

# PLA-PBAT-PLA tri-block copolymers: Effective compatibilizers for promotion of the mechanical and rheological properties of PLA/PBAT blends



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## ARTICLE INFO

### Keywords:

PLA-PBAT-PLA  
Compatibilizer  
Interfacial interaction  
Miscibility

## ABSTRACT

Poly(lactide-poly(butylene adipate-co-terephthalate)-poly(lactide) tri-block copolymers incorporating PLA blocks (LPB and HPB) with different chain lengths were synthesized as compatibilizers for PLA/PBAT blends. The structure of the tri-block copolymers could be adjusted by varying the feeding ratios of the monomer and macro-initiator, and the polymers were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, GPC, and DSC measurements. Compared to the short chains of the PLA blocks (LPB) in the copolymers, HPB was a more effective compatibilizer for two immiscible blends because the long chains achieve enhanced interpenetration of the relevant homopolymers. The elongation between the blocks of the PLA/PBAT blends with 5% HPB compatibilizer was seven times more than that of the pristine blends. The addition of compatibilizer reduced the particle size of the dispersed phase from 1.5 μm to 0.5 μm and improved the miscibility of PLA and PBAT, as confirmed by the thermal, morphological, and rheological properties. The experimental results established that tri-block copolymers improved the interfacial interaction and the miscibility between PLA and PBAT.

## 1. Introduction

In recent years, bio-based or biodegradable polymers have attracted considerable interest from researchers because these compounds are environmentally friendly and renewable [1–3]. Examples are polylactide (PLA) [4,5], poly(butylene succinate) (PBS) [6,7], poly(ε-caprolactone) (PCL) [8,9], and poly(butylene adipate-co-terephthalate) (PBAT) [10–12]. Even though some of these polymers can be processed into highly efficient materials with extensive applications, it remains difficult to satisfy the requirements of all the applications with a single polyester. Thus, materials with the desired properties have been obtained by melt blending two or more polyesters as an economic and effective way to combine their respective advantages [13–15]. For example, PLA/PBAT blends are highly promising materials on account of the considerable mechanical strength conferred by PLA and the extreme toughness contributed by PBAT [16–20]. However, a blend of PLA and PBAT only exhibits perfect performance if the two compounds are compatible in the product. Although PBAT has carbonyl groups similar to those of PLA, low interfacial adhesion and macro-phase separation between the two polyesters would lead to immiscibility. Studies found that more than 5% of PBAT is phase-separated in PLA resin, thus it is

necessary to explore an effective compatibilizer to improve the interaction between PLA and PBAT [21,22].

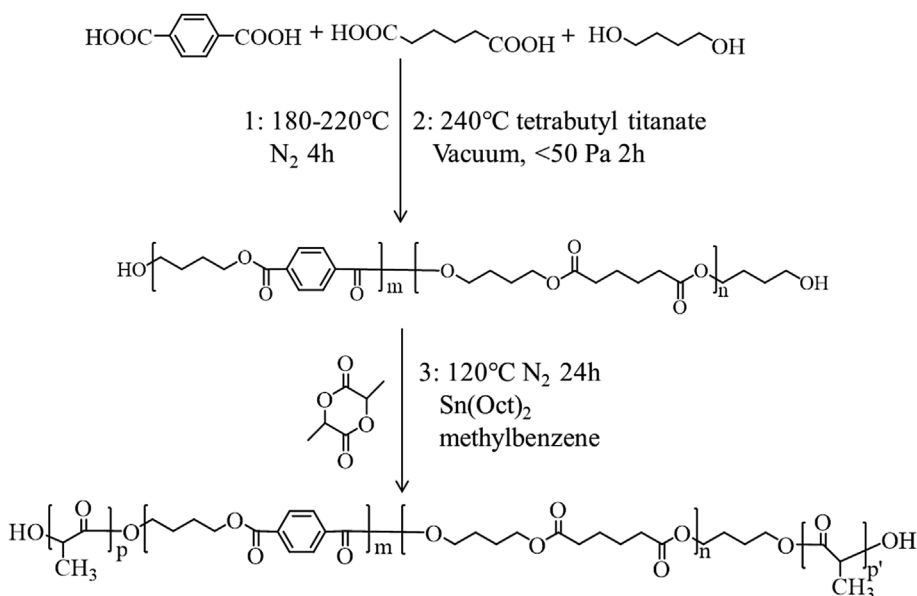
The presence of bi-, tri-, or multi-block copolymers at the interface can reduce the interfacial tension of two immiscible blends. Only small amounts of copolymers emulsify the phase interface to improve the phase morphology and interfacial adhesion of the immiscible blends [23–25]. In this regard, PLA-PBAT-PLA tri-block copolymer was previously used to improve the miscibility of PLA and PBAT. Sun [26] found that tri-block copolymers with a low molecular weight acted as carriers for high-molecular-weight tri-block copolymers to compatibilize PLA and PBAT, and that the long chain of the PLA blocks played a key role in improving the miscibility. Moreover, Kim [27] also found that the chain length of PS-*b*-PI copolymers played different roles to compatibilize PS/PI blends. Thus, the chain length of block copolymers is known to influence the compatibilization of blends in different ways.

This prompted us to investigate the effect of the chain length of PLA-PBAT-PLA tri-block copolymers on the compatibilization of PLA/PBAT blends. Two tri-block copolymers with PLA blocks with different chain lengths were synthesized: a low molecular weight tri-block copolymer with short-chain PLA blocks (LPB) and a high molecular weight tri-block copolymer with long-chain PLA blocks (HPB). The mechanical,

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**Scheme 1.** Reaction route for PLA-PBAT-PLA tri-block copolymers.

morphological, thermal, and rheological properties were studied with the aim of evaluating the effect of compatibilization.

## 2. Experimental methods

### 2.1. Materials

PLA (grade 4032D,  $M_n = \sim 100,000$  g/mol) was purchased from Natureworks. PBAT (Ecoworld,  $M_n = \sim 45,000$  g/mol) was obtained from Jinhui Zhaolong Co. Ltd. Lactide (LA), terephthalic acid (TPA), adipic acid (AA), 1,4-butanediol (BDO), tetrabutyl titanate (TBT), and stannous octoate ( $\text{Sn}(\text{Oct})_2$ ) were purchased from J&K Scientific Ltd. All of these reagents were used directly as received. Methylbenzene was treated by distillation over calcium hydride. Trichloromethane was of chromatographic grade and was used without further purification. All other solvents were of analytical grade.

### 2.2. Synthesis of HO-PBAT-OH initiator

The synthesis of the macro-initiator was conducted via condensation polymerization using tetrabutyl titanate as the catalyst (Scheme 1). In the first esterification process, calculated amounts of terephthalic acid (83 g, 0.5 mol), adipic acid (73 g, 0.5 mol), 1,4-butanediol (108 g, 1.2 mol) and tetrabutyl titanate (0.47 g, 0.3 wt% of acid) were added to a 500 mL three-necked flask equipped with a mechanical stirrer. The esterification reaction was conducted under N<sub>2</sub> atmosphere by gradually increasing the temperature from 180 °C to 220 °C where it was maintained for 2 h. In the second polycondensation process, the pressure of the reaction system was gradually decreased and polycondensation was continued at reduced pressure below 50 Pa for 2 h. During this period, the temperature was increased from 220 °C to 240 °C. Finally, the polymer was cooled to room temperature and exposed to air. The mixture was dissolved in chloroform and precipitated three times by using ethyl alcohol. The product was subsequently separated by filtration and dried at 50 °C for 12 h under vacuum. The HO-PBAT-OH macro-initiator was recovered in the form of a white powder.

### 2.3. Synthesis of PLA-PBAT-PLA tri-block copolymers

The PLA-PBAT-PLA tri-block copolymers were synthesized by the ring-opening polymerization (ROP) of lactide in methylbenzene solution using HO-PBAT-OH as the macro-initiator and  $\text{Sn}(\text{Oct})_2$  as the catalyst. First, HO-PBAT-OH (7 g,  $4 \times 10^{-4}$  mol), LA (4 g, 0.028 mol)

and 8 g, 0.056 mol), methylbenzene (10 g, 0.11 mol), and  $\text{Sn}(\text{Oct})_2$  (0.3 wt% of LA) were added to a 100 mL three-necked flask, after which the temperature was increased to 120 °C for 24 h under N<sub>2</sub> gas atmosphere. The product was subsequently separated by filtration and dried at 50 °C for 12 h under vacuum. The PLA-PBAT-PLA tri-block copolymers were recovered in the form of a white powder.

### 2.4. Blends preparation

Before melt-blending, commercial PLA and PBAT were dried in a vacuum oven for 12 h at 50 °C. PLA/PBAT blends at a fixed ratio (70/30, w/w) were prepared by melt blending in the presence of various amounts (i.e., from 0 to 1%, 3%, and 5%) of tri-block copolymer LPB or HPB. The blending process was conducted using a Thermoscientific process 11 extruder with a screw speed of 200 rpm at a temperature of 185 °C.

### 2.5. Characterization

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-300 apparatus using CDCl<sub>3</sub> as the solvent. Chemical shifts are given in parts per million referenced to tetramethylsilane. The weight contents of the polymers were calculated by obtaining the integral ratios of peaks on the <sup>1</sup>H NMR spectra.

Gel permeation chromatography (GPC Waters 410) analysis was conducted with chloroform as the eluent (flow rate: 1 mL/min) and polystyrene (PS) standards for calibration.

Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC1 instrument under nitrogen flow. The sample was measured by using a heat/cool/heat procedure from –70 °C to 200 °C. The first heating process was used to remove the heating history at a rate of 20 °C/min, and then the cooling and the second heating process were measured at a rate of 10 °C/min.

A cross-section of the blends was investigated by Hitachi S-4800 scanning electron microscope (SEM). The samples were fractured in liquid nitrogen and sputter-coated with gold.

The tensile tests were carried out by employing an Instron-5699 tester according to ASTM D638. All the samples were stretched with a 50 mm/min stretching rate at room temperature.

Dynamic analysis (DMA) was performed on a Mettler DMA/SDTA861e instrument. The experiments were carried out at a frequency of 1 Hz from –60 to 100 °C at a heating rate of 3 K/min.

Melt-rheological properties were investigated on a HAKKE

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