

# Chapter 2

## Biodegradable Polymers

Luc Avérous and Eric Pollet

**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 agropolymers (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 CO<sub>2</sub> 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 (CO<sub>2</sub>). 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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

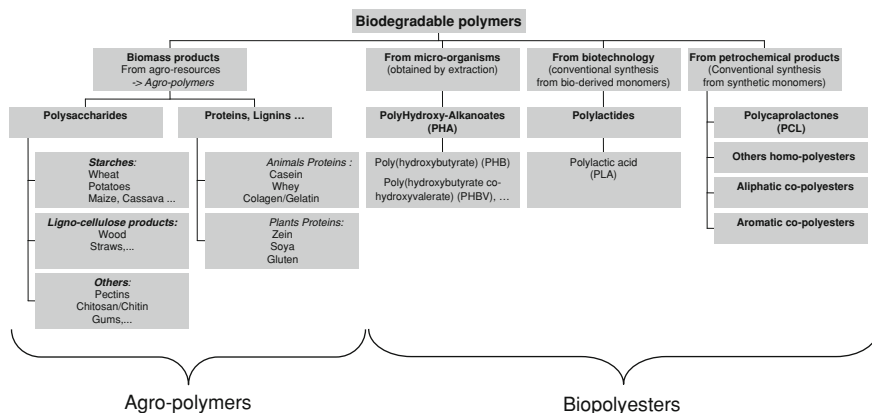
composting biodegradable plastic wastes, we can generate much-needed carbon-rich compost: humus materials. These valuable soil inputs can go back to the farmland and “reinitiate” the carbon cycle. Then, the plants growth contributes to reducing CO<sub>2</sub> atmospheric accumulation through photosynthesis 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 CO<sub>2</sub>, 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).

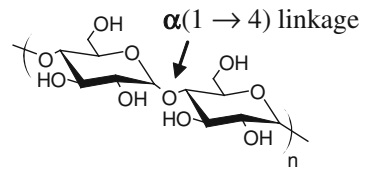
## 2.2 Agro-Polymers

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.

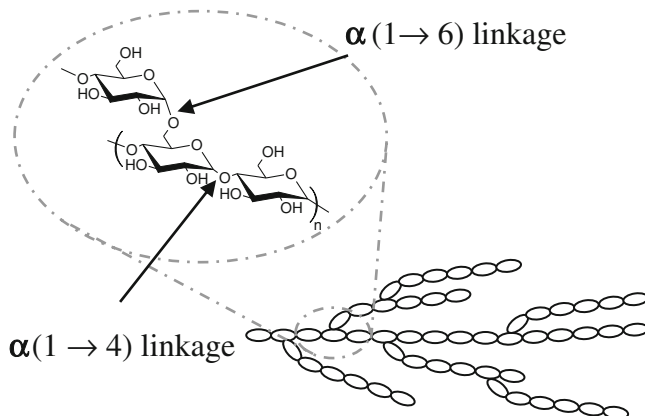
#### Native Starch Structure

Depending on the botanical origin of the plant, starch granules can have different shapes (sphere, platelet, polygon...) and size (from 0.5 to 175  $\mu\text{m}$ ). These granules are composed of two  $\alpha$ -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  $\alpha(1 \rightarrow 4)$  linkages (Fig. 2.2). These chains are partially ramified with some  $\alpha(1 \rightarrow 6)$  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  $\alpha(1 \rightarrow 4)$  linkage [15].

Amylopectin is the main starch component and has the same monomeric unit as amylose. It shows 95 %  $\alpha(1 \rightarrow 4)$  linkages and 5 %  $\alpha(1 \rightarrow 6)$  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

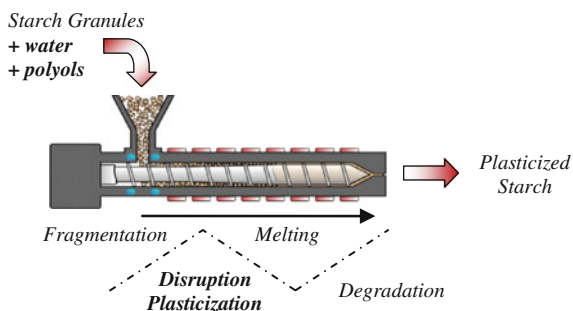
Because of numerous intermolecular hydrogen bonds existing between the chains, the melting temperature ( $T_m$ ) of starch is higher than its degradation temperature [21, 22]. Consequently, to elaborate a plastic-like material, it is necessary to introduce high water content or/and some non-volatile 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  $\beta$ ) 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  $\alpha$ ) 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

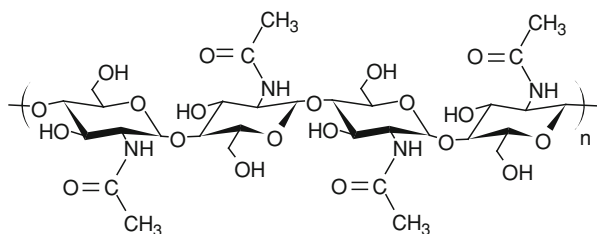


Fig. 2.5 Chitin chemical structure

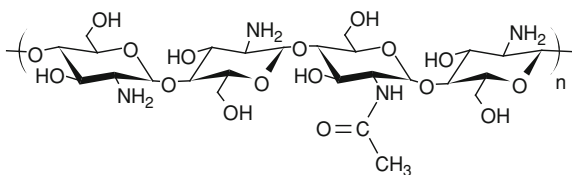
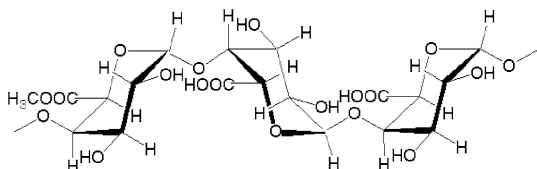
conditions. When the samples are stored below the  $T_g$ , the samples will undergo physical ageing with material densification [56]. When  $T > T_g$ , the samples will retrograde with a crystallinity increase [57]. The physical ageing is observed for materials with plasticizer content lower than 25 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  $\alpha$  and  $\beta$  [65]. A third allomorphic structure  $\gamma$  has also been reported, but it seems to be a variant of the  $\alpha$  form [66]. These two structures are organized in crystalline sheets where a number of intra-sheet hydrogen bonds tightly hold them. The  $\alpha$  form presents some inter-sheets hydrogen bonds. Such a feature is not found for the  $\beta$  form, which is consequently more prone than the  $\alpha$  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  $\beta(1\rightarrow4)$  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  $\text{g}\cdot\text{mol}^{-1}$  and acetylation degrees from 2 to 60 %.

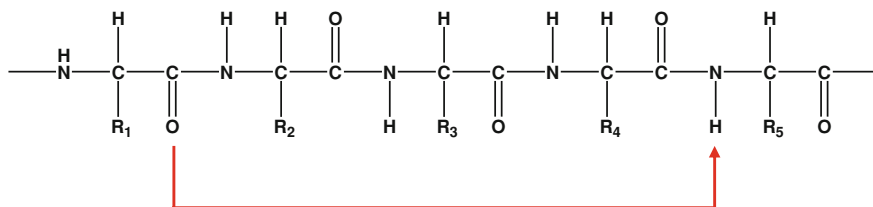
In solid state, chitosan is a semi-crystalline polymer. Its morphology has been investigated and many allomorphs have been described, depending on its acetylation degree, on the distribution of the acetyl groups along the carbohydrate chain, and on the chitosan preparation procedure [73, 74].

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  $\alpha(1\rightarrow4)$ -linked D-galacturonic acid (Fig. 2.7). This monomer unit could be partially replaced by  $\alpha(1\rightarrow2)$ -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  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  [78]. Commercial zein is made up of  $\alpha$ -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<sup>-1</sup>.

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<sup>-1</sup> 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<sup>-1</sup>. 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....

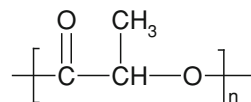
### 2.2.2.4 Casein

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<sup>-1</sup>. 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

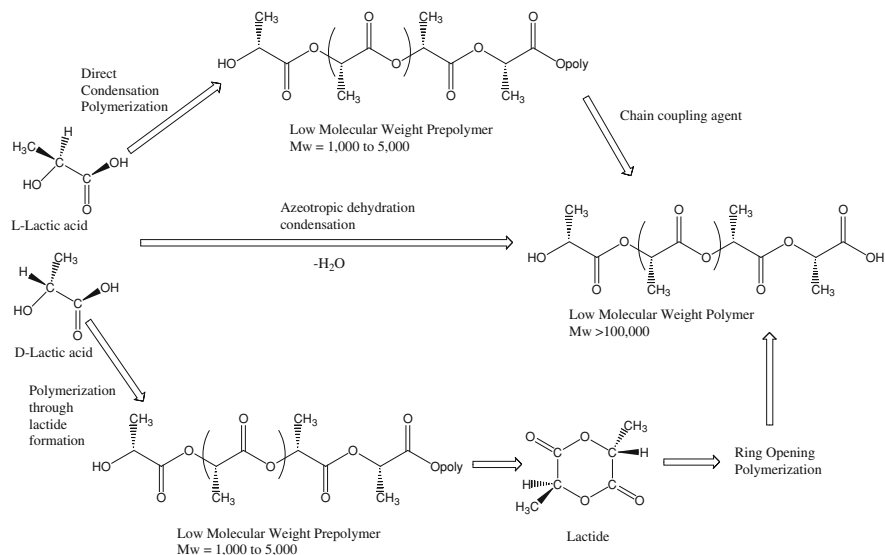
Some biobased polyesters are now largely available like PLA and PHAs, with different industrial productions.

#### 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), Futerra (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  $\alpha$ -form exhibits a well-defined diffraction pattern. This structure is more stable than the  $\beta$ -structure, with a  $T_m$  at 185 °C compared to 175 °C for the  $\beta$ -structure. This latter can be formed at a high draw ratio and high drawing temperature [28]. The  $\gamma$ -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.

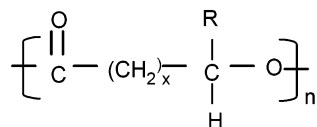
### 2.3.1.2 Polyhydroxyalkanoates

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(3H Ud)	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

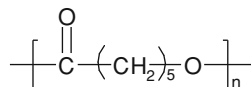
because there is a wide gap between the (press) announcements and the true production. Only the production capacities are published.

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<sup>®</sup>. 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<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup>, 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<sup>®</sup> 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

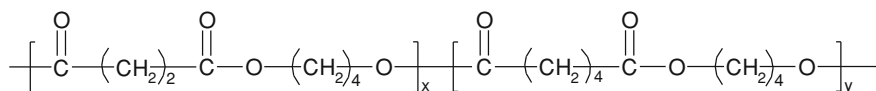
Figure 2.12 gives the chemical structure of poly( $\epsilon$ -caprolactone) (PCL).

It is usually obtained by ROP of  $\epsilon$ -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<sup>®</sup>), which has sold this activity to Perstorp (Sweden), by Dow Chemical (Tone<sup>®</sup>) and by Daicel (Celgreen<sup>®</sup>). 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.

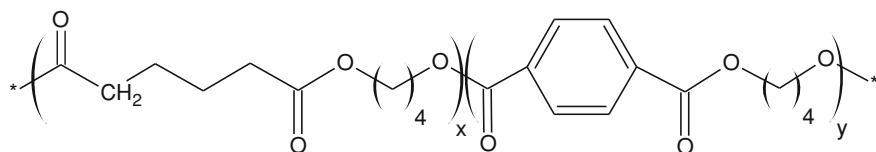
#### 2.3.2.2 Aliphatic Copolyesters

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<sup>®</sup>



**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<sup>®</sup> trademark. Skygreen<sup>®</sup>, a product from SK Chemicals (Korea), is obtained by polycondensation of 1,2-ethanediol, 1,4-butenediol with succinic and adipic acids [129]. Nippon Shokubai (Japan) also commercializes such aliphatic copolyester (Lunare SE<sup>®</sup>). 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<sup>®</sup> [95], Biomax<sup>®</sup>, and Origo-Bi<sup>®</sup> trademarks, respectively. Biomax<sup>®</sup> 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<sup>®</sup> from Eastman Chemical was stopped some years ago. This activity has been sold to Novamont, which now produces Origo-Bi<sup>®</sup>.

Ecoflex<sup>®</sup> 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<sup>®</sup>-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.

## References

1. Narayan R (2001) Drivers for biodegradable/compostable plastics and role of composting in waste management and sustainable agriculture. *Orbit J* 1(1):1–9
2. Steinbuechel A (2003) *Biopolymers, general aspects and special applications*, vol 10. Wiley-VCH, Weinheim
3. Avella M, Bonadies E, Martuscelli E (2001) European current standardization for plastic packaging recoverable through composting and biodegradation. *Polym Test* 20(5):517–521
4. Van Tuil R, Fowler P, Lawther M, Weber CJ (2000) Properties of biobased packaging materials, biobased packaging materials for the food industry: status and perspectives. KVL, Frederiksberg
5. Fritz J, Link U, Braun R (2001) Environmental impacts of biobased/biodegradable packaging. *Starch* 53(3–4):105–109
6. Karlsson S, Albertsson A-C (1998) Biodegradable polymers and environmental interaction. *Polym Eng Sci* 38(8):1251–1253
7. Kaplan DL, Mayer JM, Ball D, McCassie J, Allen AL, Stenhouse P (1993) Fundamentals of biodegradable polymers. In: Ching C, Kaplan DL, Thomas EL (eds) *Biodegradable polymers and packaging*. Technomic Pub Co, Lancaster, pp 1–42
8. Van de Velde K, Kiekens P (2002) Biopolymers: overview of several properties and consequences on their applications. *Polym Test* 21(4):433–442
9. Rouilly A, Rigal L (2002) Agro-materials: a bibliographic review. *J Macromol Sci Part C Polym Rev* C42(4):441–479
10. Chandra R, Rustgi R (1998) Biodegradable polymers. *Prog Polym Sci* 23(7):1273–1335
11. Guilbot A, Mercier C (1985) The polysaccharides. In: Aspinall GO (ed) *Molecular biology*, vol 3. Academic Press Incorporation, New York, pp 209–282
12. Della Valle G, Buleon A, Carreau PJ, Lavoie PA, Vergnes B (1998) Relationship between structure and viscoelastic behavior of plasticized starch. *J Rheol* 42(3):507–525
13. Colonna P, Mercier C (1984) Macromolecular structure of wrinkled- and smooth-pea starch components. *Carbohydr Res* 126(2):233–247
14. Hizukuri S, Takeda Y, Yasuda M (1981) Multibranched nature of amylose and the action of debranching enzymes. *Carbohydr Res* 94(2):205–213
15. Hayashi A, Kinoshita K, Miyake Y, Cho CH (1981) Conformation of amylose in solution. *Polym J* 13(6):537–541

16. Zobel HF (1988) Molecules to granules: a comprehensive starch review. *Starch-Starke* 40(2):44–50
17. Hizukuri S (1986) Polymodal distribution of the chain lengths of amylopectins, and its significance. *Carbohydr Res* 147(2):342–347
18. Jenkins PJ, Donald AM (1995) The influence of amylose on starch granule structure. *Int J Biol Macromol* 17(6):315–321
19. Van Soest JGG, Hullemann SHD, De Wit D, Vliegthart JFG (1996) Crystallinity in starch bioplastics. *Ind Crop Prod* 5(1):11–22
20. Van Soest JGG, Essers P (1997) Influence of amylose-amylopectin ratio on properties of extruded starch plastic sheets. *J Macromol Sci Part A-Pure Appl Chem* 34(9):1665–1689
21. Jang JK, Pyun YR (1986) Effect of moisture content on the melting of wheat starch. *Starch-Starke* 48(2):48–51
22. Shogren RL (1992) Effect of moisture content on the melting and subsequent physical aging of cornstarch. *Carbohydr Polym* 19(2):83–90
23. Swanson CL, Shogren RL, Fanta GF, Imam SH (1993) Starch-plastic materials-preparation, physical properties, and biodegradability (a review of recent USDA research). *J Environ Polym Deg* 1(2):155–166
24. Tomka I (1991) Thermoplastic starch. *Adv Exp Med Biol* 302:627–637
25. Cooke D, Gidley MJ (1992) Loss of crystalline and molecular order during starch gelatinisation: origin of the enthalpic transition. *Carbohydr Res* 227:103–112
26. Stevens DJ, Elton GAH (1971) Thermal properties of the starch/water system. Part I. Measurement of heat of gelatinisation by differential scanning calorimetry. *Starch-Starke* 23(1):8–11
27. Genkina NK, Wikman J, Bertoft E, Yuryev VP (2007) Effects of structural imperfection on gelatinization characteristics of amylopectin starches with A- and B-type crystallinity. *Biomacromolecules* 8(7):2329–2335
28. Averous L (2004) Biodegradable multiphase systems based on plasticized starch: a review. *J Macromol Sci Part C-Polym Rev* 44(3):231–274
29. Ollett AL, Parker R, Smith AC, Miles MJ, Morris VJ (1990) Microstructural changes during the twin-screw extrusion cooking of maize grits. *Carbohydr Polym* 13(1):69–84
30. Martin O, Averous L, Della Valle G (2003) In-line determination of plasticized wheat starch viscoelastic behavior: impact of processing. *Carbohydr Polym* 53(2):169–182
31. Della Valle G, Boche Y, Colonna P, Vergnes B (1995) The extrusion behaviour of potato starch. *Carbohydr Polym* 28(3):255–264
32. Vergnes B, Villemaire JP, Colonna P, Tayeb J (1987) Interrelationships between thermomechanical treatment and macromolecular degradation of maize starch in a novel rheometer with preshearing. *J Cereal Sci* 5:189
33. Orford PD, Parker R, Ring SG (1993) The functional properties of extrusion-cooked waxy-maize starch. *J Cereal Sci* 18(3):277–286
34. Sagar AD, Merrill EW (1995) Starch fragmentation during extrusion processing. *Polymer* 36(9):1883–1886
35. Baud B, Colonna P, Della Valle G, Roger P (1999) Macromolecular degradation of extruded starches measured by HPSEC-MALLS. In: Colonna P, Guilbert S (eds) *Biopolymer science food and non food applications. Les Colloques de l'INRA, Paris*, pp 217–221
36. Wang SS, Chiang WC, Yeh AI, Zhao B, Kim IH (1989) Kinetics of phase transition of waxy corn starch at extrusion temperatures and moisture contents. *J Food Sci* 54(5):1298–1301
37. Davidson VJ, Paton D, Diosady LL, Larocque G (1984) Degradation of wheat starch in a single screw extruder: characteristics of extruded starch polymers. *J Food Sci* 49(2):453–458
38. Davidson VJ, Parker R, Diosady LL, Rubin LT (1984) A model for mechanical degradation of wheat starch in a single-screw extruder. *J Food Sci* 49(4):1154–1169
39. Zeleznak KJ, Hosney RC (1987) The glass transition in starch. *Cereal Chem* 64(2):121–124

40. Kalichevsky MT, Jaroszkiwicz EM, Ablett S, Blanshard JMV, Lillford PJ (1992) The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydr Polym* 18(2):77–88
41. Van Soest JGG, Knooren N (1997) Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging. *J Appl Polym Sci* 64(7): 1411–1422
42. Forssell P, Mikkila J, Suortti T, Seppala J, Poutanen K (1996) Plasticization of barley starch with glycerol and water. *J Macromol Sci Part A-Pure Appl Chem* 33(5):703–715
43. Hulleman SHD, Kalisvaart MG, Janssen FHP, Feil H, Vliegthart JFG (1999) Origins of B-type crystallinity in glycerol-plasticised, compression-moulded potato starches. *Carbohydr Polym* 39(4):351–360
44. Lourdin D, Coignard L, Bizot H, Colonna P (1997) Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. *Polymer* 38(21):5401–5406
45. Van Soest JGG, De Wit D, Tournois H, Vliegthart JFG (1994) The influence of glycerol on structural changes in waxy maize starch as studied by Fourier transform infra-red spectroscopy. *Polymer* 35(22):4722–4727
46. Gaudin S, Lourdin D, Forssell PM, Colonna P (2000) Antiplasticisation and oxygen permeability of starch-sorbitol films. *Carbohydr Polym* 43(1):33–37
47. Lourdin D, Della Valle G, Colonna P (1995) Influence of amylose content on starch films and foams. *Carbohydr Polym* 27(4):261–270
48. Kalichevsky MT, Blanshard JMV (1993) The effect of fructose and water on the glass transition of amylopectin. *Carbohydr Polym* 20(2):107–113
49. Ollett AL, Parker R, Smith AC (1991) Deformation and fracture behaviour of wheat starch plasticized with glucose and water. *J MaterSci* 26(5):1351–1356
50. Shogren RL, Swanson CL, Thompson AR (1992) Extrudates of cornstarch with urea and glycols: structure/mechanical property relations. *Starch-Starke* 44(9):335–338
51. Lourdin D, Ring SG, Colonna P (1998) Study of plasticizer-oligomer and plasticizer-polymer interactions by dielectric analysis: maltose-glycerol and amylose-glycerol-water systems. *Carbohydr Res* 306(4):551–558
52. Averous L, Moro L, Dole P, Fringant C (2000) Properties of thermoplastic blends: starch-polycaprolactone. *Polymer* 41(11):4157–4167
53. Lourdin D, Bizot H, Colonna P (1997) Correlation between static mechanical properties of starch-glycerol materials and low-temperature relaxation. *Macromol Symp* 114:179–185
54. Lourdin D, Bizot H, Colonna P (1997) “Antiplasticization” in starch-glycerol films? *J Appl Polym Sci* 63(8):1047–1053
55. Godbillot L, Dole P, Joly C, Roge B, Mathlouthi M (2006) Analysis of water binding in starch plasticized films. *Food Chem* 96(3):380–386
56. Thiewes HJ, Steeneken PAM (1997) The glass transition and the sub-T<sub>g</sub> endotherm of amorphous and native potato starch at low moisture content. *Carbohydr Polym* 32(2): 123–130
57. Lu TJ, Jane JL, Keeling PL (1997) Temperature effect on retrogradation rate and crystalline structure of amylose. *Carbohydr Polym* 33(1):19–26
58. Appelqvist IAM, Cooke D, Gidley MJ, Lane SJ (1993) Thermal properties of polysaccharides at low moisture: 1—An endothermic melting process and water-carbohydrate interactions. *Carbohydr Polym* 20(4):291–299
59. Averous L, Fauconnier N, Moro L, Fringant C (2000) Blends of thermoplastic starch and polyesteramide: processing and properties. *J Appl Polym Sci* 76(7):1117–1128
60. Van Soest JGG, Borger DB (1997) Structure and properties of compression-molded thermoplastic starch materials from normal and high-amylose maize starches. *J Appl Polym Sci* 64(4):631–644
61. Van Soest JGG, De Wit D, Vliegthart JFG (1996) Mechanical properties of thermoplastic waxy maize starch. *J Appl Polym Sci* 61(11):1927–1937



62. Van Soest JGG, Hullemann SHD, De Wit D, Vliegthart JFG (1996) Changes in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystallinity. *Carbohydr Polym* 29(3):225–232
63. Campbell NA, Reece JB, Mitchell LG (1999) *Biology*, 5th edn. Addison Wesley Longman, Menlo Park
64. Rinaudo M (2006) Chitin and chitosan: Properties and applications. *Prog Polym Sci* 31:603–632
65. Rudall KM, Kenchington W (1973) The chitin system. *Biol Rev* 40:597–636
66. Atkins EDT (1985) Conformation in polysaccharides and complex carbohydrates. *J Biosci* 8:375–387
67. Minke R, Blackwell J (1978) The structure of  $\alpha$ -chitin. *J Mol Biol* 120:167–181
68. Gardner KH, Blackwell J (1975) Refinement of the structure of  $\beta$ -chitin. *Biopolymers* 14:1581–1595
69. Lu Y, Weng L, Zhang L (2004) Morphology and properties of soy protein isolate thermoplastics reinforced with chitin whiskers. *Biomacromolecules* 5(3):1046–1051
70. Paillet M, Dufresne A (2001) Chitin whisker reinforced thermoplastic nanocomposites. *Macromolecules* 34(19):6527–6530
71. Peter MGPI (2002) Chitin and Chitosan from Fungi. In: Steinbüchel A (ed) *Biopolymers*, vol 6., Polysaccharides I/Wiley-VCH, Weinheim, pp 123–157
72. Shahidi F, Arachchi JKV, Jeon YJ (1999) Food applications of chitin and chitosan. *Trends Food Sci Technol* 10(2):37–51
73. Ogawa K (1991) Effect of heating an aqueous suspension of chitosan on the crystallinity and polymorphs. *Agric Biol Chem* 55(9):2375–2379
74. Ogawa K, Yui T, Miya M (1992) Dependence on the preparation procedure of the polymorphism and crystallinity of chitosan membranes. *Biosci Biotech Biochem* 56:858–862
75. Epure V, Griffon M, Pollet E, Averous L (2011) Structure and properties of glycerol-plasticized chitosan obtained by mechanical kneading. *Carbohydr Polym* 83(2):947–952
76. Thakur BR, Singh RK, Handa AK (1997) Chemistry and uses of pectin—a review. *Crit Rev Food Sci Nutr* 37(1):47–73
77. May CD (1990) Industrial pectins: Sources, production and applications. *Carbohydr Polym* 12(1):79–99
78. Zhang L, Zeng M (2008) Proteins as sources of materials. In: Belgacem M, Gandini A (eds) *Monomers polymers and composites from renewable resources*. Elsevier, Amsterdam, pp 479–493
79. Zhang JW, Chen F (2010) Development of novel soy protein-based polymer blends. *Green Polym Chem: Biocatal Biomater* 1043:45–57
80. Domenek S, Morel MH, Guilbert S (2004) Wheat gluten based biomaterials: environmental performance, degradability and physical modifications. *Roy Soc Ch* 295:443–446
81. Guillaume C, Gontard N, Guilbert S (2011) New packaging materials based on renewable resources: properties, applications, and prospects. In: Aguilera JM, Simpson R, Welti-Chanes J, Bermudez Aguirre D, Barbosa-Canovas G (eds) *Food Engineering Interfaces*. Springer, New York, pp. 619–630
82. Arvanitoyannis I, Psomiadou E, Nakayama A (1996) Edible films made from sodium caseinate, starches, sugars or glycerol.1. *Carbohydr Polym* 31(4):179–192
83. Ofokansi K, Winter G, Fricker G, Coester C (2010) Matrix-loaded biodegradable gelatin nanoparticles as new approach to improve drug loading and delivery. *Eur J Pharm Biopharm* 76(1):1–9
84. Averous L (2008) Polylactic acid: synthesis, properties and applications. In: Belgacem N, Gandini A (eds) *Monomers, oligomers, polymers and composites from renewable resources*. Elsevier, Amsterdam, pp 433–450
85. Garlotta D (2001) A literature review of poly(lactic acid). *J Polym Environ* 9(2):63–84
86. Wee Y-J, Kim J-N, Ryu H-W (2006) Biotechnological production of lactic acid and its recent applications. *Food Technol Biotechnol* 44(2):163–172

87. Moon SI, Lee CW, Miyamoto M, Kimura Y (2000) Melt polycondensation of L-lactic acid with Sn(II) catalysts activated by various proton acids: a direct manufacturing route to high molecular weight poly(L-lactic acid). *J Polym Sci Part A: Polym Chem* 38(9):1673–1679
88. Moon S-I, Lee C-W, Taniguchi I, Miyamoto M, Kimura Y (2001) Melt/solid polycondensation of L-lactic acid: an alternative route to poly(L-lactic acid) with high molecular weight. *Polymer* 42(11):5059–5062
89. Okada M (2002) Chemical syntheses of biodegradable polymers. *Prog Polym Sci (Oxford)* 27(1):87–133
90. Albertsson A-C, Varma IK (2002) Aliphatic polyesters: synthesis, properties and applications. *Adv Polym Sci* 157:1–40
91. Vert M, Schwarch G, Coudane J (1995) Present and future of PLA polymers. *J Macromol Sci Pure Appl Chem* A32(4):787–796
92. Sinclair RG (1996) The case for polylactic acid as a commodity packaging plastic. *J Macromol Sci—Pure Appl Chem* 33(5):585–597
93. Lunt J (1998) Large-scale production, properties and commercial applications of polylactic acid polymers. *Polym Degrad Stabil* 59(1–3):145–152
94. Auras R, Harte B, Selke S (2004) An overview of polylactides as packaging materials. *Macromol Biosci* 4(9):835–864
95. Steinbuechel A, Doi Y (2002) Biopolymers: polyesters III—applications and commercial products, vol 4. Wiley-VCH, Weinheim
96. Bigg DM (1996) Effect of copolymer ratio on the crystallinity and properties of polylactic acid copolymers. *J Eng Appl Sci* 2:2028–2039
97. Perego G, Cella GD, Bastioli C (1996) Effect of molecular weight and crystallinity on poly(lactic acid) mechanical properties. *J Appl Polym Sci* 59(1):37–43
98. Martin O, Avérous L (2001) Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. *Polymer* 42(14):6209–6219
99. Yasuniwa M, Iura K, Dan Y (2007) Melting behavior of poly(L-lactic acid): Effects of crystallization temperature and time. *Polymer* 48(18):5398–5407
100. Labrecque LV, Kumar RA, Dave V, Gross RA, McCarthy SP (1997) Citrate esters as plasticizers for poly(lactic acid). *J Appl Polym Sci* 66(8):1507–1513
101. Jacobsen S, Fritz HG (1999) Plasticizing polylactide—the effect of different plasticizers on the mechanical properties. *Polym Eng Sci* 39(7):1303–1310
102. Kranz H, Ubrich N, Maincent P, Bodmeier R (2000) Physicomechanical properties of biodegradable poly(D,L-lactide) and poly(D,L-lactide-co-glycolide) films in the dry and wet states. *J Pharm Sci* 89(12):1558–1566
103. Ljungberg N, Andersson T, Wesslen B (2003) Film extrusion and film weldability of poly(lactic acid) plasticized with triacetine and tributyl citrate. *J Appl Polym Sci* 88(14):3239–3247
104. Van Tuil R, Fowler P, Lawther M, Weber CJ (2000) Properties of biobased packaging materials. In: *Biobased packaging materials for the food industry—status and perspectives*. KVL, Frederiksberg, pp 8–33
105. Lehermeier HJ, Dorgan JR, Way JD (2001) Gas permeation properties of poly(lactic acid). *J Membrane Sci* 190(2):243–251
106. McCarthy SP, Ranganathan A, Ma W (1999) Advances in properties and biodegradability of co-continuous, immiscible, biodegradable, polymer blends. *Macromol Symp* 144:63–72
107. Bastioli C (1998) Biodegradable materials—present situation and future perspectives. *Macromol Symp* 135:193–204
108. Tuominen J, Kylma J, Kapanen A, Venelampi O, Itävaara M, Seppälä J (2002) Biodegradation of lactic acid based polymers under controlled composting conditions and evaluation of the ecotoxicological impact. *Biomacromolecules* 3(3):445–455
109. De Koning GJM (1993) Prospects of bacterial poly[(R)-3-hydroxyalkanoates]. Eindhoven University of Technology, Eindhoven
110. Madison LL, Huisman GW (1999) Metabolic engineering of poly(3-hydroxyalkanoates): from DNA to plastic. *Microbiol Mol Biol Rev* 63(1):21–53

111. Doi Y (1990) *Microbial polyesters*. Wiley, New York
112. Zinn M, Witholt B, Egli T (2001) Occurrence, synthesis and medical application of bacterial polyhydroxyalkanoate. *Adv Drug Deliver Rev* 53(1):5–21
113. Amass W, Amass A, Tighe B (1998) A review of biodegradable polymers: Uses, current developments in the synthesis and characterization of biodegradable polyesters, blends of biodegradable polymers and recent advances in biodegradation studies. *Polym Int* 47(2):89–144
114. Shogren R (1997) Water vapor permeability of biodegradable polymers. *J Environ Polym Degr* 5(2):91–95
115. Kotnis MA, O'Brien GS, Willett JL (1995) Processing and mechanical properties of biodegradable poly(hydroxybutyrate-co-valerate)-starch compositions. *J Environ Polym Degr* 3(2):97–105
116. Shogren RL (1995) Poly(ethylene oxide)-coated granular starch-poly(hydroxybutyrate-co-hydroxyvalerate) composite materials. *J Environ Polym Degr* 3(2):75–80
117. Ramkumar DHS, Bhattacharya M (1998) Steady shear and dynamic properties of biodegradable polyesters. *Polym Eng Sci* 38(9):1426–1435
118. El-Hadi A, Schnabel R, Straube E, Müller G, Henning S (2002) Correlation between degree of crystallinity, morphology, glass temperature, mechanical properties and biodegradation of poly(3-hydroxyalkanoate) PHAs and their blends. *Polym Test* 21(6):665–674
119. Parikh M, Gross RA, McCarthy SP (1998) The influence of injection molding conditions on biodegradable polymers. *J Inject Molding Technol* 2(1):30
120. Dos Santos Rosa D, Calil MR, Fassina Guedes CdG, Rodrigues TC (2004) Biodegradability of thermally aged PHB, PHB-V, and PCL in soil compostage. *J Polym Environ* 12(4):239–245
121. Chiellini E, Solaro R (1996) Biodegradable polymeric materials. *Adv Mater* 8(4):305–313
122. Noda I, Green PR, Satkowski MM, Schechtman LA (2005) Preparation and properties of a novel class of polyhydroxyalkanoate copolymers. *Biomacromolecules* 6(2):580–586
123. Philip S, Keshavarz T, Roy I (2007) Polyhydroxyalkanoates: biodegradable polymers with a range of applications. *J Chem Technol Biotechnol* 82(3):233–247
124. Williams SF, Martin DP, Horowitz DM, Peoples OP (1999) PHA applications: addressing the price performance issue I. *Tissue engineering*. *Int J Biol Macromol* 25(1–3):111–121
125. Bastioli C, Cerutti A, Guanella I, Romano GC, Tosin M (1995) Physical state and biodegradation behavior of starch-polycaprolactone systems. *J Environ Polym Degr* 3(2):81–95
126. Bastioli C (1998) Properties and applications of Mater-Bi starch-based materials. *Polym Degrad Stab* 59(1–3):263–272
127. Koenig MF, Huang SJ (1994) Evaluation of crosslinked poly(caprolactone) as a biodegradable, hydrophobic coating. *Polym Degrad Stab* 45(1):139–144
128. Tokiwa Y, Suzuki T (1977) Hydrolysis of polyesters by lipases. *Nature* 270(5632):76–78
129. Lee S-R, Park H-M, Lim H, Kang T, Li X, Cho W-J, Ha C-S (2002) Microstructure, tensile properties, and biodegradability of aliphatic polyester/clay nanocomposites. *Polymer* 43(8):2495–2500
130. Muller R-J, Witt U, Rantze E, Deckwer W-D (1998) Architecture of biodegradable copolyesters containing aromatic constituents. *Polym Degrad Stab* 59(1–3):203–208
131. Yokota Y, Marechal H (1999) Processability of biodegradable poly(butylene) succinate and its derivatives. A case study. In: *Biopolymer conference*, Wurzburg, Germany, 24 Feb 1999
132. Fujimaki T (1998) Processability and properties of aliphatic polyesters, 'Bionolle', synthesized by polycondensation reaction. *Polym Degrad Stab* 59(1–3):209–214
133. Ratto JA, Stenhouse PJ, Auerbach M, Mitchell J, Farrell R (1999) Processing, performance and biodegradability of a thermoplastic aliphatic polyester/starch system. *Polymer* 40(24):6777–6788
134. Witt U, Einig T, Yamamoto M, Kleeberg I, Deckwer W-D, Muller R-J (2001) Biodegradation of aliphatic-aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. *Chemosphere* 44(2):289–299



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