Preparation and characterization of bionanocomposite fiber based on cellulose and nano-SiO$_2$ using ionic liquid

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A B S T R A C T

Microcrystalline cellulose (MCC)/nano-SiO$_2$ composite fibers were processed from solutions in 1-allyl-3-methylimidazolium chloride (AMIMCl) by the method of dry-jet wet spinning. The oscillatory shear measurements demonstrated that the gel network formed above 10 wt% nano-SiO$_2$ and the complex viscosity increased with increasing nano-SiO$_2$. Remarkably, the shear viscosity of the nanofluids was even lower than solutions without nano-SiO$_2$ under high shear rates. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images revealed that well-dispersed particles exhibit strong interfacial interactions with cellulose matrix. Measurements on wide-angle X-ray diffraction (WAXD) indicated that the regenerated cellulose and nanocomposite fibers were the typical cellulose II crystalline form, which was different from the native cellulose with the polymorph of Type I. The tensile strength of the nanocomposite fibers was larger than that of pure cellulose fiber and showed a tendency to increase and then decrease with increasing nano-SiO$_2$. Furthermore, the nanocomposite fibers exhibited improved thermal stability.

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1. Introduction

Cellulose, as the most plentiful and renewable resource in nature, is amongst the most widely used natural fibers (Chen et al., 2006; Hirano, Usutani, Yoshikawa, & Midorikawa, 1998; Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Klemm, Heublein, Fink, & Bohn, 2005; Kosan, Michels, & Meister, 2008). However, cellulose is difficult to process in solution or as a melt, because of its large proportion of intra- and intermolecular hydrogen bonds, which strictly limit its processing and applications (Cai & Zhang, 2006; Ruan, Zhang, Zhou, Jin, & Chen, 2004). Therefore, many organic and inorganic solvent systems such as *N*-methyl morpholine *N*-oxide (NMMO) (Fink, Weigel, Purz, & Ganster, 2001), lithium chloride/1,3-dimethyl-2-imidazolidinone (LiCl/DMI) (Takaragi, Minoda, Miyamoto, Liu, & Zhang, 1999), lithium chloride/N, N-dimethylacetamide (LiCl/DMAc) (McCormick and Callais, 1987; McCormick, Callais, & Hutchinson, 1985), and phosphoric acid (Northolt et al., 2001) have been investigated for regenerated cellulose fiber production. Nevertheless, most of the systems still seem to be unsuccessful from an industrial viewpoint because of their toxicity and difficult solvent recovery. Recently, ionic liquids (ILs), which are considered as desirable green solvents, have been reported to be effective and promising cellulose solvents

(Rinaldi, 2011; Song et al., 2013; Swatloski, Spear, Holbrey, & Rogers, 2002; Zhang, Wu, Zhang, & He, 2005; Zhu et al., 2006). Nowadays, ILs used for manufacturing-regenerated cellulose fibers are arousing considerable commercial interest because of their superior dissolving capacity, environmentally friendly properties, easy recycling and good recoverability (Rahatekar et al., 2009; Xu et al., 2008; Zhang et al., 2007).

Polymer nanocomposites with nanoparticles, such as organic and inorganic nanoparticals, have attracted much attention owing to their outstanding mechanical, optical, electrical (Kim, Abdala, & Macosko, 2010; Sahoo, Rana, Cho, Li, & Chan, 2010; Zhang et al., 2007), and flame retardancy properties (Dong et al., 2012; Kiliaris and Papaspyrides, 2010; Zhang, Yang, Maurer, & F, 2011; Zou, Wu, & Shen, 2008). Of these polymer nanocomposites, cellulose combined with natural polymers led to the development of a new class of biodegradable and environmental friendly bionanocomposites (Jia, Li, Ma, Sun, & Zhu, 2012; Siqueira, Bras, & Dufresne, 2010; Valodkar and Thakore, 2011). This new family of nanocomposites is expected to have remarkable improvement of material properties when compared with the matrix polymers, and it will capture new market in transportation, medical and packaging applications (Celis, Adelino, Hermosín, & Cornejo, 2012; Darder, Aranda, & Ruiz-Hitzky, 2007). However, the main challenges still exist for developing high-performance cellulose nanocomposites is how to improve the dispersion of nanoparticles in the cellulose matrix or solutions, which is of great use for modifying the physical properties of cellulose (Maniruzzaman, Jang, & Kim, 2012; Park, Liang,

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Mohanty, Misra, & Drzal, 2004). Interestingly, ILs has been exploited as key components of dispersion medium in some novel systems, such as surfactant solutions, block copolymer micelle solutions, and emulsions (Anderson, Pino, Hagberg, Sheares, & Armstrong, 2003; Greaves and Drummond, 2008; He, Li, Simone, & Lodge, 2006). Specifically, because ILs can exhibit strong interactions with some nanopatarticles, a number of novel systems with ILs have recently been reported with respect to the dispersion of solid nanoparticles (Dupont and Scholten, 2010; Fukushima et al., 2006; Wang, Chu, & Li, 2008; Wu et al., 2009). Of these solid nanoparticles, nano-SiO$_2$ is widely used with ILs as nanohybrid solid-state electrolytes (Shimano, Zhou, & Honma, 2007), ionogels (Bideau, Viau, & Vioux, 2011; Moganty et al., 2012), and other advaced soft materials (Ueno and Watanabe, 2011; Wang, Zakeeruddin, Comte, Exnar, & Grätzel, 2003). In addition, nano-SiO$_2$ can easily provide functionalities by using ILs (Trewyn, Whitman, & Lin, 2004). Therefore, the use of ILs can not only as a solvent but also as a dispersion medium for preparing of cellulose nanocomposites.

In our previous work, the phase transitions and rheological properties of cellulose/AMIMCl and cellulose/1-ethyl-3-methylimidazolium acetate (EMIMAc) solutions under both oscillatory and steady shear modes were further studied (Song, Zhang, Niu, & Wang, 2010; Song, Niu, Wang, & Zhang, 2011). For cellulose/nano-SiO$_2$/AMIMCl solutions, however, situations might be quite different due to nanoparticles drastically alter the viscoelastic properties of the system (Rahatekar et al., 2009; Ueno, Hata, Katakabe, Kondoh, & Watanabe, 2008). In the present work, we reported the rheology and a facile and economic method for preparing bionanocomposite fibers based on cellulose and nano-SiO$_2$ with IL, as well as a detailed study of structure and properties of the resulting bionanocomposites fibers. It should be noted that IL appears to play a dual role as a solvent of cellulose and a dispersion medium of nanoparticles.

2. Materials and methods

2.1. Materials

The ionic liquid of 1-allyl-3-methylimidazolium chloride (AMIMCl) was synthesized according to the procedure described in the literature. Purification of AMIMCl was carried out on the basis of our previous work (Song et al., 2010). The water content of AMIMCl measured by the Karl Fischer titration was 0.12 wt%. Microcrystalline cellulose (MCC), Vivapur 101, used in this study was purchased from the Sen-Jun Chemical Agents Accessories Co., Ltd., Shanghai, China. The viscosity-average degree of polymerization (DP) of MCC in cupriethylenediamin hydroxide solution is about 200 as measured by using Ubbelodh viscometer. The nano-SiO$_2$ used in this study, NYSi80, was purchased from BOYU GAOKE New Material Co., Ltd., Beijing, China. The primary particles of the NYSi80 are 80 nm in diameter and have hydrophilic silanol (Si—OH) groups on their surface. The silica particles were dried for 24 h in a vacuum oven at 60 °C before use.

2.2. Composites preparation

Cellulose/nano-SiO$_2$/AMIMCl solutions were prepared as follows: Six batches of 5 g MCC were added into 89.8, 89.7, 89.6, 89.5, and 89.4 g AMIMCl in six sealed reaction vessels, respectively, and the mixtures were stirred at 90 °C for 4 h to obtain a homogeneous solution. Meanwhile, six batches of 0.2, 0.3, 0.4, 0.5, and 0.6 g nano-SiO$_2$ were dispersed in 5 g AMIMCl using mortar and pestle for 1 h to obtain a homogenous paste mixture, respectively, then, the obtained nano-SiO$_2$/AMIMCl paste mixtures were correspondingly added into the above six sealed reaction vessels and stirred

for another 1 h at 90 °C until solutions were optically homogenous. Finally, 5 wt% MCC/AMIMCl solutions containing 0.2, 0.3, 0.4, 0.5, and 0.6 wt% were obtained with a total weight of 100 g, respectively. The method of preparing 7 and 9 wt% cellulose/nano-SiO$_2$/AMIMCl solutions samples were the same as above. Correspondingly, these solutions were used to prepare regenerated MCC/nano-SiO$_2$ (4, 6, 8, 10, and 12 wt%) composite fibers in the following section. The water content in each solution measured by the Karl Fischer titration was about 0.15 wt%. Before further measurements, the solutions were sealed and stored in desiccators containing P$_2$O$_5$.

Cellulose/nano-SiO$_2$ composite fibers were processed using dry-jet wet spinning with 3 cm air-gap and using deionized water as coagulation bath. For all samples, a single-hole spinneret of 200 μm was used. The fiber was first soaked in deionized water overnight and then washed with deionized water at least five times to remove AMIMCl. After, the fibers had been dried in vacuum at 80 °C for 48 h.

2.3. Rheological measurements

Rheological properties of the MCC/Nano-SiO$_2$/AMIMCl solutions under both oscillatory and steady shear modes were measured by using a TA AR2000ex stress-controlled rheometer with 25 mm and 40 mm parallel-plates geometry. The chosen gap was about 600 μm for all the measurements. Steady shear measurements and dynamic frequency sweep measurements were carried out within the shear rate range of 0.01–100 s^{-1} and frequency range of 0.1–100 rad/s, respectively. Before the oscillatory shear measurements, a strain sweep from 0.1 to 100% with a fixed frequency of 6.28 rad/s was performed for each solution to determine the linear viscoelastic regime. The selected strain of 10–15% during the frequency sweeps fell well into the linear viscoelastic regime. The experimental temperature was mainly set at 30 °C. All measurements were conducted under a nitrogen atmosphere. In our experiments, the samples of 5 wt% and 7 wt% cellulose/nano-SiO$_2$/AMIMCl solutions were performed using 40 mm parallel plate geometry, while the samples of 9 wt% cellulose/nano-SiO$_2$/AMIMCl solutions were performed using 25 mm parallel plate geometry. To ensure data accuracy and repeatability, three measurements were carried out for each sample.

2.4. Scanning electron microscopy (SEM)

The observation of composite fiber samples was taken on a JEOL SEM 6700 microscope operating at 5 kV. The fibers were frozen in liquid nitrogen, immediately fractured, and vacuum-dried. The fracture surface of the fibers was coated with platinum layer (the thick is about 20 nm) before the observation.

2.5. Transmission electron microscopy (TEM)

The ultrathin slices with a thickness of approximately 70–90 nm were obtained from composite fiber samples imbedded into an epoxy resin by ultra-microtome (Leica EM UC6 & FC6) under cryogenic conditions, and then it was placed onto a carbon-coated copper grid. The dispersion state of Nano-SiO$_2$ within cellulose was investigated by using a JEOL JEM-2200 FS at an accelerating voltage of 200 kV.

2.6. Wide-angle X-ray diffraction (WAXD)

WAXD profiles of MCC and MCC/nano-SiO$_2$ composite fibers were obtained by using an X-ray diffractometer (D/MAX-2500, Rigaku Denki, Japan) with Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 100 mA. The samples were scanned continuously from $2\theta = 5°$ to 40° at a rate of 1°/min and the WAXD profiles were recorded at an interval of 0.02°.