



Morphology, miscibility and continuity development in poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends



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ABSTRACT

In this study, the morphology and miscibility of poly(lactic acid), PLA, and poly(butylene adipate-co-terephthalate), PBAT, blends were studied in detail. Three techniques to examine the morphology of PLA/PBAT are compared: SEM using lower secondary electron imaging (LEI), SEM using low-angle backscattered electrons (LABE) and atomic force microscopy (AFM). The interfacial tension of the system was examined by fitting the Palierne model to the rheological data and the results indicate a very low value of 0.6 ± 0.15 mN/m. The miscibility in PLA/PBAT blends was studied by modulated DSC and the results show a limited one-way partial miscibility of PBAT in the PLA-rich phase with the glass transition temperature of the PLA-rich phase in PBAT showing a drop of up to 10°C , as compared to the neat PLA. Further investigations reveal that this effect depends significantly on the molecular weight of PBAT and underlines the strong entropic nature of this partial miscibility. The morphology at 1 vol.% of the dispersed phase shows that the dispersed phase exists in a stable fiber form even at these very low concentrations, an observation which is compatible with partial miscibility, with fiber diameters of 300 nm for PLA in PBAT and 150 nm for PBAT in PLA. The influence of composition on the dispersed phase fiber diameter shows a significant increase in fiber diameter with minor phase concentration which is not a result of classic coalescence, but more a result of the partial miscibility phenomenon. The region of dual-phase continuity has been examined by a rheological approach and is determined to be a wide and highly symmetric region with the lower and upper limits located between 30–40 and 60–70 vol.% of PBAT, respectively.

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1. Introduction

Bioplastics have received much attention during the past decade predominantly due to environmental concerns related to greenhouse gas production and the end of life scenarios for classic petroleum-based polymers [1]. Among bioplastics, poly(lactic acid), PLA, has shown significant commercial growth due to its bio-based and compostable nature, mechanical strength, availability in the market and lower price compared with most other bioplastics [2]. One of the most important weaknesses of PLA is its brittleness. Different methods have been proposed to overcome this drawback and, in this regard, the blending of PLA with other polymers has received much attention [3]. Polymer blends with PLA offer an economically viable approach to overcome the brittleness and also

enhance other properties, such as the crystallinity of PLA. Among different blends of PLA, blends with other polyester-based bioplastics such as polycaprolactone (PCL) [4,5] and poly(butylene adipate-co-terephthalate), a copolymer of butylene adipate (BA) and butylene terephthalate (BT) known as PBAT [6–21], have been studied more extensively due to their compatibility with PLA, high elongation at break and impact strength and biodegradability/compostability. The PLA/PBAT blend is particularly interesting since it can offer a much wider range of application temperatures and thus has significant commercial potential.

Jiang et al. [21] studied PLA/PBAT and showed that the addition of 20 wt.% of PBAT increases the elongation at break by a factor of 50. A number of other studies [6–20] have focused on the mechanical properties and, to some extent, the rheological properties, however many aspects of the morphology and miscibility of PLA/PBAT remain unclear. This can be attributed to the complexity of the characterization of this blend which originates from the very similar polyester nature of both PLA and PBAT. The complex

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morphology of some polymer blends with similar nature components was previously studied in this group. Ravati et al. [22] studied the morphology of ternary blends of PLA/PBAT/poly(butylene succinate), PBS, and PLA/PBS/polycaprolactone, PCL and showed that PLA/PBAT/PBS develops into a tri-continuous morphology while PLA/PCL/PBS has a partially wet morphology with droplets of one phase spread on the interface of the two other phases. In previous work from this group, Li et al. [23] studied the continuous and co-continuous morphology development in polymer blends with different types of the interfaces and showed that highly interacting, low interfacial tension systems demonstrate fibrillar morphologies even at low composition. This fibrillar morphology leads to a lower percolation threshold for continuity development and results in a wide region of co-continuous morphology. Marin et al. [24] and Bhadane et al. [25] also studied the morphology development in highly compatible low interfacial tension blends and observed some deviations from the features classified by Li et al. which they attributed to the partially miscible nature of the polymer blends studied. The results of these three studies clearly indicate that the level of interaction between components in low interfacial tension polymer blends and their mutual miscibility/immiscibility can have a determining effect on the morphology development. Jiang et al. [21] used dynamic mechanical analysis, DMA, to study the miscibility of PLA/PBAT blends in the composition range of 5–20 wt.% of PBAT and concluded that PLA/PBAT is an immiscible polymer blend. Yeh et al. [16], also using DMA, reported that PLA/PBAT was a miscible binary polymer blend system when PBAT was less than 5 wt.%. The miscibility/immiscibility of PLA/PBAT still remains to a large degree unresolved.

The objective of this work is to carry out a highly detailed examination of the miscibility, interfacial tension and morphology of PLA/PBAT blends. The dispersed phase and co-continuous morphology will be characterized using a variety of microscopic and rheological techniques. Finally a comprehensive conceptual model for the morphological development of these systems will be proposed.

2. Experimental

2.1. Materials

PLA 3001D (Natureworks) from Cargill and two commercial grades of PBAT, Ecoflex F BX 7011 (low molecular weight) and Ecoflex F Blend C1200 (high molecular weight) from BASF will be referred to as PLA, L-PBAT and H-PBAT respectively. All the materials were dried at 60 °C under vacuum overnight before being used in the experiments.

2.2. Molecular weight and gel permeation chromatography (GPC)

The molecular weights of the three polymers were obtained from GPC tests carried out on an Agilent 1260 Infinity Multi-Detector GPC/SEC system equipped with two Phenomenex Phenogel columns (10³ Å pore size, 5 µm bead) and a 1260 Infinity Refractive Index Detector. The solution of polymers (100 µL of 2 mg/ml in chloroform) was injected with the flow rate of 1 mL/min.

2.3. Proton nuclear magnetic resonance (¹H NMR)

In order to determine the ratio of butylene adipate (BA) to butylene terephthalate (BT) segments in PBATs, ¹H NMR spectra of L-PBAT and H-PBAT in CDCl₃ were recorded at 25 °C on a Bruker AVII-700, operating at 16.4 T (¹H frequency of 700 MHz). 64 scans with a repetition time of 7.8 s were used for all the samples.

2.4. Blend preparation

All samples were prepared using an internal batch mixer (Plasti-Corder DDR501, Brabender) with a total volume of 30 mL at 50 RPM and 180 °C under a nitrogen blanket. The average shear rate at the processing condition used was estimated as 25 s⁻¹ [26]. After 10 min of mixing, samples were cut and cooled in ice-water to freeze-in the morphology of the samples.

2.5. Field emission scanning electron microscopy (FE-SEM)

The samples were cut and microtomed under liquid nitrogen using a microtome (Leica-Jung RM 2065). Then, the sample surface was coated with a 15 nm thick gold layer and the morphology was observed with a FE-SEM machine (JSM 7600F, JEOL). Two different detectors of lower secondary electron image (LEI) and low-angle backscattered electron (LBE) were used to examine the morphology of the microtomed sample. Cryo-fractured samples were also coated with a gold layer before determining their morphology by FE-SEM.

2.6. Atomic force microscopy (AFM)

The samples were microtomed using the same procedure as mentioned for FE-SEM samples. The AFM machine was equipped with a scanning probe microscope Dimension 3100 with a Nanoscope IVa controller from Veeco Instruments. Silicon tips, model ACTA-W from AppNano, with the tip radius less than 10 nm were used in this study. Because of the differences in the modulus of PLA and PBAT, the tapping phase mode was used to determine the morphology of the samples.

2.7. Image analysis

The AFM images were analyzed by an image analysis software (SigmaScan Pro. V.5, Sigmaplot) equipped with a digitizer table (Wacom) and a pressure sensitive pen for convenient mapping of the dispersed phase. The detailed procedure for the digitizing table is described elsewhere [27]. The average dispersed phase fiber or spherical droplet diameter were determined using an average number of 350 measurements from 6 to 8 AFM images (depending on the blend structure) for each sample. In the samples with 1 vol.% of the dispersed phase, the average dispersed phase diameter was determined using an average number of 30–50 measurements. In the disk samples with spherical dispersed phase morphology for the interfacial tension measurement, the Saltikov correction was applied [28] in calculating the dispersed phase diameter. This corrects for the fact that the droplets are not cut exactly at their equator in the microtomed surface and also for polydispersity effects. The average dispersed fiber diameter in the samples with fibrillar morphology cannot be determined from the area of the dispersed fibers in the microtomed samples as the cross-sectional area depends considerably on the angle between the microtoming direction and the fiber axis. Fig. 1 schematically shows how cutting a fiber at different angles in a blend with fibrillar morphology can result in different observed cross-sectional area of the fiber in AFM images.

After cutting a fiber, its final geometry becomes a cylindrical segment in which the smallest diameter of the formed ellipse (minor axis) of the microtomed surface is always equal to the diameter of the fiber. Therefore, the average fiber diameter in this work was calculated based on the measured smallest diameter of the dispersed fibers cross-sectional area in the microtomed surfaces. The average fiber diameters are reported as XX ± YY where

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