, the Coca-Cola company announced their PlantBottle®, which contains up to 30% plant-based (bio-based) material. This was achieved by the use of bio-based ethylene glycol. In mid-2015, Coca-Cola announced PlantBottle 2.0® that contains 100% bio-based resources, with the aim to commercialize the process by 2020 (Ptonline). The terephthalic acid is produced from bio-based isobutanol through a multi-step process, which is shown in the diagram below (Figure 23.15). The bio-based isobutanol is produced via the yeast fermentation of sugars, and then is dehydrated to isobutylene. Oligomerization converts this into isooctene, which then undergoes dehydrocyclization to xylenes of which para-xylene is separated. The final step is the production of terephthalic acid by the oxidation of para-xylene. By combining the two bio-based processes in this way, a totally bio-based PET can be produced.

The range of aromatic polyesters produced from terephthalic acid can be extended by replacing the ethylene glycol used in PET with alternative diols. This gives polymers with different characteristics and properties, for example poly(trimethylene terephthalate) (PTT) and poly(butylene terephthalate) (PBT). PTT is produced by replacing ethylene glycol with 1,3- propanediol (PDO). Production of PTT was commercialized in 2000 and is currently mainly used in carpet and textile fibers. PBT is produced by replacing ethylene glycol with 1,4- butanediol (BDO). The production of BDO from succinic acid is discussed in Section 23.3.3, in connection with bio-based routes to PBS.
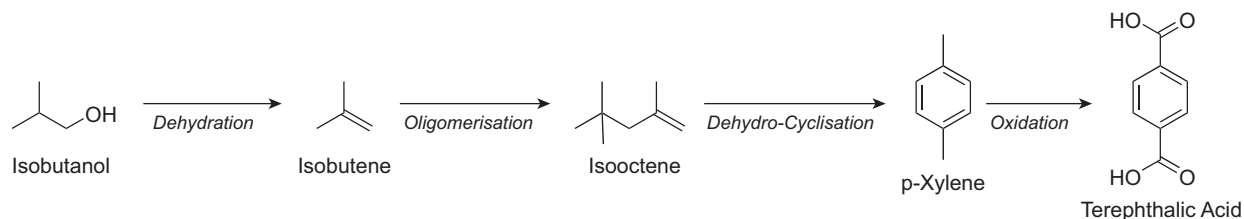

FIGURE 23.15   Bio-based route and intermediates for terephthalic acid.

Although PBT is a crystalline thermoplastic polyester (see Section 20.4), related to PET and PTT, it is more directed to specialty technical applications rather than to the commodity market. It has good chemical, thermal, and mechanical characteristics, and is mainly used to produce small precision components for electrical or electronic equipment and the automotive industries. PBT can withstand temperatures up to approximately 120 °C as well as petrol, diesel, oils and fats, and weak acids.

Bio-based processes are challenging and the subject of intensive study. Various large companies and consortia are working on the development and up scaling of bio-based diols. PDO (1,3-propanediol) is a versatile chemical building block with a market volume of around 125 kton year^{-1} (Kersh, 2011). A large part of this production volume is already bio-based, the current global production capacity of bio-based PDO is 90 kton with an expected increase to over 100 kton in 2016 (Kersh, 2011). Bio-based PDO production has been an industrial process for quite some time, with DuPont producing bio-based PDO by fermenting sugars from maize starch in a joint venture with Tate & Lyle and Genencor.

1,4-Butanediol (BDO) is a bulk product that is currently being produced in large volumes from petrochemical raw materials. BDO is used for the production of polymers, as a precursor to the solvent tetrahydrofuran (THF) and a route to fine chemicals. BDO can be produced in various ways: a large percentage is being produced from petrochemical maleic anhydride via a process that is owned by the British company Davy Process Technologies. Bio-based BDO is currently produced at demonstration levels only. It can potentially be used immediately as a drop in within the existing infrastructure as it has the same characteristics as petrochemical BDO.

The versatility of routes to bio-based polymers is the subject of on-going synthetic explorations. One such area is the development of new diacid monomers based on bio-based raw materials. In the polyester field, there are some promising alternative candidates to terephthalic acid. One of the most interesting of these is 2,5-furandicarboxylic acid (2,5-FDCA), which is an oxidation product of 5-hydroxymethylfurfural (HMF). The bio-based route to HMF is via the dehydration of sugars such as fructose, which is discussed in Section 23.3.3. Figure 23.16 highlights the structural differences between terephthalic acid and 2,5-furandicarboxylic acid.

Copolymerization of 2,5-FDCA with ethylene glycol gives poly(ethylene furandicarboxylate) (PEF), which is seen as a possible replacement for PET (Beckman, 2016). PEF shows interesting thermal properties as an alternative to PET since it has a higher thermal stability (higher glass transition temperature) than PET combined with a lower processing temperature (lower melting temperature). PEF is also seen as a superior material for bottles due to its improved gas barrier properties (de Jong et al., 2012). The ethylene glycol can also be replaced with other diols such as 1,4-butanediol (BDO) and PDO, which results in the polyesters, poly(butylene furandicarboxylate) (PBF) and poly(propylene furandicarboxylate) (PPF). One benefit of using BDO as the diol is that both components (2,5-FDCA & BDO) can be produced from the same bio-based source via HMF.

A comparative LCA study of PEF and PET showed possible savings of 40−50% for PEF on the consumption of nonrenewable energy and CO_2 emissions. Potential savings could even run up to 50−90%, although this largely depends on the raw material and processes used (Eerhart et al., 2012).

Other families of polymers that are being investigated are polyurethanes and polyamides. The progress in the field of bio-based polyurethanes is split into two parts, bio-based polyols and bio-based isocyanates, with the majority of the work focused on the polyols.

Bio-based polyols normally fall into the following bio-based categories: polyols from natural oils, polyether polyols from the diols PDO and BDO, polyether polyols based on sugars (sorbitol and sucrose), and polyester polyols from diacids (e.g., succinic acid and adipic acid).

In addition to bio-based polyols, there are also some limited developments in bio-based isocyanates. The production of isocyanates usually starts by manufacturing an amine compound, which is then converted into an isocyanate via reaction
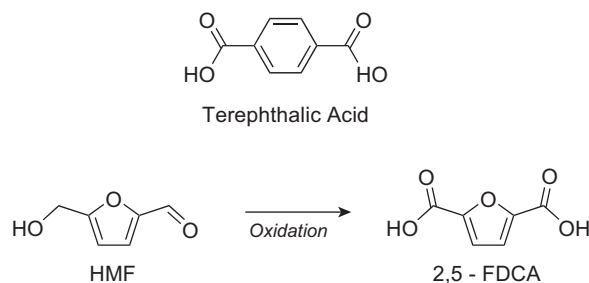

Terephthalic Acid

HMF   *Oxidation*   2,5 - FDCA

FIGURE 23.16 Aromatic diacids.

with phosgene. Isocyanates production from fatty acids is also possible, but production via this route is still limited due to the very low reactivity of the isocyanates and high costs (More et al., 2013; Noreen et al., 2016).

Polyamides are a major class of engineering plastics (see Chapter 18). They are produced via polycondensation of a diacid and a diamine, or by ROP of a lactam (Bolck et al., 2011). There is potential for a wide range of polyamides by converting just a few bio-based intermediates, from various bio-sources, oils to sugars. Perhaps one of the most important is hexanediamine, which is currently produced from petrochemical butadiene or propylene. In view of the developments surrounding bio-based propylene and butadiene, there are opportunities for the production of bio-based hexanediamine. BioAmber has plans to produce bio-based hexanediamine from renewable materials; it is looking to further extend the succinic acid platform to C6 building blocks for chemicals including hexanediamine, adipic acid, and caprolactam for the production of PA6 and PA66 (Dros et al., 2015).

A successful bio-based polyamide production on a commercial scale for many years is polyamide 11 (PA11). The monomer used is 11-aminoundecanoic acid, a derivative of castor oil (Martino et al., 2014). PA11 is a high-quality plastic; at present, Arkema is the only producer of PA 11 under the brand name Rilsan®. Other potential bio-based monomers derived from castor oil are decanediamine and sebacic acid; the latter is used in the production of PA610.

23.5 BIODEGRADATION AND COMPOSTABILITY PRINCIPLES AND TESTING PROCEDURES

This section is concerned with the end cycle in the cradle to grave cycle of bioplastics. The standards are different in different regions of the world and are in some sense arbitrary. There are three relevant standards organizations:

- ASTM—American Society for Testing and Materials (USA)
- ISO—International Organization for Standardization (International)
- CEN—European Committee for Standardization (European Union)

The most relevant current standards for the three organizations are shown in Table 23.2. Before those methods are compared, there are two unusual points to be considered. These relate to two standards that do not appear in the table: ASTM D6866 and ASTM D 6002.

ASTM D6866—Definition of Biological Content: The ASTM D6866 standard should be considered separately as it is unusual in that it is designed to assess the extent to which a particular plastic can be defined as bio-based. Essentially, this method certifies the biologically derived content of bioplastics. Cosmic rays colliding with the atmosphere mean that some atomic carbon is the radioactive isotope carbon-14. Carbon dioxide from the atmosphere is used by plants in photosynthesis, so new plant material will contain both carbon-14 and carbon-12. Under the right conditions, and over geological timescales, the remains of living organisms can be transformed into fossil fuels. After about 100,000 years, all the carbon-14 present in the original organic material will have undergone radioactive decay leaving only carbon-12. Thus, a product made from biomass will have a relatively high level of carbon-14, while a product made from petrochemicals will have no carbon-14. The percentage of renewable carbon in a material (solid or liquid) can be measured with an accelerator mass spectrometer (ASTM D6866-12, 2012). The technique used in this ASTM standard highlights the important difference between biodegradability and bio-based content. A bioplastic, such as HDPE, for example, can be 100% bio-based (i.e., contain 100% renewable carbon), yet be nonbiodegradable.

TABLE 23.2 Active Standards for Biodegradability and Compostability

	ASTM	ISO	EN
Industrial compostability	D6400	17088	13432
Anaerobic biodegradability	D5511-02	15985	
		14855-1	
	D5526	14855-2	
Aerobic biodegradability	D5338	14851	
		14855-2	

Compostability and Biodegradation: Normally polymer degradation is described as a change in the properties (tensile strength, color, shape, etc.). This can be caused by numerous factors such as heat, light, or chemicals such as acids, alkalis, and some salts. These changes are usually undesirable in conventional plastics. When describing degradation of bioplastics, however, the degradation is normally desirable. Biodegradation is defined as the process in which the molecular structure of a material is broken down through metabolic or enzymatic processes. The decomposition process occurs via enzymes secreted by naturally occurring microorganisms such as bacteria, some fungi, and so on. Biodegradation can occur in aerobic (presence of oxygen) or anaerobic (absence of oxygen) conditions. Biomass (humus) and biogas (carbon dioxide and methane) are the products of a biodegradation process. Under aerobic biodegradation, carbon dioxide is the primary gas emitted, while in the case of anaerobic biodegradation, methane is the primary gas.

A previous ASTM standard (*ASTM D 6002*) was designed to define a compostable plastic: "ASTM D 6002 method for determining the compostability of a plastic." In this standard, the word compostable was defined as: "That which is capable of undergoing biological decomposition in a compost site such that the material is not visually distinguishable and breaks down into carbon dioxide, water, inorganic compounds and biomass at a rate consistent with known compostable materials" (ASTM D6002-96(2002)e1, 1996).

This definition led to much criticism, due to the fact that, contrary to the way the word is traditionally defined, it completely divorces the process of "composting" from the necessity of it leading to humus/compost as the end product. Indeed, the only criteria this standard does describe is that a compostable plastic must look to be "disappearing" as fast as a standard that had been previously established to be compostable under the traditional definition. In January 2011, the ASTM withdrew standard ASTM D 6002, which had provided plastic manufacturers with the legal credibility to label a plastic as compostable. There is as yet no replacement for ASTM D 6002.

Current Compostability and Biodegradation Standards: For plastics to be categorized as biodegradable or compostable, they must meet the relevant standards. Biodegradability testing can be performed under "certification" or "screening" conditions. Certification conditions are required in cases where results will be required for certification and/or making public claims. There are currently 23 active standards for testing the biodegradability or bio-based content of plastics listed on the ASTM Website. The most commonly mentioned testing procedures and standards are shown in Table 23.2.

The most frequently reported testing procedures for bioplastics are those related to industrial compostability. A brief summary of what the standards involve is given here. The three standards used for industrial compostability are EN 13432, ASTM D6400, and ISO 17088.

The EN 13432 industrial standard is arguably the most internationally used for industrial compostability. This standard must be met in order to claim that a plastic product is compostable in the European marketplace. In summary, it requires biodegradation of 90% of the material to occur under laboratory conditions within 90 days. The ASTM D6400 standard contains the regulatory framework for the United States and sets a less stringent threshold of 60% biodegradation within 180 days for nonhomopolymers and 90% biodegradation of homopolymers within industrial composting conditions (temperatures at or above 60 °C).

ISO 17088 specifies procedures and requirements for the identification and labeling of plastics, and products made from plastics, that are suitable for recovery through aerobic composting. This specification is intended to establish the requirements for the appropriate labeling of plastic products and materials, including packaging made from plastics, as "compostable" or "compostable in municipal and industrial composting facilities" or "biodegradable during composting". The conditions defined by the standard for "compostable plastics" are as follows: "Degree of biodegradation for all polymers: 90% of the organic carbon (relative to a positive-control reference material which is microcrystalline cellulose) shall have been converted to carbon dioxide by the end of a test period of 180 days. Both the positive control and the test sample shall be composted for the same length of time and the results compared at the same point in time after the activity of both has reached a plateau. As an alternative, 90% (in absolute terms) of the organic carbon shall have been converted to carbon dioxide by the end of the test period."

Many starch-based plastics, PLA-based plastics, and certain aliphatic-aromatic co-polyester compounds, such as succinates and adipates, have obtained these certificates. Additive-based bioplastics sold as "photodegradable" or "oxo biodegradable" do not comply with these standards in their current form.

23.6 CONCLUSIONS

The areas of activity surrounding the bioplastics field are all in a state of dramatic development. Growth in interest in bioplastics is in many ways similar to that in bioenergy and biofuels; both are strongly influenced by a mixture of technical and political considerations. Many of the underlying technologies have been studied for years, and in fact the earliest polymers developed for practical use were of biological origin: casein, natural rubber, and cellulosics, for example.

There are two main considerations behind the growing interest in bioplastics: the first is the production of plastics materials and the second is their disposal. These two drivers have resulted in two separate, but interlinked, fields of activity. The first is the use of biological nonfossil feedstocks for the production of polymer precursors. The second is the development of materials from biological feedstocks that are themselves susceptible to "biodegradation," whether environmentally or in a biological host.

It is in the development of materials from biological feedstocks that the greatest level of activity is apparent. The last decade has seen a dramatic interest in commercial activity ranging from the industrial production of PLA to the manufacture of beverage containers from bio-sourced plastics. The greatest area of research and development activity has been in the use of modification techniques to develop a limited range of commercially available biodegradable plastics (e.g., PLA, PBS, and PHBV) into a wider range of materials that are both technically and economically competitive with conventional fossil-based commodity plastics. There is equal interest, if not commercial impetus, in biodegradable materials for medical applications. But here it is performance rather than cost that is the primary consideration.

The most widely used approach to increase the versatility of the core family of biodegradable bioplastics has been blending. It provides a versatile way to modify and improve mechanical properties and aids processability while additionally manipulating degradation behavior and potentially decreasing the price. There is an almost unlimited range of blends that can be produced ranging from simple addition of plasticizing agents to investigation of multicomponent systems. The superficial attractiveness and versatility of the blending approach is the inherent incompatibility of mixed polymer systems. In consequence, the area is far from simple but conversely offers great opportunities for the development of compatibilizers and blending techniques. Associated with this approach are the related areas of reactive processing, grafting, and biomodification. Such is the underlying need to reduce dependence on fossil-based sources of commodity plastics that interest and activity in cost-effective polymer modification techniques is certain to continue.

Associated with the various experimental approaches to bioplastics development are the two related areas of life-cycle analysis (LCA) and recycling. The relevance of these topics is underlined by the existence and political importance of ASTM D6866, which is a standard for definition of that content of a plastic that is of biological origin, independent of its biodegradability. Many assumptions are made about the relative merits of recyclable materials versus biodegradable materials. It is clear that only by careful analysis of all the cost, energy-related, and environmental consideration can the true merits of individual materials and processes be objectively determined. LCA is, relatively speaking, in its infancy and it is important that when carried out it is done so with accurate data and a complete synoptic view of all the factors in the "cradle-to-grave" lifetime of a material or component. Much more attention needs to be paid to the complementary economic assessment of both production and disposal processes as the bioplastics field continues to develop.

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