



Stereocomplexation of PLL/PDL–PEG–PDL blends: Effects of blend morphology on film toughness

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ABSTRACT

Poly(lactide) (PL) finds its use in a wide variety of applications ranging from medical devices to engineering plastics. However, the use of PL is limited to certain applications due to its brittle characteristic and low heat distortion temperature, which indicate its poor mechanical and thermal properties, respectively. This present work demonstrated the toughening of PL by stereocomplexation adopting poly(D-lactide)–poly(ethylene glycol)–poly(D-lactide) (PDL–PEG–PDL) copolymers with various PDL segment length. The DSC results showed that the complete stereocomplexation was reached when 40 wt% copolymer was blended with poly(L-lactide) (PLL). In addition, the crystallization of PEG was interrupted and, thus, prohibited by either adding PDL or PLL in the system. AFM images showed that, for the first time, the stereocomplex crystallites (Sc-crystallites) formed by the enantiomer pairs were dispersed in a continuous amorphous phase of PL and the non-crystallizing PEG. The increase of PDL segment length in the copolymer led to the increase of the Sc-crystallite size, which, consequently, resulted in the increase of the tensile strength of the blended-films. Elongation at break of the films was found to rely on the determined amorphous area. To maximize the toughness of the films, the specific ratio of PDL and PEG segment length in the copolymer must be achieved to provide the optimum balance between Sc-crystallite size and % amorphous area.

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1. Introduction

Poly(lactide) (PL), one of the well-known aliphatic polyesters, has received much interest due to its enzymatic-/hydrolytic-degradability as well as biocompatibility [1–3]. PL finds its use in a wide variety of applications ranging from medical devices to engineering plastics [4–7]. Since its monomer can be derived from renewable agricultural sources, this polymer is considered as a “green” alternative thermoplastic which can potentially replace a number of petrochemical based polymers in the next era. However, the use of PL is limited to certain applications due to its brittle characteristic and low heat distortion temperature, which indicate its poor mechanical and thermal properties, respectively. Many approaches adopted to improve heat distortion temperature of PL such as plasticization and nucleation [8,9], and blending PLL with its

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enantiomeric forms, i.e. poly(D-lactide) (PDL) and poly(L-lactide) (PLL) [10–13], mostly led to stereocomplexation by which the two enantiomeric forms of PL are simply mixed to form stereocomplexed crystallites (Sc-crystallites). Sc-crystallites, originated from stereoselective van der Waals forces, act as molecular-interlocking arrangements in the semicrystalline region. These strongly packed crystallites provide a considerable increase in the melting point, typically 50–70 °C higher than either PDL or PLL alone [14–17].

Although stereocomplexation offers a choice for increasing heat distortion temperature, the brittleness is still of concern because the increase in crystallinity generally results in low ductility [18]. So to simultaneously increase thermal stability and toughness of PL, the copolymers of its enantiomeric segments are adopted for stereocomplexation. Among the successful literatures reported [7,18–26], the copolymers of poly(ethylene glycol) (PEG) and PDL, when blending with PLL, were shown to provide good balance between crystallinity and toughness due to the plasticizing effect of the former and the specific affinity toward stereocomplexation of the latter [7,18,23,24].

It is well established that morphological features, e.g. the degree of crystallinity, the crystalline size, the chain conformation distribution of the amorphous phase and the crystallization rate, are responsible for the mechanical properties of the semicrystalline polymers, in general [23,24,27–29]. Specifically, the mechanisms for toughening of Sc-PL involving PEG were proposed to originate from a combination of various factors including lowering T_g of the amorphous phase system by PEG, the presence of PL continuous amorphous phase, the presence of a soft PEG amorphous phase within the PL amorphous region and the appearance of the α' phase, i.e. the crystalline structure formed at the temperatures below 120 °C, of PL [23]. These morphological features have been widely investigated using several techniques such as differential scanning calorimetry (DSC) [15,18], polarized optical microscopy (POM) [7,23,24], wide-angle X-ray diffraction (WAXD) [15] and infrared (IR) and Raman spectroscopy [7,23,24].

Since the aforementioned Sc-PL prepared by blending PDL and PLL is well known to improve thermal properties but the brittleness of Sc-PL still remains a problem. The present work demonstrated the toughening of PL by stereocomplexation in nonequimolar mixtures of PLL and PDL-PEG-PDL copolymers. In addition to the literatures reported, this work, for the first time, showed that the Sc-crystallites, formed by the enantiomer pairs and, then, dispersed in a continuous amorphous phase of PL and the non-crystallizing PEG can be viewed using atomic force microscopy (AFM) technique. The morphology-toughness relationship of stereocomplexed-poly(lactide) (Sc-PL) was elucidated. Also supported by DSC results, the crystallization of PEG was interrupted by the presence of PL and, instead, was incorporated into a continuous amorphous phase. AFM analysis also showed that the combination of the size of Sc-crystallites and the determined amorphous regime is attributable to the toughness of Sc-PL.

2. Experiments

2.1. Materials

Commercial grade PLL (PLL 2003D, $M_n = 1.6 \times 10^5 \text{ g mol}^{-1}$ and PDI = 2.0) was supplied by Nature Works. D-lactic acid was purchased from Musashino Chemical Laboratory. PEG ($M_n = 8000$ and 20,000) and stannous octoate, Sn(Oct)₂, were purchased from Sigma-Aldrich. All other reagents were analytical grade and used as received.

2.2. Synthesis of PDL-PEG-PDL copolymers

The PDL-PEG-PDL copolymers were synthesized by ring-opening polymerization. The predetermined amounts of D-lactide (DL) and PEG, in the presence of 1 wt% Sn(Oct)₂, were added to the reaction flask equipped with a magnetic stirrer bar at the same time under vacuum condition. Intrinsically, PDL-PEG-PDL copolymers were synthesized using PEG molecular weight 8000 and applied different DL/EG molar ratio to yield different PDL segment lengths. The polymerization was carried out at 120 °C for 24 h. After polymerization, the products were dissolved in chloroform and precipitated in methanol. The copolymers were dried under vacuum before further use.

2.3. Preparation of PLL/copolymer blended-films

PLL and the copolymer were solution-blended at a concentration of 5 g/dl in chloroform for the predetermined PLL/copolymer compositions (100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 wt%). The solutions were cast onto glass petri-dishes and left for solvent evaporation at room temperature for approximately 3 days in a vacuum oven.

2.4. Characterizations

The synthesized copolymers were subjected to structural characterized by ¹H NMR spectroscopy (Bruker 400 NMR spectrometer, Switzerland). The spectra were obtained from polymer solutions in deuterated chloroform (CDCl₃) at room temperature with TMS as an internal standard. Average molecular weights and polydispersity indices of the copolymers were determined by gel permeation chromatography (GPC, Waters 2485 size-exclusion chromatograph) operating at 35 °C using tetrahydrofuran (THF) as a solvent.

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