Microcellular injection-molding of polylactide with chain-extender

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ARTICLE INFO

ABSTRACT

The effects of adding an epoxy-based chain-extender (CE) on the properties of injection-molded solid and microcellular polylactide (PLA) were studied. PLA and PLA with 8 wt.% CE (PLA-CE) were melt-compounded using a twin-screw extruder. Solid and microcellular specimens were produced via a conventional and microcellular injection-molding process, respectively. Various characterization techniques including gel permeation chromatography, tensile testing and dynamic mechanical analysis, scanning electron microscopy and differential scanning calorimetry were applied to study the molecular weight, static and dynamic mechanical properties, cell morphology, and crystallization behavior, respectively. The addition of CE enhanced the molecular weight but decreased the crystallinity of PLA. The addition of CE also reduced the cell size and increased the cell density. Furthermore, the decomposition temperatures and several tensile properties, including specific strength, specific toughness, and strain-at-break of both solid and microcellular PLA specimens, increased with the addition of CE.

1. Introduction

In recent times much attention is made on the design, synthesis, processing and characterization of novel biodegradable polymers and developing applications to them in various fields such as packaging, structural, pharmaceutical, biomedical and environmental field [1–2]. Among many biodegradable polymers, Polylactide (PLA) is a biobased, biodegradable and biocompatible aliphatic polyester and have found many applications due to their unique set of properties [3–8]. In the biomedical industry, it is used in bone plates, bone screws, tissue repair and drug delivery [1,9–16]. In non-medical industries, it is mainly used in packaging [2]. There has been renewed interest with PLA in recent years because the cost of PLA has been greatly reduced to the point that they can be used for many commodity applications replacing some of the petroleum-based polymers. As a biobased polymer, PLA is made from renewable resources such as corn and can be naturally recycled by biological processes, thereby reducing our dependency on depleting fossil fuels and greenhouse gas emissions.

PLA is produced by ring-opening polymerization of lactide or condensation polymerization of lactic acid monomers that are produced from renewable resources via a fermentation process [17]. In this study PLA obtained from NatureWorks™ was produced by ring-opening polymerization of lactide. Although PLA presents various environmental benefits, it has certain inferior properties such as low-molecular weight, brittleness, and a low heat distortion temperature that prevent its widespread applications. Additionally, biobased thermoplastic polymers such as PLA have a narrow processing window due to their sensitivity to moisture and heat. In order to broaden the applications of biobased plastics, its material properties and processability must be improved and the component cost must be reduced.

PLA homopolymers have a glass-transition and melt temperature of about 55 °C and 175 °C, respectively, and require processing temperatures in excess of 185–190 °C [18,19]. At these temperatures, unzipping and chain scission reactions are known to occur, leading to loss of molecular weight and thermal degradations [5]. At a certain level, the depolymerization of PLA can cause a change in the physical properties such as reducing the polymer melt viscosity, melt elasticity, and mechanical and thermal properties. Thus, in order to increase the usability of PLA, its molecular weight must be maintained or increased during processing.

Recently, a large volume of research has been devoted to developing the chemical means to enhance the molecular weight of virgin, reprocessed, or recycled thermoplastics. Chief among these chemical methods has been the use of di- or multi-functional chemical compounds called "chain-extenders" [20]. Chain-extension is a reaction to obtain a high molecular-weight polymer by means of a post-polymerization reaction carried out during compounding, injection-molding, or extrusion [20–22]. Normally, these chain-extension reactions can be carried out effectively in the melt using existing melt reactors, or single or twin-screw extruders operated at normal conditions [23–25].

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Chain-extension with di-functional ($f_n = 2$) compounds such as hydroxyl, carboxylic acid, anhydride, amine, and epoxy lead to a lower enhancement in molecular weight compared with high functional ($f_n \geq 3$). This is because di-functional compounds will only couple at the two end groups, thereby leading to a linear polymer [20]. Thus, the use of chain-extenders with functionality equal or larger than three ($f_n \geq 3$) has become an attractive means to increase efficacy of the extenders, although it comes at the expense of going from linear to long chain branched structures. The multi-functional epoxy based chain-extender (CE) has a very broad processing window, which can be used in typical extrusion or injection-molding equipment without vacuum or catalysts. The mechanisms of epoxy-based chain-extension in reactive extrusion have been discussed at length in the literature [23–28].

Microcellular plastics are characterized by cell densities on the order of 10^9 cells/cm^3 or more and cell sizes on the order of 10 μm or less. Such plastics were developed in an effort to reduce the amount of material used by creating a large number of small voids without significantly compromising the mechanical properties [29]. The micron-sized cells formed in the polymer matrix may serve as crack arrestors by blunting crack tips, thereby enhancing part toughness [30], impact strength [31–36], and fatigue life [37–38]. Microcellular injection-molding employs supercritical fluid, typically nitrogen, as the foaming agent. The employment of supercritical fluid reduces the viscosity of the polymer melt [39–41] due to the formation of a single-phase polymer-gas solution, enabling the polymer to be processed at lower temperatures and pressures [29,42]. This is a very desirable feature of biobased polymers, which are moisture- and thermal-sensitive. Thus, microcellular injection-molding of biobased polymer may be able to produce biobased polymer components with increased dimensional stability, less thermal degradation, and less material while potentially improving certain material properties such as impact strength, toughness, and fatigue life [43–45]. Microcellular components also have lower costs due to the use of less materials and energy, and improved productivity.

This study investigated the effects of adding epoxy-based chain-extender on the cell morphology and mechanical properties of solid and microcellular PLA.

2. Experimental

2.1. Materials

PLA (NatureWorks™ PLA 3001D) in pellet form was obtained from NatureWorks® LLC, Minnetonka, MN, USA. It has a specific gravity of 1.24 and a melt flow index around 15 g/10 min (190 °C/2.16 kg). The CESA-Extend OMAN698502, containing 10 wt.% multi-functional epoxy-based chain-extender in a PLA resin, was obtained from
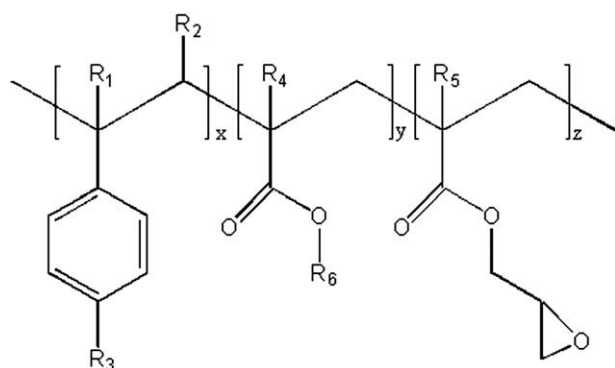
Table 1
The formulation of the PLA and PLA-CE systems.

Sample	PLA	Chain-extender	Anox (0.2 wt.%)	Alkanox (0.2 wt.%)
PLA	9.0 kg	0	18.1 g	18.1 g
PLA-CE	10.4 kg	0.9 kg (8 wt.%)	22.7 g	22.7 g

Clariant, USA. The multi-functional epoxy-based chain-extender is a styrene-acrylic oligomer with a number averaged molecular weight (M_n) less than 3000, a high number average functionality ($f_n > 4$), and a tailored polydispersity (PDI > 3), as shown in Fig. 1.

3. Methods

3.1. Processing

As shown in Table 1, two types of material systems were prepared: PLA and PLA with 8% CESA-Extend OMAN698502 (PLA-CE) (i.e., in PLA-CE, there was 0.8 wt.% multi-functional epoxy-based chain extender). Prior to injection-molding, both the PLA and CE were dried in an oven at 55 °C overnight to remove any excess moisture. Two different antioxidants (Anox and Alkanox, each at 0.2 wt.%) were then added to the PLA neat resin and PLA-CE mixtures, as tabulated in Table 1. Afterwards, both material systems, i.e., PLA and PLA-CE, were extruded using a 32 mm ($L/D = 36/1$) Davis Standard co-rotating twin screw extruder at 200 rpm. The twin screw extruder was configured with mixing elements that were capable of providing additional shear to make the mixture uniform. The melt compounding processing conditions for PLA and PLA-CE are given in Table 2. The resulting materials were then pelletized.

Tensile bars (ASTM D638-03, Type I) were injection-molded using an Arburg Allrounder 320S (Lossburg, Germany) with a 25 mm diameter screw and equipped with MuCell® technology (Trexel, Inc., Woburn, MA). Solid and microcellular tensile bars were molded at the processing conditions indicated in Table 3. Note that with conventional injection-molding, no supercritical nitrogen fluid was introduced into the barrel. Additionally, the pack/hold stage is absent in microcellular injection-molding due to the homogeneous packing pressure that results from the nucleation and growth of cells [40]. This homogeneous packing pressure was shown to drastically reduce the shrinkage and warpage of microcellular injection-molded parts when compared with conventional injection-molding, thereby greatly enhancing the dimensional stability of molded parts with a complex geometry [41,46].

3.2. Gel permeation chromatography (GPC)

The number average molecular weight (M_n) and polydispersity index (PDI) of PLA presented in all the samples, namely, pure PLA

Fig. 1. General structure of the multi-functional epoxy-based chain-extenders. Where R1–R5 are H, CH$_3$, a higher alkyl group, or combinations of them; R6 is an alkyl group.

Table 2
Melt compounding (using extrusion) parameters for the PLA and PLA-CE material systems.

	PLA	PLA-CE
End cap (°C)	168	168
Zone-1 (°C)	157	157
Zone-2 (°C)	157	157
Zone-3 (°C)	166	166
Zone-4 (°C)	166	166
Zone-5 (°C)	166	166
Zone-6 (°C)	168	168
Zone-7 (°C)	168	168
Melt temperature (°C)	182	182
Melt pressure (MPa)	1.2	1.9
RPM (rev/min)	200	200
Load (%)	50	60
Feed rate (kg/h)	11.3	11.3