Chapter 6
Biobased Polymers from Food Waste Feedstock and Their Synthesis

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6.1 Introduction

Plastics are mixtures of organic polymers of high molecular mass and other additives. The etymology of the word “Polymer” derives from two Greek words, ‘Poly’, which means many (numerous), and ‘Meros’, which means units (parts). Monomers are the chemical building blocks of polymers. A monomer can be reacted together with other monomers in a process called polymerization; monomers have the capacity to chemically bond to two other monomers or, in some cases, to more than two other monomers in cross-linked polymers.

Polymerization converts monomer molecules into a polymer. The process can be categorized into two important groups, namely step-growth and addition polymerizations. A step-growth polymerization is typical of monomers with functional groups such as –OH, $–NH_2$, –COOH, –COCl. Their reactions generate small molecular byproducts such as H_2O and NH_3 during the build-up of the polymer. In the case of water, the polymerization is called polycondensation. In contrast, addition polymerization involves the activation/addition of unsaturated monomers with a free radical or ionic initiator, yielding a much higher molecular weight polymer.

Polymerizations can be carried out in one of four different ways: in bulk, in a solvent, in suspension, and in emulsion. Reaction initiators are usually necessary. In bulk polymerization, only monomers provide the liquid portion of the reactor contents, whereas, in solution processes, the addition of solvents can control viscosity and temperature. Suspension polymerization counteracts the heat problem generated by the exothermic reaction by suspending droplets of water-insoluble monomer in an aqueous phase. These droplets are obtained by vigorous agitation of the system and are in size range from 0.01 to 0.5 cm diameter. Emulsion polymerization differs from the suspension method: the particles in the system are much smaller, from 0.05 to 5μm diameter, and the initiator is in the aqueous phase rather than in the monomer droplets. Besides monomers and an initiator, for emulsion polymerization prerequisite components are a dispersing medium, usually water, and an

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emulsifying agent. The emulsifying agents are surfactants; their amphipathic nature ensures the stability of the initial monomer emulsion and of the polymer dispersion formed. Common surfactants used in emulsion polymerization comprise fatty acids, sodium lauryl sulfate, and α-olefin sulfonate.

The product of the polymerization reaction is the polymer, which is a long-chain molecule composed of a large number of repeating units covalently bonded. The repeating unit is a part of the macromolecule whose repetition would produce the complete polymer chain (except for the end-groups). The repeating unit may comprise one or more kinds of monomeric units. If a polymer is derived from only one species of monomer, it is called homopolymer; on the converse, copolymers derive from more than one species of monomer (Cowie 2007).

If the monomer is asymmetric, it can be distinguishable from its mirror image. In this case, it is called chiral. The chirality of the resulting polymer represents the relative stereochemistry of adjacent chiral centers within the macromolecule. An important characteristic of chiral polymers is tacticity, that is, “the orderliness of the succession of configurational repeating units in the main chain of a regular macromolecule, a regular oligomer molecule, a regular block, or a regular chain” according to the IUPAC definition (Jenkins et al. 1996). In isotactic polymers all the substituents are located on the same side of the macromolecular backbone. They are usually semicrystalline macromolecules and often form a helix configuration. In syndiotactic polymers, the substituents have alternate positions along the chain. In atactic polymers, the random nature of substituents along the chain generally results in amorphous macromolecules; hence tacticity may also be inferred from the melting temperature.

Plastic polymers can also be classified as thermosetting and thermoplastic matrices. The thermoset materials have crosslinking structures, which prevent the remelting, hence they show dimensional stability and resistance to high temperatures, but cannot be recycled, reshaped, or remolded. This is the case of poly(vinyl ester), phenol-formaldehyde resins, and epoxy resins. Thermoplastic polymers are not crosslinked and can be easily recycled or remolded because they become soft when heated, even if this can be a drawback. Polyolefines and polyesters are common thermoplastics. Elastomers are rubber-like elastic polymers that can be stretched extensively beyond their original length and can retract rapidly to their original dimensions: weak binding forces enable the polymer stretching, and a few crosslinks among chains permit the polymer to retract to the original shape. Thread forming polymers are called fibers: they are characterized by strong molecular forces, which lead to strong interactions of the chains and thus impart the crystalline nature (Cowie 2007).

Polymer science and technology aim to control macromolecular synthesis as regards uniform length, branching, molecular weight distribution, composition, topology, functionality, stereospecificity etc.

Fossilbased polymers are one of the major stories of the past century. The attractive qualities of fossilbased plastics lead us, around the world, to a voracious appetite and over-consumption of plastic goods. They have become a vital asset for humanity but also the crucial emblem of waste, pollution, and ecotoxicity. The use of disposable objects is increasingly perceived by consumers as a negatively valued practice.

There are many facets to the production and use of plastics of petrochemical origin. They are durable, lightweight, low cost, water-resistant, strong and tough, chemically inert, corrosion resistant, and thermal/electrical insulators. Anyhow, these advantages turn into disadvantages from the environmental point of view, since fossilbased plastics are non-renewable goods with a high "carbon footprint" They are also very slow to degrade. They may pose public health concerns because they release toxic fumes if burnt, their recycling is expensive and not always straightforward, they are not heat resistant, and they may become brittle at low temperatures. The rapid emergence of bioplastics is one of the major stories of the last decades because consumers ask for environmentally-sustainable products, there are increased restrictions for the use of polymers with high "carbon footprint" and boosted attention to sequestration of CO_2; hence industries are stimulated to focus on the development of new biobased feedstocks.

In the event of a resource crunch, the shifting toward a biobased material policy will be crucial for a sustainable future of polymer science and technology.

The economic and environmental needs claim the development of sustainable and renewable biobased polymers to address the challenge of finite fossil resources in the polymers market (Mirabella et al. 2014).

Bioplastics or biobased polymers or bio-polymers are terms that describe several different classes of materials, depending on the background of authors. From an environmental viewpoint, the renewability of feedstocks and degradability of the polymers are the most critical factors.

According to European Bioplastics, plastic material is defined as a bioplastic if it is either biobased, biodegradable, or both (European Bioplastics 2018). Anyhow there are biobased polymers that are not plastic at all.

The nomenclature ambiguity in this field of study is addressed by the European standard CEN/TR 15932:2010 (Plastics – Recommendation for terminology and characterization of biopolymers and bioplastics) that takes into consideration the current use of biopolymer-related terms in various settings (Imre et al. 2019).

The European Standard names the polymeric materials as follows:

- Biobased polymers: they are polymers with constitutional units that are totally or in part derived from biomass. Polymers synthesized by living organisms and synthetic biobased polymers, made of monomers that derive from renewable resources, belong to this category.
- Biodegradable polymers: they are polymers that can be biodegraded according to the relevant standards, such as the European Standard EN 13432:2000, ISO 17088:2012, and the US Standard ASTM D6400, discussed in Chap. 9 (Sec. 9.5). Biodegradability biochemically depends on the structure of the polymer chain; it does not depend on the origin of the raw materials. It has to be emphasized that, in fact, all plastics materials are theoretically biodegradable; since fossilbased plastics degrade at a slow rate in the natural environment, because the vast majority of microorganisms did not develop the ability to use them as carbon source,

they are considered non-biodegradable. According to the European Society for biomaterials, biodegradation is the process in which biological agents (microbes and enzymes) play a dominant role in degradation (Williams 1986).

- Biocompatible polymers: they are polymers compatible with human or animal tissues and suitable for medical use because they do not harm the body or its metabolism while fulfilling the expected function. Actually, for implantable systems, there are stringent requirements: (i) a benign and not excessively hydrophobic material is required; (ii) the material should exhibit long-term stability in a wet, oxygen- and enzyme-rich environment and should biodegrade within a specific time, which can be different for different applications; (iii) very low toxicity of degradation products or remnants of catalysts is needed. The biocompatibility of the material with cells should be tested before in vivo studies are conducted.

It follows that the generic term ‘biopolymer’ covers a rather wide range of polymeric materials. They are a whole family of materials with different properties and applications.

Figure 6.1 illustrates a global polymer classification according to renewability and biodegradability coordinates and lists the most significant examples in each category. The horizontal axis shows the biodegradability of plastic, whereas the vertical axis features the different origins of raw materials. This categorizes plastics into four groups.

Drop-in bioplastics are the “bio-similar” copy of the petrochemical plastics made from biomass instead of fossil oil. Polyolefins, polyamides, polyurethanes, and polyethylene terephthalate are examples of drop-in bioplastics if the producer has replaced the fossilbased chemicals with biobased chemicals while using the same machinery and equipment for their production.

The drop-in bioplastics are high-priced compared to the original fossilbased plastics because of the economy of scale and smaller production and processing capacity; moreover, research and development costs are higher, and biomass cannot be transported through pipelines but in trucks. On the converse, the end-of-life options are similar as regards biodegradability. The carbon footprint for drop-in bioplastic is lower because the CO_2 that is released when the material is returned to the biosphere had been photosynthetically captured by the plant during its growth, and no additional CO_2 is brought into the atmosphere, at variance with fossilbased plastic analogs.

Generally speaking, while the price of conventional plastics oscillates with oil prices, the prices of bioplastics are higher but more stable than conventional plastics. Bioplastic costs are expected to decline as economies of scale are achieved, and logistics are fully developed. Product design may also promote price reductions. For example, PLA is stiffer than PS and less plastic is necessary to make products with comparable rigidity (Zhao et al. 2020). Furthermore, labor costs entailed in recycling plastic objects can be reduced by using biodegradable versions.

Polymer processability, mainly governed by rheological properties, such as extensional viscosities and melt strength, depends on polymer molecular weight,

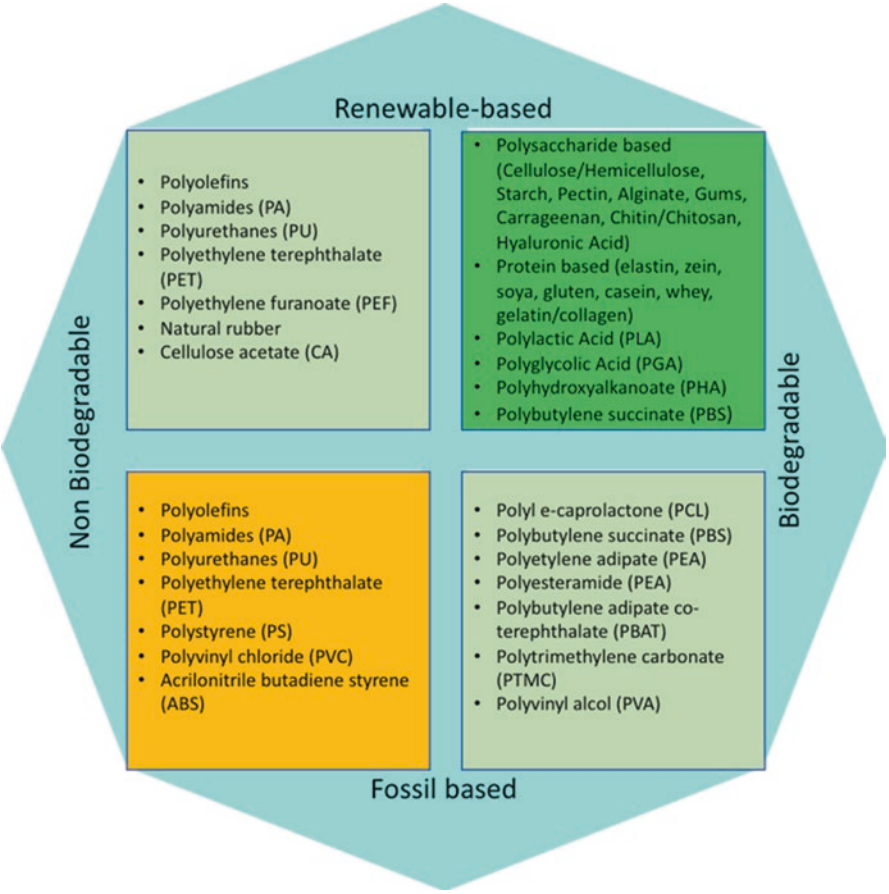


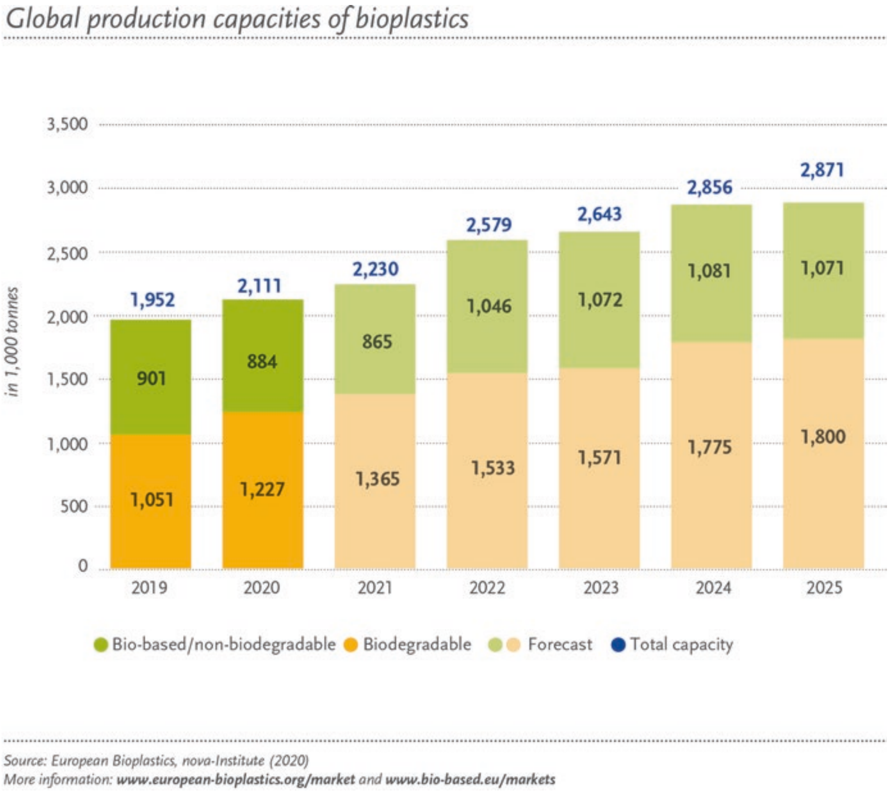
Fig. 6.1 Polymer classification according to renewability and biodegradability coordinate; abbreviations are detailed

molecular weight distribution, degree of crystallinity, and chain structure. Most biodegradable bioplastics have worse processability (via a variety of thermal techniques) than fossilbased plastics (Zhao et al. 2020).

Currently, biobased polymers production was 4.2 million tonnes, which represents about 1% of fossilbased polymers in 2020 (Skoczinski et al. 2021), with a market boom due to sophisticated biopolymers and novel applications.

Their production capacity was projected to increase from around 2.11 million tonnes in 2020 to about 2.87 million tonnes in 2025, as illustrated in Fig. 6.2. In 2020 their compound annual growth rate, 8%, is more than double the overall growth of polymers (Skoczinski et al. 2021).

The most important market segment is packaging, followed by consumers goods, textiles, and agriculture/horticulture, but biopolymers are increasingly used in many other sectors such as automotive and transport, building, and construction, coating



Source: European Bioplastics, nova-Institute (2020)
More information: www.european-bioplastics.org/market and www.bio-based.eu/markets

Fig. 6.2 Global production capacities of bioplastics 2019–2025. Reprinted with permission from the Author. (European Bioplastics 2020)

and adhesives, electrics and electronics, and others (European Bioplastics 2020), as detailed in Fig. 6.3.

The application of biodegradable biopolymers is possible and advantageous mainly in the packaging, agriculture, and the medical sector. In short service life applications, biodegradability is of utmost importance. For long-term applications, however, biodegradability might be disadvantageous.

In order to be selected as potential monomers for bioplastic production, platform chemicals need to overcome the gap between laboratory/pilot scale and commercial/industrial scale using suitable and profitable production strategies, including microbial strain development to convert renewable resources into value-added products.

Virgin bioplastic feedstocks raise the issue as to whether they have a negative impact on food supply. European Bioplastics claims there is no competition between the renewable feedstock for food, feed, and the production of bioplastics, and actually, the land used to grow the renewable feedstock for the bioplastics production was less than 0.02% of the global agricultural area (European Bioplastics 2020). Anyhow, the use of food waste (FW) instead of edible crops is an opportunity and a

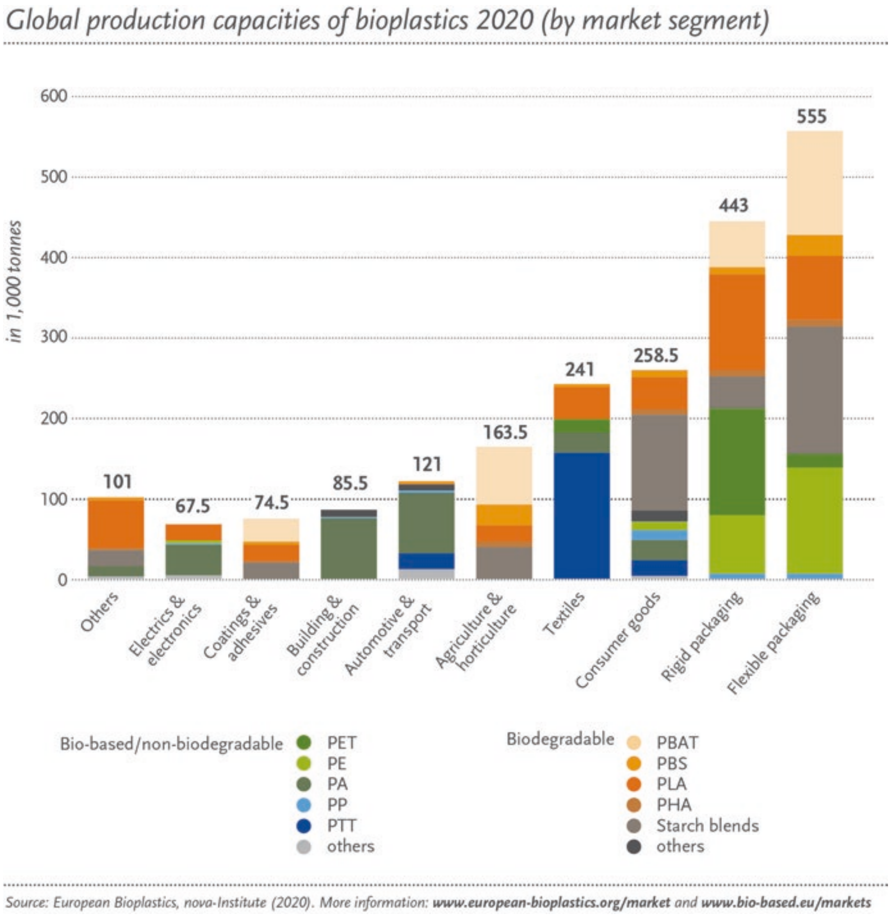


Fig. 6.3 Global production capacities of bioplastics 2020 (by market segment). Reprinted with permission from the Author. (European Bioplastics 2020)

highly feasible option that is receiving increasing attention at the academic and industrial levels.

Figure 6.4 illustrates the current global production capacity of bioplastics. Asia is a major production hub, even if one-fourth of the global bioplastics production capacity is located in Europe that ranks highest in research and development and is the industry's largest market worldwide.

Biopolymers can be present in the FW. This is the case of polysaccharides found in plants (such as starch, cellulose, agar, hemicelluloses, pectin, alginate, konjac, carrageenan, gum) or in animals (chitin/chitosan, hyaluronic acid). Protein of vegetal (zein, soy, gluten) and animal origin (casein, whey protein, collagen, gelatin, elastin, silk, fibroin) are other biopolymers. They can also be synthesized by microorganisms such as fungi (pullulan, elsinan, scleroglucan) and bacterial species (glucans, xanthan gum, polygalactosamine, curdlan, gellan, dextrans, and polyhydroxyalkanoates (PHA)).

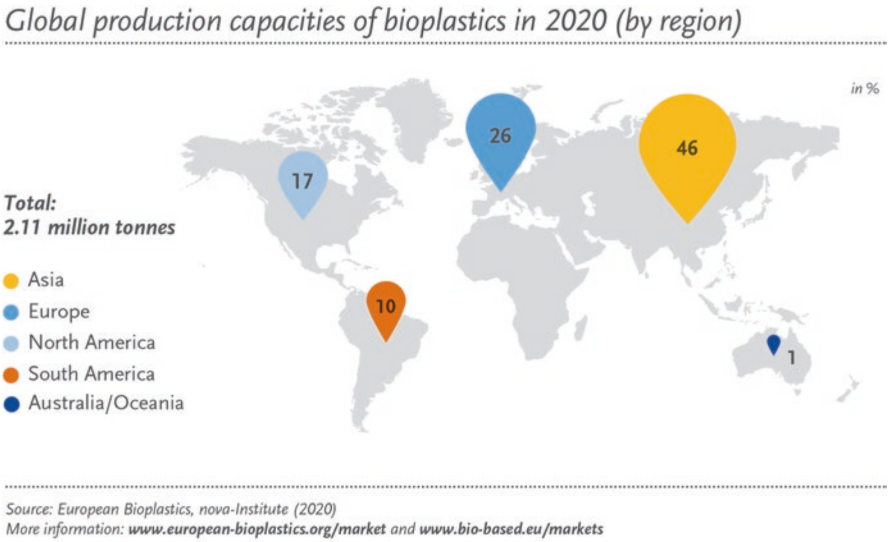


Fig. 6.4 Global production capacities of bioplastics 2020 (by region). Reprinted with permission from the Author. (European Bioplastics 2020)

Natural polymers such as polysaccharides and chitin can be converted into marketable derivatives via bulk or surface chemical modification (Cunha and Gandini 2010) that usually aims at reducing the polymer hydrophilicity (Sanchez-Vazquez et al. 2013). Similarly, cellulose-based bioplastics can be obtained via physico-chemical modification of cellulose. High-molecular-weight cellulose is highly crystalline and almost insoluble in aqueous media (Sandhya et al. 2013). Surface chemical modification gives ethers, esters, and acetals, which are the most common derivatives of the hydroxyl groups in cellulose structures. Plastic properties can be introduced into cellulose fibers by mechanical treatments and, above all, by esterification of the hydroxyl group with the acid to confer fluidity, resistance, and durability comparable to those of synthetic polymers (Abdul Khalil et al. 2016). Conversion of cellulose into polyols can also be achieved through liquefaction during the manufacture of polyurethane polyesters and foams (Wang et al. 2008a).

Apart from PHAs, directly synthesized by microorganisms, biopolymers production from a gamut of FW that ranges from agroindustrial residues to organic waste from household level, relies on polymerization of simple biomolecules accessible either through substrate fermentation by microbes, including the genetically modified ones, or by chemical processing.

Figure 6.5 illustrates the current global production capacities of bioplastics, detailed by material type. More than half the produced bioplastics are biodegradable. Today, there is a bioplastic substitute for nearly every fossil plastic material with the additional advantages of a reduced carbon footprint and additional waste management options (van den Oever and Molenveld 2017).

PLA, PCL, and PGA are hydrophobic aliphatic polyesters based on hydroxyalkanoic acids, particularly important for the biomedical sector because of their

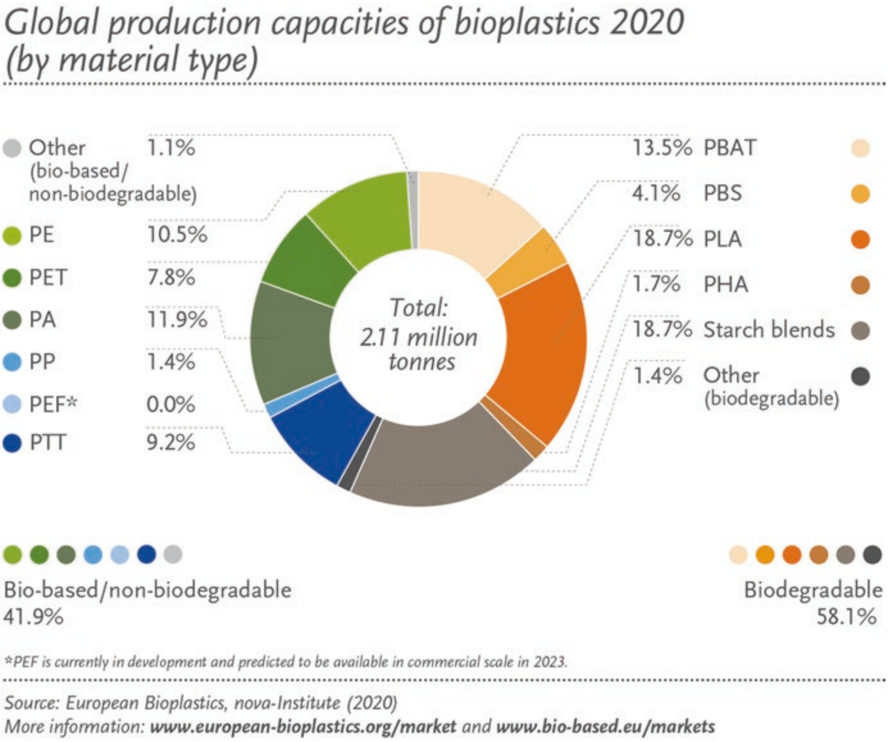


Fig. 6.5 Global production capacities of bioplastics 2020 (by material type). Reprinted with permission from the Author. (European Bioplastics 2020)

biocompatibility and low immunogenicity; they are biodegradable by enzymes and/or hydrolysis under physiological conditions. Their good mechanical properties enable their use as sutures, implants for bone fixation, drug delivery vehicles, and tissue engineering scaffolds (Oh 2011; Jacobson et al. 2008). Biodegradable polymers like PLA, PHA, PBS, PGA, PCL, etc. are high value- added products for sustained release systems, pesticides, fertilizers, packaging, paper coatings, and compost bags.

PLA and PHAs rank highest in the field of research and development and show the fastest rates of market development. Production capacities of PLA show high growth rates due to its excellent barrier properties. High-performance PLA grades are an excellent replacement for PS, PP, and ABS (acrylonitrile butadiene styrene) in challenging applications. Increased volumes of PLA production are needed since PLA was sold out in 2019. Biobased PE and PP are breaking ground, while biobases polyamides, PBAT, PHAs, and casein polymers expansion is envisioned (Skoczinski et al. 2021).

PHAs production has been in development for a while, but their commercial production capacities are projected to increase almost tenfold in the next five years due to their wide gamut of physical and mechanical properties and consumer awareness about the importance of sustainable and ecofriendly bioplastics.

As regards non-biodegradable bioplastics such as biobased PE and PET, new capacities are expected in the coming years. Biobased PP entered the market in 2019. As regards PET, the focus has shifted to the development of PEF (polyethylene furanoate). It is predicted to enter the market in 2023 as a biobased PET alternative with superior barrier and thermal properties for the packaging sector (European Bioplastics 2020).

Biobased polymers can be primarily manufactured using three principal routes: (i) partial modification of natural biobased polymers (e.g. starch, cellulose, and chitin), (ii) polymerization of biobased monomer produced by fermentation or conventional chemistry (e.g., PLA, PBS, and biobased PE) (iii) bacterial synthesis (e.g., PHA). This chapter does not focus on the modification of natural polymers into their marketable derivatives but introduces four among the most interesting biodegradable thermoplastic biopolymers, viz., PLA, PHA, PBS, and PGA with a focus on the history of their development, their properties, synthesis, commercial market, and low-cost FW-based feedstock identified for production. Biobased thermosetting polymers, copolymerization, and blending will be shortly presented. Chapter 8 details the mechanical testing and characterization of bioplastics and biocomposites

6.2 Polylactic Acid (PLA)

PLA is the most popular bioplastic, and its production capacity will increase significantly in the next years.

PLA has been studied for over a century. In the early 1800s, PLA was discovered when Pelouze condensed lactic acid by distillation of water. This polycondensation process produces low yield, low purity, and low-molecular-weight PLA and the cyclic dimer of lactic acid, namely, 3,6-dimethyl-1,4-dioxane-2,5-dione, known as lactide (Benninga 1990).

Nearly a century later, Wallace Carothers found that heating lactide in vacuum conditions produced PLA (Carothers and Arvin 1929). This method, namely ring-opening polymerization (ROP), was later patented by DuPont in 1954 (Auras et al. 2010a). This process is difficult on an industrial scale due to the high cost of purification, limititing it to the production of medical products, such as sutures, implants, and drug carriers.

Since the 1970s, PLA has been approved by the US food and drug administration (FDA) for food and pharmaceutical applications since the PLA depolymerization products are not toxic (Garlotta 2001).

In the 1990s, a commercially viable lactide ROP was developed to polymerize high-molecular-weight PLA (Auras et al. 2010a). Since then, PLA has become the emblem of biopolymers, and it currently attracts an exponentially increasing research attention.

6.2.1 FWs as Feedstocks

Lactic acid (LA) is the monomer of PLA. Lactic acid is one of the most promising value-added building blocks that can be derived from sugars, and it is a midway chemical for the production of various commodity and specialty chemicals (Bozell and Petersen 2010).

The IUPAC name is 2-hydroxy-propionic acid, it exists in two optically active enantiomers, the L(+)- and the D(−)-lactic acid (respectively L-LA and D-LA). Lactic acid can be either prepared chemically or biotechnologically. Anyhow, the fermentative biotechnological LA production is usually preferred because of the low substrate costs, moderate operating temperatures, and lower energy consumption.

During a typical LA fermentation, LA production results in a drop in pH that has an inhibitory effect on the metabolic activity of LA-producing strains. To avoid this drawback, a neutralizing agent such as calcium carbonate or hydroxide is used in industrial processes to produce calcium lactate in the fermentation broth. This salt does not inhibit further LA synthesis. Filtration removes the cell biomass and other insolubles, and then, after evaporation and recrystallization, corrosive sulfuric acid is used to liberate crude LA from calcium lactate, generating a large amount of calcium sulfate (gypsum) as solid waste. A filtration step separates gypsum; LA purification via esterification and subsequent hydrolysis is one of the most expensive stages of the production process and a reactive distillation system was advantageous for lactic acid purification (Komesu et al. 2015). The process is costly and complicated; by this scenario, the use of acid-tolerant strains, obtained by genome shuffling through protoplast fusion, gene deletion, exploitation of knockdown libraries and adaptive evolution to acidic pH, would avoid the need for neutralizers, thereby simplifying the downstream process, and lowering the overall cost of the fermentative LA production; another strategy to circumvent the toxicity of lactic acid towards microbial cells was in situ LA recovery (Singhvi et al. 2018).

Commercial LA is usually and selectively produced by the bacterial fermentation of carbohydrates by homofermentative organisms belonging to the genus *Lactobacillus* and *Bacillus*. *L. delbrueckii, L. amylophilus, L. bavaricus, L. casei, L. maltaromicus,* and *L. salivarius* predominantly produce the L(+)-isomer. Strains such as *L. lactis, L. jensenii,* and *L. acidophilus* generate either the D(–)-isomer or mixtures of both LA enantiomers. Interestingly, at variance with the chemical synthesis, only one of the two enantiomers is produced if a specific strain of lactic acid bacteria is chosen (Reddy et al. 2008). Most strains are anaerobic and convert pyruvic acid, the end-product of the Embden-Meyerhof pathway, to lactate by either of the two enzymes, L- or D-lactate dehydrogenase; pyruvate is the electron acceptor of NADH (nicotinamide adenine dinucleotide) oxidation (Singhvi et al. 2018).

Bio-production of optically pure L-LA from FW at ambient temperature relied on the regulation of key enzyme activity by sewage sludge supplementation and intermittent alkaline fermentation. Production of optically pure L-LA acid was achieved from FW at ambient temperature with a yield of 0.52 g/g of total chemical oxygen demand of the substrate (Li et al. 2015). *Streptococcus thermophilus* and *Lactobacillus bulgaricus* selectively produced L-LA from furfural residues and corn kernels with hydrolyzed yeast as cheap nutrients (Tang et al. 2013).

L-LA is the preferred building block for food and pharmaceutical application of PLA since elevated levels of D-LA are harmful to humans. The presence of a single optical lactic acid is preferable because different optical lactic acids can affect the properties of PLA, such as the rate of crystallization, the extent of crystallization, the melting point, mechanical strength, and degradability.

Most simple sugars can be fermented, but the expensive food-based sugars make their use scarcely feasible from the economic point of view. Nowadays, LA used for PLA production is mainly derived from renewable edible crops such as sugar beet and corn (Castro-Aguirre et al. 2016). To limit the land use share for bioplastics, high sugar-containing FW such as whey, coffee mucilage, corn cobs, corn stalks, rice bran, barley, wheat bran and brewer's spent grains, (Venus 2006; Venus and Richter 2006), kitchen and canteen waste (Tashiro et al. 2013; Ohkouchi and Inoue 2006) (Wang et al. 2010), pineapple syrup and grape invertase as substrate and enzyme, respectively (Ueno et al. 2003), wheat bran (Germec et al. 2019), soybean vinasse (Karp et al. 2011), *Curcuma longa* biomass (Nguyen et al. 2013), carbohydrates, starchy and lignocellulosic biomasses free from food-related concerns, glycerol, microalge, whey (Abdel-Rahman et al. 2013; Vasala et al. 2005; Vishnu et al. 2006), fruit and vegetable wastes (Wu et al. 2015) and yoghurt waste (Alonso et al. 2010) have been explored as alternative feedstocks for fermentative LA production

The production of lactic acid from these and other FWs was more extensively dealt with in Chap. 5 (Sect. 5.4.3).

A techno-economic assessment investigated the technical feasibility, profitability and extent of investment risk for LA, lactide and PLA production using FW powder as the raw material in a plant. Sensitivity analysis demonstrated that the prices of lactic acid, lactide, and PLA, as well as the marketability of byproducts (animal feed), were crucial factors for the profitability in the plant (Kwan et al. 2018).

6.2.2 Synthesis

The production of PLA can be conducted by different synthetic routes, viz. direct condensation polymerization, azeotropic dehydrative polycondensation, and polymerization through lactide formation and ROP, as illustrated in Fig. 6.6.

Since the lactic acid monomer has both –OH and –COOH groups, the reaction can take place directly by self-condensation/dehydration equilibrium. Condensation of lactic acid is usually performed in bulk by distillation of condensation water, while vacuum and temperature are progressively increased (Mehta et al. 2005).

This preparation strategy also involves ring-chain equilibrium involving the depolymerization of PLA into the dimer of lactic acid, i.e., lactide. The polymer obtained by this process has a low molecular weight because it is hard to remove water from the highly viscous reaction mixture completely. At a certain point, the

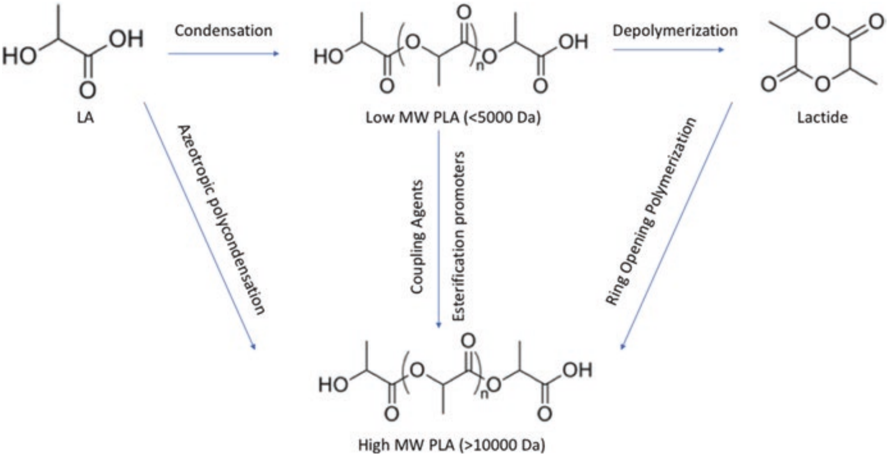


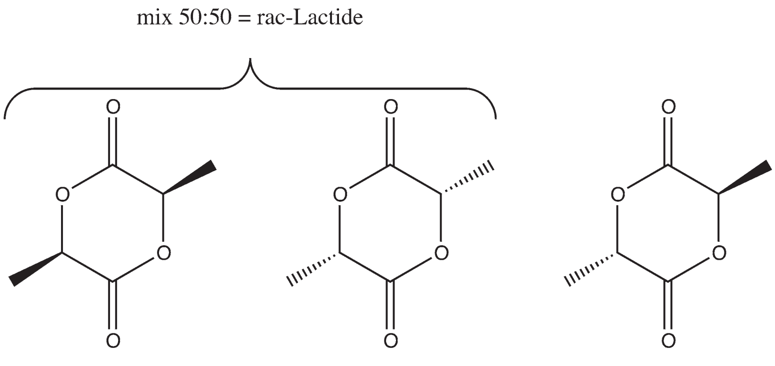
Fig. 6.6 PLA preparation technologies

polymerization and depolymerization rates are the same. A reaction temperature lower than 200 °C limits the generation of the entropically favored lactide. The low molecular weight polymer is brittle and almost unusable. External coupling agents, such as carbonyl diimidazole, bis(trichloromethyl) carbonate, and dicyclohexylcarbodiimide, are employed to increase the chain length promoting esterification between low molecular weight PLA molecules obtained in the initial condensation. These reagents produce reaction byproducts that must be removed; for example, dicyclohexylcarbodiimide forms insoluble dicyclohexylurea, which must be filtered in the purification step. Moreover, the increased number of reaction steps makes the procedure more expensive. Alternatively, reactions involving chain-extending agents are cheaper, requiring low amounts of chain-extending agents. Chain extenders are usually bifunctional low molecular weight chemicals. At variance with coupling agents, they do not bind different PLA chains but they can increase the molecular weight of polymers in a fast reaction without a separate purification step via their reaction with the hydroxyl or carboxyl end groups. Some possible chain-extending agents are isocyanates, acid chlorides, anhydrides, epoxides, thiirane, and oxazoline; isocyanates are toxic chain extending agents (Li and Yang 2006). Chain extending agents are not biodegradable or bioabsorbable and are not compatible with medical applications because of possible severe in vivo complications (Hartmann 1998).

PLA can alternatively be produced using the azeotropic dehydrative polycondensation approach. This method brought a breakthrough in increasing the molecular weight of PLA. Solvents with high boiling point are used to remove the dissociated water by means of the so-called azeotropic distillation technique. A general procedure for this route consists of reduced pressure distillation of lactic acid for 2–3 h at 130 °C to remove the majority of the condensation water. Then, the catalyst and azeotropic solvent, such as toluene, are added. The water formed during the polymerization is removed as water/solvent azeotrope. Then the water/solvent vapor condenses to give a liquid that separates in two phases. The upper one consists of the solvent, that is reintroduced in the reaction mixture. The lower phase comprises water, which is eliminated. The polymer can then be isolated as is or dissolved and precipitated for further purification. This polymerization technique requires significant amounts of catalysts. They remain as impurities in the polymer and may initiate unwanted degradation during subsequent processing work at elevated temperatures, uncontrolled polymer hydrolysis, and toxicity in medical applications (Garlotta 2001). The use of solvents increases the PLA price and makes the processes ecologically unattractive since it is hard to remove solvent totally from the end product.

The third and most exploited synthetic route is the ROP of the cyclic dimer of lactic acid. The opening of the lactide gives a unit that is acyclic. The controlled ROP of lactide is significant because it leads to high molecular weight PLA with specific and desirable properties. Due to the two asymmetric carbon atoms in the molecule, lactide exists in three different stereoisomers: DD-lactide, LL-lactide enantiomers, and *meso*-lactide, as illustrated in Fig. 6.7; the DD-lactide and LL-lactide enantiomers can form a 1: 1 racemic stereocomplex (rac-lactide), which melts at 126–127 °C (Hartmann 1998), higher than the pure isomers, which melt at 97 °C, while *meso*-lactide melts at 52°C (Ehsani et al. 2014). DD-lactide and LL-lactide are also known, respectively, as D-lactide and L-lactide and, according to the Cahn–Ingold–Prelog sequence rules, they sequentially correspond to (R-R)-Lactide and (S-S)-Lactide. The use of high-temperatures induces racemization.

Lactide is currently obtained by the depolymerization of low molecular-weight PLA (1000–5000 MW), obtained condensing lactic acid, with or without catalysts, at 110–180 °C and removing the water of condensation under vacuum 25 mm Hg under reduced pressure and high temperature. This prepolymer is then subjected to temperatures of 180–215 °C at 0.1–15 mm Hg to form and distill off the crude



(R-R) Lactide
D-Lactide

(S-S) Lactide
L-Lactide

(S-R) Lactide
meso-Lactide

Fig. 6.7 Lactide stereoisomers

lactide and remove water and acid impurities. Purification can be performed via recrystallization or distillation, even if the small difference in boiling temperatures of LL- or DD-lactide and meso-lactide makes the latter procedure quite labor-intensive. Furthermore, for the highest stereochemical purity, recrystallization is needed. The ROP, depending on the type of catalyst used, can follow three different pathways: cationic, anionic, or coordination/insertion. Both cationic and anionic ROP are usually done in solvent systems, and are susceptible to racemization and transesterification. The coordination/insertion ROP is usually performed using tin(II) 2-ethylhexanoate, $Sn(Oct)_2$, as a catalyst. Although $Sn(Oct)_2$ has been accepted as a food additive by the U.S. FDA, the toxicity associated with most tin compounds is a considerable drawback in the case of biomedical applications (Albertsson and Varma 2003; Kowalski et al. 2005). In fact, a medical PLA-based product within a tissue would releases continuously tin during the course of biosorption of PLA, potentially leading to critical tin concentrations with adverse effects on enzymes, receptors, and the whole organisms due to cyto- and genotoxicity (Yamada et al. 2008; Tanzi et al. 1994); the ecotoxicity (Mehta et al. 2005; Hege and Schiller 2014) of tin has also to be taken into account since PLA disposable products are increasingly used. The development of safe catalysts for biopolymers synthesis is of great interest. It follows that tin replacement strategies are of utmost importance. Concerns about catalyst toxicity prompted the academic study of the biocatalytic ROP of lactide using mild reaction requirements and recyclable enzymes such as *Candida antarctica* lipase B immobilized onto chitin and chitosan (Omay and Guvenilir 2013). Cerium trichloride heptahydrate is a nontoxic and easy to handle Lewis acid catalyst in organic reactivity; a new and efficient lactic acid polymerization by multimetallic cerium complexes yielded a PLA suitable for biomedical applications, in high yields up to 95% and a molecular weight ranging from 9000 to 145000 g/mol (Pastore et al. 2021). Iron-based catalysts were also successfully explored to avoid the tin-based catalysts toxicity (Hege and Schiller 2014).

6.2.3 Properties and Uses

PLA possesses high density, elongation, and tear resistance similar to PET (Lunt 1998) and PS (Zhao et al. 2020). It follows that the potential of PLA as an alternative material to conventional plastics is high if properly manufactured, since it can be lightweight with low processing temperature, no environmental pollution, and good 3D printability.

If the polymer molecular weight is not very high (<50,000 Da), PLA is amorphous, with a melting point of 130–150 °C and a glass transition temperature (see Sec. 9.2) around 45 °C (Rivero et al. 2016).

On the converse, high molecular weight PLA (>50,000 Da) has a melting temperature of 170–180 °C, a glass transition temperature of 58–65 °C, and a tensile modulus 2.7–16 GPa (Rivero et al. 2016; Södergård and Stolt 2002; Middleton and

Tipton 2000). Annealing and nucleation have been used to enhance the mechanical properties of PLA polymers (Simmons et al. 2019). Exemplary physical properties of PLA are detailed in Table 6.1 ; they strongly depend on the molecular weight of the polymer and its tacticity.

Lactic acid, which is the building block of PLA, is chiral; hence its polymerization may lead to isotactic, syndiotactic, and atactic/heterotactic PLA primary structures. L-LA and D-LA lead to two enantiomeric forms PLAs, namely, poly(L-LA) (PLLA) and poly(D-LA) (PDLA), respectively, while their mixture leads to poly(D-, L-LA) (PDLLA).

Isotactic PLLA homopolymer is a semicrystalline material with a melting temperature of about 170–180 °C (Husseinsyah and Zakaria 2011). On the converse, the atactic and heterotactic stereoblocks, with a random arrangement of L- and D-units, lead to amorphous and low-quality PLA. PLA has quickly developed into a competitive material, but the control of crystallinity is a bottleneck in extended utilization. A specific stereocomplex of PDLA and PLLA has a higher glass transition temperature, with increased crystallinity and mechanical strength (Lv et al. 2018); hence, although present day PLA is composed of mainly L-LA, an L- and D- LA strereocomplex copolymer is expected to improve the quality of PLA and expand its use (Awasthi et al. 2018) due to an enhanced melting point to over 200 °C (Rivero et al. 2016): advanced therapeutic delivery carriers and tissue engineering devices, as well as stabilization of colloidal systems in microparticles, micelles, and hydrogels, could be attained (Li et al. 2016a). An environment-friendly polyhydroxy compound, pentaerythritol, was also used as a crystallization promoter to form the PDLA/PLLA regular stereocomplex; the temperature stability is maximized when a 1:1 blend is used (Chen et al. 2019), but even at lower concentrations there is still a substantial improvement of thermal stability (Zhang et al. 2019).

The use of an aryl amide as a nucleating agent improved the crystallization rate of PLLA/PDLA blend and increased the fraction of the stereocomplex (Xie et al. 2016). Other strategies to facilitate the stereocomplex crystallization, thereby increasing the heat resistance, include copolymerization, flow-induced crystallization, and the use of a polyhydroxy compound, such as pentaerythritol, to stimulate nucleation (Chen et al. 2019).

Polylactic acid can profitably be processed like most thermoplastics into fiber (for example, using conventional melt spinning processes) and film (Zhang et al. 2019).

PLA is soluble in dioxane, acetonitrile, chloroform, methylene chloride, 1,1,2-trichloroethane, and dichloroacetic acid but it is not soluble in water, alcohols, and alkanes. Crystalline PLLA is not soluble in polar solvents, such as acetone, ethyl acetate, or tetrahydrofuran (Farah et al. 2016).

PLA is a thermoplastic aliphatic polyester that can be attacked by microorganisms but it also undergoes simple hydrolytic cleavage of the ester moieties of the polymer backbone with only little or even no assistance from enzymes resulting in the formation of non-harmful and not toxic lactic acid monomers (Pawar et al. 2014), even if the potential toxicity of additives and catalysts has to be considered. Actinobacteria belonging to the family *Pseudonocardiaceae*, and some members of the family *Micromonosporaceae*, *Streptomycetaceae*, *Streptosporangiaceae*, and *Thermomonosporaceae* can degrade PLA; PLA composting and anaerobic digestion are feasible while PLA is less degraded in the environment (Folino et al. 2020). Heterogeneous PLA was effectively composted with garden waste (Ghorpade et al. 2001). PLA can also be depolymerized to its monomer by thermal depolymerization or hydrolysis with boiling water or steam (Madhavan Nampoothiri et al. 2010).

Due to the biodegradability, not toxic nature of degradation products, and mechanical properties, PLA has been used extensively for medical application (Hamad et al. 2015) such as tissue engineering, drug delivery systems, implants, sutures, anchors, screws, scaffolds, bone grafting, reattachment of ligaments, tendons (Auras et al. 2010b).

It has been used in oral, orthopedic, auricular, and craniofacial augmentations in plastic surgery. Degradation via hydrolysis into lactic acid, which is then incorporated into the Krebs cycle, results in the resorption of the material (Athanasiou et al. 1996).

PLA is a crucial biobased polyesters for food packaging that is one of its major applications because of its superior transparency, ease of processing, and availability in the market. In this context, the major drawback of PLA is its brittleness and low toughness (Auras et al. 2004). According to IUPAC, a plasticizer is a substance or material incorporated in a material that increases its flexibility, workability, or distensibility. The addition of plasticizers increases the flexibility of PLA and makes it more useful in the packaging sector (Madhavan Nampoothiri et al. 2010). Phthalates are commonly used, but health concerns about them stimulated research about the possibility to use low molecular weight, not volatile molecules such as polyols (namely: glycerol, ethylene glycol, diethylene glycol, triethylene glycol and sorbitol, mannitol and xylitol), glucose monoesters and partial fatty acid esters, and triethyl citrate as nontoxic plasticizers. To avoid the use of phthalates to mitigate the brittleness of PLA, oligomers of lactic acid (with molar mass around 1000 Da) are blended with commercial PLA to improve ductility, obtaining transparent and ductile materials able for films manufacturing. These oligomers are proposed as innovative and fully compatible and biodegradable plasticizers for PLA (Burgos et al. 2014) (Madhavan Nampoothiri et al. 2010).

As a food contact substance, PLA is one of the most attractive biopolymers with many short-term or disposable applications, such as disposable cutlery (plates, cups, lids, and drinking straws), upholstery, disposable garments, personal care products, covers, and diapers (Farah et al. 2016).

PLA is becoming one of the most popular alternatives to traditional petroleum-based plastics in automotive applications; designed plasticizers and impact modifiers confer adequate levels of ductility while maintaining rigidity and strength, making PLA an interesting competitor of mineral-filled polypropylene for automotive parts possibly subjected to serious loading and unfavorable conditions (Notta-Cuvier et al. 2014).

PLA is used as a feedstock material for 3D printers (Rajpurohit and Dave 2019). Pure PLLA is used as a long-lasting volume enhancer in dermatologic surgery (Mazzuco and Sadick 2016).

PLA-based polymeric drug delivery systems were used for custom-made 3D printing of pharmaceutical products for controlled drug release (Water et al. 2015). 3D printing of PLA biomedical devices was realized using patient-specific anatomical data (Farah et al. 2016).

Durable applications of PLA have been significantly impaired by its inherent brittleness and limited thermal stability. These points, therefore, represent the main key-parameters to be improved for its industrial implementation.

Blending or copolymerization of PLA with another polymer are used to overcome these limitations, as illustrated in Sect. 6.5.

6.3 Polyhydroxyalkanote (PHA)

PHAs are linear polyesters of hydroxyacids synthesized by a wide range of bacteria through bacterial fermentation (Reis et al. 2011). Polyhydroxybutyrate was the first member of PHA to be discovered in 1926 (Li et al. 2016b). PHAs, particularly, are natural storage polymers of many bacterial species similar to polyethylene and polypropylene. PHAs synthesis is stimulated by unbalanced growth as part of a survival mechanism of the microbes (Hassan et al. 2013b). PHAs are storage biopolymers that accumulate in bacteria cytoplasm within granules of 0.2–0.7μm in diameter, especially if bacteria are grown in a media that is limited in a nutrient essential for growth (typically nitrogen or phosphorus) or under stressful conditions. If the carbon source is abundant, bacteria convert the extracellular carbon into these intracellular storage biopolymers that are energy and carbon reserve materials (Venkateswar Reddy and Venkata Mohan 2012). PHAs are then degraded and used for growth when the limiting nutrient is available and the starvation conditions for nitrogen and/or phosphorus are over (Reis et al. 2011).

Today there are more than 150 classes of PHAs, but the presence of refractive intracellular bodies due to these biopolymers was already reported by Beijerinck in 1888. The French microbiologist Maurice Lemoigne in 1925 determined that the formula of those granular inclusions in *Bacillus megaterium* was $(C_4H_6O_2)n$ (Lemoigne 1926). Researches and patents for the production of PHAs actually started only in the '70s (Albuquerque and Malafaia 2018).

The general molecular structure of PHAs is presented in Fig. 6.8. Depending on the carbon numbers in the 3-hydroxyalkanoate units, more than 150 different PHAs monomers are known, which renders them the largest group of natural polyesters.

Among others, poly(3-hydroxybutyrate) (PHB), poly(3-hydroxyvalerate) (PHV), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) can be easily obtained from fermentation reactions (Sudesh et al. 2000).

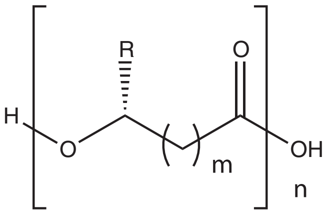


Fig. 6.8 PHA structure. Poly(3-hydroxybutyrate): R = methyl, m=1; Poly(3-hydroxyvalerate): R = ethyl, m=1; Poly(3-hydroxyhexanoate): R = propyl, m=1; Poly(3-hydroxyoctanoate): R = pentyl, m=1; Poly(3-hydroxydecanoate): R = heptyl, m=1; Poly(3-hydroxydodecanoate): R = nonyl, m=1

Over the past decade, enormous efforts have been put into the valorization of FW into PHAs, yet, technological advances to convert FW into PHAs are needed to profit from their commercialization with economic viability. The simplest and most common type of PHA is PHB.

PHAs have become one of the key drivers of the biodegradable polymers market after a long development stage; their production capacities continue to grow in the next years (Briassoulis and Giannoulis 2018).

Although 250 types of natural PHAs producers have been identified, including deep-sea bacteria (Numata et al. 2013), only a few prokaryotic microorganisms have been exploited for the commercial production of PHAs. *Alcaligenes latus, Bacillus megaterium, Cupriavidus necator, and Pseudomonas oleovorans*, are the most effective PHAs producers (Reddy et al. 2003). Marine bacteria, such as *Halomonas hydrothermalis, H. campaniensis LS21*, manifested a huge potential for bioplastic production since they do not need freshwater and can grow in FW-like mixed substrates (Tsang et al. 2019; Yue et al. 2014).

PHAs accumulating prokaryotic microorganisms can be broadly subdivided into two groups according to the chain length of the monomers they produce. Short-chain-length PHAs (SCL-PHAs) and medium-chain-length PHAs (MCL-PHAs) have monomers ranging from 3 to 5 carbons or from 6 to 16 carbons, respectively, in length.

6.3.1 FWs as Feedstocks

PHAs production cost is significantly higher than the capital cost of equipment and strongly influences the final PHAs price (Van Wegen et al. 1998). The current industrial expense for PHAs production (due to complicated bioprocessing, low conversion of carbon substrates, poor growth of microorganisms, difficult downstream separation, and high temperature fermenters sterilization) is the major hurdle for viable marketability of PHAs (Koller et al. 2005; Chen et al. 2020). Unadulterated cultures and mixed cultures are different cultivation strategies. Compared with pure culture technology, mixed culture costs less on sterilization. Genetic engineering is crucial to develop strains that are capable of efficiently producing PHAs from affordable renewable resources and contamination resistant bacteria, especially extremophiles, may push PHAs productions towards cost competitiveness and reproducible molecular weights, structures, and thermo- mechanical properties (Chen et al. 2020).

For these reasons, the substitution of virgin feedstock with FW represents a turning point because utilization of cheap FW as a carbon source seems a promising strategy. Wastewater from palm oil, olive oil, and hydrolysates of starch (e.g., corn and tapioca), cellulose, and hemicellulose are good putative feedstocks, viable from the economic point of view (Reis et al. 2011). Other food wastes used for PHAs production were banana residue (Naranjo et al. 2014), spent coffee grounds (Obruca et al. 2014a; Obruca et al. 2014b) distillery spent wash (Amulya et al. 2014), and margarine waste (Morais et al. 2014), dairy waste (RamKumar Pandian et al. 2010), whey (Amaro et al. 2019; Berwig et al. 2016), paddy straw (Sandhya et al. 2013), and other FW (Venkateswar Reddy and Venkata Mohan 2012).

Follonier et al. evaluated the potential of sugars and fatty acids derived from nine different fruit pomace and waste frying oil for the low-cost production of medium chain length PHAs by *Pseudomonas resinovorans* and waste frying oil as a resource for the bio-production of medium chain length polyhydroxyalkanoates. Apricot pomace was characterized by the lowest level of inhibitors, but the maximum PHAs production (21.3 g/L) was observed with grape pomace (Follonier et al. 2014).

Un-utilizable and toxic molasses spent wash was the feedstock for the production of PHB; a 52% removal of chemical oxidation demand was concomitant to a PHB accumulation of 28% (Khardenavis et al. 2009).

Several research groups focused on the bioplastic production cost analysis. Three case studies of biorefineries provide information on techno-economical possibilities and cost analysis of the PHAs production. Its economic viability is contingent on several factors (e.g., type, cost, and availability of waste generated in the selected area, processing and transport cost of the biomass, and general industrial expenses). The first case study focused on palm oil waste; the milling activity results in 50–70 tons of biomass waste per ha of palm plantations (Tsang et al. 2019). The waste biomass can be further utilized for the generation of biofuels for combined heat and power plants, ethanol and methane production, or composting, briquette and medium-density fiberboard construction, and pulp and paper manufacture (Chiew and Shimada 2013). Anyhow, non-food sugars produced from palm fronds (i.e., around 42.8 wt% of glucan, 12.5 wt% of xylan, and 2.3 wt% of arabinan) can be used for economical production of the most frequently studied and characterized PHA, that is PHB (Zahari et al. 2015) (Tsang et al. 2019). Its cost can be drastically reduced compared to using commercial glucose by using the renewable sugars contained in palm frond.

In the second case, the rejected and wasted proportions of total banana crops, which can be more than 30%, were used as a precious source for glucose, ethanol, and PHB production in a biorefinery (Naranjo et al. 2014; Quinaya and Alzate 2014). The study demonstrated that if the PHAs production is embedded into a multiproduct biorefinery, the economic and environmental availability of the process through energy and mass integration strategies is improved: the former can reduce up to 30.6% the global energy requirements of the process, and the latter allows a 35% in water savings. The optimal use of energy and water resources decreases both the production cost and the negative environmental impacts (Naranjo et al. 2014).

In the third case, techno-economic and environmental analysis for the production of ethanol, PHB, and electricity from sugarcane bagasse demonstrated that the use of a biorefinery could reduce the selling price of PHB by 50%, making it competitive with typical fossil plastic (Moncada et al. 2013).

6.3.2 Biosynthesis

PHA is biosynthesized via glycosylation or β-oxidation pathway. For example, the genes for the synthesis of PHB reside within an operon that includes a β-ketothiolase, an acetoacetyl- coenzyme A reductase, which synthesize the monomeric substrate 3-hydroxybutyryl CoA, and a PHA synthase, which polymerizes this monomer to form PHAs (Pohlmann et al. 2006). With respect to the synthesis of PHAs by the β-oxidation pathway, 2-enoyl-CoA hydratase and 3-ketoacyl-acyl carrier protein reductase are known to be responsible for converting 3-enoyl-CoA and 3-ketoacyl-CoA into (R)-3-hydroxyacyl-CoA (Fiedler et al. 2002). The PHA synthase plays a crucial role in the synthesis of high-performance PHAs because its substrate specificity and specific activity affect the monomeric compositions of the resulting PHA (Rehm 2003).

The biosynthesis process of PHA practically goes through as substrate preparation, enzymatic hydrolysis, PHA-accumulating fermentation, and PHA extraction and drying from the PHA-rich biomass (Serafim et al. 2008).

An initial acidogenic fermentation of the feedstock often proved to be very important for the PHA synthesis. The initial acidogenic fermentation is needed to make the waste suitable for PHAs production; in fact, waste carbohydrates would be stored as glycogen and not PHA; on the converse, VFA obtained in the acidogenic fermentation of carbohydrates are readily convertible into PHAs (Reis et al. 2011). A three-stage biotechnological process made use of waste-based feedstocks, and comprised an initial acidogenic fermentation of the feedstock, the second phase of selection of PHA-storing bacterial biomass, and the last phase in which PHA was stored in batch conditions (Reis et al. 2011). Integration of acidogenic fermentation with PHA production increased the biopolymer yield (Venkateswar Reddy and Venkata Mohan 2012: Amulya et al. 2015) due to the ready availability of VFA. Zhang et al. (2014) highlighted that the consumption of even-numbered VFAs or odd-numbered VFAs was correlated, respectively, with the PHB or PHV synthesis. Interconnections of biotechnological pathways enable the co-production of biofuels and bio-products, thereby maximizing FW utilization (Venkateswar Reddy et al. 2014).

6.3.3 Properties and Uses

PHAs have great potential as a substitute for traditional plastics since they are strong, tough, and moisture resistant; their performance regarding heat resistance and barrier properties may mimic that of PVC and PET even if they are more rigid and less thermally stable than many fossilbased plastics (Zhao et al. 2020); their characteristics are tunable by the monomeric composition, selection of microbial production strain, substrates, process parameters during production, and post-synthetic processing. They are acknowledged as better oxygen barrier (than PE and PET), better water vapor barrier (than PP), and good fat/odor barrier. Their biodegradability and rubbery-like properties, their thermoplastic properties (similar to those of the fossilbased plastics) as well as their peculiar properties have prompted their usage in various fields. They represent biological alternatives for diverse technomers of petrochemical origin. Their hydrolytic degradation products are nontoxic and demonstrate their potential for applications in the medical sector. Similarly to PLA, PHAs can be biodegraded via composting and under anaerobic conditions: in the first case, the process lasts less than four months, while only two weeks are needed for the anaerobic biodegradation; biodegradability is less than and 10% and 50% in aquatic and soil environments, respectively, after one year (Folino et al. 2020).

PHA can be processed with usual methods such as injection molding, extrusion, thermoforming, film blowing, etc. For example, PHA can be transformed into injection-molded items such as film and sheet, fibers, laminates, and coated articles. There is a broad range of PHA-based marketable products for a variety of applications, including food packaging, disposable bottles, and water-resistant film, paints, adhesives, nonwoven fabrics, synthetic paper products, waxes, foams. They are important for agroindustrial applications (carriers and matrices for controlled release of nutrients, fertilizers, and pesticides), therapeutic applications (controlled release of active pharmaceutical ingredients), as well as for medical and pharmaceutical applications (bone, nerve, cardiovascular, and cartilage tissue engineering, 3D constructs, implants, chiral substrates for drug synthesis and drug delivery) (Van Wegen et al. 1998; Ahmed et al. 2018; Chen and Patel 2012; Liang and Qi 2014; Koch and Mihalyi 2018).

Unfortunately, the applications of PHAs are restricted due to several undesirable physical properties.

Due to poor PHA mechanical properties and the high costs for their microbial production, insufficient production volume, relatively slow crystallization rates, narrow thermal processing window, high hydrophobicity, and high brittleness, PHA exploitation was mostly limited to academic research (Chen et al. 2013), and the utilization of PHAs as direct substitutes for synthetic plastics was a major challenge.

For example, large crystals in PHB cause poor mechanical properties; its thermal processing window is narrow because the melting and decomposition temperatures are similar, and this renders PHB susceptible to thermal degradation. Modification of PHA properties by side-chain adjustment does not tackle the optimization of the properties efficiently, hence blending or copolymerization was also explored (Li et al. 2016b).

Copolymerization, blending, and composite making have been explored in order to modify PHA properties; in this context, the reduction of hydrophobicity and the increase of biodegradability are the focus of interest of biomedical application research (Samui and Kanai 2019). Cost competitiveness and reproducible molecular weights, structures, and thermo- mechanical properties can be obtained by genetically engineered strains and contamination resistant bacteria (Chen et al. 2020).

6.4 Polybutylene Succinate (PBS)

Succinic acid and 1,4-butanediol are building blocks for synthesizing PBS (Su et al. 2019), whose structure is illustrated in Fig. 6.9.

PBS is a well-known biobased thermoplastic aliphatic polyester with interesting thermo-mechanical properties comparable to polypropylene, the second largest polymer (~55million t/year worldwide); thus the potential application area is enormous (EU 2015) also taking into account its proven biodegradability and compostability (according to DIN EN 13432). However, PBS would hardly be a polypropylene competitor due to the cheapness of the latter (EU 2015). PBS is used for blending with starch polymers to improve properties.

In the 1930s, Wallace Hume Carothers, capitalized on previous work by Lourenço (1863), Davidoff (1886), and Voländer (1894) about the esterification of succinic acid and ethylene glycol and begun a more systematic study of succinic acid based polyesters. The elimination of water on a continuous distillation process leads to polymers with molar masses significantly higher than what was previously synthesized (Carothers and Arvin 1929). The study was prompted by the need to find a synthetic alternative to natural silk fiber; since the properties of the final products

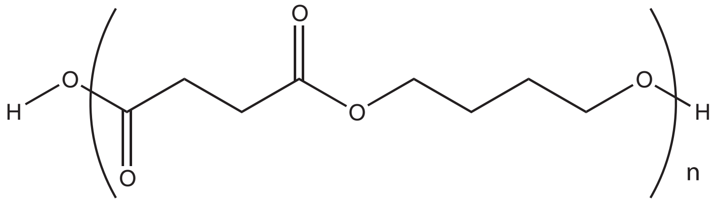


Fig. 6.9 PBS structure

did not show the expected qualities, Carothers focused on polyamides and invented with his colleague Julian Hill Nylon 6,6.

At the beginning of the 1990s, after being forgotten for more than 40 years (Flory and Leutner 1952), these polymers came into the spotlight due to the increasing demand for biodegradable and biobased polymers. PBS is commercially available since 1993 (Gigli et al. 2016).

6.4.1 FW as Feedstocks

For a complete biobased PBS, its biobased building blocks, namely succinic acid and 1,4-butanediol, are required.

Succinic acid was recognized as a key sugar-based building block; according to the U.S. Department of Energy, it is a platform molecule with high-value niche applications such as personal care products and food additives, but also large volume applications such as bio-polyesters, polyurethanes, resins, and coatings. Moreover, it can be used as the precursor of various commodity chemicals, including 1,4-butanediol, which is the other building block of PBS, but also tetrahydrofuran and γ-butyrolactone, which have a wide range of applications ranging from detergents to pharmaceuticals (Werpy and Petersen 2004; Bozell and Petersen 2010; EU 2015). Succinic acid has mostly been produced by chemical processes from fossil feedstocks, via hydrogenation of maleic anhydride, but the biotechnological production of succinic acid from renewable biomass by anaerobic bacteria came into the limelight because succinic acid is an intermediate of the tricarboxylic acid cycle; it is a dicarboxylic acid produced as a fermentation product of anaerobic metabolism (Gottschalk 1986). Various FW have been explored as succinic acid feedstock, and several microorganisms have been screened and tested for the biotechnological production of succinic acid with good yields, as discussed in Sect. 5.4.2 (Bechthold et al. 2008).

1,4-Butanediol is a colorless, viscous liquid industrially used as a solvent in industrial cleaners and in the manufacture of valued polymers such as polybutylene terephthalate, synthetic polyether polyurea fibers, and polyurethanes. It was first commercially manufactured in 1930 through the reaction of formaldehyde with acetylene and subsequent hydrogenation (Reppe process), and this process still accounts for about 42% of global production. Anyhow, in the petrochemical industry, 1,4-Butanediol can be produced in various ways from maleic anhydride, propylene oxide, and butadiene (EU 2015). Biobased 1,4-Butanediol is regarded as a direct drop-in chemical. Its production can either take place via direct fermentation of sugars or via the hydrogenation of biobased succinic acid. The biobased 1,4-butanediol manufacture process is not performed worldwide on a large scale yet, but its production is increasingly supplemented by biotechnological processes; recently, a genetically modified *Escherichia coli* strain was used under microaerobic conditions to convert glucose into 1,4-Butanediol (Pooth et al. 2020). Metabolic engineered bacterial synthesis represents an emerging and advantageous technology, alternative over the succinic acid hydrogenation route, with a lower risk of market fragmentation, thanks to the use of more abundant and low-cost feedstock, such as wheat straw (Forte et al. 2016). Although a complete sugar-based PBS can be made, nowadays, it is mostly fossilbased; oil price fluctuations and consumers' inclination for biobased products will probably influence future PBS production (Zhao et al. 2020).

6.4.2 Synthesis

A two steps esterification of succinic acid with 1,4-butanediol is the most common way to produce PBS. First, an excess of the diol is condensed with the diacid to form PBS oligomers with the elimination of water. Secondly, these oligomers are trans-esterified, in the presence of titanium-, zirconium-, tin- or germanium-based organometallic or metal-oxide catalysts, under vacuum, to form a high molar mass polymer. Titanium(IV) butoxide is the most common catalyst (Su et al. 2019). PBS can be produced via melt polycondensation at moderate costs.

Diisocyanates, typically hexamethylene diisocyanate, are used as chain extenders to obtain high molecular weight PBS, reducing brittleness and increasing elongation at break (Gigli et al. 2012b).

The enzymatic synthesis of PBS made use of lipase from *Candida Antarctica* (Azim et al. 2006). The ability of lipases to catalyze the direct polycondensation of a linear aliphatic diacid and a diol increases with increasing the monomer chain length. The diffusion of this greener route was hampered by enzyme leaching and inactivation, and the use of solvents to avoid polymer precipitation (Gigli et al. 2016). Further optimization of the process is likely to reduce biobased PBS price.

6.4.3 Properties and Uses

PBS is a semicrystalline polymer with high crystallization ability (35–45%) (Soccio et al. 2008), and its melting temperature (115 °C) (Gigli et al. 2012b; Xu and Guo 2010) is important for applications that require a high temperature range. Noteworthy, its mechanical performance mimics that of PP and PE (Zhao et al. 2020). Due to a glass transition temperature much lower than room temperature, PBS has a wide processing/temperature window (Fabbri et al. 2014).

Its wide temperature window for thermoplastic processing makes the resin appropriate for extrusion, injection molding, thermoforming, and film blowing; however, its stiffness and melt viscosity for processing are often insufficient for various end-use applications (Gigli et al. 2016).

PBS commercialization is mainly devoted to biodegradable food packaging (tea cups, plates and bowls, coffee capsules, food service ware, and catering products) and compostable bags, and other disposable items; PBS is also used in agriculture and fishing sectors for the production of mulching films and fishing nets, respectively; nonwoven textiles, diapers, and foams in PBS were also produced. PBS is also significant in the automotive sector (wood-PBS composites, composites with natural fibers), in electronics and other consumer goods applications. PBS and its copolymers are particularly expedient in biomedicine emerging topics, such as controlled drug release by microspheres or nanocarriers and tissue engineering via films and scaffolds (produced by salt leaching, electrospinning, or extrusion) but only a few examples of in vivo studies regarding PBS and PBS-based systems are present in the literature; hence more exploration on its biocompatibility is needed to validate the possibility to employ this polymer in biomedicine (Gigli et al. 2016).

Materials must fulfill strict requirements to be employed as biomaterials regarding biocompatibility, mechanical properties, and biodegradation rate (Vert 2009). The quite slow hydrolysis rate under physiological conditions (due to the high crystallinity and hydrophobicity of this polymer (Soccio et al. 2012)) and low flexibility of PBS could hinder its uses for certain applications; therefore, blending and/or copolymerization have been used to fine tune surface wettability, degree of crystallinity, mechanical properties and biodegradation rate; chitosan and hydroxyapatite, are important fillers in this respect (Gigli et al. 2016). Polybutylene Succinate Adipate (PBSA) is one of the most promising PBS copolymers.

As regards PBS biodegradation, *Amycolatopsis* sp. HT-6 and several thermophilic actinomycetes such as *Microbispora rosea*, *Excellospora japonica*, and *E. viridilutea* can degrade PBS (Tokiwa et al. 2009). PBS can be biodegraded by composting (90% in three months), but the biodegradation in anaerobic (landfill), soil, and aquatic environments is not easy (Folino et al. 2020). PBS ionomers with improved hydrodegradability containing sulfonated succinate units have been synthesized and characterized (Bautista et al. 2015).

Table 6.1 illustrates exemplary physical properties of PBS, PBSA, PLA, PHA (explained in Chaps. 8 and 9) compared to fossilbased polymers: it has to be emphasized that reported data may be different from other literature data for the same physical properties of the same material because of the difference in molecular weight, production processes, and so on.

6.5 Polyglycolic Acid (PGA)

Polyglycolic acid is the simplest polyester; it is a thermoplastic and biodegradable linear, aliphatic biopolymer. Similarly to PLA, it can be prepared starting from glycolic acid by means of polycondensation or ROP. PGA has been known since 1954, and since it is a tough fiber-forming polymer, in 1962, it was used to develop the first synthetic absorbable suture (Gilding and Reed 1979).

Table 6.1 Exemplary physical properties of PBS, PBSA, PLA, PHA (explained in Chaps. 8 and 9) compared to fossilbased polymers (Xu and Guo 2010; Weise et al. 2018; Farah et al. 2016; Su et al. 2019 ; Rivero et al. 2016; Johansson et al. 2012; Kim et al. 2005; Totaro et al. 2016; Bugnicourt et al. 2014; Chaiwutthinan et al. 2013; Avérous and Pollet 2012; Ojijo et al. 2012b; Sasa et al. 2011; Gigli et al. 2016; Numata et al. 2013; Bugnicourt et al. 2014; Zhao et al. 2020; Södergård and Stolt Stolt 2002; Middleton and Tipton 2000)

	PBS	PBSA	PLA	PHA	HDPE	LDPE	PS	PP
Glass transition temperature (Celsius)	−32	−45	55–65	2	−120	−120 to −40	105	−5
Melting point (Celsius)	114–115	83.1−96	140–180	160–175	129	110	Amorphous	163–186
Heat distortion temperature (HDT-B, Celsius)	97	69	55	–	82	49	95	110
Tensile strength (MPa)	26.5–34	19	50–70	15–40	24–32	10–12	24–60	33–34.5
Tensile modulus (GPa)	0.71	0.16	2.7–16	1–2	0.5	0.3	3.4	1.4
Elongation at break (%)	8–560	807	4–7	1–17	150–700	300–500	3–4	100–415
Flexural strength (MPa)	36.5	–	48–110	–	21	6	80	49
Notched Izod impact (J/m)	300	>400	29	22–35	40	>400	19–150	20
Degree of crystallinity (%)	34–45	20–30	0–40	40–70	69	49	0	56-60
Density (g/cc)	1.22	1.23	1.25	1.17–1.25	0.95	0.92	1.05	0.91–0.94

6.5.1 FWs as Feedstocks

The monomer of PGA is glycolic acid (GA); it is a platform chemical that is currently produced by petrochemical synthesis, in a process where formaldehyde is carbonylated, but its biotechnological and sustainable production from renewable resources is receiving substantial interest.

GA is formed from the glyoxylate shunt route. D-glucose, D-xylose, ethanol, and acetate have been experienced as substrates by using hosts *E. coli*, *C. glutamicum*, *S. cerevisiae,* or *K. lactis*. Genetic modifications aim to enhance the flux from isocitrate to GA via accumulation of isocitrate (through deletion of genes encoding isocitrate dehydrogenase and malate synthase) or overexpression of isocitrate lyase and glyoxylate reductase encoding genes (Salusjärvi et al. 2019).

It is important to design metabolic pathways that make use of naturally producing glycolic acid microorganisms (chemolithotrophic iron-and sulfur-oxidizing bacteria, *Alcaligenes sp*. ECU0401, and a variety of yeast and acetic acid bacteria) and enable utilization of several carbon sources at the same time from various renewable feedstocks as FW streams rich in sugars and starch, lignocellulosic waste, and even gaseous substrates (CO_2, CO and H_2) (Salusjärvi et al. 2019; Jha and Kumar 2019).

6.5.2 Synthesis

Low molecular weight PGA was first synthesized in 1932 by Carothers (Carothers et al. 1932). In the 1950s, DuPont patented a method for synthesizing high-molecular-weight PGA (Lowe 1954). It was known as a tough fiber-forming polymer. Nowadays, it is an extremely expensive, high value-added product; it follows that technology to permit inexpensive mass production is highly desirable.

High-molecular-weight PGA is commonly synthesized via a ROP from highly purified glycolide (GL) in the bulk condition since polycondensation starting from glycolic acid would only give oligomers, as shown in Fig. 6.10. Unfortunately, the viscosity of the generated polymer increases with increasing polymerization time as the chain length increases during the reaction. Agitation difficulties impair the efficiency of the method, which needs to be manufactured in batches using small-scale apparatuses. A process to obtain high-molecular-weight PGA continuously from the intermediate GL, with high levels of purity, was experienced in a commercial production plant at a lower cost than previously possible using a temperature range

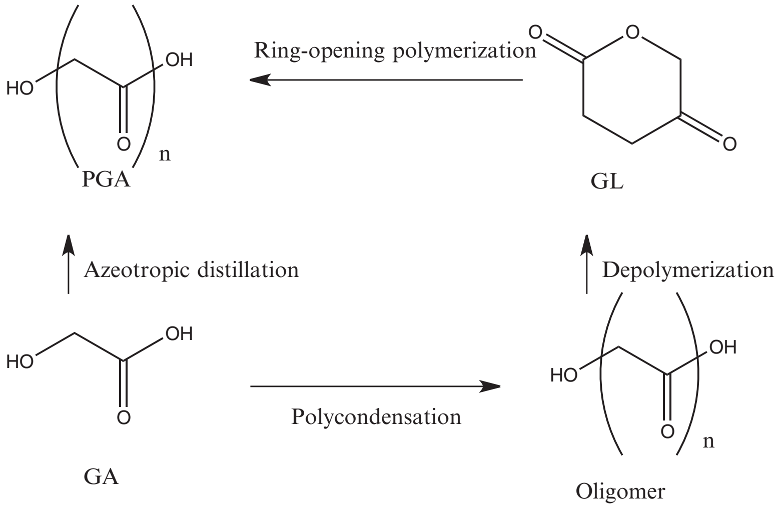


Fig. 6.10 PGA preparation technologies

between the melting point of the GL (~90 °C) and the melting point of high-molecular-weight PGA (~220 °C). This way, the polymerization is firstly induced in the molten state, then the polymer is precipitated as a solid, and polymerization is promoted in the solid state so that high-molecular-weight PGA is generated (Yamane et al. 2014).

The ROP was considered restrictive because of the high cost of the raw material (glycolide) and the associated high energy consumption. The direct synthesis of PGA via an azeotropic distillation (Fig. 6.10) parallels that for the PLA production; it enables tunable molecular weights, better solubility in organic solvents, and faster degradation than reference PGA (Sanko et al. 2019).

The cationic alternating copolymerization of formaldehyde (from trioxane) and carbon monoxide (CO), a sustainable C1 feedstock obtainable from biomethanol or biogas, constitutes an inexpensive and efficient pathway for the synthesis of PGA, by-passing the standard route involving glycolide. PGA was successfully synthesized with yields up to 92% from trioxane and CO, with triflic acid initiator at 170 °C over 3 days. The chemico-physical characterization of the polymer via ^{1}H NMR, ^{13}C NMR, and FT-IR spectra, is consistent with that of the commercial one, prepared from the ROP of glycolide. Molecular weight analysis suggested the formation of oligomers, which can be converted into high molecular weight PGA *via*: (i) their post-polymerization polycondensation, catalyzed by $Zn(OAc)_2 \cdot 2H_2O$; (ii) inclusion of glycerol as a branching agent during the C1 copolymerization (Göktürk et al. 2015).

6.5.3 Properties and Uses

The glass transition temperature of polyglycolide is between 35 and 40 °C and its melting point is in the range of 225–230 °C. The high degree of crystallinity, around 45–55%, results in its insolubility in water and almost all common organic solvents (Budak et al. 2020). It offers high mechanical strength and high gas-barrier performance. The ester linkage in the PGA backbone provides hydrolytic instability. The degradation process is erosive: the polymer is converted back to its monomer glycolic acid due to water diffusion firstly into the amorphous (non-crystalline) regions and then into the crystalline regions of the polymer matrix, cleaving the ester bonds. Under physiological conditions, PGA is hydrolyzed, and it is also broken down by certain enzymes, especially those with esterase activity; hence biodegradation is faster in vivo than in vitro. The glycolic acid monomers can enter the tricarboxylic acid cycle, or they can be excreted by urine (Wada 2007).

PGA finds important applications in the biomedical practice because of its expedient mechanical, biocompatible, and biodegradable properties (Budak et al. 2020). Its hydrolytic instability is a drawback for many applications, but currently, polyglycolide and its copolymers with lactic acid, ε-caprolactone, and trimethylene carbonate are widely used for the synthesis of absorbable sutures, and are being evaluated for other applications in the biomedical field. The bioresorption /

degradation process in the body into water-soluble absorbable monomers lasts a few weeks depending on the PGA molecular weight; it has been explored for implantable medical devices (anastomosis rings, pins, rods, plates, and screws) and tissue engineering or controlled drug delivery. PGA nerve conduits proved to be an effective artificial biodegradable peripheral nerve regeneration-inducing tube (Fujimaki et al. 2019). Production of high molecular weight PGA is needed to achieve sufficient mechanical stability for biomedical applications (Sanko et al. 2019) and for food packaging applications; in this case, tin (II) based catalyst needed to give high molecular weight PGA should rather be removed from the produced PGA since tin (II) compounds are known to be toxic (Budak et al. 2020). Copolymerization and blending are often used for a fine tuning of PGA properties, as described below. The use of ultra-strong and biodegradable PGA in shale gas and oil exploration is of great interest (Yamane et al. 2014).

6.6 Biobased Thermosetting Polymers

6.6.1 Phenolic Resins

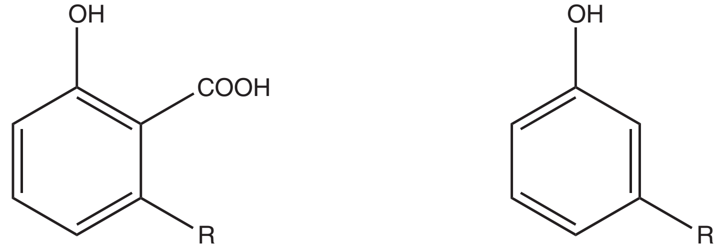
Phenolic resins are synthesized from phenol (or substituted phenols) with formaldehyde. They were the first commercial synthetic plastics (Bakelite), widely used for the production of molded products, including billiard balls, coatings, and adhesives, and the first circuit boards.

There are many variations in both production and input materials that are used to produce a wide variety of resins for special purposes.

Biobased phenols from FW have been studied for fully biobased phenolic resins. Cashew nut shell liquid, an agricultural by-product of cashew *(Anacardium occidentale)* processing, is abundantly available in tropical countries. It represents one of the major and economical resources of naturally occurring phenols. Cashew nut shell liquid is a reddish-brown viscous fluid containing four major components, namely cardanol, cardol, anacardic acid and 2-methylcardol (Voirin et al. 2014). They are phenolic lipids, illustrated in Fig. 6.11, with varying degree of unsaturation in C15 alkyl side chain at the meta position.

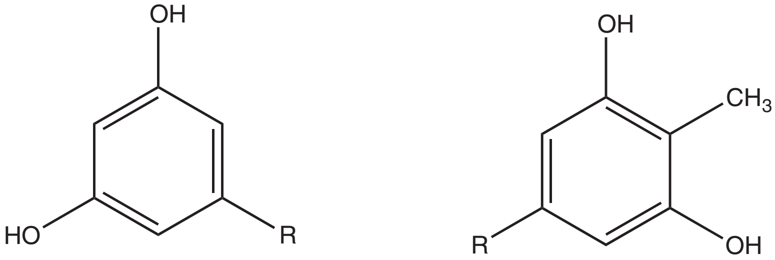
Cardanol can react with formaldehyde to form novolac resin (using excess phenol and an acid or metal salt catalyst) or resole resins (using excess formaldehyde and a basic catalyst) with improved flexibility compared with conventional analogs (Quirino et al. 2014) due to the side chains. They also impart a hydrophobic nature to the polymer, making it resistant to moisture and weathering.

Chemical modifications of cardanol can be made at the reactive phenolic group, or on the mono/di/tri unsaturated side chain in the meta position; π-π stacking and functionalization of the aromatic ring have also been studied and a wide gamut of cardanol-based amphiphiles and other functionalized monomers are reported for the synthesis of fine chemicals and polymers (John et al. 2019).



Anacardic Acid

Cardanol



Cardol

2-Methyl cardol

Fig. 6.11 Phenolic compounds present in cashew nut shell liquid

Lignin is a by-product derived from the wood pulp in the paper industry, but it is also contained in many agro-industry wastes. Up to 98% of overall lignin is utilized as a (bio)fuel. Due to its phenolic moieties (Laurichesse and Avérous 2014), lignin is a good candidate as another natural substitute for phenolic building block for phenolic based resins with innovative macromolecular architectures (Kouisni et al. 2011).

Tannin compounds extracted from vegetal sources can also be considered renewable building blocks in the design of phenolic resins (Barbosa et al. 2010).

6.6.2 Epoxy and Polyurethane Resins

Epoxy resin is a thermosetting material whose synthesis relies on the high reactivity of the epoxy moiety to many functional groups such as carboxyl, amino, and hydroxyl groups. Polyepoxide networks represent a major class of thermosetting polymers. Owing to their singular mechanical and electrical properties, chemical resistance, and minimal shrinkage after curing, they are extensively used as coatings, in electronic materials and integrated circuit boards, in adhesives and structural carbon fiber adhesives, as in structural applications as well.

Most epoxy resins are industrially manufactured from bisphenol A via the glycidylation route with epichlorohydrin to produce the diglycidyl ether of bisphenol A. Bisphenol A is considered an endocrine disruptor; its toxicity, due to significant hormonal activity, and legal issues stimulate an increasing number of studies on its replacement with natural sources of epoxy monomers both from the academic and industrial sides (Ng et al. 2017).

Waste oils represent a potential low-cost material for the production of resins. The main constituents of oils are triglycerides. They are formed from glycerol and three fatty acids whose chains contain from 8 to 24 carbons. They can be saturated or comprise up to 5 non-conjugated C=C double bonds in the cis- configuration. Longer chain fatty acids characterize marine fats.

The composition of fatty acid differentiates one vegetable oil from another; for example, ricinoleic acid characterizes castor oil, a vegetable oil of significant importance to the industry. The most common fatty acids are detailed in Fig. 6.12.

Oils are quite nonreactive raw materials but the introduction of functional groups at sites suitable for the chemical attack (double bonds, ester bonds, and allylic positions to double bonds) make them more reactive. Different synthetic strategies for the preparation of useful polymeric materials starting from waste oils are possible. The direct polymerization of the double bonds suffers the lack of active functional groups, but heating the oil above 300 °C induces the formation of conjugated diene (if fatty acids containing more than one double bond are present); the presence of dienophiles makes the process proceeds through Diels-Alder addition (Petrović 2010); anyhow this kind of triglyceride-based materials is not very useful for structural applications.

For this reason, triglycerides are often chemically modified and then polymerized. Vegetable oils can be converted into useful polymerizable monomers by epoxidation with a peroxy acid (Prilezhaev-epoxidation), catalytic epoxidation via acidic ion exchange resin, metal-catalyzed epoxidation, or chemo-enzymatic epoxidation. The latter epoxidation method is safe, environmentally friendly, and has a high conversion rate of epoxidation (90%) (Tan and Chow 2010).

Soybean oil, fish, and castor oil can be epoxidized at the C=C double bonds. Figure 6.13 illustrates epoxidized linolein, one of the major components of epoxidized soybean oil.

Epoxidized oils as such are used as plasticizers and hydrochloric acid scavengers in PVC items such as cling film for wrapping foods and toys, among others.

Anyhow, the importance of epoxidized vegetable oils (soybean and linseed oils) stems from the fact that they are among the few biobased epoxy building blocks that reach industrial-scale production and can replace the glycidyl ether of bisphenol A, which is the main epoxy monomer.

The possibility of using epoxidized vegetable oils as sustainable substitutes of epoxy monomers for biobased epoxy thermosetting polymers (Petrović 2010) has

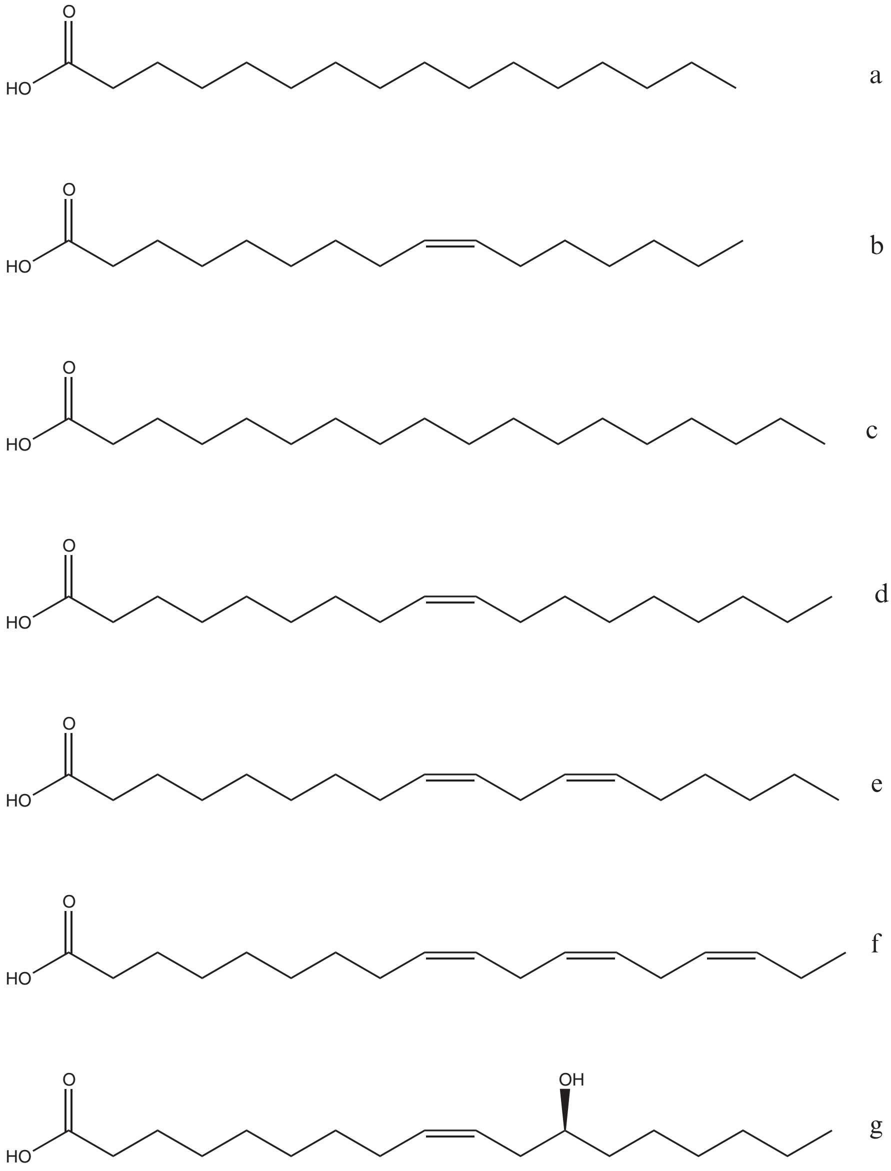


Fig. 6.12 Common fatty acid found in vegetable oils. (**a**) palmitic (C16:0); (**b**) palmitoleic (C16:1); (**c**) stearic (C18:0); (**d**) oleic (C18:1), (**e**) linoleic (C18:2); (**f**) linolenic acids (C18:3), (**g**) ricinoleic acid (C18:1, OH)

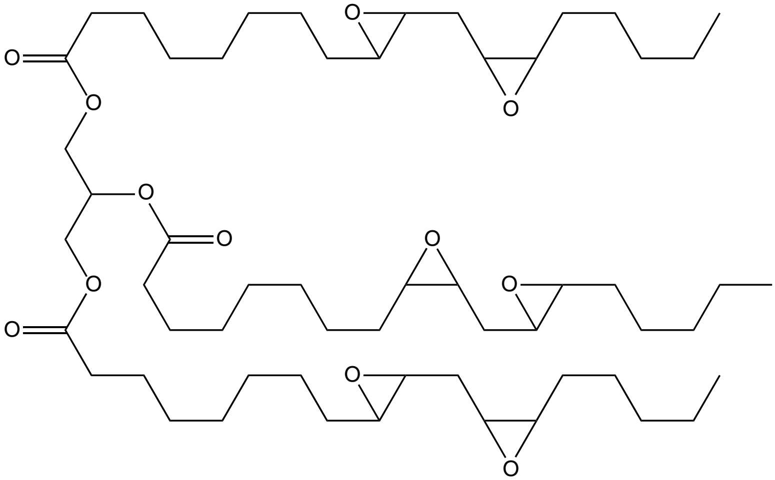


Fig. 6.13 Epoxidized linolein

been known for decades. The oxirane ring is more reactive than the double bond, thus providing an energetically favorable site for the reaction. Epoxidation of the double bonds of waste oils and on the *meta* alkyl chain of cardanol was also used for the preparation of epoxy resins (John et al. 2019).

Novel biobased epoxy resins were prepared from waste vegetable oil by epoxidation using hydrogen peroxide in acetic acid. Acid hardeners such as citric acid, tartaric acids, sebacic acids, and succinic anhydride were used. Thermal stability up to 350 °C, biodegradability, and biocompatibility based on blood clotting studies were demonstrated (Yemul et al. 2016).

Unfortunately, due to the lack of cycloaliphatic or aromatic rigid structures, the resulting polymers usually have a low strength; hence they have been considered for non-structural, additive applications, such as plasticizers or stabilizers. The replacement of the diglycidyl ether of bisphenol A, which allows covering all applications by a single biobased epoxy monomer, is still difficult. Biobased rigid aromatic epoxy monomers are needed in order to enable replacement of bisphenol A and obtain a compromise between easy processing and good properties; in this respect, natural sources of aromatic moieties, bearing reactive groups suitable for the introduction of epoxy moieties, include (i) eugenol extractable from natural plant oils, (ii) polyphenolic cross-linked polymers such as tannins and lignin that can be functionalized or depolymerized into smaller fragments prior to epoxidation steps, (iii) terpenes, terpenoids and their synthetic derivatives, such as carvacrol, which can be synthetically obtained from limonene or directly isolated from oregano and thyme essential oils (Ng et al. 2017).

Recently a fully biobased epoxy resin from fatty acids and lignin was designed to counterbalance for that deficit of stiffness: lignin reacts with the epoxidized vegetable oil, and it gets incorporated in the structure; epoxy groups still available after the reaction were cured, as usual, upon addition of a diamine (Ortiz et al. 2020).

Glycidyl esters of epoxidized fatty acids derived from soybean oil and linseed oil proved to yield mechanically stronger polymerized materials than materials obtained using epoxidized oils. They were synthesized using epichlorohydrin to have higher oxirane content and increased reactivity. They have the potential for fabrication of structural epoxy matrixes (Wang and Schuman 2012).

Sugar-based glucopyranoside- and glucofuranoside-based renewable epoxy resin were also investigated: they can be useful if bending stresses higher then the tensile ones are required (Niedermann et al. 2015).

Epoxidized vegetable oils can also undergo oxirane ring-opening with hydrochloric acid, hydrobromic acid, methanol, hydrogen, and water; hence, the resulting polyol structures can be halogenated, methoxylated, and vicinal hydroxy groups are also possible (Guo et al. 2000; Petrović 2010). These variegated biobased polyols can further react with diisocyanates made from petroleum-resources to provide polyurethanes comparable in many aspects with those obtained from petrochemical polyols (Lligadas et al. 2010).

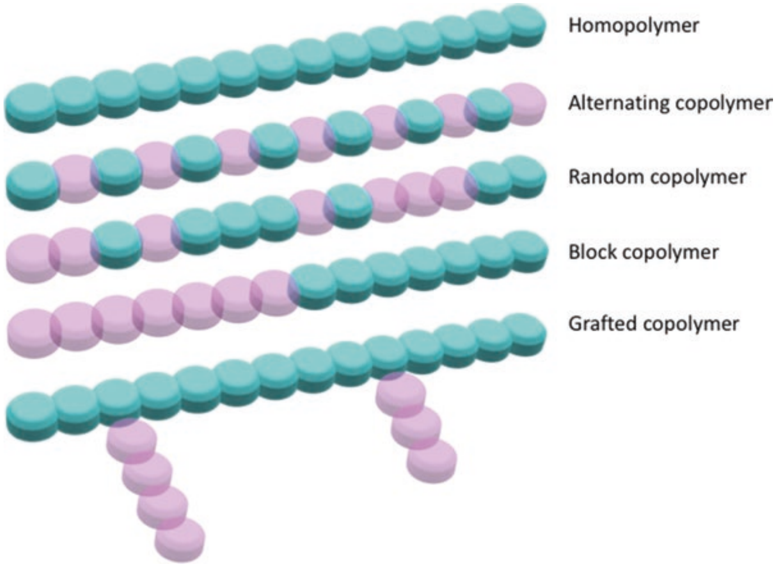


Fig. 6.14 Common types of polymers

6.7 Copolymerizarion and Blending

Processability and tailor-made modifications of the properties of polymers have attracted the attention of both academia and industry to meet specific needs. Copolymerization and blending and are the frequently used methods to alter the properties of polymers.

Copolymerization is the polymerization of more than one monomer species into copolymers; it follows that copolymers consist of at least two types of constituent units. Copolymers architecture can be linear or nonlinear, as illustrated in Fig. 6.14.

Linear copolymers are classified as alternating, periodic, random (statistical), and block copolymers according to the composition and arrangement of the repeating units. In stereoblock copolymers, the units differ only in the tacticity of the monomers.

Nonlinear copolymers are classified as branched copolymers with varying architectures. Graft copolymers are characterized by side chains structurally distinct from the main chain. For example, the main chain repeating unit is the monomer, and branches are formed from another species monomer: the side-chains have constitutional or configurational features that differ from those in the main chain. Moreover, the individual chains of a graft copolymer may be homopolymers or copolymers.

Blending is obtained when at least two thermoplastics macromolecular substances (polymers or copolymers) are mechanically mixed together in the melt state to create a new material with different and hopefully improved physical properties. Polymer blending aims at the suppression of the drawbacks of the parent components. Normally, the physical and mechanical properties of polymer blends can be tailor-made by the judicious selection of the components, optimization of the blend composition and adequate tuning of the preparation conditions. Plastic blends parallel metal alloys and their development represents an easy and cost-effective method of developing versatile polymeric materials for commercial applications.

Polymer blends can be broadly classified as:

- heterogeneous (immiscible polymer blends): in this case, that is the most common, two glass transition temperatures will be observed because the blend is not a single-phase structure
- homogeneous (miscible polymer blends): the single-phase structure results in a single glass transition temperature.
- compatible polymer blends: they are immiscible polymer blend that exhibits macroscopically uniform physical properties because of the strong interactions between the component polymers.

Physical blending is often challenged by the compatibility of most polymer pairs; the performance may be impaired by blending, and quantitative analyses of miscibility-structure-properties correlations (Imre and Pukánszky 2013) are needed to get insights into the chemistry of the process.

According to the rule of mixtures (Eq. 6.1), the properties of homogeneous polymer blends (σb) are obtained from the linear combination of the respective properties of the components (σ1 and σ2) multiplied by their volumetric fraction in the blend (f represents the volumetric fraction of component 1):

$$\sigma b = f\sigma 1 + \left(1 - f\right)\sigma 2 \tag{6.1}$$

The mechanical behavior of immiscible polymeric blends generally deviates from the rule of mixtures.

Most polymer pairs are thermodynamically immiscible because of their poor interactions. Compatibility in such polymeric systems is a function of the chemical structure and interfacial interactions. The vast majority of biopolymer-based blends available on the market are compatibilized. Different strategies of compatibilization can be distinguished. In the case of nonreactive compatibilization, pre-made amphiphilics, (Imre et al. 2019) able to interact with the respective polymers in both phases, are often used. The compatibilizer is often a diblock or triblock copolymer with a chemical structure identical to that of the main components, which exerts its activity at the components interface in order to enhance interfacial adhesion and to decrease the interfacial tension. Similarly, the use of low molecular weight compounds, ionomers, or a third polymer at least partially miscible with both blend components has also been explored (Imre and Pukánszky 2013).

Reactive methods are more efficient than nonreactive compatibilization because the blocky structures possess reactive groups that act as compatibilizers during blending (Imre and Pukánszky 2013). Reactive groups can eventually be created by the chemical modification of one of the components. Biopolymers often contain various reactive groups; hence the reactive compatibilization is plausible and convenient. The addition of a compound reactive towards the functional groups of one component and miscible with the other component results in the in situ formation of grafted or block-copolymers acting as versatile compatibilizers. The grafting of an element with anhydrides, resulting in the formation of carboxylic groups prone to react with hydroxyls in the other component, is a typical example. Unsaturated anhydrides, and maleic anhydride, in particular, are very useful in this respect.

Recently, nanofillers proved to be expedient to improve the phase morphologies of immiscible blends and act simultaneously as compatibilizers and nanoreinforcements. They can also provide tailor-made barrier, thermal, and mechanical properties, as well as shape memory (Mochane et al. 2020).

The commercial development of new copolymers and blends of biobased polymers seems endless. In the following, we particularly turn our attention to copolymers and blends of fully biobased components. We limit our analysis to a few examples of recent advances in this hotly debated field of research.

6.7.1 Copolymers

PLA copolymers are intensively studied. They are generally synthesized by ROP of LA and other monomers, initiated with hydroxyl- and amine-functionalized initiators.

Copolymers of glycolic and lactic acids (PGLA) are extensively used in surgical sutures, in tissue engineering, and the development of drug delivery systems.

The ROP of LA and GA requires harsh conditions and tin (II) 2-ethylhexanoate as the catalyst to increase the copolymer randomness. The higher reactivity of glycolic acid would result in longer glycolic acid blocks and a decreased elasticity of the polymer. The replacement of the tin-based catalyst with nontoxic 'biometals' such as magnesium or zinc analogs was successfully studied (Nifant'ev et al. 2018).

Enantiomeric alternating Poly(L-LA-co-GA)] and Poly(D-LA-co-GA) with an average molar mass of 5×10^3 g/mol were reported. Wide-angle X-ray diffractometry indicated that the stereocomplex crystalline modification is different from those reported for enantiomeric homopolymers of PLLA and PDLA. The stereocomplex formation did not largely influence the FTIR peak shape and frequency. The sufficiently high melting temperature values, the high mechanical performance, and high thermal stability suggest that stereocomplex crystallization between enantiomeric alternating lactic acid-based copolymers is a versatile method for the preparation of high-performance biodegradable materials with a wide range of physical properties (Tsuji et al. 2019).

Graft copolymerization of L-lactide onto chitosan using $Ti(OBu)_4$ as a catalyst in DMSO at 90 °C in nitrogen atmosphere gave graft copolymers with increased hydrophilicity and biodegradation (Luckachan and Pillai 2006).

Other studied cyclic monomers for LA copolymerization include caprolactone, a cyclic carbonate monomer, dipropargyl glycolide, and allyl glycidyl (Oh 2011; Gaucher et al. 2010).

For successful biological and biomedical applications of PLA and its copolymers, one serious challenge is associated with their hydrophobicity. The hydrophobicity of PLA may impair its use in sutures, implants for bone fixation, drug delivery vehicles, and tissue engineering scaffolds. This issue was addressed by the synthesis of PLA-based copolymers comprising amphiphilic monomers such as poly(meth) acrylates, poly(ethylene glycol), polypeptides, polysaccharides, and polyurethanes (Oh 2011). These PLA amphiphilic block copolymers are synthesized by radical, ring- opening, or condensation polymerization methods. They are of utmost interest as drug delivery and imaging platforms of self-assembled nanoparticles and tissue engineering of cross-linked hydrogels. In fact, the carboxylic acid (–COOH), amino ($–NH_2$), and hydroxyl (–OH) functional groups are utilized for bioconjugation with targeting biomolecules to achieve active targeting of specific cells.

A new stereo pentablock copolymers (PLLA-PDLA-PBS-PDLA-PLLA) was synthesized by two-step ROP of D- and L-lactides in the presence of bis-hydroxyl-terminated PBS prepolymer that has been prepared by the ordinary polycondensation. The direct connection of the PLLA and PDLA blocks allows easy formation of the stereocomplex crystals. At the same time, the introduction of the semicrystalline PBS block is effective not only for altering the crystallization kinetics but also for conveying an elastomeric property (Lee et al. 2016).

Copolymerization of PHA solve the drawbacks of PHA blending with natural raw materials such as starch, cellulose, and lignin or with other bioplastics such as PLA: blending enables the facile modification of physical and mechanical properties; anyhow these properties would fall within the extremes yielded by the blended polymers, and this represents a limitation; furthermore, the blending of polymers is complicated by poor interfacial interactions, which result in deterioration of properties during material aging. The bacterial development of new PHA copolymers involves a complicated genetic engineering process: for example, poly(3- hydroxybutyrate-co-4-hydroxybutyrate) can be obtained using specific bacteria and nutrient source, with elongated cells expected to provide more space for the biopolymer; anyhow, the most promising route to drastically modify the PHA properties is the PHA chemical functionalization and the synthesis of copolymers in various block/graft architecture (Samui and Kanai 2019); in this way, a hydrophobic polymer can be rendered amphiphilic. The grafting of poly(N-vinylpyrrolidone) groups onto PHBV backbones was used to improve thermal stability and hydrophilicity, restrict the crystallization process, and decrease the flexibility of PHBV (Wang et al. 2008b).

Tailor-made physical properties, and superior mechanical properties of PBS can be achieved by random copolymerization with different types of comonomer units such as adipic acid, terephthalic acid, methyl succinic acid, 2,2-dimethyl succinic acid, benzyl succinic acid, ethylene glycol, and 1,3-propanediol, etc. (Xu and Guo 2010).

Poly(butylene succinate-co-terephthalate (PBST) and Polybutylene Succinate Adipate are the most common PBS copolymers. Copolymerization was also explored to obtain a tunable biodegradation rate of PBS. Random copolymers obtained by copolycondensation with tin-based catalyst were prevalently reported.

The synthesis of a variety of multiblock copolymers such as poly(butylene thiodiglycolate) (Gigli et al. 2012a), poly(thiodiethylene succinate) (Soccio et al. 2012), multiblock copolyesters comprising butylene succinate and triethylene succinate with different block lengths (Gualandi et al. 2012b), a multiblock bioresorbable copolyester, poly(butylene/diethylene glycol succinate (Gualandi et al. 2012a), poly(butylene diglycolate) (Gigli et al. 2013), and poly[(butylene terephthalate)-co-poly(butylene succinate)-block -poly(ethylene glycol)] (Wang et al. 2004) was explored for biomedical application, in most cases. Recently, sugar-based subunits (Zakharova et al. 2015) were introduced along the PBS backbone.

Random copolymerization usually decreases the melting point, degree of crystallinity, heat distortion temperature, and tensile strength of the copolymer. On the converse, the elongation at break and impact strength usually rise with copolymerization.

PGA copolymers, such as poly(lactic-co-glycolic acid) with lactic acid (Tsuji et al. 2019), poly(glycolide-co-caprolactone) with ε-caprolactone and poly (glycolide-co-trimethylene carbonate) with trimethylene carbonate are precious materials in the biomedical field. Biocompatible and biodegradable poly(lactic-co-glycolic acid) (PLGA) nanosystems provide tumor-targeting and diagnostic properties since PLGA can be modified with therapeutic cargos in the internal space or adsorbed onto the surface of PLGA nanoparticles. The introduction of imaging modalities to PLGA-based nanoparticles can enable drug delivery guided by in vivo imaging (Kim et al. 2019).

6.7.2 Blends

PLA blending epitomizes biopolymer modification through the blending technique in order to achieve suitable properties for different applications; in fact, PLA blending has received significant attention over the past decade. PLA-based blends are usually developed for applications demanding better performance as engineering polymers whose high price can be better tolerated. Among the family of biodegradable polyesters, PLA is not toxic, and it has a high mechanical performance. However, the thermal stability of PLA is generally not high enough in many commercial polymers applications. In order to enhance it, an enantiomeric polymer blending of PLLA and PDLA showed higher thermal stability, compared with pure PLLA and PDLA (Tsuji and Fukui 2003). Another goal of PLA blending is the increase of PLA degradation. A variety of PLA mixtures are available, as detailed in the following. Melt-blending of PLA with a small amount of poly(aspartic acid-co-lactide) or poly(sodium aspartate-co-lactide) accelerated the hydrolytic degradation of PLA (Shinoda et al. 2003).

Polysaccharides represent a major part of FW resources and they are a cheap blending feedstock. Blends of starch and PLA in the presence of various water contents and various compatibilizers and plasticizers, including diisocyanate, dioctyl maleate, and poly(vinyl alcohol), have been investigated to improve the interfacial interactions (Ke and Sun 2003; Yu et al. 2006) but the poor miscibility is still an issue (Hamad et al. 2018).

Edible coatings or films made of chitosan have been used in packaging; blending of chitosan with PLA was studied to improve the water vapor barrier of chitosan (Suyatma et al. 2004). The improved strength and ductility of PLA films fabricated with 10 wt.% chitosan compared to those of neat PLA films can make them competitive candidates for food packing applications; nonetheless, the decomposition of chitosan during melt mixing makes the fabrication of this system challenging (Hamad et al. 2018).

PLA/biopolyester blends are very common. Since PCL has a low glass transition temperature, blending PLA with PCL was successfully researched in an attempt to decrease the brittleness of PLA. In particular, the addition of a small amount of low-molecular-weight PCL and long mixing time improved both the tensile strength and ductility of PLA/PCL blends (Cock et al. 2013). PLA/PCL blends compatibilized with lysine triisocyanate showed improved mechanical performance (tensile strength and elongation-at-break) compared with the non-compatibilized blend, while the use of dicumyl peroxide gave a blend with characteristics similar to those of high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) (Harada et al. 2008; Semba et al. 2006).

Due to the commercial availability of PLA and PBS and the increasing requirements for using biobased chemical building blocks, the application potential of PLA/PBS blends has been intensively researched in the last two decades (Su et al. 2019). PBS usually has a lower melting point and is less brittle than PLA. This combination of properties makes PBS/PLA blends especially interesting for bioplastics producers but also for 3D printing applications. Due to the biodegradability, good thermal resistance and melt processability of PBS, the aliphatic copolyester has been used to improve the melt processability and ductility of PLA (Park et al. 2010). Unfortunately, the improvement of ductility of PLA/PBS blends was at the cost of tensile strength, which markedly decreased (Hassan et al. 2013a). Blends consisting of PLA and PBS are characterized by a thermodynamically favored biphasic composition that often restricts their applications. Better compatibility for tailored and improved material properties was the focus of interest of many academicians. Lysine triisocyanate was proposed for the reactive processing to enhance the compatibility and improve the mechanical performance of PLA/PBS blends (Harada et al. 2007) thanks to the reaction of the isocyanate groups and the terminal hydroxyl or carboxyl groups of PLA and PBS. Maleic anhydride (Persenaire et al. 2014) and twice functionalized organoclay (Chen et al. 2005) were also successfully investigated for the compatibilization of PLA/PBS blends. The biodegradation and disintegration of PLA/PBS blends and their recycling are of priority interest. Other PBS blends include those with poly(L-lysine) (Tan et al. 2014), poly(3-hydroxybutyrate-co-valerate) and PHB (Ma et al. 2012), and PCL (Gumede et al. 2018).

PLA blends with polybutylene succinate-co-adipate, an aliphatic biodegradable polyester prepared from a butylene succinate adipate random copolymer, were investigated. Again, blending with PBAS was explored in order to enhance the ductility and injectability of PLA (Pivsa-Art et al. 2015): higher impact strengths and improved biodegradability were reported, but the poor compatibility of PLA and PBSA resulted in poor tensile strength and ductility. PLA/PBSA blends, compatibilized by reactive extrusion with triphenyl phosphite (Ojijo et al. 2012a, 2013), resulted in both improved tensile properties and its impact strength. The polymer chain extension due to the compatibilizer resulted in ligament-like fibrils located at the interphase, leading to some level of interfacial adhesion.

Polybutylene adipate-co-terephthalate (PBAT) was considered a good candidate for PLA blends because it is a fully biodegradable and tough aliphatic-aromatic copolyester (Jiang et al. 2006). Compared with neat PLA, the non-compatibilized PLA/PBAT blends show improved ductility and toughness but lower tensile strength and elastic modulus. To obtain an improvement in all properties, compatibilizers, and tetrabutyl titanate, in particular, were necessary (Lin et al. 2012). PLA/PBAT blends have an important potential as fully compostable high-performance materials.

PLA/PHA blends (Sudesh et al. 2000; He et al. 2014; Zhou et al. 2015; Zembouai et al. 2014) were investigated with the aim of obtaining a wide range of physical properties and improved processibility (Ohkoshi et al. 2000), but, above all, to increase both the biocompatibility and biodegradability of neat PLA and the thermal stability of neat PHA.

PHA performance can be improved by blending with natural materials or other biopolymers, such as cellulose derivatives, starch, and PCL, or by chemical modification, such as block and graft copolymerizations (Li et al. 2016a, b).

The compatibility of PLA/PHBH blends was enhanced using a reactive epoxy as a bifunctional compatibilizer (Zhou et al. 2015), but the poor toughness was the major drawback.

Poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHHx) and its dominant blends with PHB are promising from the biomedical point of view: the presence of PHBHHx in PHB reduced crystallization; films with a fairly regular and smooth surface allowed cell attachment and growth, thus strongly improving the biocompatibility of PHB, thereby demonstrating the feasibility of using this polymer blend as scaffold materials for tissue engineering (Kai et al. 2003). The blends of PHB or poly((R)-3-hydroxybutyrate-co-3-hydroxyvalerate) were studied to improve the inherent brittleness, and reduce high production costs associated with microbial polyesters (Yu et al. 2006). The experimental evidence indicates that chitosan is miscible with either PHB or poly((R)-3-hydroxybutyrate-co-3-hydroxyvalerate) at all compositions (Cheung et al. 2002).

PBS characteristichs have been improved through blending with PHB, PLA, PCL, poly(vinylphenol), polyethylene succinate, and fibers (Zeng et al. 2012).

6.8 Improvement of Bioplastic Properties to Bridge the Gap to Conventional Plastics

The biobased polymers market boom is partially hindered by their prohibitive expensiveness and their scarce competitiveness with fossilbased plastics. It follows that only novel technological advances will promote their use. The production of bioplastics is a key strategy that can maximize the use of FW and increase the potential revenue of the entire FW processing, thereby decreasing the environmental burdens arising from waste disposal (e.g., water contamination and GHG emissions).

The improvement of bioplastic properties to bridge the gap to conventional plastics is crucial.

Mechanical reinforcement should be pursued since brittleness and rigidity are the common problems faced by bioplastics. External plasticization, which increases polymer chain mobility, leading to improved flexibility, suffers from the tendency of plasticizers to leach from the plastic or phase separate from the polymer. Internal plasticization via copolymerization or grafting a second monomer to the polymer structure is more efficient than external plasticization, and no plasticizer leaching occurs. The most common, practical, and cost-effective technique to improve polymer mechanical performance is, however, blending with other polymers.

Copolymerization, grafting, blending, modification of the crystallization rate, and the use of fillers have been used to enhance bioplastic flexibility and toughness. These strategies are also used to improve the thermal properties of the biopolymers (Zhao et al. 2020).

Bioplastic barrier properties, discussed in Chap. 9 (Sec. 9.4), are crucial for food packaging; they can be improved by various strategies. Lamination with barrier petroleum-based and non-biodegradable plastics is not a fully biobased option, even if it is effective. Metallization by vacuum coating silicon (or aluminum) dioxide onto PLA film, increased the oxygen and water vapor barrier of up to 8–10 and 6–8 times, compared to those of pristine PLA (Zhao et al. 2018). Nanofillers such as nanoclay and zeolites decrease moisture/gas diffusion (Priolo et al. 2015; Zhao et al. 2020). The introduction of hydrophobic materials, waxes, and hydrolyzed keratin improves the moisture barrier (Morillon et al. 2002). Increasing polymer crystallinity using a nucleating agent is another option to enhance the moisture and gas barriers (Jost and Langowski 2015). Section 10.3.1 deals with biobased barriers useful to prevent migration from conventional packaging materials.

As regards processability, PLA and PHAs cannot be easily processed as normal thermoplastics through conventional plastic processing techniques because their chain linearity results in low resistance to stretching of the melt polymer; this, in turn, causes issues that require film blowing and blow molding or adjustment on processing parameters or the presence of compatibilizers (Wei and McDonald 2015). PLA and PHAs degrade at temperatures close to their melting points, making thermal processing very changeling due to a narrow processing window (Larsson et al. 2016). PLA and PHAs processability can be improved by: (i) long chain branching, (ii) grafting, (iii) peroxide induced crosslinking through reactive melt processing (Wei and McDonald 2015), and (iv) chain extension by using multifunctional chain extenders such as tris(nonylphenyl) phosphite and polycarbodiimide and epoxy-functionalized oligomeric acrylic copolymer (Tiwary and Kontopoulou 2018; Jaszkiewicz et al. 2014). These techniques increase polymer molecular weight and molecular weight distribution and polymer chain entanglement, thereby increasing resistance to untangling during thermal processing. Other techniques to improve processability include blending with elastomers, the use of plasticizers (epoxidized soybean oil, acetyl tributyl citrate, poly(ethylene glycol), limonene (Panaitescu et al. 2017; Arrieta et al. 2014)), nucleation and reinforcement with the addition of nanoclay (Zhao et al. 2020).

6.9 Conclusions

While global bioplastic production keeps sharply increasing because of consumers' environmental awareness, new policies and legislation, as well as technological advancements, the estimated market share of bioplastics still has not exceeded 1% of the global plastics production. Increasing the market share of bioplastics would reduce the dependence on and the environmental impact of fossilbased plastics in a biobased society within the framework of a circular economy approach.

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