



Poly[(R)3-hydroxybutyrate] (PHB)/poly(L-lactic acid) (PLLA) blends with poly(PHB/PLLA urethane) as a compatibilizer



Kai-Wei Lin ^a, Ching-Hung Lan ^a, Yi-Ming Sun ^{a, b, c, *}

^a Department of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li, 320, Taiwan, ROC

^b Graduate School of Biotechnology and Bioengineering, Yuan Ze University, Chung-Li, 320, Taiwan, ROC

^c R&D Center for Membrane Technology, Chung Yuan University, Chung-Li, 320, Taiwan, ROC

ARTICLE INFO

Article history:

Received 30 October 2015

Received in revised form

2 September 2016

Accepted 16 September 2016

Available online 18 September 2016

Keywords:

Poly(3-hydroxybutyrate)

Poly(lactic acid)

Blend

Bio-based

Compatibilizer

ABSTRACT

Poly(PHB/PLLA urethane) (poly(ester urethane), PEU) was synthesized with telechelic poly[(R)3-hydroxybutyrate]-diol (PHB-diols) and poly(L-lactic acid)-diol (PLLA-diols). The miscibility of cast PHB/PLLA blends was enhanced by adding PEU as a compatibilizer, as observed by DSC, WAXS, SAXS, alkaline solution etching test and mechanical properties measurement. It is shown that the crystalline unit cells of PHB and PLLA didn't interfere with each other and the biphasic separation was kept in the blends with PEU. However, the miscibility of PHB/PLLA in the amorphous phase of the blends was improved due to the presence of PEU. The changes of their thermal properties and morphology of the phase boundaries indicated the enhanced miscibility of PHB/PLLA blends by adding PEU. The mechanical properties of PHB/PLLA blends with PEU were amended due to the better entangled amorphous polymer chains. The results demonstrated that PEU was a good compatibilizer for PHB/PLLA blends.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polyhydroxyalkanoates (PHAs) are a class of biologically synthesized polyesters accumulated in many strains of bacteria as an intracellular carbon and energy storage material [1–3]. The earliest discovered and most extensively studied PHA is poly[(R)3-hydroxybutyrate] (PHB). PHB is a thermoplastic polyester that has comparable mechanical strength to polypropylene (PP) and many advantageous properties in terms of biodegradability, biocompatibility, and bio-based nature; therefore, it has been considered as an environment-friendly polymeric material. However, the applications of PHB are limited by its brittleness due to its high crystallinity, substantial hydrophobicity, and narrow processability window due to thermal instability near its melting point of 180 °C [4–6]. In order to overcome the disadvantages of PHB and get some useful applications based on PHB, it has been proposed to improve the properties of PHB either by introducing various hydroxyalkanoate monomers to yield copolyesters [7,8], physical blending with other polymers [9–22], using plasticizers [23–25], or adding inorganic nano-fillers to make nanocomposites [26–28].

Poly(lactic acid) (PLA) is also a biodegradable thermoplastic

polyester derived from renewable and bio-based resources [29,30]. Poly(L-lactic acid) (PLLA) is produced by the catalytic ring-opening polymerization of L-form lactide monomers, which are obtained from fermentation of corn starch in commercial scale. PLLA can hydrolyze easily under wet environment and eventually degrades into nontoxic lactic acid. However, the manufacture of PLLA products is quite sophisticated since the crystallization rate of PLLA is quite slow due to its relatively high T_g (~60 °C) [30].

Both PHB and PLA (or their copolymers) have been widely studied or applied as biomedical materials such as the tissue engineering scaffolds and drug/gene delivery vehicles due to their biocompatibility and biodegradability [31–36]. The mechanical properties and biodegradability of the materials are crucial criteria in many applications. The blends of PHB and PLA provide a simple way to modify the properties of each other for various purposes [37]. Our previous study [38] showed that the degradation behaviors of a PHA/PLA blend could be adjusted by various blending ratios. This could be an important advantage for biomedical applications. Furthermore, there are also some applications of PHB/PLA blends for food packaging due to their compostability [39,40]. It is well known that the apparent properties of a polymer blend depend on the miscibility between blended polymers. The miscibility and crystallinity of binary blends of PHB and PLLA have been investigated [12–19]. The miscibility of PHB/PLLA blends depends on the molecular weight of PHB, and the growth rate of spherulites and the crystallinity of PLLA are affected by the addition of the low

* Corresponding author. Department of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li, 320, Taiwan, ROC.

E-mail address: cesunym@saturn.yzu.edu.tw (Y.-M. Sun).

molecular weight ($L-M_w$) PHB component [14]. Hu et al. [14] analyzed the miscibility and crystallization of $L-M_w$ -PHB/PLLA blends by using differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, and wide-angle X-ray scattering (WAXS), and indicated that the PLLA showed no miscibility with high molecular weight PHB ($\overline{M}_w = 650,000 \text{ g mol}^{-1}$) in the PHB/PLLA blends. On the other hand, it showed some limited miscibility with low molecular weight PHB ($\overline{M}_w = 5,000 \text{ g mol}^{-1}$).

In order to improve the miscibility, compatibilizers or plasticizers could be added to a polymer blend system. Few studies have focused on the effects of compatibilizers or plasticizers on the PHB/PLLA blends. Yoon et al. [41] investigated the compatibility of PHB/PLLA blends with and without a compatibilizer. The copolymer of poly(ethylene glycol) (PEG) and PLLA were synthesized and used as a compatibilizer. However, the results showed that the mechanical properties of PHB/PLLA blends containing PEG-b-PLLA copolymer as a compatibilizer were not improved very much. Abdelwahab et al. [37] applied a newly developed polyester plasticizer (Lapol 108, MW > 80,000 Da) in a PLA/PHB blend, and they found that the blends showed a good distribution of the major components and absence of phase separation. El-Hadi tried to find out the effect of PVAc on PHB/PLLA blend, and he indicated that the PVAc could be used as a compatibilizer and improved the compatibility between PHB and PLLA [42].

In this article, blends of PHB and PLLA of various weight ratios were prepared with or without the addition of poly(PHB/PLLA urethane), which is a block copolymer of PHB and PLLA, as a compatibilizer. The copolymer of poly(PHB/PLLA urethane) was synthesized from low molecular weight poly[(R)3-hydroxybutyrate]-diol (PHB-diol) and low molecular weight poly(L-lactic acid)-diol (PLLA-diol) using 1,6-hexamethylene diisocyanate (HMDI) as a coupling reagent. The focus of this study is to discuss the miscibility, chain packing and phase separation behavior of the crystalline/crystalline blend of PHB and PLLA with or without poly(PHB/PLLA urethane). The thermal properties and the crystallization behavior of the PHB/PLLA blends were investigated using differential scanning calorimetry (DSC), small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS). The mechanical properties and phase separation behavior of the blends were characterized by the tensile test and etching experiments, respectively.

2. Experimental

2.1. Materials

Biosynthetic poly[(R)3-hydroxybutyrate] (PHB) were supplied by the Graduate School of Biotechnology and Bioengineering of Yuan Ze University (GSBB, YZU). The received PHB were purified by being dissolved in chloroform followed by filtration and subsequent precipitation in cold methanol before use. The chemical identity of PHB was confirmed by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). The \overline{M}_n and \overline{M}_w of the purified PHB are 3.8×10^5 and 7.8×10^5 , respectively, as measured by gel permeation chromatographic (GPC).

A commercial grade poly(L-lactic acid) (4032-D, L/D = 98/2) was obtained from Wei Mon Industry Co., Ltd., a local distributor of NatureWorks LLC. The \overline{M}_n and \overline{M}_w of the PLLA are 1.7×10^5 and 2.7×10^5 , respectively, as measured by GPC.

L-Lactide and stannous octoate ($\text{Sn}(\text{Oct})_2$) were from Alfa, chloroform was from Mallinckrodt, toluene and ethylene glycol were from Tedia, diglyme, 1,4-butanediol (BDO), and 1,6-hexamethylene diisocyanate (HMDI) were from ACROS. Dibutyltin dilaurate (DBTDL) was from Strem Chemicals.

2.2. Synthesis of poly(PHB/PLLA urethane)

Telechelic PHB-diol were prepared by the transesterification between biological PHB and ethylene glycol using dibutyltin dilaurate (DBTDL) as a catalyst in diglyme according to the procedures proposed by Hirt et al. [43]. Telechelic PLLA-diol were prepared by the ring opening polymerization of L-lactide with 1,4-butanediol (BDO) using $\text{Sn}(\text{Oct})_2$ as a catalyst in toluene as reported previously [44].

Poly(PHB/PLLA urethane) was synthesized from telechelic PHB-diol and PLLA-diol (1:1, molar ratio) using HMDI as a coupling agent and DBTDL as a catalyst. The amount of HMDI added was equivalent to that of the reactive hydroxyl group in the solution. Freeze-dried 0.48 g PHB-diol and 0.82 g PLLA-diol were dissolved in 5 ml anhydrous chloroform in a flask. When the mixture was dissolved, 4×10^{-4} mol HMDI and two drops of DBTDL were added sequentially. The reaction mixture was stirred under dried nitrogen at 60 °C for two days. After reaction, the solution was precipitated with cold methanol. The product was dried under vacuum at 40 °C for 1 day; a sample of white solid polymer powders was obtained. The preparation procedure for poly(PHB/PLLA urethane) is shown in Scheme 1. Since poly(PHB/PLLA urethane) is a kind of poly(ester urethane) (PEU), it is also called as poly(ester urethane) or PEU in short later on.

2.3. Blend preparation

PHB and PLLA with/without PEU were blended in chloroform in various weight ratios: (1) PHB/PLLA blends of 100/0, 80/20, 50/50, 20/80, and 0/100, and (2) blends of PHB/PLLA as above with 10% PEU, respectively. B100 and L100 are used to represent pure PHB and PLLA, respectively, and B80L20, B50L50, and B20L80 are denoted to the ratio of PHB/PLLA blends of 80/20, 50/50, and 20/80, respectively. All the samples were prepared by solution casting, and dried under vacuum at ambient condition. Membranes of the PHB/PLLA blends with or without 10% PEU with a thickness about 200–300 μm were obtained after the solvent was evaporated.

2.4. Solution etching

In order to observe the phase separation behavior and miscibility of PHB/PLLA blends with/without 10% PEU, samples were prepared by preferentially removing PLLA using alkaline hydrolysis. Surface-etching was performed by immersing the samples in 1 wt% sodium hydroxide solution to remove PLLA component under shaking at 60 rpm at 40 °C for 24 h. The treated samples were washed with distilled water and dried thoroughly under vacuum. The samples were coated with gold for 40 s, and scanning electron microscopy (SEM) images were taken using a JEOL JSM-56000 microscope operated at an acceleration voltage of 20 kV.

2.5. Characterization

Gel permeation chromatographic (GPC) system was built up with three columns (PLgel 5 μm MIXED-C, 7.5 \times 300 mm, \overline{M}_w : 200 to 2,000,000; PLgel 5 μm 10⁴ Å, 7.5 \times 300 mm, \overline{M}_w : 10,000 to 600,000; PLgel 3 μm MIXED-E, 7.5 \times 300 mm, \overline{M}_w : up to 25,000; Polymer Laboratories, UK) connected in series and a refractive index (RI) detector (L-2490, Hitachi, Japan). Chloroform was used as an eluent at a flow rate of 1 ml/min. An oven (Super CO-150N, Enshine, Taiwan) was used to maintain the column temperature at 40 °C. Mono-dispersed polystyrene standards (EasiCal, Agilent, USA) were used to obtain a calibration curve. Perkin-Elmer Spectrum 100 (USA) was used to obtain the FTIR spectra. Samples were mixed with potassium bromide (KBr) powder, and pressed into a

Download English Version:

<https://daneshyari.com/en/article/5200880>

Download Persian Version:

<https://daneshyari.com/article/5200880>

[Daneshyari.com](https://daneshyari.com)