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Reinforcement effect of poly(butylene succinate) (PBS)-grafted cellulose nanocrystal on toughened PBS/polylactic acid blends

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ABSTRACT

Poly(butylene succinate) (PBS)/polylactic acid (PLA) blends modified with dicumyl peroxide (DCP) were reinforced by PBS-*g*-cellulose nanocrystal (CNC) through melt mixing. PBS-*g*-CNC was prepared through *in situ* polymerization and its structure was confirmed by FTIR, ^{13}C NMR, XPS and GPC analysis after saponification. The morphological analysis of PBS/PLA/PBS-*g*-CNC composites before and after etched by CH_2Cl_2 shows that the addition of DCP and PBS-*g*-CNC could decrease the size of PBS as a dispersed phase in PLA matrix and improve the dispersion of PBS-*g*-CNC in both PBS and PLA phases, which could affect the crystallization and mechanical properties of composites. The crystallinity of PLA α'-phase crystal in PBS/PLA/PBS-*g*-CNC composites is increased obviously by the addition of PBS-*g*-CNC, leading to an increase of the crystallinity of the composites. PBS/PLA blends modified by DCP have high Notched Izod impact strength and moduli, and the values are increased by the addition of PBS-*g*-CNC. Both storage modulus and glass translation temperature of PBS/PLA blend are increased by DCP and PBS-*g*-CNC, which is proved by DMA results, showing a weak molecular segment mobility of PBS/PLA matrix. The addition of DCP decreases the crystallization temperature and crystallinity of PBS/PLA composite, but increases the thermal stability of composites, mostly because of the crosslink effect of DCP on PBS/PLA matrix.

1. Introduction

Polylactic acid (PLA) is a bio-degradable polymer, and can be used as an environmental friendly plastic (Wang, Wang, Zhang, Wan, & Ma, 2009b). But the high production costs, brittle nature and slow crystallization rate of PLA restricts its applications as common polymers (Nerkar, Ramsay, Ramsay, Vasileiou, & Kontopoulou, 2015). Various modification methods have been employed to overcome these limitations of PLA (Anderson, Schreck, & Hillmyer, 2008; Rasal, Janorkar, & Hirt, 2010; Nagarajan, Zhang, Misra, & Mohanty, 2015). Modification of PLA by physical blending is a useful and economical way to improve the toughness. For example, some flexible biodegradable polymers such as poly(butylene succinate) (PBS) (Shibata, Inoue, & Miyoshi, 2006; Cherykhunthod, Seadan, & Suttiruengwong, 2015; Shibata, Teramoto, & Inoue, 2007), poly(butylene adipate-*co*-terephthalate) (PBAT) (Jiang, Wolcott, & Zhang, 2006) and poly(butylene succinate-*co*-adipate) (PBSA) have been used to toughen PLA. However, these blends prepared by simple melt blending could not achieve good mechanical properties due to the phase separation and poor interfacial adhesion between the two components.

As a crosslinking agent, dicumyl peroxide (DCP) was used to modify PLA/polyesters composites *via in situ* compatibilization (Zeng, Li, & Du, 2015). Ji et al. (2014) studied the effect of DCP on the morphology and properties of PLA/PBS composites, and found that the interfacial adhesion between PLA and PBS was increased significantly as evidenced by the decreased PBS particle size with increasing DCP content, which resulted in significant improvement in mechanical properties. Similarly, DCP was also used to improve the interfacial adhesion between PLA and PBAT (Signori et al., 2015; Ma et al., 2014). The addition of DCP could decrease the PBAT phase size and led to the formation of PBAT gel which had a toughing effect on PLA. However, PLA/polyesters blends still have poorer thermal stability and mechanical properties especially lower impact strength than those commodity plastics such as polypropylene.

Cellulose nanocrystal (CNC) may be a good choice to reinforce PLA-based composites, because it is a promising biopolymer filler used to reinforce many bio-based polyesters, such as PLA (Lizundia, Vilas, & León, 2015), PBS (Lin, Yu, Chang, Li, & Huang, 2011b), PBSA (Zhang & Zhang, 2015) and PBAT (Ludvik, Glenn, Klamczynski, & Wood, 2007) with appealing intrinsic properties such as good mechanical properties (longitudinal modulus

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close to 150 GPa), high aspect ratio (10–70) and high surface area (Kargarzadeh, Sheltami, Ahmad, Abdullah, & Dufresne, 2015; Arrieta, Fortunati, Dominici, López, & Kenny, 2015). To improve the dispersion of CNC and its adhesion to polymers, some CNC surface modification methods, such as acetylation (Lin, Huang, Chang, Feng, & Yu, 2011a), and reactions with castor oil (Shang et al., 2013), waterborne epoxy (Xu, Girouard, Schueneman, Shofner, & Meredith, 2013) and polyurethane (Rueda et al., 2013). All the methods could successfully improve the dispersion of CNC in bio-based polymers, but the improvement in their adhesion was still limited, which is partially because of the limited compatibility of those modifiers with the polymer matrices. On this occasion, *in situ* polymerization method was used to prepare polymer grafted CNC composites, and to improve the compatibility of CNC and polymeric matrix. Cao, Habibi, and Lucia (2009) prepared waterborne polyurethane/CNC composites successfully *via in situ* polymerization, and observed that a co-continuous phase between the matrix and CNC was formed which enhanced the interfacial adhesion and consequently contributed to an improvement in the thermal stability and mechanical strength of the composites.

In this study, poly(butylenes succinate)-grafted cellulose nanocrystal (PBS-*g*-CNC) was prepared through *in situ* polymerization. PBS-*g*-CNC was then used to reinforce DCP modified PBS/PLA composites in order to have a good dispersion and compatibility with PBS component. The structure of PBS-*g*-CNC was characterized with FTIR, ^{13}C NMR, XPS as well as gel permeation chromatography (GPC) and the morphology of composites was observed by scanning electron microscope. The effects of PBS-*g*-CNC and DCP on the compatibility of PBS and PLA were studied. The crystallization behavior, mechanical properties and thermal stability of the composites were also investigated.

2. Experimental

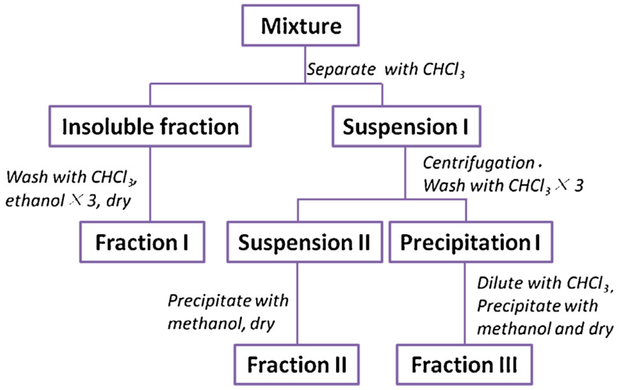
2.1. Materials

PLA (Revode 190) with number average molecular weight (M_n) of 9.7×10^4 g/mol, polydispersity index (PDI) of 1.2, and L-lactate unit content of 98.5% was kindly supplied by Zhejiang Hisun Biomaterials Co., Ltd. (China). PBS (Bionolle 1001MD) was produced by Showa Denko Group (Japan) with M_n of 8.8×10^4 g/mol and PDI of 2.2. DCP, 1,4-butanediol (BDO), succinic acid (SA) and microcrystalline cellulose (MCC) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Titanium butoxide (97%), purchased from Sigma-Aldrich (USA), was used as a catalyst. CNC with length of 100–250 nm and diameter of 15–30 nm was extracted from MCC in sulfuric acid solution with a similar method used in the study of Lin et al. (2013).

2.2. Synthesis of PBS-g-CNC via in situ polymerization

Synthesis of PBS-*g*-CNC consisted of two steps: the esterification of BDO, CNC and SA to obtain an oligomer, and the synthesis of high-molecular weight PBS-*g*-CNC by condensation polymerization.

CNC, BDO and SA were added into a four-necked flask with a weight ratio of 20:33:67, and heated to 180 °C until SA was completely dissolved in BDO under N_2 atmosphere. When no more water was distilled out under normal pressure, titanium butoxide (0.1% of total amount of the reactants) as a catalyst was added into the flask and the reaction system was heated to 220 °C under high vacuum and kept for 4 h to obtain a mixture of *in situ* condensation polymerization.



Scheme 1. Extraction and separation procedure of the PBS-*g*-CNC copolymer.

2.3. Extraction of PBS-g-CNC

The mixture was added in chloroform and stirred for 24 h at room temperature to form a suspension (noted as Suspension I) and an insoluable fraction floating on the surface of the suspension. The insoluable fraction was washed by chloroform and ethanol for 3 times, respectively. To remove PBS homopolymer and residual reactants, and the residue was vacuum-dried at 60 °C for 6 h and named as Fraction I.

To remove PBS homopolymer, Suspension I was subjected to 3 times of centrifugation at 10,000 rpm for 30 min to get a suspension (Suspension II) and precipitation (Precipitation I). After each centrifugation, the precipitate in suspension was separated and diluted again in chloroform. 5 min ultrasonic treatment was necessary to obtain a uniform suspension before next centrifugation. Suspension II was deposited in methanol and vacuum-dried to obtain Fraction II (possibly PBS). Precipitation I was first dispersed in chloroform to get a suspension, and then precipitated by methanol and vacuum-dried at 60 °C for 24 h to get Fraction III (PBS-*g*-CNC). The procedure details of separation are presented in Scheme 1. In order to control the veracity of the following tests, Fraction III was subjected to Soxhlet extraction with chloroform for 24 h.

To investigate the PBS molecular structure connected onto the surface of CNC, PBS-*g*-CNC composite was subjected to a saponification in order to cleave the PBS chains from CNC. 1 g PBS-*g*-CNC composite was dispersed in 50 mL sodium hydroxide solution with a sodium hydroxide concentration of 0.5 mol/L, and the saponification was started at 30 °C with magnetic stirring. Samples were taken out every 5 min, and the PBS component in each sample was then separated from CNC by suction filtration and Soxhlet extraction for gel permeation chromatography test using chloroform as solvent. The bore diameter of Teflon filter paper used in suction filtration was 200 nm.

2.4. Preparation of PBS/PLA/DCP/(PBS-g-CNC) composites via melt blending

PBS and PLA were first vacuum-dried for 12 h at 80 °C. PBS/PLA(30/70) blend was prepared using a Haake rheometer at a rotor speed of 60 rpm and 190 °C for 10 min, and compression molded for 10 min at 200 °C to get sheets with the thickness of 1 and 3 mm for measurements. For PBS/PLA/DCP/(PBS-g-CNC) composites, DCP/(PBS-g-CNC) ratio was as follows: 0/0, 0/2, 0.2/0, 0.2/0.5, 0.2/1.0, 0.2/2.0.

2.5. Characterization

Infrared spectra were obtained by using a Spectrum 100 Fourier transform infrared spectra (FTIR) Spectrometer (Perkin Elmer,