Research Paper

Biodegradable regenerated cellulose-dispersed composites with improved properties *via* a pickering emulsion process

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A B S T R A C T

Reinforcement of biodegradable polymers with nanocellulose is attractive yet the effectiveness is often compromised by uneven dispersion. In this work, a general method of preparing reinforced biodegradable composites using regenerated cellulose (RC) was developed. From an oil-in-water Pickering emulsion of PLA/methylene chloride stabilized with RC, uniformly dispersed RC/PLA composites was obtained. The resulting RC/PLA composites showed enhanced crystallization and tensile strength of up to 34% compared with the native PLA, while the transmittance in the visible range remained above 70%. The Pickering emulsion-based composition procedure is simple, environment friendly and cost effectively, which could be applied to preparation of other RC-reinforced biodegradable composites.

1. Introduction

During the last few decades, biodegradable polymers derived from renewable resource have attracted great attention and interest as replacement for petroleum-derived polymers (Nagarajan, Mohanty, & Misra, 2016; Xu et al., 2012; Yang et al., 2015). Despite highly valued for being sustainable, renewable and biodegradable (Gupta, Revagade, & Hilborn, 2007; Nagarajan et al., 2016; Thakur, Thakur, Raghavan, & Kessler, 2014), biodegradable polymers nevertheless suffered from some drawbacks that limit their extensive applications. For example, poly (lactic acid) (PLA) were limited by inherent brittleness, low thermal stability and low crystallization rate (Goffin et al., 2011; Lim, Auras, & Rubino, 2008).

Nanocomposites, *i.e.* polymer filled with nanoparticles, tend to have exceptional properties due to peculiar increase of the matrix-filler interface (Paul & Robeson, 2008). Several nanoparticles, such as layered silicates (Giannelis, 1996), carbon nanomaterial (Moniruzzaman & Winey, 2006) and silica nanoparticles (Slowing, Trewyn, Giri, & Lin, 2007), have been extensively studied in the field of nanocomposites. However, due to growing concerns on sustainability and environmental protection, biodegradable and renewable nanocellulose has widely attracted researches' attention as reinforcing agents (Fujisawa, Togawa, & Kuroda, 2016; Klemm et al., 2011; Wang et al., 2015). Cellulose-based nanofillers such as cellulose nanocrystal (CNC) and cellulose nanofibril (CNF) have high surface area-to-volume ratio, high

aspect ratio and impressive mechanical properties (Jonoobi, Harun, Mathew, & Oksman, 2010; Kamal & Khoshkava, 2015; Scaffaro, Botta, Lopresti, Maio, & Sutera, 2017; Zhou et al., 2013).

However, the studies devoted to the preparation of regenerated cellulose (RC)-based composites were scarce (Soheilmoghaddam, Wahit, & Akos, 2013; Yu, He, & Dufresne, 2017). Recently, it was reported RC suspensions could be prepared by dissolving cellulose in phosphoric acid followed by controllable regeneration by adding water (Hao et al., 2015; Jia et al., 2014; Jia et al., 2013). This preparation process of RC is simple with yields of up to 86%, and therefore minimum costs. RC thus generated could be nanoscale aggregates stably suspended in water, making it a promising reinforcing agent in the field of green nanocomposites.

The difficulty of dispersing hydrophilic nanocellulose in hydrophobic polymers such as PLA remains the major drawback to the preparation of nanocellulose composites (Jonoobi et al., 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Thakur & Thakur, 2014). Considerable efforts have been made to improve the dispersibility of cellulose in polymeric matrix *via* hydrophobic modification (Klemm, Heublein, Fink, & Bohn, 2005). Surface modification techniques including silylation (Pei, Zhou, & Berglund, 2010), acetylation (Lin, Huang, Chang, Feng, & Yu, 2011; Tomé et al., 2011), esterification (Pasquini, de Morais Teixeira, da Silva Curvelo, Belgacem, & Dufresne, 2008) and polymer grafting(Muiruri, Liu, Teo, Kong, & He, 2017; Xiao et al., 2012) have been explored. However, the

mechanical properties of the final composites were inevitably compromised due to the loss of H bond-forming hydroxyl groups. In addition, most surface modification of nanocellulose require the use of hazardous solvents, which would offset the environmental advantages brought by using cellulose.

As reported in our previous work (Zhang et al., 2017), we have developed a Pickering emulsion approach to prepare CNF – reinforced PLA composites. CNF could be evenly dispersed in PLA matrix. In this work, the Pickering emulsion approach was used to prepare RC/PLA composites. RC was shown to effectively stabilize oil-in-water emulsions. A uniformly mixture of pristine was obtained by slowly evaporation of CH_2Cl_2 from the RC stabilized Pickering emulsion. The RC/PLA composites formed by hot-pressing the mixture at 180 °C, showed good crystallization, high strength and optical transparency even at low RC content.

2. Materials and methods

2.1. Materials

PLA (2003D, D-lactic acid: 1.4%, L-lactic acid: 98.6%, granules form, density of 1.24 g/cm^3) with number-average molecular weight (M_n) of ~150,000 Da and weight-average (M_w) of ~200,000 Da, respectively) was supplied by Natureworks, U.S.A. Wood Pulp was obtained from Xinxiang Natural chemical co., Ltd. The viscosity-average degree of polymerization was estimated to be 870 according to measurements using an Ubbelohde viscometer in cupric ethylene diamine hydroxide solution (CUEN). Dichloromethane (CH_2Cl_2) and 85 wt% phosphoric acid (H_3PO_4) were supplied by Sinopharm Chemical Reagent CO., Ltd.

2.2. Preparation of regenerated cellulose

The phosphoric acid (Yisi, BL, China) and deionized water were pre-cooled to 4 °C before use. Wood pulp (2 g) was pre-wetted with 6 ml deionized water and then mixed with 200 ml 85% phosphoric acid to reach a homogenous state. The wood pulp suspensions obtained were incubated in a shaking bath at 5 °C and speed at 300 rpm for 24 h to obtain a clear solution. Then, 1 l of deionized water was used to dilute the cellulose solution to obtain a milky dispersion. The dispersion was subjected to centrifugation at 12,000 r (Thermo, USA) for 20 min. The supernatant was discarded, and the precipitate pellet was washed with deionized water repeatedly until a constant pH was achieved. A high pressure homogenizer (APV-2000 Homogenizer, Germany) was used to re-disperse RC at 800 bar for 2 times before use. The concentration of cellulose in the final dispersion was determined gravimetrically to be 1.47% w/v.

2.3. Preparation of RC/PLA composites

An RC dispersion was diluted with deionized water to obtain cellulose dispersions at concentrations of 0.05, 0.075 and 0.1% w/v. The RC to PLA ratio (1, 1.5 and 2 wt.%) was adjusted to deliver the desired solid contents of RC to the composites. CH_2Cl_2 solution of PLA (10 ml, 100 mg/ml) was added to the RC aqueous dispersion (50 ml). And the CH_2Cl_2/water emulsion stabilized by RC, was formed by homogenization (IKA T18 homogenizer, Germany) at 12,000 rpm for 3 min followed by ultrasonication (SCIENTZ, JY 92-IIDN, China) for 3 min. CH_2Cl_2 was let evaporated at ambient temperature over the course of 24 h. The precipitates were vacuum filtered using a filter screen (500 mesh). The paste collected on the filter screen was vacuum dried at 60 °C for 24 h. The RC/PLA composites were generated by hot-pressing the dried paste on a Carver Laboratory Press (Carver Inc., USA) at 180 °C and 1500 kg for 5 min.

2.4. Characterizations

2.4.1. Transmission electron microscopy

The morphology of RC was characterized using transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) operated at 100 kV. TEM observations were performed on one dried drop of a 0.05% aqueous suspension of RC on a carbon coated grid (200 mesh).

2.4.2. Fluorescence microscopy

The fluorescence photographs of O/W emulsions were captured using an Eclipse microscope equipped with a digital camera (Nikon 80i, Japan). Calcofluor White was used as the fluorescent dye of cellulose at a concentration of 0.1% w/v. A drop of Calcofluor White solution was added on the slide followed by the addition of a drop of emulsion.

2.4.3. Scanning electron microscope

A field-emission scanning electron microscope (FE-SEM) (S-4800, Hitachi) was used to analyze the surface structure of RC/PLA composites before hot pressing and the fracture surface of the composites after hot pressing. Secondary electron images were obtained at an acceleration voltage of 1 kV with about 5 nm osmium coating by an osmium coater (Neo Osmium Coater, Meiwafosis) at 5 mA for 5 s.

2.4.4. X-ray diffraction

X-ray diffraction (XRD, Rigaku D/max 2550PC, Japan) was used to study the crystallinity of RC and RC/PLA composites. The samples were exposed for 1.5 s for each angle of incidence (θ) using a Cu K X-ray source with a wavelength of 1.541E. The angle of incidence is varied from 4 to 50 by steps of 0.02 s.

2.4.5. Differential scanning calorimetry

The neat PLA and the RC/PLA composites were analyzed using differential scanning calorimetry (DSC, 204 F1, NETZSCH, Germany). Under nitrogen purge, the samples were heated from 25 to 200 °C, held at 200 °C for 5 min to eliminate thermal history, cooled to 25 °C, and heated again to 200 °C. The heating rate was 10 °C/min, and the cooling rate was 2 °C/min. Crystallization temperature (T_c) and crystallization enthalpy ($\triangle H_c$) were determined from the cooling scan. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), cold crystallization enthalpy ($\triangle H_{cc}$) and melting enthalpy ($\triangle H_m$) were determined from the second heating scan. The crystallinity (χ) of PLA and RC/PLA composites was calculated by:

$$X(\%) = \left(\frac{\Delta H_m + \Delta H_{cc}}{\Delta H_m^0 * \left(1 - \frac{wt.\% filler}{100} \right)} \right) * 100. \tag{1}$$

Where ΔH_m^0 is the melting enthalpy of a 100% crystalline polymer matrix (93.0 J/g) for PLA, and wt.% filler is the weight percentage of RC.

2.4.6. Thermogravimetric analysis

The thermal properties of the neat PLA and RC/PLA composites were evaluated by thermogravimetric analysis (TG, NETZSCH 209F1, Germany). Under nitrogen purge, the samples were heated from 30 to 600 °C. The heating rate was 10 °C/min.

2.4.7. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed in single cantilever mode using a TA Instruments Q800 analyzer (New Castle, DE). The test samples dimensions were approx. 35 × 10 × 0.5 mm (long × wide × thick). The measurements were performed at a constant frequency (1 Hz), amplitude of 15 μm, a temperature range from 30 to 120 °C, and with a heating rate of 3 °C/min.