Research Paper

Combined effect of cellulose nanocrystals and poly(butylene succinate) on poly(lactic acid) crystallization: The role of interfacial affinity

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ABSTRACT

Poly (lactic acid) (PLA)/cellulose nanocrystals (CNC), poly(butylene succinate) (PBS)/CNC and PLA/PBS/CNC composite films were prepared using a solution-casting technique. CNCs can be used to enhance the crystallization of PLA by offering more nucleation sites, and PBS can increase spherulite growth rate of PLA by providing flexible chains. However, CNCs and PBS together tend to interfere with each other and thus enhancement in the crystallization of PLA is lost. FTIR, contact-angle measurements, and dissolution experiments were used to characterize the materials. It was found that the interfacial affinity was greater in the CNC–PBS system than the CNC–PLA system. It was therefore concluded that the PBS chains occupy most of the CNC surfaces in the molten state before cooling. Consequently, PLA was mainly blocked from the CNCs and the nucleation effect was greatly weakened. The binary and ternary composite systems are discussed in terms of their crystallization processes.

1. Introduction

Poly(lactic acid) (PLA), derived from renewable resources, has always received considerable attention in the search for sustainable and environmentally friendly materials (Chen & Patel, 2011). It is an aliphatic thermoplastic polyester with high modulus, high strength and good clarity. However, the poor toughness and relatively slow crystallization rate are the main disadvantages that restrict its wider application (Auras, Harte, & Selke, 2004; Saeidlou, Huneault, Li, & Park, 2012; Sinba, 2012).

In order to achieve desired mechanical properties without compromising its biodegradability, PLA can be blended with a plasticizer such as poly(butylene succinate) (PBS). PBS is an attractive material with environmental and ecological advantages. It is flexible and tough, and blending PLA with PBS has generated great interest from many research groups (Park & Im, 2002; Park, Hwang, Moon, Im, & Yoo, 2010; Shibata, Inoue, & Miyoshi, 2006; Yokohara & Yamaguchi, 2008; Zhang, Liu, Shi, Ye, & Zhou, 2017). The addition of PBS has been reported to accelerate the spherulite growth rate of PLA. Nanoparticles are also good nucleation agents (Harris & Lee, 2008; Pan & Qiu, 2010; Ye, Hou, & Zhou, 2016; Yu, Liu, Zhao, Lu & Wang, 2012), and they can enhance the nucleation ability of a polymer matrix, exhibiting increased nucleation sites and crystallization rates (Zhao & Qiu, 2015).

Cellulose nanocrystals (CNC) have received increasing attention as they have unique morphology, low density, and high mechanical strength, and because they are renewable and biodegradable (Habibi, Lucia, & Rojas, 2010). CNC can be derived from cellulose, which is one of the most abundant substances in nature. Subsequently, CNCs can be used as a 'green' nucleation agent as well as a source for polymer reinforcements, which is essential to enhance the mechanical properties of the composite. Numerous researchers (Barrau et al., 2011; Kamal & Khoshkava, 2015; Lin, Huang, Chang, Feng, & Yu, 2011; Lizundia, Vilas, & León, 2015; Lizundia et al., 2016; Luzi et al., 2016) have doped PLA with CNCs and a resultant increase in the crystallization rate as well as an enhancement in the mechanical properties were generally found.

CNCs have also been reported to reinforce PBS by serving as additional nucleation sites (Hu, Lin, Chang, & Huang, 2015; Lin, Chen, Hu, & Huang, 2015). Therefore, it would be interesting to see how CNCs and PBS work together to affect PLA. Would there be a synergistic effect (Yang et al., 2013) or an interference (Mao et al., 2016) of the two materials on PLA in the PLA/PBS/CNC composite? The ternary system is entirely biodegradable and is promising in the application of environmental protection and renewable resources. Luzi and coworkers (Luzi et al., 2016) found an improvement in the barrier properties due to the combined nucleation effect of CNCs and PBS in the PLA matrix with the PBS content predetermined to be 20%. Zhang's group (Zhang, & Zhang, 2016) grafted CNCs to PBS and investigated their

toughening effect in the PBS/PLA blend, and found that the impact strength and moduli were both increased.

In this work, PLA/CNC, PBS/CNC and PLA/PBS/CNC composite films were prepared by the solution-cast method and the crystallization behavior of PLA was evaluated by DSC. Further, FTIR, contact-angle measurements and dissolution experiments were successively employed to characterize the interfacial interactions in the binary and ternary systems. To the best of our knowledge, this is the first time interfacial affinity has been used to systematically investigate how CNCs and PBS function together to affect the crystallization of PLA. This work will advance our understanding and promote the development of multi-component materials when exploring CNCs.

2. Experimental

2.1. Materials

Commercially available PLLA with the trade name 4032D was supplied by NatureWorks® LLC, USA. The number-average molecular weight (M_n) and the polydispersity index (PDI) were 1.34×10^5 g/mol and 1.86, respectively. Poly(butylene succinate) (PBS) was provided by Xinjiang Lanshan Tunhe Polyester Co., Ltd., China. The intrinsic viscosity of PBS was 1.11 dL·g^{-1} in phenol and 1,1,2,2-tetrachloroethane (50:50 w/w) mixed solvent at 25 °C. The melting temperature of PBS is 115.6 °C. Microcrystalline cellulose (MCC) and dimethylformamide (DMF) were purchased from Tianjin Guangfu Fine Chemical Research Institute. The granularity of MCC was reported in the range of 20–100 μm. Sulfuric acid (H_2SO_4), chloroform ($CHCl_3$), tetrahydrofuran (THF) and other analytical-grade reagents were purchased from Beijing Chemical Plant.

2.2. Extraction of cellulose nanocrystals

CNCs were prepared by H_2SO_4 hydrolysis of MCC. First, 3 g MCC was mixed with 60 wt% H_2SO_4 aqueous solution (45 ml) and then stirred vigorously at 50 °C for 2 h. A ten-fold volume of deionized water was then applied to stop the hydrolysis reaction. The solution was left undisturbed for a day, and the resultant suspension was centrifuged at 10^4 r/min for 10 min to separate the crystals, which were subsequently washed with distilled water. The centrifugation process was repeated three times before dialysis was performed overnight against distilled water to reach approximate neutrality. Finally, CNCs in the form of loose powder were obtained after freeze–drying.

2.3. Preparation of composite materials

PLA/CNC, PBS/CNC and PLA/PBS/CNC composite films were prepared by a solvent casting method. The content of CNCs was kept at 3 wt%, and the ratios of the polymers varied. The weighed polymers (1 g) were dissolved in 25 mL DMF with vigorous stirring at 70 °C for 12 h. The dissolved solution was then poured onto a 9–cm diameter Petri dish and heated at 70 °C for 4 h. All samples were subsequently placed in a vacuum oven at 40 °C for 12 h in order to remove the residual solvent.

2.4. Characterizations

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

WAXD measurements were performed on a Bruker AXS D8 instrument using a graphite-filtered *Cu K$_\alpha$* radiation target (λ = 0.154 nm) at ambient conditions. Data were collected in the 2θ interval from 5° to 40° with a scan rate of 2°/min.

2.4.2. Transmission electron microscopy (TEM)

TEM observation of CNCs was carried out on an FEI F20 transmission electron microscope. A mass of 10 mg of CNCs was well dispersed in 10 ml of distilled water for 30 min with ultrasonic treatment.

2.4.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the powdered CNCs, as well as the nanocomposite sheets, were recorded on a Bruker Tensor II spectrometer under the ATR mode by signal averaging over 32 scans at a resolution of 4 cm^{-1}. The powder samples were analyzed using a KBr-pellet method.

2.4.4. Differential scanning calorimetry analysis (DSC)

Thermal analysis of the samples was conducted using DSC (204 F1, NETZSCH) under argon atmosphere. For non-isothermal melt crystallization, the samples were heated from 25 to 195 °C, held isothermally for 5 min to remove thermal history, and then cooled to 25 °C. The heating and cooling rates were 10 °C/min and 5 °C/min, respectively. For isothermal melt crystallization, the samples were heated from 25 to 195 °C, held isothermally for 5 min to remove thermal history, and then quench-cooled to 126 °C.

2.4.5. Contact-angle (CA) measurements

The interfacial tensions between the components in the composites were determined using a CA instrument (DCAT21, Dataphisca, Germany) at 20 °C. Before measurement, films of pure PLA and pure PBS were prepared through compression molding at 195 °C. Measurement of a given contact angle was carried out at least five times and the values were averaged. Double-distilled water and ethylene glycol were used as probe liquids.

3. Results and discussion

3.1. Characterizations of CNC

Sulfuric acid has been used extensively for decades to hydrolyze cellulose (Marchessault, Morehead, & Walter, 1959). Upon hydrolysis, the amorphous regions of MCC were preferentially reacted while the crystalline regions remained intact. The WAXD pattern of the CNCs is shown in Fig. 1A. The diffraction peaks of the 2θ angles at approximately 14.8°, 16.6°, 22.3° and 34.4° are consistent with what has been reported (Cao, Habibi, & Lucia, 2009; Jonoobi, Mathew, Abdi, Makinejad, & Oksman 2012; Lin, Huang, Chang, Feng, & Yu, 2011; Tingaut, Zimmermann, & Lopez-Suevos, 2010). The degree of crystallinity of CNC was calculated (Park, Baker, Himmel, Parilla, & Johnson, 2010) to be 75%

TEM was used to examine the morphology and the rod-like structure of CNCs and the results are shown in Fig. 1B. CNCs possessed a diameter of 10–20 nm with their length in the range of 70–300 nm. The large distribution range in size was expected, due to the diffusion-controlled nature (Cao, Habibi, & Lucia, 2009) upon acid hydrolysis. The chemical structures of CNCs were also analyzed by FTIR and the absorption spectrum is presented in Fig. 1C. The broad band at 3400 cm^{-1} are assigned to the free $-OH$ groups. The vibrations at approximately 2900 cm^{-1} and 1640 cm^{-1} were associated with the stretching of $C-H$ and the absorbed water, respectively. All the characterizations agreed well with literature values (Cao, Habibi, & Lucia, 2009; Jonoobi, Mathew, Abdi, Makinejad, & Oksman 2012; Lin, Huang, Chang, Feng, & Yu, 2011; Tingaut et al., 2010).

3.2. Crystallization behavior

Both non-isothermal and isothermal crystallization behavior was analyzed by DSC. Fig. 2A illustrates the melt-crystallization DSC curves of neat PLA, PLA/CNC, PBS/CNC and PLA/PBS/CNC composites. Neat PLA showed no crystallization on cooling while a crystallization peak appeared at around 116.5 °C with the addition of CNC, and is attributed to the nucleation effect of the addition (Fortunati et al., 2012; Kamal & Khoshkava, 2015). Similarly, the crystallization of PBS was also enhanced by introducing CNC, as evidenced by the increase in T_c