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Simultaneous improvement of thermal stability and redispersibility of cellulose nanocrystals by using ionic liquids

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ABSTRACT

Cellulose nanocrystals (CNCs) are predominantly obtained by the traditional sulfuric acid hydrolysis process. However, as-prepared CNCs powder features low thermal stability and poor redispersibility due to the existence of sulfonate groups and the hydrogen bond interaction among particles. Herein, by mixing the ionic liquid [BMIm][BF_4] with freshly prepared CNCs without dialysis through a simple rotary evaporate procedure, the simultaneous improvement of thermal stability and redispersibility of CNCs has been achieved. By combining FTIR, TGA and DLS measurements, the critical role of rotary evaporates process for improving the thermal stability of CNCs has been discussed. Furthermore, the poly(lactic acid) (PLLA)/IL-CNC nanocomposites with enhanced mechanical properties were prepared by the melt-mixing method. This study provides a green and simple strategy for preparing dried CNC powders, which has a great potential in large-scale production of fully bio-based nanocomposites.

1. Introduction

As a biomass nanofiller extracted from natural fibers, cellulose nanocrystals (CNCs) have received considerable attention due to their properties including inherent renewability, sustainability, high modulus and low density (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Miao & Hamad, 2016; Zhu et al., 2016). Based on these excellent characters, people believe that CNCs have great potential application for fabricating fully-biobased polymer nanocomposite with bioplastic such as poly(L-lactide) (PLLA) for lightweight automotive components (Yao et al., 2014).

CNCs are normally obtained through sulfuric acid hydrolysis, which will introduce sulfonate groups on its surface (Eichhorn et al., 2010; Marchessault, Morehead, & Koch, 1961; Revol et al., 1994). The electrostatic repulsion induced by the sulfonate groups endows the CNCs with stable dispersion in water. Nevertheless, a dry CNC powder is more desired when CNCs/polymer nanocomposites are prepared in industrial-scale by melt-mixing process (Dhar, Tarafder, Kumar, & Katiyar, 2016). Moreover, powder form of CNCs has the advantage for transportation and it can also inhibit deterioration caused by bacterial and fungi. However, there are two main issues for the use CNC powder derived from sulfuric acid hydrolysis process. First, CNCs will form extensive hydrogen bond networks between the −OH groups of CNCs as dried from suspension, which lead to irreversible particle aggregation (Dong & Gray, 1997; Lu, Askeland, & Drzal, 2008). Thus, CNC powder can hardly be re-dispersed in water or molten polymer matrices (Beck, Bouchard, & Berry, 2012). Second, sulfonate groups introduced on the CNC surface usually sacrifice the thermal stability of CNCs. The poor thermal stability of CNCs (degradation starting from ca. 90 °C) cannot endure the typical melt-processing temperatures (close to 200 °C or above) of polymeric matrices for preparing CNC/biopolymer nanocomposites (Roman & Winter, 2004).

To avoid these problems, solution blended with surfactant (Habibi, 2014; Hu, Ballinger, Pelton, & Cranston, 2015), aqueous polymer (Paralikar, Simonsen, & Lombardi, 2008; Roohani et al., 2008; Samir, Alloin, Sanchez, & Dufresne, 2004) and surface chemical modifications (Arias, Heuzey, Huneault, Ausias, & Bendahou, 2015; Cheng et al., 2015) prior to drying of CNC suspensions have been attempted. For example, through the esterification reaction, Menezes, Siqueira, Curvelo, and Dufresne, (2009) modified the surface of CNCs by grafting aliphatic chains. The functionalized nanoparticles exhibited improved thermal stability and nano-disperibility in polyethylene matrices. However, the chemical modification method is cumbersome and complicated, which is not suitable for large scale production. In another simple strategy, freeze drying of this PEO-adsorbed CNC dispersion was used to melt-mix with PE for preparing PE/CNC nanocomposites

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(Azouz, Ramires, Fonteyne, Kissi, & Dufresne, 2012; Lin & Dufresne, 2013). Compared to neat CNC-based nanocomposites, both improved dispersibility and thermal stability were realized. But the adsorbed PEO chains were prone to slip, resulting in partial self-aggregation in matrices. Recently, Nagalakshmaiah, El Kissi, and Dufresne, (2016) reported a flexible procedure to modify the surface of CNCs by building ionic interactions with quaternary ammonium salt bearing long alkyl chain. Nevertheless, the surfactant in polymer/CNC nanocomposites is hard to be removed and it may bring the adverse effect for the performance of polymer nanocomposites (Bondeson & Oksman, 2007).

Ionic liquids (ILs), a green solvent with negligible vapor pressure, has multiple functions in polymer modification. For example, it has been reported ILs can improve the dispersibility of nanofiller, such as graphene (Zhou et al., 2010) and carbon nanotubes (Fukushima et al., 2003) in polymer matrices. Meanwhile, the high polarity and non-volatile character of ILs makes them an ideal candidate as a new generation of plasticizers for polymer (Scott et al., 2002). Furthermore, the properties of ILs can be easily modified by changing the structure of cations or anions, which make them attractive to a broad field of applications (Murray et al., 2013; Fox et al., 2016). In our previous work, ionic liquid, AmimCl, was used to plasticize iridescent CNC films on account of its ability to break H-bonds of cellulose. Surprisingly, the plasticized CNC films also exhibit improved thermal stability (Liu, Guo, Nan, Duan, & Zhang, 2017). Inspired by this finding, we think that modifying CNC by simple blend with ionic liquids may be a new route for obtaining the dried CNC powder with high performance. In the present study, imidazolium-based ionic liquid, [BMIm][BF_4], with high thermal stability and better miscibility with PLLA, was selected to functionalize CNCs. It was found that the simultaneous improvement of thermal stability and redispersibility of CNCs could be achieved by mixing the [BMIm][BF_4] with freshly prepared CNCs through a simple rotary evaporate procedure. Moreover, the PLLA/IL-CNC nanocomposites with high transparency were successfully prepared by the melt-mixing method.

2. Experimental

2.1. Materials

Cotton linter pulps (CLP) was obtained from Hubei Chemical Fiber Co. The degree of polymerization (DP) was 700 measured by the viscosity method (Huggins, 2002). Sulfuric acid (H_2SO_4, 98 wt%, analytically pure, Yantai. China), sodium hydroxide (NaOH, analytically pure, Tianjin, China), [BMIm][BF_4] (Lanzhou Greenchem ILS, LICP. CAS. China) were used as received without further purification. Double-distilled water was used for all experiments. A commercial grade poly(L-lactide) was supplied by Zhejiang Haizheng Co. The weight-average molecular weight (Mw) was 9.8×10^4 g mol^{-1}.

2.2. Preparation of cellulose nanocrystals

CNC suspension was prepared by sulfuric acid hydrolysis of CLP. In brief, CLP milled with a food processor was soaked by 4 wt% NaOH solution for 24 h at room temperature. Then, the obtained slurry was thoroughly washed with distilled water till a neutral pH and dried at 60 °C in a vacuum oven for 24 h. Subsequently, 5 g of pretreated CLP was dispersed in a 64 wt% sulfuric acid solution at room temperature (CLP/acid = 1 g/18.6 mL). The mixture was stirred at 50 °C for 50 mins. The acid hydrolysis was then stopped with deionized water (approximately ten times the volume of the acid used). The resulting suspension was centrifuged and repeatedly washed with deionized water until the pH was close to 2. Finally, acidic CNC suspension with a solid content around 1 wt% was obtained, which was directly without dialysis.

The morphology of the as-prepared CNC was analyzed by AFM (Fig. S1a). A typical TEM image (Fig. S1b) reveals that the CNC rod is about 130 nm in length and with a diameter of 5–10 nm. Dynamic light scattering (DLS) profile (Fig. S1c) was used to evaluate the size distribution of the as-prepared CNC. The sulfur content detected by full energy-dispersive X-ray (EDX) is 2.18 wt% (To avoid interference with dissociative sulfonate ion, the samples measured by EDX were dialyzed in advance and then pH was calibrated to 7 using sodium hydroxide).

2.3. Preparation of functionalized CNCs powder with ionic liquid

In a typical procedure for preparing functionalized CNC powder with [BMIm][BF_4], 1 wt% CNCs (pH = 2) aqueous suspension was firstly sonicated for 3 mins for better dispersion. Then, 2 mL [BMIm][BF_4] was added into CNC suspension (the molar ratio of glycosyl unit to [BMIm][BF_4] was 1:0.7). After that, the mixture was continuously concentrated by rotary evaporation at 60 °C. After 2 h, the mixed CNC/[BMIm][BF_4] suspension was spray-dried to get functionalized CNC powder (IL-CNC). As a control, spar-dried CNC without the addition of [BMIm][BF_4] was also prepared. In order to investigate the effect of CNC and ILs ratio on the thermal stability and redispersibility of IL-CNC, IL-CNCs with molar ratios of glycosyl unit to [BMIm][BF_4] in 1:0.1, 1:0.5, 1:1, 1:2 were prepared and named as IL-CNC-0.1, IL-CNC-0.5, IL-CNC-1, IL-CNC-2 respectively.

2.4. Preparation of PLLA/IL-CNC nanocomposites

PLLA/IL-CNC nanocomposites were prepared by twin-screw extrusion. A predetermined amount of PLLA and IL-CNC were mixed in a twin-screw compounder with 60 rpm under 175 °C. The total blending time was 10 min. After the melt-mixing process, the specimens were hot pressed at 180 °C and 20 MPa for 2 min and then quenched in ice water. The transparent films of PLLA and nanocomposites with 1 wt%, 3 wt%, and 5 wt% of IL-CNC were prepared and coded as PLLA, PLLA-1, PLLA-3 and PLLA-5 respectively. As a contrast, PLLA/CNC composite film containing 1% CNC were also prepared and coded as PLLA/CNC. The resultant films with a thickness of ca. 1 mm were then cut into dumbbell-type spline.

2.5. Characterizations

Thermogravimetric analyzer (TGA) measurement was conducted on a TA Instruments Q500. The temperature was set from 40 to 600 °C with a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. FTIR was performed on a Bruker VERTEX 70 spectrometer using a spectral width ranging from 4000 to 600 cm^{-1} with a 2 cm^{-1} resolution. Atomic force microscope (AFM) image was performed by using a Multimode V (VEECO) under contact mode. CNC suspension and IL-CNC redispersion were coated on a mica substrate for AFM measurements via spin-coating at 2000 rpm for 1 min.

To investigate the redispersibility of CNC and IL-CNC, spray dried CNC and IL-CNC powders were redispersed in deionized water and sonicated 30 s using ultrasonic bath (KQ3200DE Kunshan, Shumei Ultrasonic Instrument Co. Ltd., China, 150 W, 40 kHz). The dispersion of CNC and IL-CNC were set a different concentration to reach the value of 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt% and 3 wt%. Digital photographs were taken immediately and subsequently after 1 d, 7 d. To evaluate the chiral liquid-crystal assembled behavior of as-prepared IL-CNC, the IL-CNC suspension with high concentration was introduced in a glass vials and equilibrated for 7 days. The chiral nematic structure of the IL-CNC suspension was examined by viewing the sample glass vials between crossed polarizers. Polarizing optical micrographs were obtained by polarizer optical microscope (Leica DM2500P) equipped with a CCD camera. Zeta potential of IL-CNC treated by various rotary evaporation time was performed on a Malvern Nano ZS90 light scattering instrument at 25 °C (all samples had been dialyzed in advance and the pH was calibrated to 7 using sodium hydroxide).

The tensile properties were measured using a Zwick z005 tensile testing machine. Films were cut into specimens with 20 mm length and