

Chapter 2

Biodegradable Polymers

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Abstract In the recent years, bio-based and biodegradable products have raised great interest since sustainable development policies tend to expand with the decreasing reserve of fossil fuel and the growing concern for the environment. These polymers bring a significant contribution to the sustainable development in view of the wider range of disposal options with minor environmental impact. As a result, the market of these environmentally friendly materials is in rapid expansion, 10–20 % per year. Consequently, biodegradable polymers are the topics of much research. Biodegradable polymers can be mainly classified as agro-polymers (starch, chitin, protein...) and biodegradable polyesters [polyhydroxyalkanoates, poly(lactic acid)...]. These latter, also called biopolyesters, can be synthesized from fossil resources but main productions are obtained from renewable resources. This chapter intends to present these polymers regarding the synthesis, the structure, properties and their applications.

2.1 Introduction

Increasing concern exists today about the preservation of our ecological systems. Most of today's synthetic polymers are produced from petrochemicals and are not biodegradable. Persistent polymers generate significant sources of environmental pollution, harming wildlife when they are dispersed in nature. For example, the disposal of non-degradable plastic bags adversely affects sea-life. It is widely

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accepted that the use of long-lasting polymers in products with a short life-span, such as engineering applications, packaging, catering, surgery, and hygiene, is not adequate. Moreover, incineration of plastic waste presents environmental issues as well since it yields toxic emissions (e.g., dioxin). Material incineration is also limited due to the difficulties to find accurate and economically viable outlets. In addition, plastic recycling shows a negative eco-balance due to the necessity, in nearly all cases, to wash the plastic waste as well as the energy consumption during the recycling process phases (waste grinding and plastic processing). As plastics represent a large part of the waste collection at the local, regional, and national levels, institutions are now aware of the significant savings that compostable or biodegradable materials would generate. For these different reasons, reaching the conditions of conventional plastic replacements by degradable polymers, particularly for short-term applications (packaging, agriculture...), is of major interest to the society as a whole, from the plastic industries to the citizens.

The potential of biodegradable polymers has been recognized for a long time since they could be an interesting way to overcome the limitation of the petrochemical resources in the future. The fossil fuel and gas could be partially replaced by green agricultural resources, which would also participate in the reduction of CO₂ emissions [1]. However, till now, biodegradable polymers have not found extensive applications in industries to largely replace conventional plastic materials, reasons being their high production costs and sometimes their underperformed properties.

2.1.1 Renewability and Sustainable Development

Renewability is linked to the concept of sustainable development. The UN World Commission on “Environment and Development in Our Future” defines sustainability as the development which meets the needs of the present time without compromising the ability of future generations to meet their own needs. According to Narayan [1], the manufactured products must be designed and engineered from “conception to reincarnation”, the so-called “cradle-to-grave” approach. The use of annually renewable biomass must be understood in a complete carbon cycle. The carbon cycle is a complex process by which carbon is exchanged between the four main reservoirs of carbon on the planet i.e., the lithosphere (e.g., limestone), the biosphere (plant and animal), the hydrosphere (e.g. bicarbonate dissolved in the oceans), and the atmosphere (CO₂). Recent human activities (burning fossil fuel and massive deforestation) lead to an important imbalance in the carbon cycle with a huge and rapid release of CO₂ to the atmosphere, which cannot be fully compensated by the photosynthesis activity and the dissolution in the oceans. It results in a large accumulation of CO₂ in the atmosphere, which contributes to the global warming. People are now aware that efforts have to be made to re-balance the carbon cycle by reducing the amount of CO₂ production. Part of the carbon cycle re-balancing concept is based on the development and manufacture of products based on renewable and biodegradable resources. By collecting and

composting biodegradable plastic wastes, we can generate much-needed carbon-rich compost: humus materials. These valuable soil inputs can go back to the farmland and “reinitiate” the carbon cycle. Then, the plants growth contributes to reducing CO₂ atmospheric accumulation through photosynthesis activity. Besides, composting is an increasing key point to maintain the sustainability of agricultural systems by reducing the consumption of chemical fertilizers.

2.1.2 Biodegradability and Compostability

According to ASTM standard D-5488-94d and European norm EN 13432, “biodegradable” means “capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, and biomass”. The predominant mechanism is the enzymatic action of microorganisms, which can be measured by standard tests over a specific period of time, reflecting available disposal conditions. There are different media (liquid, inert, or compost medium) to analyze biodegradability. Compostability is material biodegradability using compost medium. Biodegradation is the degradation of an organic material caused by biological activity (biotic degradation), mainly microorganisms’ enzymatic action. The end-products are CO₂, new biomass, and water (in the presence of oxygen, i.e. aerobic conditions) or methane (in the absence of oxygen, i.e., anaerobic conditions), as defined in the European Standard EN 13432-2000. Depending on the type of standard to follow (ASTM or EN), different composting conditions (humidity and temperature cycle) must be realized to determine the compostability level [2]. Therefore, the comparison of the results obtained from different standards seems to be difficult or impossible. We must also take into account the amount of mineralization as well as the nature of the residues (commonly called “by-products”) left after biodegradation [3]. The accumulation [4] of contaminants with toxic residues can cause plant growth inhibition. The key issue is to determine the environmental toxicity level for these by-products, which is known as eco-toxicity [5]. Some general rules enable the determination of the biodegradability evolution. For example, an increase in parameters such as the hydrophobicity, the macromolecules molecular weights, and the crystallinity or the size of crystalline domains decreases the biodegradability [6].

2.1.3 Biodegradable Polymers Classifications

Biodegradable polymers represent a growing field [7–9]. A vast number of biodegradable polymers (e.g. cellulose, chitin, starch, polyhydroxyalkanoates, polylactide, polycaprolactone, collagen and other polypeptides...) have been synthesized or are formed in natural environment during the growth cycles of

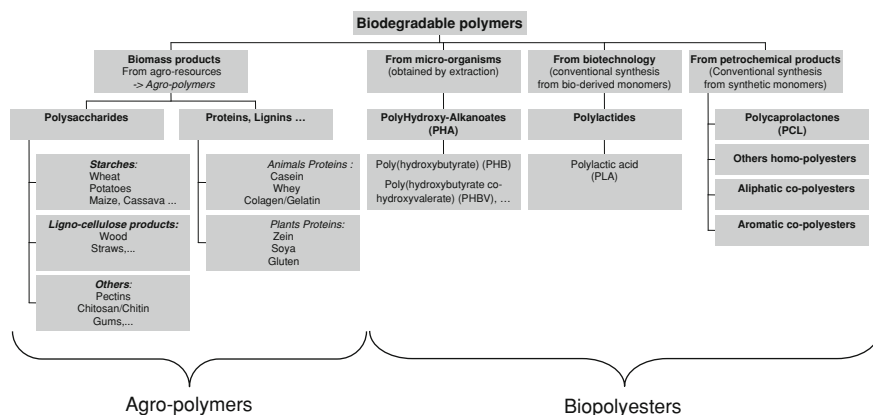


Fig. 2.1 Classification of the main biodegradable polymers

organisms. Some microorganisms and enzymes capable of degrading such polymers have been identified [7, 10].

Different classifications of various biodegradable polymers have been proposed. We propose to classify the biodegradable polymers according to their synthesis process (Fig. 2.1): (i) polymers from biomass such as agro-polymers from agro-resources (e.g., starch or cellulose), (ii) polymers obtained by microbial production such as the polyhydroxyalkanoates (PHAs), (iii) polymers conventionally and chemically synthesized from monomers obtained from agro-resources, e.g., the polylactic acid (PLA), and (iv) polymers obtained from fossil resources. Only the first three categories (i–iii) are obtained from renewable resources.

We can further classify these biodegradable polymers into two main categories: the agro-polymers (category i) and the biodegradable polyesters or biopolyesters (categories ii–iv).

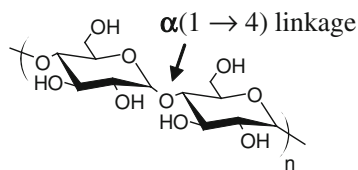
2.2 Agro-Polymers

Main agro-polymers presented in this chapter are the polysaccharides and the proteins. They are often used to elaborate multiphase materials.

2.2.1 Polysaccharides

Polysaccharides are the most abundant macromolecules in the biosphere. These complex carbohydrates constituted of glycosidic bonds are often one of the main structural elements of plants and animals exoskeleton (cellulose, carrageenan,

Fig. 2.2 Amylose chemical structure



chitin...). The polysaccharides presented in this chapter are starch, chitin, chitosan, and pectins, successively.

2.2.1.1 Starch

Starch is mainly extracted from cereals (wheat, corn, rice...) and from tubers (potatoes, manioc...). It is stocked in seeds or roots and represents the main plant energy reserve.

Native Starch Structure

Depending on the botanical origin of the plant, starch granules can have different shapes (sphere, platelet, polygon...) and size (from 0.5 to 175 μm). These granules are composed of two α -D-glucopyranose homopolymers, the amylose and the amylopectin. Their proportions in the granules depend directly on the botanical source [11]. In addition, starch also contains, in much smaller proportions, other compounds such as proteins, lipids and minerals.

The amylose is mainly a linear polysaccharide composed of D-glucose units linked by $\alpha(1\rightarrow4)$ linkages (Fig. 2.2). These chains are partially ramified with some $\alpha(1\rightarrow6)$ linkages. Depending on the botanical source and the extraction process, amylose molecular weight varies from 10^5 to 10^6 $\text{g}\cdot\text{mol}^{-1}$ with a polydispersity ranging from 1.3 to 2.1 [12–14]. The amylose chains show a single- or double-helical conformation with a rotation on the $\alpha(1\rightarrow4)$ linkage [15].

Amylopectin is the main starch component and has the same monomeric unit as amylose. It shows 95 % $\alpha(1\rightarrow4)$ linkages and 5 % $\alpha(1\rightarrow6)$ linkages (Fig. 2.3). These latter are found every 24–79 glucose units [16] and bring to the amylopectin a highly branched structure. Consequently, the amylopectin structure and organization can be seen as a grape with pending chains (Fig. 2.3) [17].

The starch granule organization consists in alternation of crystalline and amorphous areas leading to a concentric structure [18]. The amorphous areas are mainly constituted of amylose chains and amylopectin branching points. The crystalline parts are mainly composed of amylopectin side chains. Some co-crystalline structures with amylose chains have been also identified [19, 20]. Four allomorphic starch structures exist [19]. Depending on the botanical origin, starch granules present a crystallinity varying from 20 to 45 %.

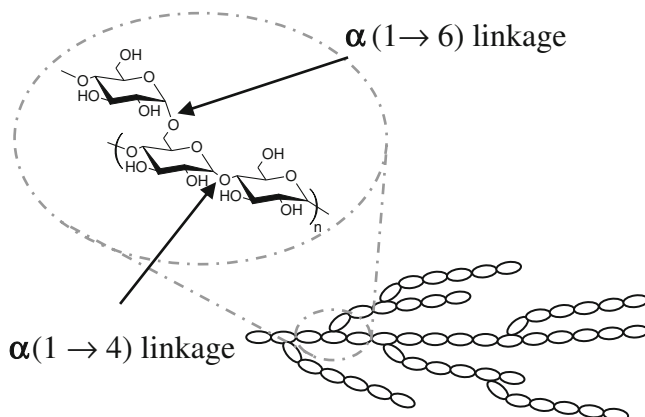


Fig. 2.3 Amylopectin chemical and grape structure (From Hizukuri, reproduced with kind permission from ©Elsevier 2011 [17])

Plasticized Starch: Elaboration and Properties

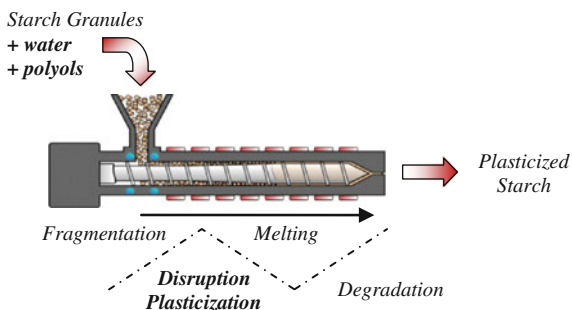
Because of numerous intermolecular hydrogen bonds existing between the chains, the melting temperature (T_m) of starch is higher than its degradation temperature [21, 22]. Consequently, to elaborate a plastic-like material, it is necessary to introduce high water content or/and some non-volatile plasticizers (glycerol, sorbitol,...) which decrease the glass transition temperature (T_g) and the T_m [23, 24]. These plasticized materials are currently named “thermoplastic starch” or “plasticized starch”. To be transformed, the starch granular structure has to be disrupted. The disruption can be obtained either by a solvent-casting process or by a melting process where starch and plasticizers are mixed under thermo-mechanical treatment.

Solvent-assisted disruption of starch granules is mostly carried out with water. At ambient temperature, starch remains insoluble in water and keeps its granular structure. The increase of water temperature induces an irreversible swelling process named “gelatinization”. During gelatinization, the amylose is well solubilized, the granular semi-crystalline structure disappears, and the granules swell rapidly. This phenomenon occurs at a given temperature defined as “gelatinization temperature” (T_{gel}) which depends on the starch botanical origin [25–27]. To obtain a quite full starch solubilization, hot DMSO is often used as a solvent. Then, this solvent can be volatilized under vacuum and heat.

The starch melting process is often carried out in association with plasticizers to obtain a homogeneous molten phase. During the thermo-mechanical process, e.g., extrusion, different and successive phenomena occur (Fig. 2.4) [28].

The disruption of starch granules being dependent on the specific mechanical energy provided during processing, this material could be described as a “thermo-mechanical-plastic” material [29, 30].

Fig. 2.4 Schematic representation of the starch extrusion process



During processing, amylose and amylopectin degradation occurs and this phenomenon is obviously dependent on the thermal and mechanical energy brought to the system. Numerous studies were conducted to determine the degradation mechanism and to understand the contribution of each parameter [31–38].

Since starch is a hydrophilic material, water is the best plasticizer [24, 39–41]. Nevertheless, the water content and thus the plasticized starch properties are strongly dependent on the storage conditions (temperature and atmosphere relative humidity). This drawback is partially solved with the use of less volatile plasticizers, which present lower plasticization efficiency. These compounds (polyols), bearing hydroxyl groups, can interact with the starch chains through hydrogen bonds. Glycerol is the most common plasticizer [42–45], but numerous other polyols, such as sorbitol [46], xylitol [47], fructose [48], glucose, [49], and glycols [50], can also be used as plasticizers. Nevertheless, these plasticizers are more hydrophilic than starch and are also sensitive to the relative humidity.

Depending on the plasticizer content, starch may display one or two relaxations, corresponding to a homogeneous or multiphase material. Some authors [44, 51] have demonstrated that a phase separation occurs for glycerol content higher than 27 wt% on dry-basis. The corresponding second relaxation (named β) is consistent with the glycerol glass transition and occurs around -50 to -70 °C. This secondary transition is dependent on the glycerol concentration and more particularly on the ‘free’ glycerol [52, 53]. The main relaxation (named α) is attributed to the plasticized starch T_g and this temperature decreases when the glycerol content increases from 0 to 25 wt% [54].

Several studies were also performed in order to highlight the different interactions taking place in water/glycerol/starch multiphase systems and to determine the influence of the water content at equilibrium [44, 55]. The results have shown that the higher the water content, the lower the T_g of plasticized starch.

The great influence of water and glycerol contents on starch properties has also been highlighted by the “so-called” anti-plasticization effect [46, 54]. For example, with glycerol content below 12 wt%, a remarkable behavior occurs, leading to the hardening of the material.

The mechanical properties of plasticized starch evolve with time due to molecular reorganization, which is dependent on processing protocol and storage

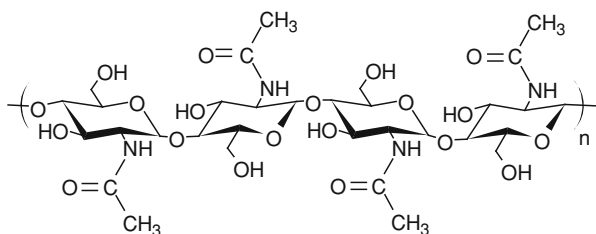


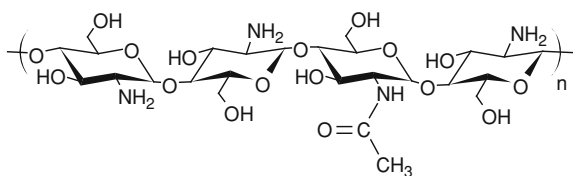
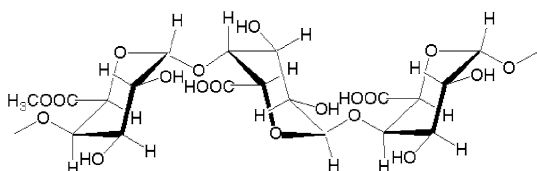
Fig. 2.5 Chitin chemical structure

conditions. When the samples are stored below the T_g , the samples will undergo physical ageing with material densification [56]. When $T > T_g$, the samples will retrograde with a crystallinity increase [57]. The physical ageing is observed for materials with plasticizer content lower than 25 wt% [22, 58]. This phenomenon induces hardening and a decrease in the strain at break. The retrogradation takes place after the amylose crystallization and concerns the amylopectin crystallization. This phenomenon is slow since it lasts for more than a month [52, 59] and induces a strong variation of mechanical properties [20, 60–62]. Thus, even if these two phenomena are different, both of them induce internal stresses in the material, which lead to embrittlement characterized by a stiffness increase correlated to a decrease in the strain at break.

2.2.1.2 Chitin and Chitosan

Chitin is the second most abundant agro-polymer produced in nature after cellulose. It appears in nature as ordered crystalline microfibrils forming structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeasts [63, 64]. It is an acetylated polysaccharide composed of *N*-acetyl-D-glucosamine groups linked by $\beta(1 \rightarrow 4)$ linkages (Fig. 2.5). From chitin, chitosan is obtained by deacetylation.

Depending on the source, chitin occurs in two allomorphic forms named α and β [65]. A third allomorphic structure γ has also been reported, but it seems to be a variant of the α form [66]. These two structures are organized in crystalline sheets where a number of intra-sheet hydrogen bonds tightly hold them. The α form presents some inter-sheets hydrogen bonds. Such a feature is not found for the β form, which is consequently more prone than the α form to water swelling [67, 68]. Like cellulose, the semi-crystalline structure of chitin microfibrils can be treated with acid to produce whisker-shaped nanofillers which can be incorporated into polymers to elaborate nano-hybrid materials [69, 70]. Contrary to chitin, chitosan is not widespread in nature. It is found in some mushrooms (zygote fungi) and in the termite queen's abdominal wall. It is industrially obtained by partial and controlled chitin deacetylation [71]. Its chemical structure, represented in Fig. 2.6,

Fig. 2.6 Chitosan chemical structure**Fig. 2.7** Pectin chemical structure

is a random linear chaining of N-acetyl-D-glucosamine units (acetylated unit) and D-glucosamine (deacetylated unit) linked by $\beta(1 \rightarrow 4)$ linkages.

Thanks to its amino group and compared to chitin, chitosan shows some particular properties. In acid conditions, when the amino groups are protonated, it becomes a water soluble polycation. Some polysaccharides like carrageenan can have a polyelectrolyte behavior, but these agro-polymers are mainly polyanions [72]. The chitosan is characterized by its acetylation degree and by its molecular weight. These last parameters influence its viscosity and solubility. Depending on the source (shrimp, crab, mushrooms...), industrial chitosan has molecular weight varying from 5,000 to 1,000,000 g.mol^{-1} and acetylation degrees from 2 to 60 %.

In solid state, chitosan is a semi-crystalline polymer. Its morphology has been investigated and many allomorphs have been described, depending on its acetylation degree, on the distribution of the acetyl groups along the carbohydrate chain, and on the chitosan preparation procedure [73, 74].

Chitosan can be plasticized with glycerol to obtain a kind of thermoplastic material like, for instance, plasticized starch [75].

2.2.1.3 Pectin

Pectin is a linear macromolecule constituted of $\alpha(1 \rightarrow 4)$ -linked D-galacturonic acid (Fig. 2.7). This monomer unit could be partially replaced by $\alpha(1 \rightarrow 2)$ -linked L-rhamnose leading to a new structure named rhamnogalacturonan I. A third pectin structural type is rhamnogalacturonan II, which is a less frequent, but complex and highly branched polysaccharide [76].

In nature, around 80 % of the galacturonic acid carboxyl groups are esterified with methanol. This proportion depends on the extraction conditions. Since the ratio of esterified/non-esterified galacturonic acid determines the behavior of pectin in food applications, pectins are classified as high- or low-ester pectins [77]. The non-esterified galacturonic acid units can be either free acid or salts, with

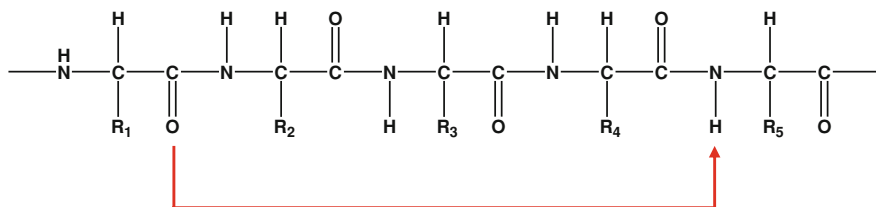


Fig. 2.8 Protein chemical structure. Hydrogen bonds interaction between the amino-acids (arrow)

sodium, potassium, or calcium as the counter ion. The partially esterified pectin salts are named pectinates. If the degree of esterification is below 5 %, the salts are called pectates.

2.2.2 Proteins

Proteins are agro-polymers. They are an important renewable resources produced by animals, plants, and bacteria. The term “protein” comes from the Greek, *proteios*, for “primary, first and foremost”. A certain number of proteins have received much attention as biodegradable polymers but few have led to actual industrial scale-up due to the high production cost and the low product performance. In terms of potential sources, soy protein, corn protein (zein...) and wheat proteins (gluten...) are among the main plant proteins. Casein, collagen protein or gelatin, and keratin are important animal proteins. Lactate dehydrogenase, chymotrypsin, and fumarase constitute the main bacterial proteins.

Most proteins consist of linear polymers built from a series of up to 20 different amino acids (Fig. 2.8). The side chains of the standard amino acids have a great variety of chemical structures and properties. It is the combined effect of all of the amino acid side chains that determines the final 3D structure and the chemical reactivity. Most proteins fold into unique 3D structures. Biochemists often refer to four distinct aspects of a protein’s structure [78]:

- Primary structure: the amino acid sequence (Fig. 2.8).
- Secondary structure: regularly repeating local structures stabilized by hydrogen bonds (Fig. 2.8) such as the alpha helix or the beta sheet. Different zones with various secondary structures can be present in the same protein.
- Tertiary structure: the overall shape of a single protein molecule; the spatial relationship of the secondary structures to another. Tertiary structure is generally stabilized by nonlocal interactions with the formation of a hydrophobic core. The tertiary structure is what controls the basic function of the protein.
- Quaternary structure: the structure formed by numerous proteins, which function as a single protein complex.

Proteins can be classified according to the shape and solubility as fibrous, globular, or membrane [78]. Fibrous proteins tend to have relatively simple, regular linear structures. Globular proteins are roughly spherical. The polypeptide chain is compactly folded so that hydrophobic amino acid side chains are in the interior of the molecule and hydrophilic side chains are on the outside exposed to the solvent. They are very soluble in aqueous media. Membrane proteins are found in association with various membrane systems of cells. For interaction with the non-polar phase within membranes, membrane proteins have hydrophobic amino acid side chains oriented outwards. They are mainly insoluble in aqueous media.

Proteins can be processed with the same kinds of approaches developed for starch-based materials, e.g., formulation with plasticizers, cross-linkers....

2.2.2.1 Soybean Proteins

Typically soybean proteins contain 38–42 % crude protein, 16–20 % triglycerides, and around 33 % carbohydrates, on dry basis. Soy proteins are the isolated proteins from soybean. It is made of dehulled, defatted soybean meal. Dehulled and defatted soybeans are processed into three kinds of high protein commercial products: soy flour, concentrates, and isolates. More recently, Soy proteins have been the subject of studies regarding the health effects of soy protein consumption. Soy protein contains phytoestrogens and some studies suggest that high levels of phytoestrogens may increase the risk of certain forms of cancer. Then, these proteins could be rather developed for non-food applications in the future [79].

2.2.2.2 Corn Proteins

Proteins form about 9 % of the dry weight of corns. They are mainly composed of zein (a highly hydrophobic protein, soluble in alcohols), glutelin (soluble in aqueous alkaline solutions), albumins, and globulins.

Zein comprises about 40 % of the total kernel protein on dry basis. It is one of the few cereal proteins extracted in a relatively pure form and is a unique and complex biopolymer. Zein comes from the alcohol soluble protein of corn, classified as a prolamin. It is the principle storage protein of corn and constituting 45–80 % of endosperm protein. Zein is a mixture of proteins varying in molecular weight and solubility, which can be separated by differential solubility to give four related zeins named α , β , γ and δ [78]. Commercial zein is made up of α -zein, which is by far the most abundant, accounting for around 70 % of the total. The molecular weight of zein is between 9,600 and 44,000 g.mol⁻¹.

The cost of purified zein is €15–50 per kg depending on the grade and purity. The cost and also its poor water resistance are two main issues of this protein to find a large range of applications.

2.2.2.3 Wheat Gluten

Wheat gluten is a protein carbohydrate complex of which proteins are the major component. Two main fractions are present. Gliadin is soluble in neutral 70 % ethanol, made of single chain polypeptides with an average molecular weight of 25,000–100,000 g.mol⁻¹ by intramolecular disulphide bonds. The second fraction is glutenin, which is an alcohol-insoluble fraction consisting of gliadin-like subunits stabilized by intermolecular disulphide bonds in large aggregates with molecular weight greater than 100,000 g.mol⁻¹. Thus, the term “gliadin” defines a group of proteins extracted from gluten by 70 % ethanol. Gliadins and glutenins are present in almost equivalent quantities in wheat gluten and have comparable amino acid compositions, with high concentrations in glutamine and proline. The amount, size distribution, and macromolecular architecture of glutenins and gliadins greatly influence the rheological, processing, mechanical, and physico-chemical properties of the gluten [80]. Wheat protein-based materials has greatly attracted attention during the two last decades and some material applications have already been found for them [81]. Some targeted areas are molded objects for interior use such as toys, leather imitation for office products (covers), design articles and pieces of furniture....

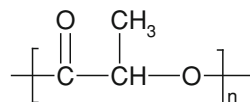
2.2.2.4 Casein

Caseins are animal proteins and are commonly found in mammalian milk, making up 80 % of the proteins in cow milk and between 60 and 65 % of the proteins in human milk. Casein molecular weight is between 1,000 and 20,000 g.mol⁻¹. Caseins include four different types. Casein is the predominant phosphoprotein and is characterized by an open, random coil structure. By treating acid-precipitated caseins with alkali solution, caseinates are produced. Both caseins and caseinates form transparent films from aqueous solutions without any treatment based on hydrogen bonds [82]. Caseins have shown to be useful in a great number of fields such as adhesives, controlled releases, and biomedical applications.

2.2.2.5 Gelatin

Gelatin is a natural material based on animal proteins. It is derived from collagen, which is elongated fibrils and mostly found in fibrous tissues such as tendon, ligament, and skin. It is also abundant in cornea, cartilage, bone, blood vessels, gut, and intervertebral disc. Gelatin is commonly used for biomedical applications due to its biodegradability and biocompatibility in physiological environments, in contact with living tissues [83]. Two different types of gelatin can be produced depending on the method in which collagen is pretreated, prior to the extraction process. Alkaline process targets the amide groups of asparagines and glutamine and hydrolyzes them into carboxyl groups, thus converting many of these residues

Fig. 2.9 Chemical structure of poly(lactic acid) (PLA)



to aspartate and glutamate. In contrast, acidic pre-treatment does little to affect the amide groups and the gelatin processed with an alkaline pre-treatment is electrically different in nature from acidic-processed gelatin. Gelatin has shown to be useful in a great number of fields such as adhesives, and pharmaceutical and biomedical applications.

2.3 Biodegradable Polyesters

We distinguish biobased (PLA, PHA...) and non-renewable polyesters (PCL, PBSA, PBAT...) in the following.

2.3.1 Polyesters Based on Agro-Resources

Some biobased polyesters are now largely available like PLA and PHAs, with different industrial productions.

2.3.1.1 Poly(Lactic Acid)

Lactic acid is a chiral molecule existing as two stereoisomers, L- and D-lactic acid which can be produced by different ways, i.e., biologically or chemically synthesized [84].

In the first case, lactic acid is obtained by fermentation of carbohydrates by lactic bacteria belonging mainly to the genus *Lactobacillus*, or fungi [85, 86]. This fermentative process requires a bacterial strain but also a carbon source (carbohydrates), a nitrogen source (yeast extract, peptides...), and mineral elements to allow the growth of bacteria and the production of lactic acid. The lactic acid as-formed exists almost exclusively as L-lactic acid and leads to poly(L-lactic acid) (PLLA) with low molecular weight by polycondensation reaction (Fig. 2.9). However, Moon et al. [87, 88] have proposed an alternative solution to obtain higher molecular weight PLLA by polycondensation route.

In contrast, the chemical process could lead to various ratio of L- and D-lactic acid. The chemical reactions, leading to the formation of a cyclic dimer, the lactide, as an intermediate step to the production of PLA, could lead to long macromolecular chains with L- and D-lactic acid monomers. This mechanism of

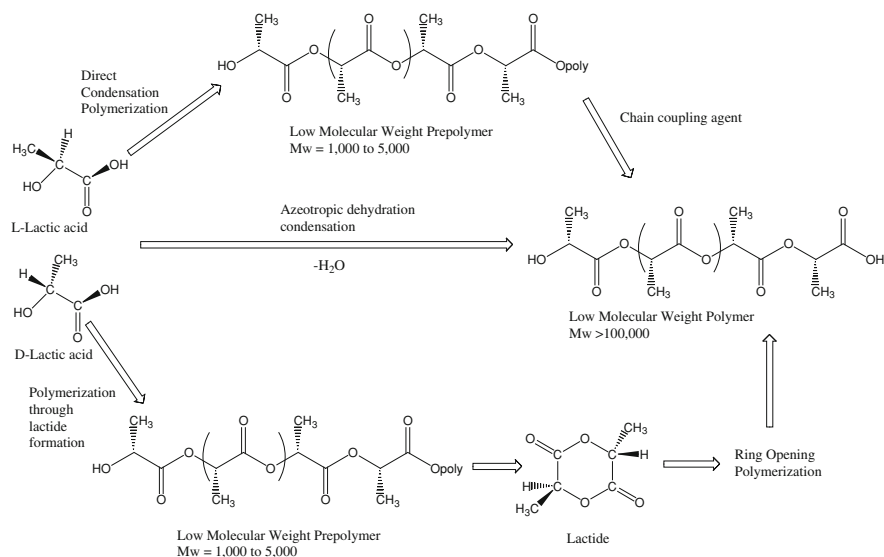


Fig. 2.10 Chemical structure of PLA and Synthesis methods for obtaining high molecular weight (Adapted from Averous. With kind permission from ©Elsevier 2011 [84])

ring-opening polymerization (ROP) from the lactide explains the formation of two enantiomers. This ROP route has the advantage of reaching high molecular weight (Fig. 2.10) and of allowing the control of PLA final properties by adjusting the proportions and the sequencing of L- and D-lactic acid units [7, 85, 89, 90].

At present, due to its large availability on the market and its relatively low price [91–94], PLA shows one of the highest potential among biopolyesters, particularly for packaging [92, 94] and medical applications. For instance, Cargill has developed processes that use corn and other feedstock to produce different PLA grades (NatureWorks®) [93, 95]. In this company, the actual production is estimated to be 140,000 tons/year. Presently, it is the highest and worldwide production of biodegradable polyester. Its price is lower than 2€/kg. Different companies such as Mitsui Chemicals (Japan), Mitsubishi (Japan), Shimadzu (Japan), Futerro (Total/Galactic—Belgium), Purac (Netherlands), Teijin (Japan), and Zhejiang Hisun Biomaterials (China) produced different PLA products with a wide range of L/D ratios. PLA consumption is only around 200,000 tons/year. At present, only ~30 % of lactic acid is used for PLA production. Thus, this biopolymer presents a high potential for development.

Commercially available, we can find 100 % PLLA which present a high crystallinity (C-PLA) and also copolymers of PLLA and poly(D,L-lactic acid) (PDLLA) which are rather amorphous (A-PLA) [95–97].

Properties of PLA, as well as other polymers, depend on their molecular characteristics as well as ordered structures such as crystalline thickness, crystallinity, spherulite size, morphology, and degree of chain orientation.

The physical properties of polylactide are related to the enantiomeric purity of lactic acid stereo-copolymers. Homo-PLA is a linear macromolecule having a molecular architecture that is determined by its stereo-chemical composition. PLA can be produced totally amorphous or up to 40 % crystalline. PLA resins containing more than 93 % of L-lactic acid are semi-crystalline. But, PLA with 50–93 % L-lactic acid is completely amorphous. Therefore, the L/D ratio induces or restrains polymer crystallinity. Both meso- and D-lactides induce twists in a very regular poly(L-lactide) architecture. Macromolecular imperfections are responsible for the decrease in both the rate and extent of PLLA crystallization. Practically most PLA are made up of L- and D,L-lactide copolymers since PLA production contains often some meso-lactide impurities.

Depending on the preparation conditions, poly(L-lactide) crystallizes into different forms [84]. The α -form exhibits a well-defined diffraction pattern. This structure is more stable than the β -structure, with a T_m at 185 °C compared to 175 °C for the β -structure. This latter can be formed at a high draw ratio and high drawing temperature [28]. The γ -form is found by epitaxial crystallization. It has been observed that a blend with equivalent PLLA and PDLA contents gives stereo-complexation (racemic crystallite) of both polymers. This stereo-complex gives mechanical properties higher than those of pure PLLA or PDLA and a high T_m equal to 230 °C. Literature reports different density data for PLA. Mainly, crystalline parts give a density of 1.29 compared to 1.25 for the amorphous material.

PLA is a slowly crystallizing polymer similar to PET. The PLA crystallization kinetics have been extensively studied. As PET, PLA can be oriented by processing. Chain orientation increases the mechanical strength of PLLA plastics. If orientation is performed at low temperature, the resulting PLLA has enhanced modulus without a significant increase in crystallinity. To determine crystallinity levels by DSC, the value, most often referred in the literature concerning the PLA melt enthalpy at 100 % crystallinity, is 93 J/g [98].

Crystallization of the thermally crystallizable but amorphous PLA can be initiated by annealing at temperatures between 75 °C and T_m . The annealing of crystallizable PLA copolymers often produces two melting peaks. Different hypothesis have been presented. Some authors [99] found double melting points in PLLA polymers and attributed them to the slow rates of crystallization and recrystallization.

The typical T_g of PLA ranges from 50 to 80 °C while the T_m ranges from 130 to 180 °C. For instance, enantiomerically pure PLA is a semi-crystalline polymer with a T_g of 55 °C and a T_m of 180 °C. For semi-crystalline PLA, the T_m is a function of the different processing parameters and the initial PLA structure. T_m increases with the molecular weight (Mw) until a maximum value. Besides, the crystallinity decreases with increasing Mw. T_g is also determined by the proportion of the different types of lactide. T_m depends on the presence of meso-lactide in the structure which produces a T_m reduction [84].

PLA can be plasticized using oligomeric lactic acid (o-LA) [98], citrate ester [100], or low molecular weight polyethylene glycol (PEG) [98, 101–103]. The effect of plasticization increases the chain mobility and then favors the PLA

organization and crystallization. After plasticization, a crystallinity ranging between 20 and 30 % is obtained.

PLA presents a medium water and oxygen permeability level [94, 104] comparable to polystyrene [105]. These different properties associated with its tunability and its availability favor its actual developments in different packaging applications (trays, cups, bottles, films...) [92, 94, 95]. McCarthy (1999) [106] showed that A-PLA presents a soil degradation rate much slower compared to e.g., PBSA. PLA is presumed to be biodegradable although the role of hydrolytic versus enzymatic depolymerization in this process remains open to debate [107]. Regarding biodegradation in compost, adequate conditions are only found in industrial units with a high temperature (above 50 °C) and a high relative humidity (RH%) to promote chain hydrolysis. According to Tuominen et al. (2002) [108], PLA biodegradation does not exhibit any eco-toxicological effect.

2.3.1.2 Polyhydroxyalkanoates

PHAs are a family of intracellular biopolymers synthesized by many bacteria as intracellular carbon and energy storage granules. PHAs are mainly produced from renewable resources by fermentation. A wide variety of prokaryotic organisms [109, 110] accumulate PHA from 30 to 80 % of their cellular dry weight. Biotechnological studies revealed that PHB is produced under balanced growth conditions when the cells become limited for an essential nutrient but are exposed to an excess of carbon [111]. Depending on the carbon substrates and the metabolism of the microorganism, different monomers, and thus (co)polymers, could be obtained [112]. Besides, PHAs are considered as biodegradable and thus suitable for e.g., short-term packaging, and also considered as biocompatible in contact with living tissues and can be used for biomedical applications (e.g., drug encapsulation, tissue engineering...). PHA can be degraded by abiotic degradation, i.e., simple hydrolysis of the ester bond without requiring the presence of enzymes to catalyze this hydrolysis. During the biodegradation process, the enzymes degrade the residual products till final mineralization (biotic degradation).

PHAs are generally classified into short-chain-length PHA (sCL-PHA) and medium-chain-length PHA (mCL-PHA) by the different number of carbons in their repeating units. For instance, sCL-PHAs contain 4 or 5 carbons in their repeating units, while mCL-PHAs contain 6 or more carbons in the repeating units. The term mCL was coined because the number of carbons in the monomers roughly corresponds to those of medium-chain-length carboxylic acids. PHA nomenclature and classification may still evolve as new structures continue to be discovered. The main biopolymer of the PHA family is the polyhydroxybutyrate homopolymer (PHB), but also different poly(hydroxybutyrate-co-hydroxyalkanoates) copolyesters exist such as poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHx),

Fig. 2.11 Generic chemical structure of the polyhydroxyalkanoates

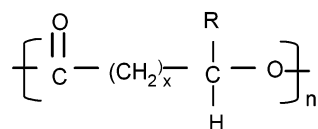


Table 2.1 Main PHAs homopolymer structures based on the Fig. 2.11

| Chemical name | Abbreviation | x value | R group |
|---|--------------------|---------|---------------|
| Poly(3-hydroxypropionate) | P(3HP) | 1 | Hydrogen |
| Poly(3-hydroxybutyrate) | P(3HB) | 1 | Methyl |
| Poly(3-hydroxyvalerate) | P(3HV) | 1 | Ethyl |
| Poly(3-hydroxyhexanoate) or poly(3-hydroxycaproate) | P(3HHx) or P(3HC) | 1 | Propyl |
| Poly(3-hydroxyhexanoate) | P(3HH) | 1 | Butyl |
| Poly (3-hydroxyoctanoate) | P(3HO) | 1 | Pentyl |
| Poly (3-hydroxynonanoate) | P(3HN) | | Hexyl |
| Poly(3-hydroxydecanoate) | P(3HD) | 1 | Heptyl |
| Poly(3-hydroxyundecanoate) or | P(3HUD)or P(3Hud) | 1 | Octyl |
| Poly(3-hydroxydodecanoate) | P(3HDD) or P(3HDd) | 1 | Nonyl |
| Poly(3-hydroxyoctadecanoate) | P(3HOD) or P(3Hod) | 1 | Pentadecanoyl |
| Poly(4-hydroxybutyrate) | P(4HB) | 2 | Hydrogen |
| Poly(5-hydroxybutyrate) | P(5HB) | 2 | Methyl |
| Poly(5-hydroxyvalerate) | P(5HV) | 3 | Hydrogen |

Table 2.2 Main PHA abbreviations

| Conventional abbreviations (short) | Full abbreviations | Structures |
|------------------------------------|--------------------|-------------|
| PHB | P(3HB) | Homopolymer |
| PHV | P(3HV) | Homopolymer |
| PHBV | P(3HB-co-3HV) | Copolymer |
| PHBHx | P(3HB-co-3HHx) | Copolymer |
| PHBO | P(3HB-co-3HO) | Copolymer |
| PHBD | P(3HB-co-3HD) | Copolymer |
| PHBOd | P(3HB-co-3Hod) | Copolymer |

poly(hydroxybutyrate-co-hydroxyoctanoate) (PHBO), and poly(hydroxybutyrate-co-hydroxyoctadecanoate) (PHBOd) (Tables 2.1, 2.2).

Figure 2.11 shows the generic formula for the PHAs where x is 1 or higher, and R can be either hydrogen or hydrocarbon chains of up to around C16 in length. The main members of the PHA homopolymer family are presented in Table 2.1.

A wide range of PHA homopolymers and copolymers have been produced, in most cases at laboratory scale. A few of them have attracted industrial interest and were commercialized in the past decade.

Copolymers of PHAs vary in the type and proportion of monomers, and are typically random in sequence. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or

Table 2.3 Main PHA commercial productions

| Company | Country | Trade name | PHA | Pilot/industrial scale |
|-------------------------------|---------|-----------------|--------------------------------------|------------------------|
| PHB industrial/ copersucar | Brazil | Biocycle | PHB, PHBV | Pilot/ind. (?) |
| Biomatera | Canada | Biomatera | PHBV | Pilot scale |
| PolyFerm Canada | Canada | VersaMer PHA | PHBV and copolymers | Pilot scale |
| Tianan | China | Enmat | PHBV | Ind. |
| Tianjin & DSM | China | GreenBio | PHB—copolymers based on 3 and 4HB | Pilot/ind. (?) |
| Tianzhu | China | Tianzhu | PHBHx | Pilot scale |
| Biomer | Germany | Biomer | PHB, PHBV | Pilot scale |
| Bio-On | Italy | Minerv PHA | PHB, PHBV | Pilot scale |
| Kaneka | Japan | Kaneka | PHBHx | Pilot/ind. (?) |
| DaniMer/Meredian | US | ? | Copolymers | Pilot/ind. (?) |
| Telles (Metabolix/ ADM) | US | Mirel | Copolymer | Ind. |

P(3HB-*co*-3HV) is based on a random arrangement of two monomers with R = methyl and with R = ethyl. Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) consists of two monomers with R = methyl and propyl. Some examples of homo and copolymers are shown in Table 2.2.

PHB is a highly crystalline polyester (above 50 %) with a high melting point, $T_m=173\text{--}180\text{ }^{\circ}\text{C}$, compared to the other biodegradable polyesters. The T_g is around $5\text{ }^{\circ}\text{C}$. The homopolymer shows a narrow window for the processing conditions. To ease the transformation, PHB can be plasticized with citrate ester. In contrast, PHBV copolymer processing is easier. Material properties can be tailored by varying the HV content. An increase of the HV content induces an increase in impact strength and decreases in T_m and T_g [113], crystallinity [114], water permeability [114], and tensile strength [115]. Besides, PHBV properties can evolve when plasticization occurs, e.g., with citrate ester (triacetin) [115, 116]. PHAs, like the PLAs, are sensitive to processing conditions. Under extrusion, we obtain rapid decreases in viscosity and molecular weight due to macromolecular chain cleavage by increasing the shear level, the temperature, and/or the residence time [117]. Regarding the biodegradable behavior, the kinetic of enzymatic degradation is variable according to the crystallinity, the structure [6, 118], and then to the processing history [119]. Bacterial copolyesters biodegrade faster than homopolymers [120] and synthetic copolyesters [121].

Table 2.3 shows that PHA production is shared among a great numbers of companies. Worldwide, more than 24 companies are known to be engaged in PHA production and applications. Compared to PLA, the world production of PHA is lower, largely less than 50,000 tons/year. But, it is difficult to have a precise idea

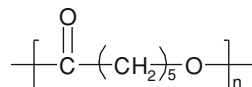
because there is a wide gap between the (press) announcements and the true production. Only the production capacities are published.

The story of PHA industrial production is very long and starts in the 1950s. In the seventeenth, Zeneca (formerly ICI) produced several tons of PHA copolymers under the trade name Biopol[®]. In the nineteenth, Zeneca UK produced P(3HB-*co*-3HV) in a pilot plant by bacterial fermentation using a mixture of glucose and propionic acid. In 1996, Zeneca sold its Biopol business to Monsanto, who continued the investigations started by Zeneca to produce PHA from genetically-modified crops. Monsanto commercially produced Biopol[®] P(3HB-*co*-3HV) with HV contents reaching 20 % by means of fermentation. The production was ceased at the end of 1999. Metabolix bought Biopol[®] assets in 2001. In 2007, Metabolix and Archer Daniels Midland (ADM) formed a joint venture, Telles, to produce PHAs under the trade name Mirel. ADM started in 2010 to build a first plant in Clinton, Iowa (US), which was expected to produce 50,000 tons of resin per year. This joint venture stopped in January 2012. Metabolix has developed production of PHA from genetically-modified crops, and announced in 2010 that it had completed a field trial of genetically engineering of tobacco into PHA biobased polymers. This company has also declared that, in greenhouse trials, switchgrass plants engineered using multi-gene expression technology can produce significant amounts of PHA bioplastics from leaf tissues.

Different small companies currently produce bacterial PHA. For instance, PHB Industrial (Brazil) produces PHB and PHBV (HV = 12 %) with 45 % crystallinity, from sugar cane molasses [118]. Biocycle[®] production is planned to be 4,000 tons/year, and then to be extended to 14,000 tons/year. In 2004, Procter & Gamble (US) and Kaneka Corporation (Japan) announced a joint development agreement for the completion of R&D leading to the commercialization of Nodax[®], a large range of polyhydroxybutyrate-*co*-hydroxyalkanoates (PHBHx, PHBO, PHBOd) [122]. Although the industrial large-scale production was planned with a target price around 2€/kg, the Nodax[®] development stopped in 2006 [123]. In 2007 Meredian Inc. purchased P&G's PHA technology. Meredian plans to produce over 270,000 tons annually in connection with DaniMer. Tianan, a Chinese company also announced to increase the capacity from the current 2,000 tons to 10,000 tons/year. The Dutch chemical company DSM announced to invest in a PHA plant together with a Chinese bio-based plastics company—Tianjin Green Bio-Science Co. The company will start up the production of PHA with an annual capacity of 10,000 tons. The Japanese company Kaneka planned to start the production of 50,000 tons/year of PHBHx in 2011.

The production of PHA is intended to replace synthetic non-degradable polymers for a wide range of applications [123]: packaging, agriculture, leisure, fast-food, hygiene as well as medicine and biomedical [112, 124] since PHA is biocompatible.

Fig. 2.12 Chemical structure of Polycaprolactone (PCL)



2.3.2 Petroleum-Based Polyesters

A large number of biodegradable polyesters are based on petroleum resources, obtained chemically from synthetic monomers [89–93, 95, 96]. According to the chemical structures, we can distinguish polycaprolactone, aliphatic copolyesters, and aromatic copolyesters. All these polyesters are soft at room temperature.

2.3.2.1 Polycaprolactone

Figure 2.12 gives the chemical structure of poly(ϵ -caprolactone) (PCL).

It is usually obtained by ROP of ϵ -caprolactone in the presence of metal alkoxides (aluminium isopropoxide, tin octoate...) [89, 90, 121]. PCL is widely used as a PVC solid plasticizer or for polyurethane applications, as polyols. But, it finds also some applications based on its biodegradable character in domains such as biomedicine (e.g. drugs controlled release) and environment (e.g. soft compostable packaging). Different commercial grades were produced by Solvay (CAPA[®]), which has sold this activity to Perstorp (Sweden), by Dow Chemical (Tone[®]) and by Daicel (Celgreen[®]). PCL shows a very low T_g (-61°C) and a low T_m (65°C), which could be a handicap in some applications. Therefore, PCL is generally blended [52, 107, 125, 126] or modified (e.g., copolymerisation, cross-linking [127]). Tokiwa et al. [128] have discussed the hydrolysis of PCL and biodegradation by fungi. They have shown that PCL can easily be enzymatically degraded. According to Bastioli [107], the biodegradability can be clearly claimed but the homopolymer hydrolysis rate is very low.

2.3.2.2 Aliphatic Copolyesters

A large number of aliphatic copolyesters based on petroleum resources are biodegradable copolymers. They are obtained by the combination of diols such as 1,2-ethanediol, 1,3-propanediol or 1,4-butanediol, and of dicarboxylic acids like adipic, sebacic or succinic acid. Showa Highpolymer (Japan) has developed a large range of polybutylene succinate (PBS) obtained by polycondensation of 1,4-butanediol and succinic acid. Anqing Hexing Chemical Co (China) also commercializes this aliphatic polyester.

Figure 2.13 gives the chemical structure of polybutylene succinate/adipate (PBSA). It is obtained by addition of adipic acid to 1,4-butanediol and succinic acid polycondensation. These copolymers are commercialized under the Bionolle[®]

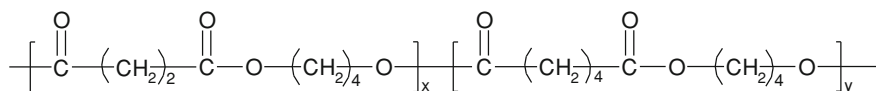


Fig. 2.13 Chemical structure of poly(butylene succinate adipate) (PBSA)

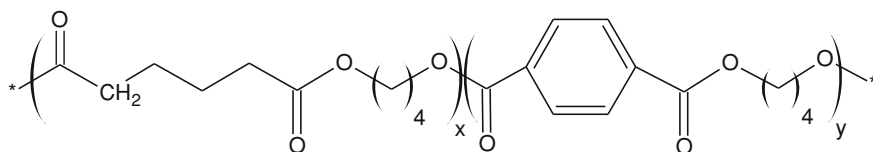


Fig. 2.14 Chemical structure of poly(butylene adipate-co-terephthalate)

trademark [95]. Ire Chemical (Korea) commercialized exactly the same kind of copolyesters under EnPol[®] trademark. Skygreen[®], a product from SK Chemicals (Korea), is obtained by polycondensation of 1,2-ethanediol, 1,4-butanediol with succinic and adipic acids [129]. Nippon Shokubai (Japan) also commercializes such aliphatic copolyester (Lunare SE[®]). The properties of these copolyesters depend on the structure [130] i.e., the combination of diols and diacids used. The biodegradability of these products depends also on the structure. The addition of adipic acid, which decreases the crystallinity [131], tends to increase the compost biodegradation rate [132]. According to Ratto et al. [133], the biodegradation results demonstrate that, while PBSA is inherently biodegradable, the addition of starch filler can significantly improve the rate of degradation.

2.3.2.3 Aromatic Copolyesters

Compared to totally aliphatic copolyesters, aromatic copolyesters are often based on terephthalic acid. For instance, Fig. 2.14 gives the chemical structure of poly(butylene adipate-co-terephthalate) (PBAT).

BASF, DuPont, and Novamont have commercialized aromatic copolyesters under Ecoflex[®] [95], Biomax[®], and Origo-Bi[®] trademarks, respectively. Biomax[®] shows a high terephthalic acid content which modifies some properties such as the T_m (200 °C). However, according to Muller et al. [130], an increase of terephthalic acid content tends to decrease the degradation rate. The production of Eastar Bio[®] from Eastman Chemical was stopped some years ago. This activity has been sold to Novamont, which now produces Origo-Bi[®].

Ecoflex[®] biodegradation had been analyzed by Witt et al. [134]. They concluded that there is no indication of environmental risk (ecotoxicity) when aliphatic-aromatic copolyesters of the Ecoflex[®]-type are introduced into composting processes.

2.4 Conclusion

Biodegradable polymers have been the topics of many studies for the last two decades. The development of these polymers (10–20 % per year) is a significant contribution to sustainable development in view of the wider range of disposal option at lower environmental impact.

Legislative attention able to properly address this issue could become a further incentive to the development of biodegradable products and maximize the environmental, social, and industrial benefits. The success of such highly innovative products is linked to the achievement of high quality standards. In this domain, quality mainly means environmental quality. Standards such as European EN 13432:2000 on the compostability and biodegradability norms at international level are now in place to partially control this bio-value.

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