

STUDY OF BIODEGRADABLE PLASTICS PRODUCED BY INJECTION MOLDING

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Abstract

This contribution deals with the processability of PLA (polylactic acid) based biopolymers. In the past, biopolymers were mainly used in medical applications due to their bioabsorbable nature. At present, there is a trend to apply biodegradable polymers in packaging applications. Such an application will lead to less waste production and more renewable products. In this contribution, basic aspects of processability of biodegradable polymers via injection molding technology are discussed.

Key words

biodegradable polymers, PLA (Poly-lactic-acid = Polyacid), injection molding

Introduction

Thermoplastic polymers have many properties ideal for use in packaging and other consumer products, such as low weight, low process temperature (compared to metal and glass), low energy consumption for raw material production. Today, most plastics are derived from non-renewable crude oil and natural gas resources. While some plastics are being recycled and reused, the majority are disposed in landfills. Over the past decade, there has been a sustained research interest in compostable polymers derived from renewable sources as one of the solutions to alleviate solid waste disposal problems and to lessen the dependence on petroleum-based plastics [1].

Biodegradable polymers are defined as those that undergo microbially induced chain scission leading to the mineralization. Specific conditions in term of pH, humidity, oxygenation and the presence of some metals are required to ensure the biodegradation of such polymers. Biodegradable polymers may be made from biosources like corn, wood cellulose etc. or can also be synthesized by bacteria from small molecules like butyric acid or valeric acid that give polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV) [3,2]. Other biodegradable polymers can be derived from the petroleum sources or may be obtained from mixed sources of biomass and petroleum [4,2]. The best known petroleum source-derived biodegradable polymers are aliphatic polyester or aliphatic-aromatic copolyesters, but

biodegradable polymers made from renewable resources like polylactides (PLA) are attracting much more attention because of more eco-friendliness from their origin as contrast to the fully petroleum-based biodegradable polymers and control of carbon dioxide (CO₂) balance after their composting [2].

PLA (Poly lactic – acid) is a compostable polymer derived from renewable sources (mainly starch and sugar). Until the last decade, the main uses of PLA have been limited to medical applications such as implant devices, tissue scaffolds, and internal sutures, because of its high cost, low availability and limited molecular weight. Recently, new techniques which allow economical production of high molecular weight PLA polymer have broadened its uses. Since PLA is compostable and derived from sustainable sources, it has been viewed as a promising material to reduce the societal solid waste disposal problem. Its low toxicity, along with its environmentally benign characteristics, has made PLA an ideal material for food packaging and for other consumer products [1].

Characteristics of material

The starting material for PLA is lactide acid, which is derived from corn by means of biochemical processes. The lactide acid is then polymerized into polylactide acid (PLA) [5].

PLA is linear aliphatic thermoplastic polyester. Molecular structure of PLA is schematically presented in Fig. 1.

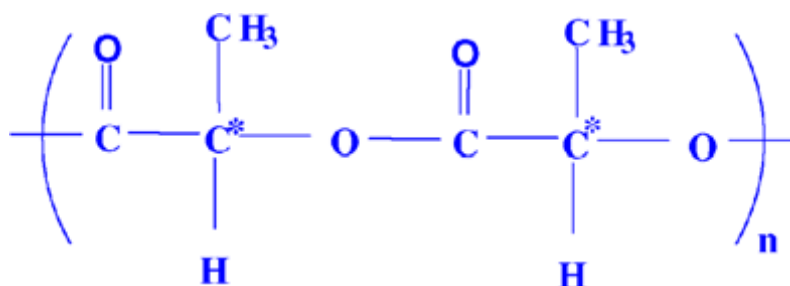


Fig. 1 Molecular structure of polylactide.

High-molecular-weight PLA is generally produced by the ring-opening polymerization of the lactide monomer. The conversion of lactide to high-molecular-weight polylactide is achieved by two routes. Recently, Cargill–Dow used a solvent-free process and a novel distillation process to produce a range of polymers [6,7]. The essential novelty of the process lies in the ability to go from lactic acid to a low-molecular-weight polylactic acid, followed by controlled depolymerization to produce the cyclic dimer, commonly referred to as lactide. This lactide is maintained in the liquid form and purified by distillation. Catalytic ringopening polymerization of the lactide intermediate results in the production of PLA with controlled molecular weights. The process is continuous with no necessity to separate the intermediate lactide. A more detailed description of the Cargill–Dow process is illustrated schematically in Fig. 2(a). In contrast, Mitsui Toatsu (presently Mitsui Chemicals) utilizes a solvent-based process, in which a high-molecular-weight PLA is produced by direct condensation using azeotropic distillation to remove the water of condensation continuously [6, 8]. Fig. 2(b) illustrates the steps involved in these two processes.

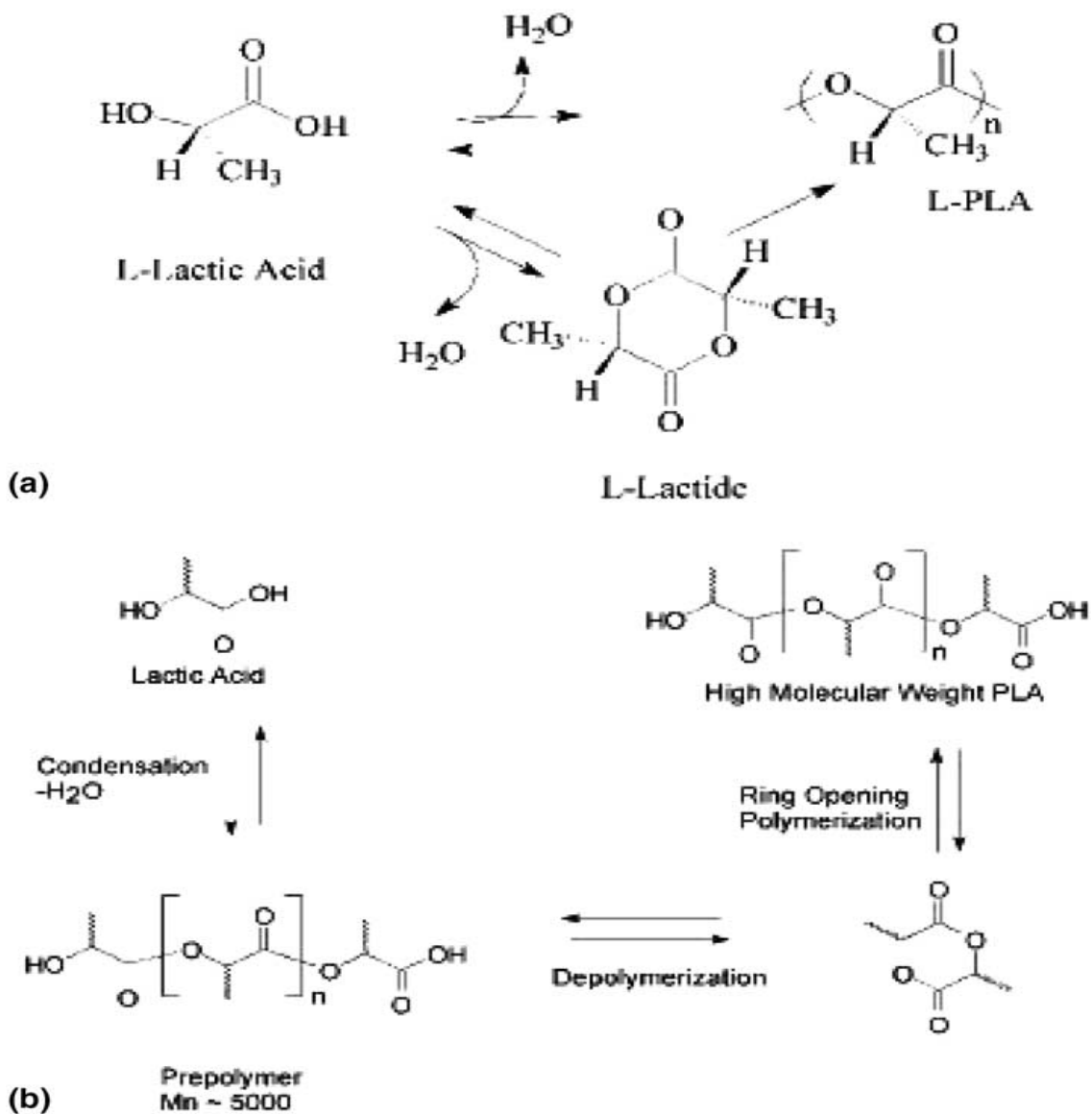


Fig. 2 (a) Polymerization route to polylactide [6,7]. Reproduced from Drumright, Patrick and Henton by permission of Wiley-VCH Verlag GmbH, Germany. (b) Schematic of PLA produced via prepolymer and lactide [6,7]. Reproduced from drumright, Patric and henton by permission of Wiley-VCH verlat GmbH, Germany [6]

Commercially available PLA grades are copolymers of poly(L-lactide) with mesolactide or D-lactide. The amount of D enantiomers is known to affect the properties of PLA, such as melting temperature, degree of crystallinity and so on. PLA has good mechanical properties, thermal plasticity and biocompatibility, and is readily fabricated, and is thus a promising polymer for various end-use applications. Even when burned, it produces no nitrogen oxide gases and only one-third of the combustible heat generated by polyolefins, and it does not damage the incinerator and provides significant energy savings. So, increasing realization of the various intrinsic properties of PLA, coupled with knowledge of how such properties can be improved to achieve the compatibility with thermoplastics processing, manufacturing, and end-use requirements has fuelled technological and commercial interest in PLA [6].

PLA belongs to the family of aliphatic polyesters derived from α -hydroxy acids. PLA has reasonably good optical, physical, and mechanical properties compared to existing petroleum-

based polymers [1,9]. For instance, the permeability coefficients of CO₂, O₂, N₂, and H₂O for PLA are lower than for polystyrene (PS), but higher than PET (poly-ethylene-terephthalate). Mechanically, unoriented PLA is quite brittle, but possesses good strength and stiffness. Tensile and flexural moduli of PLA are higher than high density polyethylene (HDPE), polypropylene (PP) and PS, but the Izodimpact strength and elongation at break values are smaller than those for these polymers [1,10]. Today, the main methods for PLA are based on melt processing. This approach involves heating the polymer above its melting point, shaping it to the desired forms, and cooling to stabilize its dimensions [1].

PLA has a glass transition temperature of between 55 and 65° C and a density of 1.25 g/cm³, and is only slightly less transparent than polystyrol or PET. Moreover, it has great tensile strength, which means that the thickness can be reduced, thus minimizing both weight and cost [11].

Methods

Processing of PLA

Injection molding

Injection molding is the most widely used process for thermoplastic articles, especially for those that are complex in shape and require high dimensional precision. All injection molding machines have an extruder for plasticizing the polymer melt. Most injection molding machines for PLA are based on the reciprocating screw extruder, although two-stage systems, which integrate a shooting pot and extruder in a single machine, have also been deployed for injection molding of preforms for PLA bottles. The two-stage system consists an in-line extruder integrated to a shooting pot. The extruder plasticizes and feeds the melt into the shooting pot under relatively low injection pressure, from which the melt is injected into the hot runner under high pressure by a plunger in the shooting pot. The machine must stop the screw during the injection and packing phases. The two-stage system presents some advantages over its reciprocating counterpart, including shorter cycle time, small screw motor drive, and more melt quality [12, 13].

A typical cycle for an injection molding machine is presented in Fig.3.

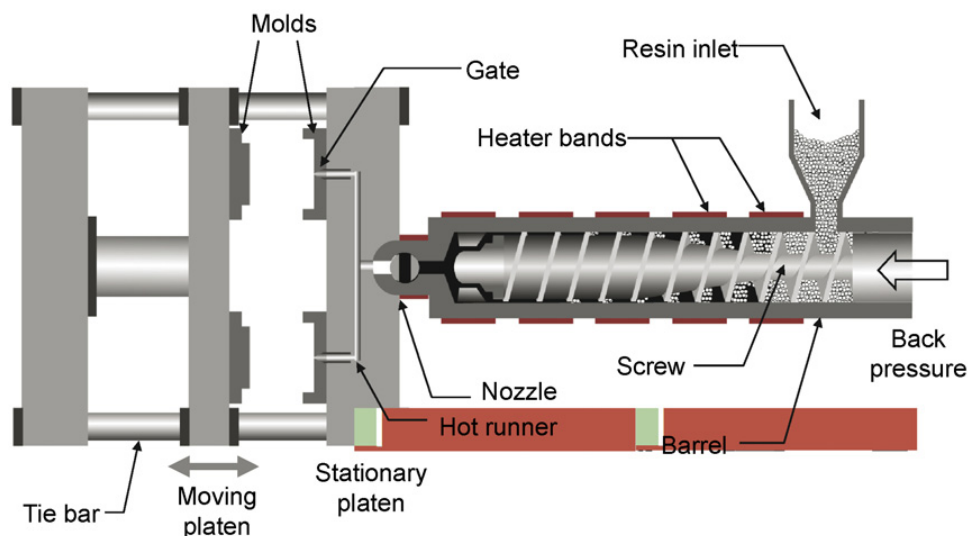


Fig. 3 Major components of an injection molding machine showing the extruder (reciprocal screw) and clamp units

The beginning of mold close is usually taken as the start of an injection molding cycle. Immediately after the molds clamp up, the nozzle opens and the screw moves forward, injecting the polymer melt into the mold cavity. To compensate for the material shrinkage during cooling in the mold, the screw is maintained in the forward position by a holding pressure. At the end of the holding phase, the nozzle is shut off and the screw begins to recover, while the part continues to be cooled in the mold. During the recovery phase, the screw rotates and conveys the polymer forward along the screw. At the same time, the screw is allowed to slide backward within the barrel. In the molding cycle, heat removal takes place predominantly during the fill, hold and cool phases, although mold opening phase also contributes to partial cooling [12, 13].

Nevertheless, the propensity of lactide condensation on the cold tooling surfaces, which can affect the surface finish and weight of the molded articles, limits the minimum temperature that can be used during injection molding of PLA to 25–30 °C. The use of molds with polished surfaces, in conjunction with an increased injection speed during fill, can also reduce the deposition of the lactide layers [16].

Flow properties It is well known that low melt viscosity is required for injection moulding of thin walled or complex shaped parts. Furthermore, high flow ability enables processing at lower temperatures, requires lower injection pressure and enhances productivity by reduction of cycle time. Due to lower temperature and injection pressure needed for processing, less energy is consumed and thermal degradation of natural fillers is reduced. Implementation of natural fibres into thermoplastic matrices generally increases the melt viscosity. This increase depends on the filler content and is also influenced by the particle size [14, 15].

Results

The drawbacks of processing PLA in the molten state is its tendency to undergo thermal degradation, which is related both to the process temperature and the residence time in the extruder and hot runner [17]. By and large, thermal degradation of PLA can be attributed to:

- a) hydrolysis by trace amounts of water,
- b) zipper-like depolymerization,
- c) oxidative, random main-chain scission,
- d) intermolecular transesterification to monomer and oligomeric esters,
- e) intramolecular transesterification resulting in formation of monomer and oligomer lactides of low *M_w* (molecular weight).

During extrusion on a production machine and injection moulding changes of biopolymers or fibre load do not require adaptations of the temperature profile. This eases processing on a production scale by enabling savings of time and energy. By blending biopolymers with wood flour, shrinkmarks and warpages of injection molded parts are easily avoided. Injection moulding of biocomposites can be performed with fibre loads up to 65%. However, the strongly decreased flow ability and the increased brittleness injection moulding of blends with filler loads above 50% is occasionally associated with some difficulties. In these cases employing tools with large gates is recommended [14, 15].

Conclusion

PLA is a highly versatile biodegradable polymer which can be tailor-made for processing into a wide spectrum of products. More importantly, the polymer can be processed using the

conventional production infrastructure with minimal equipment modification. New technologies for processing PLA, such as using supercritical processes for foaming and electrospinning for producing nanofibres, will further expand the use of this polymer. From the environmental viewpoint, the compostable characteristics of PLA are well suited for many recycling applications, reuse and recovery of products are not feasible. Since the raw materials for PLA are based on agricultural feedstock, the increased demand for PLA resins will create a positive impact on the global agricultural economy. Nevertheless, there is a number of areas which still need to be improved, especially in the applications, where PLA is intended to be used as a substitution for existing thermoplastics. Some of these challenges are expected to overcome through blending PLA with other polymers, formation of micro- and nanocomposites, and polymer modification. Research and development in these areas may open up new opportunities for PLA for use as high performance biodegradable materials [14, 15].

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