



Bio-based solution-cast blend films based on polylactic acid and polyhydroxybutyrate: Influence of pyromellitic dianhydride as chain extender on the morphology, dispersibility, and crystallinity



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ABSTRACT

Bio-based solution-cast blend films are a particular class of materials used in various fields such as coatings and their use is taking big steps in view of their eco-friendly nature. Blend of biopolymers can bring about complementary properties for replacing the petroleum-based polymer with renewable ones to minimize the environmental damaging. In this work, bio-based solution-cast blend films based on PLA and PHB are prepared and characterized. The thermal, crystallinity and morphology of the cast films are studied as well. Bio-based blends of polyhydroxybutyrate and polylactic acid (PHB/PLA) films were prepared *via* solvent-cast method and PDMA was utilized as chain extender. FTIR, DSC, WAXD and SEM analyses were performed for evaluating the properties under the influence of PDMA. A fall in glass transition temperature was observed upon increasing PDMA content which exhibited good correlation with Fox Equation. PMDA due to the ring opening substitution from carbonyl group coupled to both polymers, hence, affected the crystallinity. Addition of PDMA exhibited gigantic effect on the crystallization behavior/rate of samples. Due to this behavior, film properties can be adjusted by altering the PMDA content. The results of this work can be applied in developing bio-coatings based on blends of other types of biopolymers.

1. Introduction

Nowadays, environmental pollutions caused by plastics from one side and the limitation of irreplaceable sources from the other side necessitate replacement of immortal plastics with biodegradable and renewable polymers. Based on this attitude, application of bio-based polymers such as alginate, agarose, polylactic acid, and polyhydroxybutyrate (hereafter referred to as PLA and PHB, respectively) has been progressively examined [1–3]. PLA is a promising biodegradable polyester that is chemically synthesized, but its brittleness poses question on its suitability for various applications such as coating [4,5], textile fabrication [6], packaging [7] and tissue engineering [8,9]. Under physiological condition, PLA can be easily hydrolyzed and degraded to lactic acid, which is safe and non-toxic. To conquer PLA weak points, it can be blended with other polymers having suitable properties [10].

As one of the most favorable polymers, PHB has been occasionally blended with PLA. PHB, due to its high crystallinity and its melting point resemblance with PLA, could be an appropriate couple of PLA [11]. PHB is a biological polymer synthesized with microorganism;

hence, it can be degraded in soil with bacteria. Since PHB properties resemble some petroleum-based polymers, it has been attracted numerous attentions as a substitution for petroleum-based polymers. By fine tuning the PHB crystallinity, it can be considered for various applications [12]. When blended with other polymers, depending on composition, filler addition, compatibilizer addition and fabrication process, PHB exhibits a wide range of properties—what gives it credit for industrial applications [13].

PLA/PHB blend has various applications; however, some materials should be added to the blends to endow the desired properties. For example, to achieve antibacterial feature, Ag ions can be added to the blend [14]. Some other properties of PLA/PHB such as miscibility, crystallinity and mechanical properties have also been studied. Solubility parameter of PLA and PHB are around 19.5–20.5 MPa^{1/2} and 18.5–20.1 MPa^{1/2}, respectively [15,16]. Therefore, it brings about the idea that they should be miscible, but, the value and distribution pattern of molecular weight, degree of crystallinity, mixing method and processing condition can strongly affect their miscibility window and, hence, their final properties. PHB molecular weight has a profound effect on the blend miscibility; moreover, it governs PLA crystallinity

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and spherulites growth rate. Blend composition is another important factor affecting the PLA/PHB blend properties. Typically, low molecular weight ingredients can form into miscible blends, while higher molecular weights result in phase separation [17]. It was reported that the PLA blend with low molecular weight PHB prepared through solution-cast method and compression molding appears miscible and the PHB content increment facilitates PLA crystallization [18]. However, PLA crystallization remains intact juxtaposing with high molecular weight PHB [19]. Process temperature exhibited a significant effect on the miscibility between PLA and PHB. High temperature facilitates the transesterification reaction between PLA and PHB. It was reported that PLA/PHB samples with various composition prepared through solution-cast method were immiscible, however, raising the temperature up to 200 °C enhanced blend miscibility [20].

Reports demonstrate that PLA/PHB blend is brittle; hence, its film preparation was encountered with serious difficulties. Improving the blend properties necessitates the usage of plasticizer or compatibilizer [21]. Various plasticizers have been used for this aim like glycerol and poly(ethylene glycol). It was also reported that PLA and PHB in the form of blend or composite suffer from degradation and mismatching properties [22]. Compensating for such weak points, chain extenders have been widely used in blend and composite preparation. Overall, addition of chain extender affects crystallization process [23]. Crystallization of PLA in the presence of clay nanoplatelets was studied applying various chain extenders. Polycarbodiimide enhanced the crystallization temperature and reduced the crystallinity percentage [24]. Elsewhere, it was addressed that tris(nonylphenyl) phosphite because of chain end reduction enhances the crystallization degree [25]. Moreover, Joncryl due to formation of long-chain branching structure disrupts the chain packing and decreases the crystallization degree [26].

Based on above discussion, appropriate selection of plasticizers and chain extenders compensates for the brittleness and poor processing features of PLA/PHB blends. In this study, we sought to determine the PLA/PHB blend properties with using the pyromellitic dianhydride (PMDA) as a chain extender, which, to the best of our knowledge, has not been reported before. Due to the aforementioned immiscibility concerns, PMDA was utilized to bring about interaction and linkages between PLA and PHB components. Bio-based solution-cast blends were characterized by FTIR, DSC, WAXD, acid number and SEM test were performed to study the behavior of PLA/PHB blend.

2. Materials and methods

Poly(3-hydroxy butyrate), PHB, was purchased from Biomer Company, Germany, (Biomer – P209 (UK5782) grade, Batch 138T285/10/1112). This PHB was composed of a mixture of 15% of PHB with a molecular weight of 490 kDa and 85% of PHB with a molecular weight of 560 kDa leading to a blend with polydispersity index (PDI) varying between 2 and 3. PLA (2003-D) was purchased from Nature Works LLC, USA, which contained 1.5–2% of D isomer (PLA-002D grade) with onset degradation of 290 °C, having an average molecular weight of 2.71×10^5 g/mol, number-average molecular weight of 1.30×10^5 , PDI of 2.08 and melt flow rate of 12.4 g/10 min. PMDA and chloroform were purchased from Merck Company, Germany. All materials were utilized without further purification.

2.1. Samples preparation

PLA/PHB blends were prepared by solvent casting method. Various compositions of PLA/PHB blend (100/0, 75/25, 50/50, 100/0) with different amounts of PMDA (0, 0.5, 1 wt.%) were kept under reflux through the night to achieve uniform mixtures of blend solution. After that, the solution was casted and dried at 50 °C for two days to achieve bio-based solution-cast films.

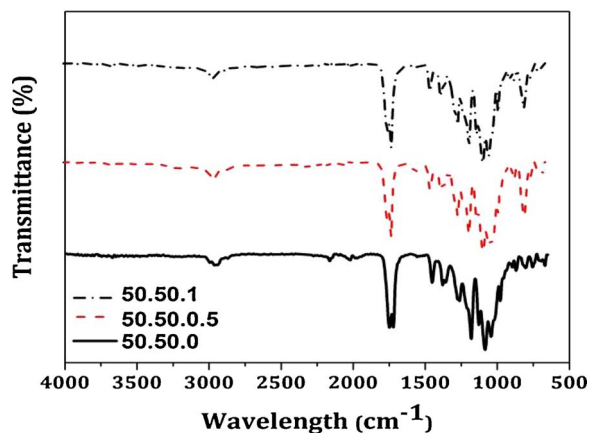


Fig. 1. FTIR spectra of PHB/PLA blend with various contents of PMDA.

2.2. Fourier-transform infrared spectroscopy (FTIR) spectroscopy

FTIR spectroscopy was performed for characterization of chemical bonding between the ingredients when they formed as films. FTIR spectroscopies of samples were conducted on a Bomem, Canada in the wavelengths range of 400–4000 cm^{-1} with 4 cm^{-1} resolution. KBr was used for FTIR spectroscopy sample preparation.

2.3. Differential scanning calorimetry (DSC)

Thermal behavior including the degree of crystallinity, glass transition temperature (T_g), cold crystallization temperature, melting point, and the miscibility of samples were studied using DSC apparatus model METTLER 882c. Samples were heated from -20 to 200 °C with heating rate of 10 °C/min, and the samples' thermal history was erased by maintaining them at 200 °C for 5 min. After that, samples were cooled down to -20 °C and reheated up to 200 °C. The crystallinity of each phase was calculated through the following equation [27]:

$$X_c = \frac{\Delta H_c}{w \times \Delta H_0} \times 100 \quad (1)$$

where X_c is the percent of crystal phase, ΔH_c is the enthalpy of crystallization of PET or PLA in the blend, w is the weight fraction of each phase in the blend and ΔH_0 is the enthalpy of for 100% crystalline PHB (146 J/g) and for 100% crystalline PLA (93 J/g) [28,29]. Fox Equation (Eq. (2)) was used for determining the blend glass transition temperature.

$$1/Tg_{\text{blend}} = W_1/Tg_1 + W_2/Tg_2 \quad (2)$$

2.4. Wide angle X-ray diffraction (WAXD) analysis

Wide-angle X-ray analysis (WAXD) was conducted on a X-ray diffractometer (Philips PANalytical X'pert PRO) with Cu $K\alpha$ radiation having $\lambda = 1.540598$ Å at a generator voltage of 35 kV and 45 mA current at ambient temperature. Based on Bragg's law, i.e. $n\lambda = 2d \sin \theta$, the crystallographic spacing (d) of the samples were calculated. The 2θ scanning of X-ray intensity was altered in the range of 2 – 90 ° with a scanning rate of 1.2 ° min^{-1} . The degree of crystallization was calculated using the Eq. (3)

$$X_c(\%) = 1/(1 + I_a/I_c) \cdot 100 \quad (I_{\text{tot}} = I_a + I_c) \quad (3)$$

In this equation, X_c , I_a , I_c and I_{tot} are the degree of crystallization, the intensity of amorphous, crystalline, and total area under peak area and total areas, respectively.

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