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Toughening semicrystalline poly(lactic acid) by morphology alteration

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ABSTRACT

The incorporation of the triblock copolymer (PDLA-PEG-PDLA) into Poly(L-Lactic Acid) (PLLA) has produced a semicrystalline polymer of substantial modulus and strength. These improvements in mechanical properties could potentially increase the utility of this biomass-based polymer. The blended samples have a continuous amorphous phase with crystalline regions being the discontinuous portion. Micro-Raman spectroscopy revealed that a stereocomplex involving PDLA and PLLA chains exists in the crystalline region. It can be concluded that the poly(ethylene glycol), the flexible midblock component, is necessarily dispersed in these crystalline regions. Both morphological features can contribute to the improvement in mechanical properties. Therefore, the successful toughening of PLA may be achieved due to several mechanisms working synergistically.

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1. Introduction

Poly(lactic acid) (PLA) is a biodegradable polymer derived from renewable resources having applications ranging from minute cardiovascular stents to large side panels for automobiles [1]. The cost of manufacture (raw materials and processing) is no longer an impediment to commercialization. However, because of its inherent brittle nature and low thermal stability [2], PLA needs to be modified to be suitable for use in various applications where mechanical properties are important. There have been a considerable number of studies to toughen PLA with the goal of balancing and increasing tensile strength, impact strength and modulus while retaining the biocompatible and biodegradable nature [3–7]. One strategy of toughening is to blunt the sharp tip of crack propagation [8]. Improvements in mechanical properties can involve alteration of morphology (e.g. soft regions or voids) or interface (e.g. polymeric compatibilizer). Several attempts to toughen PLA have included blending two or more polymers with, or without, block copolymers as compatibilizers [9–29]. In addition, Others have explored triblock thermoplastic elastomers based on PLA as an approach to obtain toughened PLA based polymers [30,31].

Blending polymers is one of the most straight forward ways to alter physical properties with well-defined phase separated morphologies [32]. We report a new concept for toughening semi-crystalline PLLA. A PDLA-PEG-PDLA triblock copolymer capable of forming a stereocomplex with the PLLA matrix was used as the sole toughening agent to improve the physical toughness of PLLA. Our hypothesis was that the stereocomplex forming triblock copolymer could perform multiple functions. It can act as a nucleating agent, the compatibilizer, as well as a toughening agent. It is well established that the stereocomplex involving PDLA and PLLA have specific affinity for each other and with significantly higher melting temperature as compared to either the all L or the all D isomers [33]. By employing PDLA-PEG-PDLA triblocks, the end blocks act as compatibilizers, forming the favorable stereocomplex, while the soft midblock may serve as the toughening agent. Because stereocomplex will preferentially form sooner relative to PLLA or PDLA at specific crystallization temperature, it is anticipated that unique morphologies can be formed.

PEG is also an attractive polymer for biomedical applications because of its biocompatible nature. It has been found that PEG shows great promise as a plasticizing agent for PLA as it gives a large increase in ultimate elongation with the smallest decrease in tensile strength [3,34,35]. However, previous studies have shown that PLLA/PEG blends are not stable and the attractive properties are lost over time because of phase separation at ambient temperature leading to formation of amorphous PLA-rich and PEG-rich phases [36]. There have been some studies regarding the use of

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triblock copolymer systems as compatibilizers [8,37]. A recent study used PDLA based triblock copolymers as nucleating agents for PLLA [30]. The morphological features of this sample and effects on mechanical properties were not elucidated. In this study, Raman microscopy has revealed the details of how morphological features evolve, suggesting that very different toughening mechanism may be present.

2. Experimental

2.1. Materials

D-Lactide was kindly provided by Purac (Netherlands) and was recrystallized from toluene prior to use. PEG 1000 (Mn: 1000; Đ: 1.1) was obtained from Alfa Aesar and dried using azeotropic distillation with toluene followed by further drying under reduced pressure at 60 °C. Stannous octoate [Sn(Oct)$_2$: tin-2-ethylhexanoate] was obtained from Aldrich. PLA 2002D (4.2%D) was supplied by Natureworks (Minnesota, USA).

2.2. Triblock synthesis

The Triblock copolymer was synthesized by ring-opening polymerization (ROP) of D-lactide using PEG 1000 as an initiator and stannous octoate as a catalyst. The required amount of dry PEG 1000 was placed in a flame dried Schlenk flask and D-lactide was added under a nitrogen atmosphere. The flask was evacuated and back filled with nitrogen three times, and then placed in an oil bath maintained at 160 °C. After 15 min, the required amount of stannous octoate in ∼0.2 ml toluene was injected into the flask. At the end of 4 h the polymer obtained was dissolved in dichloromethane, precipitated in diethyl ether and dried in vacuo.

2.3. Blends prepared

Two types of samples were used in this study. Blends of the triblock copolymer and PLA 2002D were prepared in a DSM twin screw mini-extruder (Volume 15 cc). Dog-bone samples for tensile testing were obtained using a DSM 10 cc injection mold. Blend 6 refers to a 94.3 (PLLA)-5.7 (triblock) (w/w) composition, while the Blend 15 refers to a 85–15 (w/w) composition. The dog-bone samples were annealed at 80 °C for 4 h and then kept at room temperature for 24 h before testing. In order to have a better understanding of crystallization process in the blends, an isothermal crystallization experiment was performed.

2.4. Characterization

^{1}H NMR (300 MHz) spectra were obtained on a Bruker DPX-300 NMR spectrometer. The spectra were measured in CDCl$_3$, and the chemical shifts were calibrated to the solvents' residual proton signal (^{1}H NMR signal: 7.26 ppm for CHCl$_3$). The molecular weight and dispersity were determined by GPC (chloroform) (Agilent). The molecular weights measured were with respect to polystyrene standards. Thermal characterization was performed on a TA Q100

differential scanning calorimeter (DSC) (TA Instruments) which was calibrated against an indium standard. The samples (5–10 mg) were heated at the rate of 10 °C min^{-1}. Spherulite/Dendrite growth in the blends was observed using an Olympus (Tokyo, Japan) Polarized Optical Microscope (BH-2) equipped with a heating stage. The samples for optical observation were prepared by the following procedure. First a sample of ∼8 mg was placed between a glass slide and a Kapton film and was heated to melt completely; it was then pressed to obtain a thin film and then cooled down to room temperature. Subsequently, the sample was again melted and transferred to a hot stage which was maintained at 160 °C. All crystallization experiments were followed using the birefringence developed for samples between two polarizers with an orthogonal polarization axis. Images were taken with a digital camera. Microstructure analysis was performed using infrared and Raman spectroscopy and mechanical properties were evaluated using an Instron universal testing machine. Mechanical properties were evaluated at 80 °C using a crosshead speed of 100 mm/min, and at 20 °C using a crosshead speed of 1 mm/min.

3. Results and discussion

3.1. Properties achieved

Triblock copolymer with the structure PDLA$_{23}$PEG$_{23}$PDLA$_{23}$ was synthesized by the ring-opening polymerization of D-Lactide using PEG as a macroinitiator and tin octoate as catalyst. The degree of polymerization of the lactide end blocks was calculated using ^{1}H NMR and was found to be in close agreement with the theoretical value. The molecular weight obtained by GPC was 6700 g/mol (with respect to PS standard) with a dispersity of 1.18. The compositions of the blends prepared are tabulated in Table 1. It should be noted that the amount of PEG 1000 in the blends is extremely small at <4 wt%. The dramatic improvements in mechanical properties obtained for these blends are shown in Fig. 1. The injection molded dog-bone samples were annealed at 80 °C for 4 h and aged at room temperature for 24 h before testing. It can be seen that as the triblock content increases the elongation at break, stress at break and toughness increases. At 80 °C the samples are ductile with increasing triblock content. At room temperature, only the blend containing 15% triblock (Blend 15) is ductile. This may be due to the fact that the Blend 6 sample contains only ∼1% PEG, an amount insufficient to cause any observable change in properties. It should be noted that under these testing conditions (Draw rate: 1 mm/min, Draw Temperature: 20 °C) significant improvement in elongation at break is observed with negligible loss in modulus for samples containing as little as 3% PEG. The elongation at break increases by 250% while the modulus is ∼95% of the modulus of pure PLLA (Table 1). At least three samples were tested for each blend.

3.2. Morphological features observed

The optical micrographs of the samples with, or without, triblock copolymer are shown in Fig. 2. There are clear differences

Table 1
Composition and mechanical properties of the blends.

| Sample	% Triblock in blend	%PEG in triblock	%PEG in blend	%PDLA in blend	%PLLA in blend	Modulus (MPa)	Strain at Break (%)
PLA2002D	0	NA	0	0	100	1876 ± 56	20 ± 5
Blend 6	5.7	23.4	1.33	4.37	94.3	1830 ± 350	13 ± 6
Blend 15	15	23.4	3.51	11.49	85	1752 ± 42	72 ± 2

All values are %w/w.
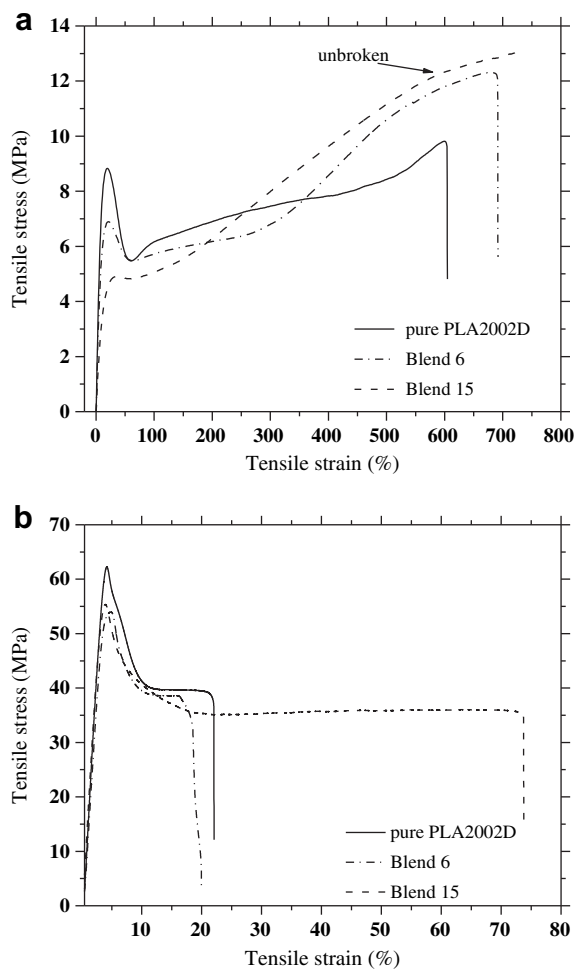
Fig. 1. Tensile stress–tensile strain curves of pure PLA and its blends with a draw rate of (a) 100 mm/min at 80 °C (b) 1 mm/min at 20 °C.

between the all L isomer and the sample containing the triblock. There are significant differences in the size of spherulites in the two samples. There is also the existence of micron size "bands" of isotropic regions surrounding each spherulite in the sample containing triblock copolymers. The relationship between the strikingly different morphological features of the two types of samples and the associated mechanical properties obtained is of obvious interest. In theory, the morphological differences can be explained by the differences in the melting temperatures associated with each system. The melting temperature of a PLA stereocomplex is at least 50° higher than either all D or all L PLA. Therefore, at any crystallization temperature, formation of the stereocomplex is favored. Because of the specific affinity between the D and L isomers of PLA [38,39], stereocomplex crystallites will be the first to nucleate and grow, trapping the soft PEG segments within the amorphous regions of the crystalline lamellae. The decrease in chain mobility because of the stereocomplex crystals formed will then trap the rest of polymers into the amorphous phase.

The differences in morphological features can best be characterized using micro-Raman. This technique provides high spatial resolution to "map" the chemical composition and morphological features in each region. There are specific Raman active features associated with this structure and the Raman spectra obtained for PLA containing triblocks at various locations are shown in Fig. 3. It has been established that PLA crystals have characteristic C=O stretching vibrations in the 1700 cm^{-1} region [33,40–42]. Raman mapping on dendrites of the Blend 15 sample grown by isothermal crystallization at 160 °C is shown in Fig. 3. The crystalline regions (dendrites) show the characteristic peaks of the PLA stereocomplex. The isotropic regions around each dendrite consist of only amorphous poly(lactic acid). Because of the low percentage and the lack of intense Raman active vibration, no definitive PEG signal was observed.

The Raman spectra also reveal the possibility of the coexistence of both the stereocomplex and the presence of the α or α′ crystalline phase of PLA. This is to be expected because of the composition of the sample. The coexistence of the two crystalline phases is seen in both thermal analysis and infrared data (Fig. 4). The formation of the stereocomplex can be confirmed by the occurrence of a higher temperature melting endotherm in the DSC trace of the blends in addition to the homopolymer melting endotherm. Other useful information obtained from DSC is that the blends exhibit a single, but broad, glass transition temperature (T_g), between the T_g of the two components, implying miscibility between the amorphous regions of the two components. The absence of a melting endotherm at ~50 °C (melting point for PEG 1000) implies that the PEG 1000 is in the amorphous state in these blends. Because of sample thickness, the injection molded, annealed dog-bone samples were characterized using attenuated total reflectance infrared spectroscopy (ATR-IR) (Fig. 4). For blends, the band at 909 cm^{-1} characteristic of the 3$_1$ helix associated with the stereocomplex is present [33]. In addition, the 922 cm^{-1} band characteristic of the 10$_3$ helix of the α or α′ phase is also observed. This indicates the existence of both the stereocomplex and traditional PLA α or α′ crystals in the blends incorporating triblocks. As expected, the intensity of the stereocomplex band is higher in the 15% blend as this blend has a higher PDLA content (~11.5wt%).
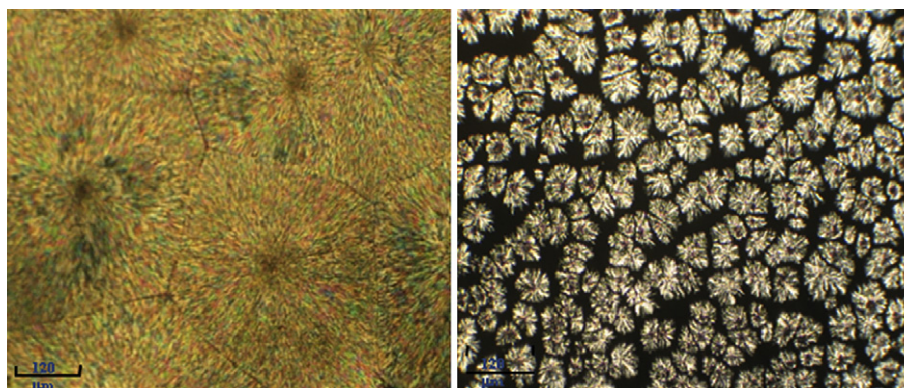
Fig. 2. Optical micrograph of (left) PLA 2002D (isothermal crystallization 140 °C); (right) Blend 15 (isothermal crystallization 160 °C).
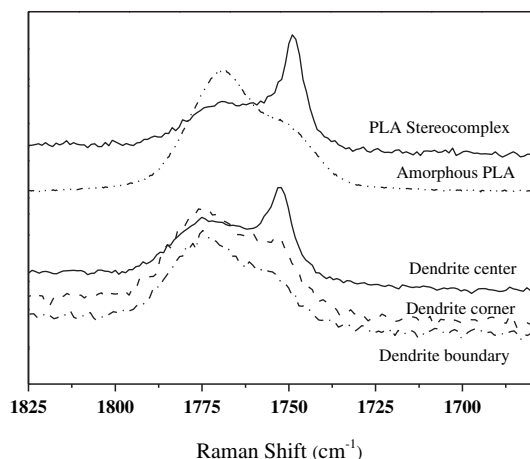
Fig. 3. Raman mapping on dendrites of Blend 15 grown by isothermal crystallization at 160 °C (top: reference spectrum of PLA stereocomplex and amorphous PLA, bottom: Raman spectra at center, corner and boundary of dendrites).

3.3. Possible mechanisms for property improvements

Based on this data the following description of the mircostructure of the blend can be drawn. The blend is a multiphase system consisting of varying composition amorphous phases and one or more crystalline phases depending on the composition of

Fig. 4. (a) Infrared spectra in the 970—890 cm^{-1} region obtained for pure PLA and its blends (b) DSC traces of pure PLA and its blends.

the blend. The crystalline phase acts as reinforcing filler in a continuous amorphous phase. The mechanism responsible for the exceptional mechanical properties obtained is not definitively known at this moment and will be the focus of future studies. Based on the structures reported here for the PLA samples containing triblocks, there can be at least three possibilities: 1. The softening of the samples due to the presence of PEG/PLA blends thus lowering the glass transition temperature (T_g); 2. The existence of a continuous amorphous phase; 3. The presence of a soft dispersed amorphous PEG-rich phase within the amorphous regions of the crystalline lamellae. It is possible that more than one mechanism is responsible for the dramatic increase in the mechanical properties obtained. In addition, the presence of the α' phase cannot be excluded. Its structural parameters and associated physical properties are different from the α phase [43].

Although there is no doubt that crystalline phases are important in the determination of physical properties of semicrystalline polymers, including PLA. It should be noted that the amorphous fraction may play a very critical role in determining the properties obtained. The drop in T_g is important. In the blend samples, the T_g can be lowered by as much as 30° as compared to the neat PLA, depending on the molecular weight of the soft block and the blend composition. This value is consistent with a sample containing different volume fractions of PLA and PEG and usually approximated using the Fox equation [34]. Although we have not found direct evidence showing the location of PEG in the samples, it can speculated that the presence of PEG certainly has altered the structure and property of PLA to lower the T_g of the amorphous PLA. The as extruded samples are amorphous in nature. This is confirmed by the presence of an infrared active vibration at 955 cm^{-1} and the absence of a crystalline vibration at 922 cm^{-1}. The samples crystallize only after annealing at 80 °C for 2 h. The relative intensity of the band at 922 cm^{-1} assignable to either the 10_3 helix in α or α' crystal, the 909 cm^{-1} band characteristic of 3_1 helix in stereocomplex crystal depend on the composition of the blend and thermal history.

It is hypothesized that the improvement in mechanical properties is directly associated with the incorporation of the soft PEG segments. The presence of this component is responsible for the morphology formed. Whether this component is directly responsible for the property enhancement has yet to be confirmed. The end blocks of the triblock form stereocomplex with the matrix PLLA which nucleates crystallization of the matrix polymer. In this process the soft midblock of the triblock is trapped within the semicrystalline polymer matrix thus forming a multiphase structure consisting of hard domains dispersed in a continuous amorphous phase.
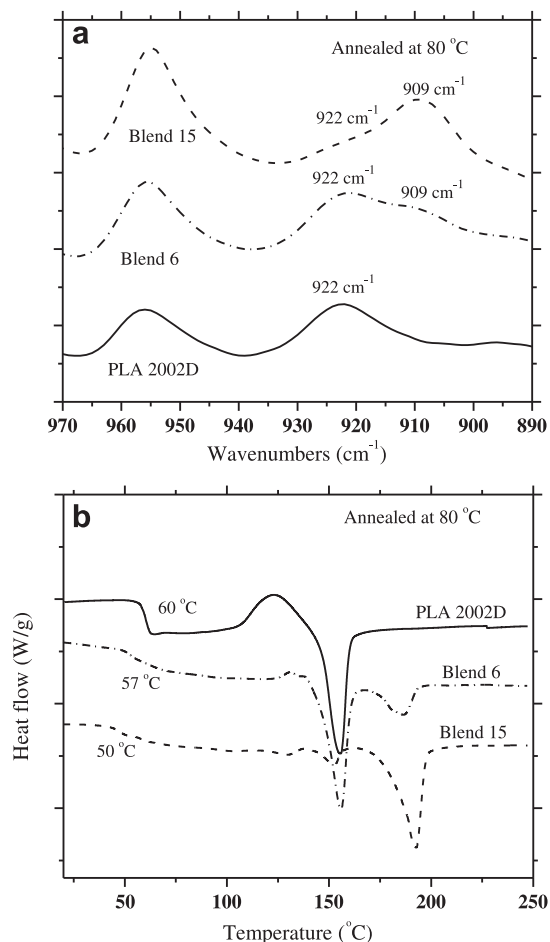
4. Conclusions

This study has shown a new morphology responsible for toughening chiral semicrystalline polymers. Samples with high thermal stability can also be obtained. This concept is based on blends of stereocomplex forming triblock copolymers with semicrystalline PLLA. Additional studies on morphology of these systems will provide a better understanding of the mechanism of toughening. Use of longer soft blocks may also provide an opportunity to further improve the mechanical properties. This study is currently being extended to optimize the molecular weight of the soft block and the composition of the blends. As these blends were prepared without involving solvents at any stage, this could prove to be an industrially viable concept for toughening PLA.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.07.032.

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