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Processing technologies for poly(lactic acid)

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ABSTRACT

Poly(lactic acid) (PLA) is an aliphatic polyester made up of lactic acid (2-hydroxy propionic acid) building blocks. It is also a biodegradable and compostable thermoplastic derived from renewable plant sources, such as starch and sugar. Historically, the uses of PLA have been mainly limited to biomedical areas due to its bioabsorbable characteristics. Over the past decade, the discovery of new polymerization routes which allow the economical production of high molecular weight PLA, along with the elevated environmental awareness of the general public, have resulted in an expanded use of PLA for consumer goods and packaging applications. Because PLA is compostable and derived from renewable sources, it has been considered as one of the solutions to alleviate solid waste disposal problems and to lessen the dependence on petroleum-based plastics for packaging materials. Although PLA can be processed on standard converting equipment with minimal modifications, its unique material properties must be taken into consideration in order to optimize the conversion of PLA to molded parts, films, foams, and fibers. In this article, structural, thermal, crystallization, and rheological properties of PLA are reviewed in relation to its converting processes. Specific process technologies discussed are extrusion, injection molding, injection stretch blow molding, casting, blown film, thermoforming, foaming, blending, fiber spinning, and compounding.

Contents

Abbreviations: BD, 1,4-butanedial; BDI, 1,4-butane diisocyanate; DSC, differential scanning calorimetry; BUR, blow-up-ratio; ΔH_{rel}, endothermic enthalpy relaxation; ΔH_c, heat of crystallization; ΔH_m, heat of fusion; HDPE, high density polyethylene; HIPS, high impact polystyrene; HMDI, hexamethylene diisocyanate; ISBM, injection stretch blow molding; LDPE, low density polyethylene; MD, machine direction; MDO, machine direction orientation; MFI, melt flow index; MMT, montmorillonite; M_n, number-average molecular weight; M_w, weight-average molecular weight; OPLA, oriented poly (lactic acid); OPP, oriented polypropylene; OPS, oriented polystyrene; PEG, poly(ethylene glycol); PET, poly(ethylene terephthalate); PDI, polydispersity index; PDLLA, poly(D,L-lactic acid); PHA, polyhydroxyalkanoate; PHO, poly(3-hydroxyloctanoate); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); PP, polypropylene; PS, polystyrene; PVT, pressure–volume–temperature; TD, transverse direction; TDO, transverse direction orientation; T_g, glass transition temperature; T_m, melting temperature; WAXS, wide angle X-ray scattering; WVTR, water vapor transmission rate; η_0, zero-shear viscosity.

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1. Introduction

Thermoplastic polymers exhibit many properties ideal for use in packaging and other consumer products, such as light weight, low process temperature (compared to metal and glass), variable barrier properties to match end-use applications, good printability, heat sealable, and ease of conversion into different forms. 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 due to end-use contamination. In 2005, plastics were recovered at a rate lower than 10% in the USA [1]. Over the past decade, there has been a sustained research interest on 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.

Poly(lactic acid) (PLA) 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 [2]. 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 [3,4]. Its low toxicity [5], along with its environmentally benign characteristics, has made PLA an ideal material for food packaging and for other consumer products [6].

PLA belongs to the family of aliphatic polyesters derived from α-hydroxy acids. The building block of PLA, lactic acid (2-hydroxy propionic acid), can exist in optically active D- or L-enantiomers. Depending on the proportion of the enantiomers, PLA of variable material properties can be derived. This allows the production of a wide spectrum of PLA polymers to match performance requirements. PLA has reasonably good optical, physical, mechanical, and barrier properties compared to existing petroleum-based polymers [7]. For instance, the permeability coefficients of CO_2, O_2, N_2, and H_2O for PLA are lower than for polystyrene (PS), but higher than poly(ethylene terephthalate) (PET) [8–10]. The barrier properties of PLA against organic permeants, such as ethyl acetate and D-limonene, are comparable to PET [11]. Mechanically, unoriented PLA is quite brittle, but possesses good strength and stiffness. Oriented PLA provides better performance than oriented PS, but comparable to PET [9]. Tensile and flexural moduli of PLA are higher than high density polyethylene (HDPE), polypropylene (PP) and PS, but the Izod impact strength and elongation at break values are smaller than those for these polymers [12]. Overall, PLA possesses the required mechanical and barrier properties desirable for a number of applications to compete with existing petroleum-based thermoplastics.

Today, the main conversion 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. Thus, understanding of thermal, crystallization, and melt rheological behaviors of the polymer is critical in order to optimize the process and part quality. Some of the examples of melt processed PLA are injection molded disposable cutlery, thermoformed containers and cups, injection stretch blown bottles, extruded cast and oriented films, and melt-spun fibers for nonwovens, textiles and carpets [6,13,14]. PLA also finds uses in other less conventional applications, such as for the housing for laptop computers electronics [14–17]. Recently, PLA has also been processed in conjunction with other filler materials to form composites which possess various unique properties, including those based on nanoclays [18–23], biofibers [16,24,25], glass fibers [26] and cellulose [27,28]. The aim of this review is to discuss the key process technologies for PLA and summarize the properties of PLA related to the processing techniques used.

2. Structural composition

The basic building block of PLA, lactic acid, can be produced by carbohydrate fermentation or chemical synthesis. Currently, the majority of lactic acid production is based on the fermentation route. Various purification technologies for lactic acid and lactide can be found in a recent review by Datta and Henry [2]. One of the main drivers for the recent expanded use of PLA is attributable to the economical production of high molecular weight PLA polymers (greater than ∼100,000 Da). These polymers can be produced using several techniques, including azeotropic