



Non-planar ring contained polyester modifying polylactide to pursue high toughness



Jia Qiu, Fei Liu, Junwu Zhang, Haining Na^{**}, Jin Zhu^{*}

Ningbo Key Laboratory of Polymer Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, PR China

ARTICLE INFO

Article history:

Received 24 September 2015
Received in revised form
3 March 2016
Accepted 14 March 2016
Available online 17 March 2016

Keywords:

Polymers
Fracture toughness
Impact behaviour
Elastic properties

ABSTRACT

Non-planar ring contained polyester is synthesized as an effective toughening agent to modify polylactide (PLA). By systematically researching the relation between molecular structure and properties, the two key factors to pursue high toughness of PLA with non-planar ring contained polyester are carefully distinguished. For one thing, the polyester must own the ability to be well compatible with PLA. For the other, the polyester should have a rigid molecular chain but “non-rigid” aggregation structure. By suitably controlling the molecular design, poly(butylene adipate-co-1,4-cyclohexanedicarboxylate) (PBAC) is obtained. After using PBAC to toughen PLA, the elongation extremely increases to $196.1 \pm 3.6\%$ and the notched impact strength is also effectively improved with several times. Finally, our research establishes an important methodology to toughen PLA and thus fabricates tough PLA based blends.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polylactide (PLA) is a typical biobased and biodegradable polyester with excellent mechanical properties such as high strength and modulus [1,2]. These advantages enable PLA suitable in various application fields, including packaging, biomedical devices, and so on [3]. Nevertheless, the inherent brittleness including low flexibility and low impact strength is inevitable [4]. This disadvantage becomes the key restriction of PLA for wider applications.

Blending PLA with a secondary polymer is recognized as a simple but effective way to achieve toughening [5–8]. In practice, many secondary polymers such as poly(ϵ -caprolactone) (PCL) [9,10], poly(butylene succinate) (PBS) [11], poly(hydroxy butyrate) (PHB) [12], poly(propylene carbonate) (PPC) [13], and poly(butylene succinate-co-adipate) (PBSA) [14] have been respectively tried. However, due to the lack of the necessary guidance in theory to choose the secondary polymers, the improvement in toughness of PLA is unsatisfying. In fact, the significant improvement of toughening PLA starts from using compatibilizer [15]. After many attempts, for instance, using triphenyl phosphite (TPP) [16], epoxide soybean oil [17], tung oil anhydride [18], epoxidized

itaconic acid [19], epoxidized cardanol [20], epoxidized citric acid [21], etc, the interfacial adhesion between PLA and the modifier is improved and thus enhances the toughness. But, compatibilizer is not usually a good choice. Generally, the molecular weight of compatibilizer is low and thus results in unexpected exudation to extremely reduce the overall mechanical properties.

Recently, poly(butylene adipate-co-terephthalate) (PBAT) attracts great attention [22–24]. Though literature [24] believes PBAT is a good material to modify PLA, the ratio of aromatics and aliphatics in PBAT (particular commercial PBAT) is in fact rather fixed. Increasing the amount of aliphatic chains in PBAT will lead to the obviously decrease in mechanical strength and modulus. And, the increase of benzene rings in PBAT will reduce the environmental friendly [25,26]. For example, poly(butylene terephthalate) is resistant to microbial attack [27]. Thus, the properties of PBAT are almost not adjustable.

According to the studies made by our group [28,29] and other researchers [30–32], non-planar ring structures have been proved to own good rigidity and toughness simultaneously. And, the toughness of non-planar ring contained polymers can be controlled through the transition of the stereostructure. Study [33] has proved the *cis*-1,4-cyclohexylene ring moiety (*cis*-CHRM) introduces kinks into the main chain, which act as defects and can hinder the formation of crystallinity, resulting in well flexibility. Accordingly, in this paper, we decided to design controllable non-planar ring contained polyester as the toughening agent for PLA. By

* Corresponding author.

** Corresponding author.

E-mail addresses: nahaining@nimte.ac.cn (H. Na), jzhu@nimte.ac.cn (J. Zhu).

researching the relation between molecular structure and properties, we would like to establish an effective methodology to toughen PLA. Thus, the PLA/polyester blend with high toughness and general properties is expected to be fabricated.

2. Experiment

2.1. Materials

The analytical pure 1,4-butanediol (BDO), adipic acid (AA), and tetrabutyl titanate were purchased from Aladdin Reagent (Shanghai, China). 1,4-cyclohexanedicarboxylic acid (mix-CHDA, *cis:trans* = 1:1) and 99% *trans*-CHDA were bought from Kangmanlin Chemical Reagent Company (Nanjing, China). Mix-CHDA was purified to obtain *cis*-CHDA with high purity (above 85%). PLA (4032D) was supplied by NatureWorks (Minnesota, USA). It was vacuum dried at 80 °C for 8 h prior to use.

2.2. Synthesis of PBC and PBAC

PBC was synthesized from *cis*-CHDA and BDO using tetrabutyl titanate as catalyst following with the experimental steps of Ref. [37]. PBAC was synthesized from 99% *trans*-CHDA, BDO, and AA. Firstly, using *trans*-CHDA and BDO, AA and BDO to obtain bis(1,4-hydroxybutyl)*trans*-1,4-cyclohexanedicarboxylate (*trans*-BHBC) and bis(1,4-hydroxybutyl)adipate (BHBA), respectively, with tetrabutyl titanate as catalyst. PBAC was then obtained by polycondensation with *trans*-BHBC and BHBA, the feed weight ratio of *trans*-BHBC to BHBA was 4:1 with tetrabutyl titanate as catalyst. Finally, both PBC and PBAC were vacuum dried for 2 h at 40 °C and 80 °C, respectively.

2.3. Preparation of PLA/PBC and PLA/PBAC blends

PLA/PBC and PLA/PBAC (a number is followed to present the weight fraction of PBC or PBAC in the blends) were melt-blended in a twin screw extruder (Brabender, Germany), respectively. Whereafter, the melting blends were water-cooled and sent to a LQ-25 granulator (Hengxi Machinery Manufacturing Co., Ltd., Taizhou, China) to make pellets. Then, the pellets were dried at 80 °C in a vacuum-drying oven for 12 h. Lastly, they were injected into standard test bars via a HTF90W injection molding machine (Haitian Plastics Machinery, Ningbo, China).

2.4. Characterization

The structures of polyesters were determined by proton nuclear magnetic resonance (¹H NMR) in CDCl₃ solvent using a Bruker AVIII400 NMR spectrometer. Molecular weights and polydispersity (*PD*, molecular weight distributions) were measured on a PL-GPC220 gel permeation chromatograph (GPC) at 40 °C with a normal flow rate of 1.0 mL/min. Thermal decomposition temperature (*T_d*) was measured using a METTLER-TOLEDO TGA/DSC thermogravimetric analyzer (TGA). Each TGA specimen was heated from 50 °C to 600 °C at a rate of 10 °C/min under nitrogen atmosphere. Thermal properties were investigated using a differential scanning calorimetry (DSC) instrument (METTLER-TOLEDO DSC 1). Each DSC specimen was heated from room temperature to 200 °C at 20 °C/min and hold for 2 min to eliminate any thermal history. Then cooled to -35 °C at 5 °C/min and hold for 5 min to obtain crystallization temperature (*T_c*). The glass transition temperature (*T_g*), cold crystallization temperature (*T_{cc}*), as well as melting temperature (*T_m*) were obtained by the second heating at 10 °C/min to 200 °C. All the DSC tests were under nitrogen atmosphere. The degree of crystallinity (χ_c) of blends was determined as follow,

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Phi \Delta H_m^\theta} \times 100\% \quad (1)$$

ΔH_m and ΔH_{cc} is the enthalpy of melting of blends and cold crystallization, respectively. ΔH_m^θ is the enthalpy of fusion assuming 100% crystalline PLA (93.7 J/g) [34]. Φ is the weight fraction of PLA in the blends.

According to GB/T 1040.1–2006 (China), tensile test was carried out at 200 mm/min and 10 mm/min for polyesters and blends, respectively, on Instron 5567 apparatus. The notch impact test was performed on a mechanical impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd., Chengde, China), according to GB/T 1843–2008 (China). Before the test, samples were notched on a WAY-240 universal sampling machine (Chengde Kecheng Testing Machine Co., Ltd., China). The bending test was performed by Instron5567 apparatus according to GB/T 9341–2008 (China) at 2 mm/min. At least five samples for each blend were tested in these mechanical tests.

The microstructural morphology of blends were characterized by environmental scanning electron microscopy (SEM, Hitachi S4800, Japan) at 8 kV, 7uA. After immersing in liquid nitrogen for 20 min, samples were fractured by vice, and then rupture surfaces were coated with gold prior to observation.

The number-average diameter (d_i) of the separated phases was determined by a software (Nano Measurer 1.2) and 50 sets were analyzed per sample. The average diameter (d) and its distribution (σ) were calculated by the following equations:

$$d = \frac{\sum_{i=1}^{50} d_i}{50} \quad (2)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{50} (d_i - d)^2}{50}} \quad (3)$$

3. Results and discussion

3.1. PBC and PBAC

The molecular structures of PBC and PBAC are carefully

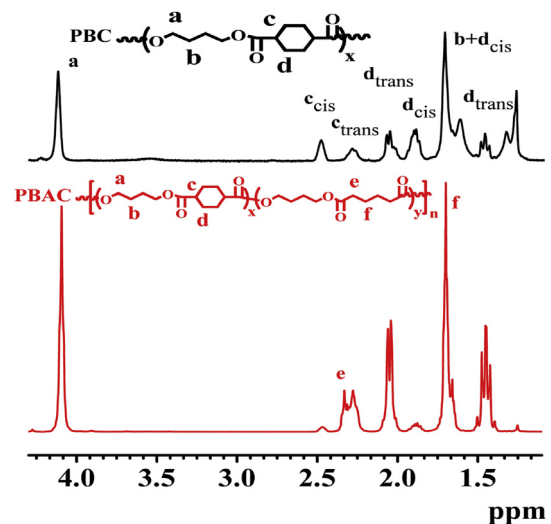


Fig. 1. ¹H NMR spectra of PBC and PBAC.

Download English Version:

<https://daneshyari.com/en/article/819889>

Download Persian Version:

<https://daneshyari.com/article/819889>

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