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Polylactic Acid: Synthesis, Properties and Applications

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ABSTRACT

Polylactic acid (PLA) is at present one of the most promising biodegradable polymers (biopolymers) and has been the subject of abundant literature over the last decade. PLA can be processed with a large number of techniques and is commercially available (large-scale production) in a wide range of grades. It is relatively cheap and has some remarkable properties, which make it suitable for different applications. This chapter deals with the different syntheses to produce this biopolymer, its diverse properties and various applications. Its biodegradability is adapted to short-term packaging, and its biocompatibility in contact with living tissues is exploited for biomedical applications (implants, sutures, drug encapsulation …).

Keywords

Polylactic acid, Biopolymer, Biodegradable, Properties, Synthesis, Process, Application, Packaging, Biomedical

21.1 INTRODUCTION

Tailoring new materials within a perspective of eco-design or sustainable development is a philosophy that is applied to more and more materials. It is the reason why material components such as biodegradable polymers can be considered as 'interesting' – environmentally safe – alternatives. Besides, ecological concerns have resulted in a resumed interest in renewable resources-based products.

Figure 21.1 shows an attempt to classify the biodegradable polymers into two groups and four different families. The main groups are (i) the agro-polymers (polysaccharides, proteins, etc.) and (ii) the biopolyesters (biodegradable polyesters) such as polylactic acid (PLA), polyhydroxyalkanoate (PHA), aromatic and aliphatic copolyesters [1]. Biodegradable polymers show a large range of properties and can now compete with non-biodegradable thermoplastics in different fields (packaging, textile, biomedical, etc.). Among these biopolyesters, PLA is at present one of the most promising biopolymer. PLA has been the subject of an abundant literature with several reviews and book chapters [2–8], mainly during the last decade. PLA can be processed with a large number of techniques. PLA is commercially and largely available (large-scale production) in a wide range of grades. It has a reasonable price and some remarkable properties to fulfil different applications. For instance, the PLA production capacity of Cargill (USA) in 2006 was 140 kT per year at 2–5 Euros per kg [9]. Other companies, such as Mitsui Chemical (Lacea-Japan), Treofan (Netherland), Galactic (Belgium), Shimadzu Corporation (Japan), produce smaller quantities. Some of them are only focused on the biomedical market like Boeringher Ingelheim (Germany), Purac (Netherland) or Phusis (France), because the constraints of this market are very specific. However, according to different sources, PLA consumption in 2006 was only about 60 000 tons per year and, at present, only ~30 per cent of lactic acid is used for PLA production. Thus, this biopolymer presents a high potential for development.

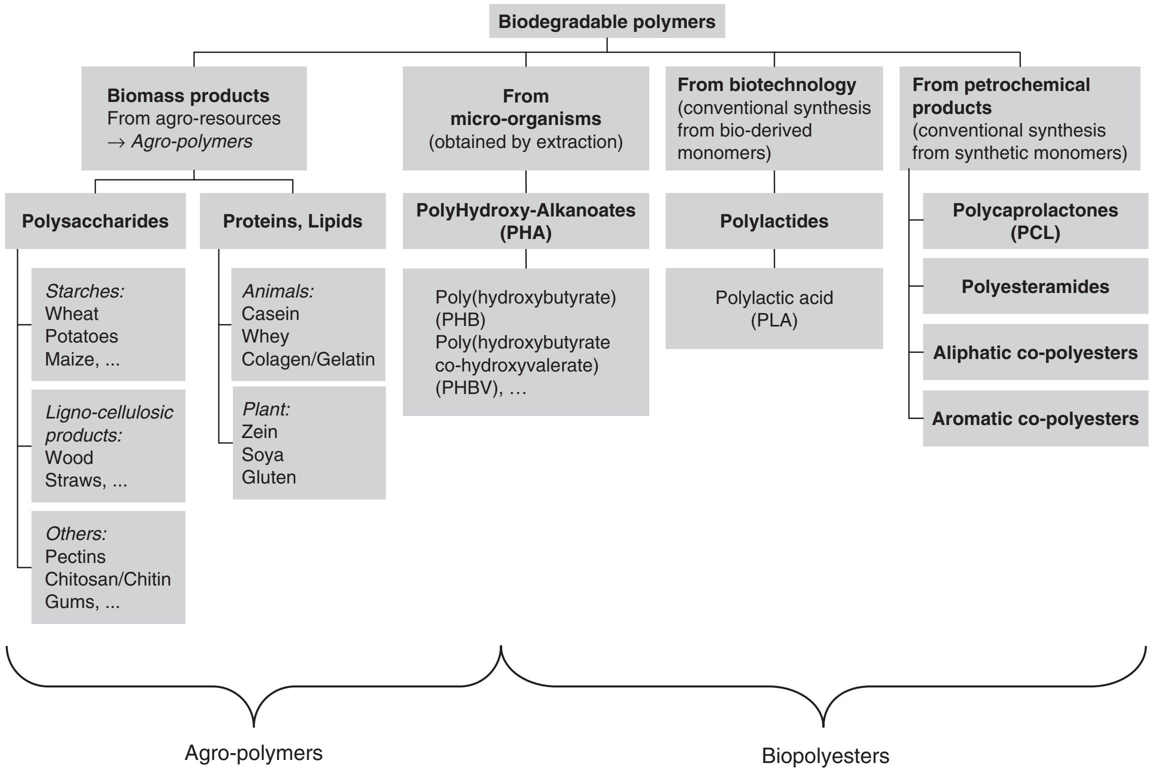

Figure 21.1 Classification of the biodegradable polymers. (Adapted from Reference [1].)

PLA belongs to the family of aliphatic polyesters commonly made from α-hydroxy acids, which also includes, for example, polyglycolic acid (PGA). It is one of the few polymers in which the stereochemical structure can easily be modified by polymerizing a controlled mixture ofland D isomers (Fig. 21.2) to yield high molecular weight and amorphous or semi-crystalline polymers. Properties can be both modified through the variation of isomers (l/d ratio) and the homo and (d,l)copolymers relative contents. Besides, PLA can be tailored by formulation involving adding plasticizers, other biopolymers, fillers, etc.

PLA is considered both as biodegradable (*e.g.* adapted for short-term packaging) and as biocompatible in contact with living tissues (*e.g.* for biomedical applications such as implants, sutures, drug encapsulation, etc.). PLA can be degraded by abiotic degradation (*i.e.* simple hydrolysis of the ester bond without requiring the presence of enzymes to catalyze it). During the biodegradation process, and only in a second step, the enzymes degrade the residual oligomers till final mineralization (biotic degradation).

As long as the basic monomers (lactic acid) are produced from renewable resources (carbohydrates) by fermentation, PLA complies with the rising worldwide concept of sustainable development and is classified as an environmentally friendly material.

21.2 SYNTHESIS OF PLA

The synthesis of PLA is a multistep process which starts from the production of lactic acid and ends with its polymerization [2–4, 6–7]. An intermediate step is often the formation of the lactide. Figure 21.2 shows that the synthesis of PLA can follow three main routes. Lactic acid is condensation polymerized to yield a low molecular weight, brittle polymer, which, for the most part, is unusable, unless external coupling agents are employed to increase its chains length. Second route is the azeotropic dehydrative condensation of lactic acid. It can yield high

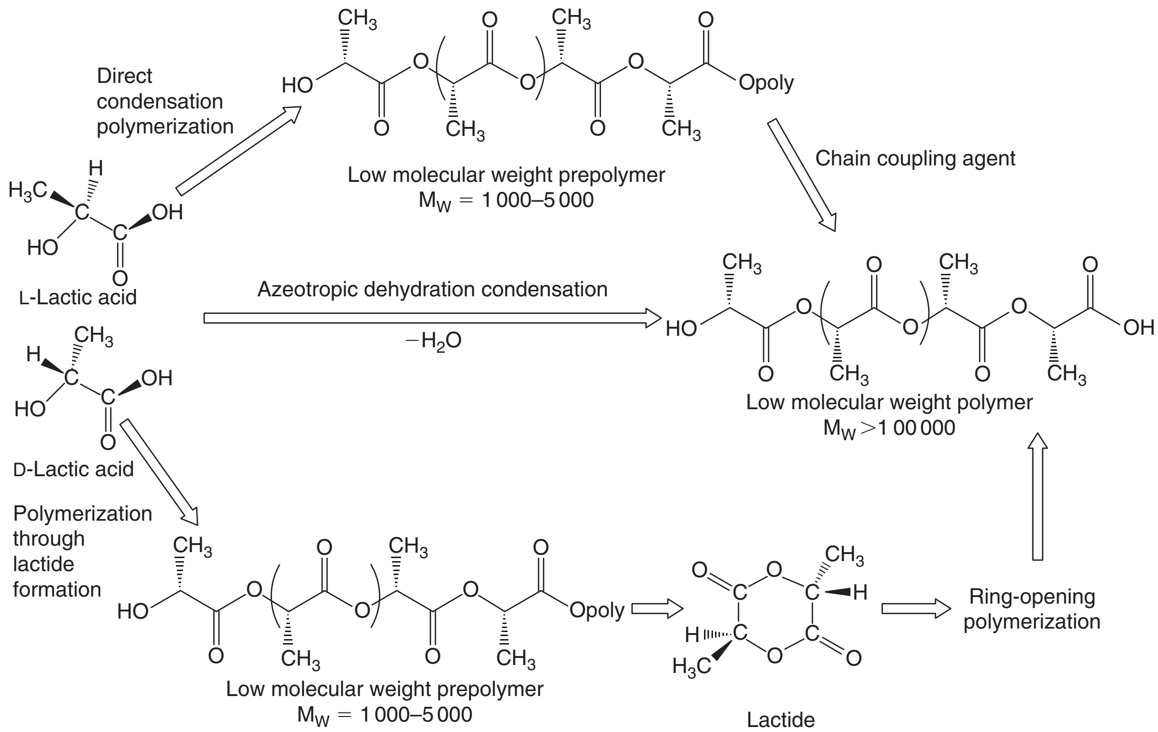

Figure 21.2 Synthesis methods for obtaining high molecular weight. (Adapted from Reference [3].)

molecular weight PLA without the use of chain extenders or special adjuvents [3]. The third and main process is ring-opening polymerization (ROP) of lactide to obtain high molecular weight PLA, patented by Cargill (US) in 1992 [8–9]. Finally, lactic acid units can be part of a more complex macromolecular architecture as in copolymers.

21.2.1 Precursors

21.2.1.1 Lactic acid

Lactic acid is a compound that plays a key role in several biochemical processes. For instance, lactate is constantly produced and eliminated during normal metabolism and physical exercise. Lactic acid has been produced on an industrial scale since the end of the nineteenth century and is mainly used in the food industry to act, for example, as an acidity regulator, but also in cosmetics, pharmaceuticals and animal feed. It is, additionally, the monomeric precursor of PLA. It can be obtained either by carbohydrate fermentation or by common chemical synthesis. Also known as 'milk acid', lactic acid is the simplest hydroxyl acid with an asymmetric carbon atom and two optically active configurations, namely the L and D isomers (Fig. 21.2), which can be produced in bacterial systems, whereas mammalian organisms only produce the L isomer, which is easily assimilated during metabolism.

Lactic acid is mainly prepared in large quantities (around 200 kT per year) by the bacterial fermentation of carbohydrates. These fermentation processes can be classified according to the type of bacteria used: (i) the hetero-fermentative method, which produces less than 1.8 mol of lactic acid per mole of hexose, with other metabolites in significant quantities, such as acetic acid, ethanol, glycerol, mannitol and carbon dioxide; (ii) the homo-fermentative method, which leads to greater yields of lactic acid and lower levels of by-products, and is mainly used in industrial processes [3]. The conversion yield from glucose to lactic acid is more than 90 per cent.

The majority of the fermentation processes use species of *Lactobacilli* which give high yields of lactic acid. Some organisms predominantly produce the L isomer, such as *Lactobacilli amylophilus*, *L. bavaricus*, *L. casei* and