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Morphology, crystallization and rheological behavior in poly(butylene succinate)/cellulose nanocrystal nanocomposites fabricated by solution coagulation

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ABSTRACT

Nanocomposites consisting of poly(butylene succinate) (PBS) and cellulose nanocrystals (CNC) were fabricated by solution coagulation method. Morphology analysis indicated that CNC dispersed well in PBS matrix and rheological analysis suggested that PBS and CNC showed strong interactions. Thermal analysis indicated that the nanocomposites showed slightly increased glass transition temperature, significantly enhanced crystallization temperature and different melting behavior, compared to neat PBS. Study on crystallization indicated that small loading of CNC could significantly increase overall crystallization rate of PBS, meanwhile the crystallization mechanism and crystal structure remained unchanged. The significant enhancement in overall crystallization was attributed to the increased nucleation ability by incorporation of well dispersed CNC nanoparticles. Tensile testing indicated that the tensile strength and modulus were gradually improved with increasing CNC content, while the elongation at break decreased and even brittle fracture occurred when the content of CNC increased to 1.0 wt%.

1. Introduction

Indiscriminate use of fossil-based and non-degradable polymers has brought about significant pollutions on the environment, which has led to a renewed and increased interest in polysaccharides like cellulose, starch and chitin (Wang, Lu, & Zhang, 2016; Zeng, He, Li, & Wang, 2012; Zeng, Jiao et al., 2011; Zhang, Wang, Zhao, & Wang, 2012; Zhang, Zhang, Wang, Chen, & Wang, 2009; Zhu, Dong, Wang, & Wang, 2010). Their attraction comes from the annual renewability, easy availability and excellent biodegradability. Cellulose is the most abundant polysaccharide which is a structural polymer found in various plants, animals and even in some primeval organisms such as bacteria, fungi, algae and amoebas (Lin, Huang, Chang, Feng, & Yu, 2011). Cellulose nanocrystal (CNC), obtained from partial acidolysis of cellulose, has many attractive intrinsic properties such as nanoscale dimensions, large surface area, high mechanical strength and modulus, thus has attracted a great deal of attentions in polymer nanocomposites (Habibi, Lucia, & Rojas, 2010). In addition, CNC is also biodegradable and sustainable, which makes it an ideal reinforcing agent for biobased and biodegradable polyesters such as poly(lactic acid) (PLA) (Fortunati, Peltzer et al., 2012; Kamal & Khoshkava, 2015; Lin, Huang et al., 2011; Miao & Hamad, 2016), poly(butylene succinate) (PBS) (Hu, Lin, Chang, & Huang, 2015; Lin, Chen, Hu, & Huang, 2015; Lin, Yu, Chang, Li, & Huang, 2011), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Yu, Yan, & Yao, 2014).

It is well-known that the final properties of polymer nanocomposites depend strongly on the dispersion state of nanofillers (Du, Yang, Zhao, Wang, & Zeng, 2016). Good dispersion of nanoparticles with very small amount would impart the matrix polymer with various significantly improved properties such as enhanced crystallization, reinforced mechanical performance, improved rheological properties (Wang, Deng, Du, Zhao, & Zeng, 2015; Zeng, Hu, Wang, Zhang, & Zeng, 2016; Zhao et al., 2016). Therefore, achieving good dispersion of nanoparticles is one of the key issues to fabricate polymer nanocomposites. The simplest way to incorporate pristine CNC into polymer matrix is casting-evaporation with water as a solvent or dispersion medium due to the hydrophilic nature of CNC (Habibi et al., 2010). This method is useful for the composite with water soluble or water dispersible polymer as the matrix, such as poly(vinyl alcohol) (Fortunati et al., 2013; Paralikara, Simonsen, & Lombardi, 2008), water-borne polyurethane (Gao et al., 2012;

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Santamaria-Echart et al., 2016), and natural rubber latex (Mariano, El Kissi, & Dufresne, 2016). However, this method is unadoptable for biodegradable polyesters, due to their water insolubility and non-dispersibility.

Biodegradable polyesters are soluble in some organic solvents. Casting-evaporation with organic solvent was also used in preparation of CNC reinforced biodegradable polyester nanocomposites (Fortunati, Armentano et al., 2012; Fortunati, Peltzer et al., 2012; Miao & Hamad, 2016 Zhou, He, Jiang, & He, 2015). PBS/CNC nanocomposites were fabricated by casting-evaporation of mixtures of PBS chloroform solution and CNC chloroform dispersion, which was prepared with aid of ultrasound (Lin, Yu et al., 2011). It is worth noting that hydrophilic CNC dispersion in chloroform is not stable due to the different polarities. Therefore, aggregation of CNC was not inevitable during the long evaporation process. Acetylation would decrease of hydrophilicity of CNC and thus stabilize dispersion of CNC in organic solvent to effectively prevent aggregation during evaporation process. In this way, PLA/CNC and PBS/CNC nanocomposites were prepared (Hu et al., 2015; Lin, Huang et al., 2011). However, acetylation would reduce the cost efficiency in CNC reinforced polymer nanocomposite. Furthermore, the loading of modified CNC was still relatively high (more than 1 wt%) in order to achieve designed objective. Therefore, it is still a challenge to well disperse original CNC in biodegradable polyesters to fabricate bio-nanocomposites.

In contrast to casting-evaporation, solution coagulation provides an efficient way in preventing aggregation of nanoparticles, because long time evaporation is avoided. This method has been widely used in fabrication of polymer nanocomposites consisting of water insoluble polymers and water dispersible nanoparticles such as graphene oxide (Huang, Xu, Fan, Xu, & Li, 2013), graphene and carbon nanotubes (Wang et al., 2015; Xu et al., 2010), and modified carbon nanotubes (Du et al., 2016; Zeng et al., 2016; Zhao et al., 2016). The electronic conductivity, crystallization, rheological, and mechanical properties of the related biodegradable polyesters were significantly improved with small addition of the corresponding nanoparticles, usually less than 1.0 wt%. Although this method succeeded in fabricating polymer nanocomposite, it has not been employed in preparation of CNC reinforced biodegradable polyester nanocomposite. In addition, solution coagulation is an eco-friendlier method than casting-evaporation, since solvent evaporation is avoided.

In this study, we evaluate the feasibility of solution coagulation in fabrication of original CNC reinforced PBS nanocomposites. It was reported that original CNC was dispersible in N, N-dimethyl formamide (DMF) and the dispersion was as stable as in aqueous dispersion (Samir, Alloin, Sanchez, El Kissi, & Dufresne, 2004). Therefore, we use DMF as a solvent for PBS to mix with CNC water dispersion firstly and then use excess water as coagulation agent for the well-dispersed PBS/CNC dispersion to coagulate the PBS/CNC nanocomposites. CNC with various loadings from 0.1 to 1.0 wt% was incorporated into PBS. The dispersion of CNC in the composites was investigated by scanning electron microscope. The crystallization behavior of the PBS nanocomposites with small addition of original CNC was studied with differential scanning calorimetry, polarized optical microscope, and X-ray diffraction in detail. In addition, the rheological and mechanical properties of the PBS/CNC nanocomposites were also investigated. To our knowledge, no literature has been reported on the fabrication of PBS/CNC nanocomposites by solution coagulation and on the investigation of morphology and crystallization in small amount CNC reinforced PBS nanocomposites.

2. Experimental section

2.1. Materials

Cellulose nanocrystals (CNC) water dispersion with concentration of 1.0 wt% was provided by Haojia nanocellulose science and technology Ltd. (Tianjin, China). It was prepared by acidolysis of cotton pulp. The average diameter and length were 7–10 and 200 nm, respectively. Poly(butylene succinate) (PBS) with molecular weight of 1.2×10^5 g/mol was obtained from Anqing Hexing Chemical Co., LTD (Anhui, China). *N*, *N*-dimethyl formamide (DMF) was procured from Kelong Chemical Co., LTD (Chengdu, China). All the materials were used without further purification.

2.2. Fabrication of CNC filled PBS nanocomposites

PBS/CNC nanocomposites with CNC contents various from 0.1 to 1.0 wt% were prepared by solution coagulation method with DMF as solvent for PBS and water as CNC dispersion medium and coagulating agent, respectively. Taking a nanocomposite containing 0.1 wt% CNC as an example, the detailed procedures are as follows: dissolving 14.98 g PBS in 200 mL DMF by magnetic stirring at 80 °C for 1 h, then dropping 2 mL CNC water dispersion into the magnetically stirred PBS solution, after mixing for 10 min, adding excessive deionized water into the solution to precipitate the coagulated composites. Four PBS/CNC nanocomposites containing 0.1, 0.3, 0.5 and 1.0 wt% CNC were prepared and named after PBS/CNC-0.1, PBS/CNC-0.3, PBS/CNC-0.5 and PBS/CNC-1.0, respectively. Neat PBS was also treated with the same procedure for property comparison. The samples were collected by filtration and vacuum dried at 60 °C for 2 days. Then, the sample sheets with thickness of 1 mm were prepared by compression molding at 130 °C under 10 MPa pressure for further characterization.

2.3. Characterization

Morphology of PBS/CNC nanocomposites was observed on a XL–30 s FEG (Philips, Holland) scanning electron microscope (SEM) with an accelerating voltage of 5 kV. The cryo-fractured surfaces were used for observation and were sputtered with a layer of gold prior to measurement.

Rheological behavior of neat PBS and PBS/CNC composites was tested on a TA DHR-1 rotational rheometer in dynamic frequency sweep mode from 0.1 to 100 rad/s at 140 °C with an oscillation strain of 1.0%.

Thermal property and non-isothermal crystallization of neat PBS and PBS/CNC nanocomposites were measured by a NETZSCH differential scanning calorimeter (DSC-214). About 6 mg sample sealed in aluminum pan was first heated to 140 °C and kept at this temperature for 3 min to remove thermal history, then cooled to −60 °C at a cooling rate of 10 °C/min, and finally reheated to 140 °C at the same rate. The measurement was performed under N_2 atmosphere. Both the cooling and the second heating scans were recorded for data analysis.

Isothermal crystallization kinetics of neat PBS and PBS/CNC nanocomposites was carried out on the NETZSCH DSC-214 equipment. About 6 mg sample sealed in aluminum pan was first melted at 140 °C for 3 min to remove thermal history, and then quickly cooled to 80 °C at a cooling rate of 60 °C/min, and finally kept at the temperature until crystallization finished. All measurements were carried out under N_2 atmosphere. The exothermic curves were recorded for analysis.

Spherulitic morphology of neat PBS and PBS/CNC nanocomposites was studied on an Olympus BX51 polarized optical microscope (POM) with a RT600 temperature controller. The sample film