Solvent Regulation Approach for Preparing Cellulose-Nanocrystal-Reinforced Regenerated Cellulose Fibers and Their Properties

Zeming Jiang, Lan Tang, Xin Gao, Wentao Zhang, Jiwei Ma, and Liping Zhang*

Beijing Key Laboratory of Lignocellulosic Chemistry, MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, Beijing Forestry University, No. 35 Tsinghua East Road, Haidian District, Beijing 100083, P. R. China

Supporting Information

ABSTRACT: An electrolyte and aprotic solvent mixture were used to prepare cellulose solutions containing cellulose nanocrystals (CNCs). All-cellulose composite fibers were then produced by dry–wet spinning these solutions. The presence of CNC in the all-cellulose fibers was demonstrated, and the effects of the CNC on the fiber properties were investigated. The all-cellulose fibers were characterized by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, and electronic tensile measurements. These results showed that CNCs were present in the mixture and that their structure was maintained in the all-cellulose fibers. No compatibility problems between the CNC and cellulose II matrix were observed. Introducing CNC enhanced the crystallinity, thermal stability, and mechanical properties of the composite fibers.

INTRODUCTION

Cellulose is an important green resource and is the most abundant biopolymer on earth, with 1.5 × 10¹² tons produced each year. Cellulose has been widely studied for use in numerous applications, leading to the development of cellulose-based composites, which can be found in a wide range of industries such as biomedicine, textiles, and food.

Cellulose-based materials can generally be categorized as either raw cellulose materials or regenerated cellulose materials. Raw cellulose materials possess a cellulose I structure and include materials such as paper. Regenerated cellulose materials possess a cellulose II structure and include materials such as regeneration cellulose fiber (e.g., viscose and lyocell fibers), cellophane, and cellulose aerogel. A previous study showed that the different structural morphologies of cellulose I and cellulose II result in the different properties of the raw and regenerated cellulose materials. Notably, crystalline cellulose and amorphous cellulose degrade below 427 °C, which is much lower than their melting temperatures; hence, the only practical way of shaping cellulose is by dissolution methods. Many solvent systems have been developed for dissolving cellulose, such as 4-methylmorpholine N-oxide (NMMO), NaOH/urea, 1-allyl-3-methylimidazolium chloride (AmimCl), 1-butyl-3-methylimidazolium chloride (BminCl), tetra-butylammonium fluoride (TBAF), dimethyl sulfoxide (DMSO), and LiCl/dimethylacetamide (DMAc).<ref>

Cellulose solutions can act as dispersing media for nanoparticles, and many nanomaterials have been incorporated into cellulose to improve its performance and function, such as carbon nanotubes, graphene oxide, ZnO, and SiO₂. However, the inherent chemical incompatibility of cellulose and reinforcement materials often result in weak interfacial bonding among the phases.

Monocomponent or single-polymer composites have been prepared in an effort to overcome this incompatibility. In 1975, Capiati and Porter produced high-density polyethylene composites that possessed a gradually changing morphology between the reinforcing fibers and matrix material. This resulted in an improved interfacial shear strength, which was within the range of those of glass-fiber-reinforced polyester and epoxy resin. A new class of monocomponent composites has since emerged: the so-called all-cellulose composites (ACCs). The concept of an ACC was first proposed by Nishino et al. in 2004 and involved preparing green composites to eliminate chemical incompatibilities between the reinforcement and the matrix using cellulose for both components.

Many subsequent studies on ACC have been reported. The reinforcing phases of ACC can generally be divided into two types. One type is based on materials remaining after selective dissolution. Specifically, some portion of cellulose (e.g., surface or amorphous regions) is initially dissolved in a solvent and the remaining undissolved cellulose becomes the reinforcing phase. Examples of this method were reported by Nishino et al. who converted a selectively dissolved fiber surface into a matrix. The other type of reinforced phase is high crystallinity, highly aligned cellulose I matrices, such as bleached fibers that come from plants. This matrix processing route involves a bonding process, in which dissolved cellulose is poured onto the matrix.

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The mixture undergoes a hot-pressing treatment and is then regenerated. Relevant examples of these materials have been reported by Adak et al., and in these studies, all cellulose laminates were manufactured from a lyocell fabric by a hand lay-up and compression molding-based surface-selective dissolution technique. The excellent performance of cellulose I has led to the use of cellulose whiskers as reinforcing materials in ACC.

A key issue for preparing CNC-reinforced ACC is obtaining a stable mixture containing dissolved cellulose and insoluble CNC. LiCl/DMAc,22 NaOH/urea,23 and some ionic liquids24 have been used as dispersing/dissolution media for preparing ACC. We recently reported that controlling the tetrabutylammonium acetate ratio in mixed solvents could regulate cellulose solubility.25 This finding provided a straightforward method for preparing CNC-regenerated cellulose composites. In this study, we incorporate high-aspect-ratio CNC into a cellulose matrix, using a solvent mixture. A schematic diagram of the experiment is shown in Figure 1. A dry−wet spinning process was used to improve the orientation and crystallinity of the all-cellulose fibers. The obtained all-cellulose fibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and electronic tensile measurements. These results demonstrate the existence of CNC within the composite and allow the study of the effects of CNC on composite properties.

## RESULTS AND DISCUSSION

Photographs of the mixed liquids (Figure 2a–f) illustrate their different appearances. The particle size distribution of the CNC in DMSO is shown in Figure 2g. The main equivalent particle size distribution of the CNC was approximately 70 nm. A transmission electron microscopy image of the CNC is shown in Figure S1.

The properties of cellulose fibers are closely related to the rheological properties of their solutions. To analyze the states of the mixtures, the rheological properties of the mixtures were tested. The dynamic viscosity characteristics of the mixtures are shown in Figure 3a. The flow curves of all mixtures were similar to those reported for typical polymer solutions, and the mixtures exhibited typical shear thinning behavior as the shear rate increased. The shear thinning phenomenon of the mixture is likely caused by a shearing-induced decrease in the amount of entanglement. The high CNC concentration (C10) also resulted in a critical shear rate for the non-Newtonian flow transition and shifted it to a lower shear rate, similar to that of previous reports of cellulose solutions. Figure 3a also shows that the shear viscosity increased as the concentration of CNC increased. This result is likely caused by the CNC-enhanced entanglement of molecular chains. The viscosities of the mixtures were low compared with that of cellulose solution (8 wt %), which we attribute to the low solid content. The non-Newtonian indices of all mixtures were less than 1, and the shear stress curve reflected typical pseudoplastic fluid characteristics (Figure 3b). Sol systems are generally considered to be typical pseudoplastic fluids, whereas the gel polymer and the general dispersion have a dilatant flow. These data indicate that addition of CNC/DMSO did not alter the structural characteristics of the solution and did not promote gelation of the solution.
The storage modulus ($G'$) and loss modulus ($G''$) reflect the state of CNC in the mixture, as shown in Figure 3c. When CNCs were dissolved in the mixture, the values of $G'$ and $G''$ increased considerably, owing to the increased cellulose molecular chains in solution. Many reports have shown that a certain molecular chain content is sufficient to influence $G'$ and $G''$. If the degree of

Figure 3. Rheological properties of the cellulose solution/CNC mixtures: (a) viscosity–shear rate curves, (b) flow curves, (c) storage and loss moduli curves, and (d) phase angle.

Figure 4. FT-IR spectra of the all-cellulose composite fibers with different CNC contents.
gellation of the mixture increases, the storage modulus ($G'$) will increase considerably and the intersection of $G'$ and $G''$ will move to a lower frequency. The storage modulus ($G'$) and loss modulus ($G''$) of the mixture are shown in Figure 3c. For all mixtures, $G'$ increased more rapidly with $G''$ as the frequency increased. In terms of the absolute values of the modulus, both $G'$ and $G''$ increased slightly as the CNC concentration increased from 0 to 10.0%. In comparing the C10 and C0 moduli intersections, the intersection of C10 shifted to a lower frequency, which also suggested that the intermolecular distance of molecular chains in solution decreased. These results indicate that the degree of entanglement in the solution was not markedly increased and the degree of gellation was not notably enhanced. The increase of $G'$ and $G''$ might be caused by the high aspect ratio of the solution in the mixture of the CNC and solvent, owing to the entanglement of molecular chains. Figure 3d shows phase angle data for the mixtures, with a phase angle of 90° for liquids and 0° for solids. As the frequency increased, the phase angles of all of the mixtures decreased and the phase angle of C10 remained the smallest. Hence, the solid properties of the solution increased slightly after addition of CNC. The above data indicate that addition of CNC/DMSO only slightly changed the mixture structure.

FT-IR spectra of the pure regenerated cellulose fiber and the all-cellulose composite fibers were recorded to investigate their interactions with the regenerated cellulose (Figure 4). All spectra exhibited similar profiles. The absence of additional peaks in the spectra of the composite fibers indicated that all samples had similar molecular structures, consisting only of cellulose, and no other derivatives were formed during the preparation.

All spectra contained peaks at 3379, 2903, 1641, 1434, 1038, and 899 cm$^{-1}$, which were assigned to the O–H stretching, C–H stretching, O–H bending of water in amorphous regions, C–O–C stretching, C–H deformation vibrations, and O–H bending vibrations, respectively. The wavenumber of the O–H stretching band shifted as the CNC content increased, from 3438 cm$^{-1}$ for the neat regenerated cellulose fibers to 3423 cm$^{-1}$ for composite fibers containing 5.0 and 7.5 wt % of CNC. This shift may have resulted from enhanced hydrogen bonding interactions between the –OH groups of the CNC and the cellulose matrix as a greater amount of CNC was added. In addition, the 2900 cm$^{-1}$ peak is composed of two small peaks near 2903 and 2893 cm$^{-1}$. Notably, 2900 cm$^{-1}$ is the –CH vibration of cellulose I and 2893 cm$^{-1}$ is the –CH vibration of cellulose II. Hence, the cellulose composite fiber is a typical mixed crystalline cellulose material in which the crystal structure of nanocellulose is retained.

TGA and derivative thermogravimetry (DTG) curves of the samples are shown in Figure 5a. Incorporating CNC improved the thermal stability of the all-cellulose fibers. The initial degradation temperature ($T_i$) and maximum degradation temperature ($T_d$) of the all-cellulose fibers increased with the increasing CNC content. The $T_i$ and $T_d$ of C10 were 282.8 and 341.3 °C, respectively, which were 10.5 and 14.9 °C higher than the corresponding values for the pure regenerated cellulose fiber (272.3 °C for $T_i$ and 326.4 for $T_d$). Figure 5b shows that all peaks of the composite moved to higher temperatures after addition of CNC. This result indicates that the presence of CNC improved the thermal stability of the all-cellulose fibers. Cellulose I is thermally more stable than cellulose II. Thus, adding CNC improved the thermal stability of the all-cellulose composite fibers. The char residues of C10, C7.5, and C5.0 were higher than that of the neat regenerated cellulose fiber. This result might be attributed to the surface of the CNC exhibiting flame-retardant properties, which acted as a catalyst for dehydration and thermal degradation of CNC, resulting in the increased char residue. The char residue acted as an insulator and mass transport barrier to the volatile products generated during decomposition of the cellulose matrix.

The tensile strength, elongation at break, and Young’s modulus of the all-cellulose fibers were measured to investigate the effects of CNC on their mechanical properties. The mechanical properties of the cellulose fiber were also measured for comparison. These data are summarized in Figure 6. The addition of CNC at any concentration improved the tensile strength of the all-cellulose fibers. When the CNC content was 2.5 wt %, the tensile strength was 300.2 MPa, which was slightly higher than that of the neat cellulose fiber. When the CNC content was increased to 5.0 wt %, the tensile strength increased to 365 MPa. The CNC contents of 7.5 and 10.0 wt % resulted in tensile strengths of 384 and 400.3 MPa, respectively. This finding could be related to the percolation model. In this study, the percolation threshold was 2.5–5.0 wt %. When the CNC...
content was lower than the percolation threshold, the tensile strength was slightly higher than C0. The main reason for the enhanced tensile strength was that the CNC had better mechanical properties than the regenerated cellulose. The addition of CNC also improved the degree of crystallinity of the all-cellulose fibers. At CNC concentrations higher than the percolation threshold, the CNC formed a network, which markedly improved the mechanical properties of the all-cellulose fibers. Similar results were observed for the Young’s modulus of the all-cellulose fibers. When the CNC contents were 2.5, 5.0, 7.5, and 10.0 wt %, the Young’s moduli were 822, 1194, 2160, 2688, and 2994 MPa, respectively. Adding 2.5 wt % CNC slightly improved the elongation at break of the all-cellulose fibers; however, CNC concentrations higher than 5.0 wt % reduced the elongation at break. We conclude that the network of CNC resulted in all-cellulose fibers, which had a high stiffness leading to a low elongation at break. This phenomenon has also been observed for other CNC composites.34,35

The XRD patterns of the CNC and the all-cellulose composites are shown in Figure 7. The diffraction peaks at 14.9, 16.2, 20.5, 22.4, and 34.3° 2θ were the characteristic of cellulose I,10,36 and those at 12.4, 20.4, and 34.2° 2θ were the characteristic of cellulose II.37,38 In the XRD patterns of the CNC, peaks at 14.9, 16.2, 20.5, 22.4, and 34.3° 2θ were observed. Their presence indicated that the CNCs were composed of typical natural cellulose with a cellulose I crystal structure. The degree of crystallinity was 72.3%, as calculated by the Jade 5.0 software package. For the all-cellulose composite fibers, the intensities of the cellulose I and cellulose II diffraction peaks increased with the increasing CNC content. C2.5 had a similar profile to that of C0, which indicated that its structure had not notably changed. The XRD patterns of C5.0, C7.5, and C10.0 showed a peak at 12.6° 2θ, which indicated that adding CNC enhanced crystallization of cellulose II. The degrees of crystallinity of C5.0, C7.5, and C10.0 were 37.1, 40.6, and 45.1%, respectively. The characteristic diffraction of the CNC at 22.2° 2θ was also detected in the XRD patterns of C7.5 and C10.0, owing to their higher CNC content. This result indicated that CNCs with a cellulose I structure were present in the composite fibers.

The densities of C0 and C10 were 1.37 and 1.41 g/cm³, respectively (Table 1). These differences are related to the mechanical properties, and the increase of the density is attributed to the increase of crystallinity caused by high-density CNC addition and crystallization effects. These results are consistent with our XRD findings.

SEM images of the cross sections and surfaces of the all-cellulose fibers (Figures 8 and 9) showed that increasing the CNC content did not notably affect the morphology. The composite fibers exhibited smooth surfaces and uniform cross sections. The phase interface could not be detected in the cross-sectional SEM images; hence, the compatibility between the matrix and reinforcing phase was good because both were composed of cellulose. The surface SEM images of the all-cellulose fibers showed cylindrical structures with smooth surfaces. Increasing the CNC content resulted in a small number of defects appearing on the surfaces of the all-cellulose fibers. This result might be caused by a small degree of agglomeration of CNC dispersed in the all-cellulose fibers.

## CONCLUSIONS

A cellulose solution containing CNC was prepared with a TBAA/DMSO/cellulose solution and a suspension of CNC in DMSO. All-cellulose composite fibers were then prepared by dry−wet spinning of the mixtures. The structures, morpholo-
cies, and mechanical properties of the all-cellulose composite fibers were characterized. FT-IR spectroscopy and XRD confirmed the presence of CNC within the composite fibers. SEM images showed that the morphology of the composite fibers did not markedly change as the CNC content increased from 2.50 to 10.0 wt %. The addition of CNC enhanced the crystallinity, tensile strength, and Young’s modulus of the fibers. The tensile strength of the cellulose fiber was 320 MPa and increased to 400 MPa upon addition of 10.0 wt % CNC. Addition of CNC initially increased and then subsequently decreased the elongation at break of the all-cellulose fibers. DTG and TGA measurements showed that the presence of CNC increased the thermal stability of the all-cellulose fibers.

**EXPERIMENTAL SECTION**

**Materials.** Needle wood pulp with DP = 650 and α-cellulose content 92 wt % was supplied by Asia Symbol Co., Ltd., Rizhao, P. R. China. Cellulose powder (W100, α-cellulose content of ≥95%) was supplied by Nippon Paper Industries Co., Ltd., Tokyo, Japan. Tetrahydroammonium acetate was purchased from Tokyo Chemical Industry Co., Ltd., Shanghai, P. R. China. Dialysis tubing with a molecular weight cutoff of 8000–14 000, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), and sodium bromide (NaBr) were provided by Aladdin Industrial Co., Shanghai, P. R. China. Analytically pure dimethyl sulfoxide (DMSO), sodium hydroxide (NaOH), hydrochloric acid (HCl aq.), and sodium hypochlorite (NaClO aq.) were purchased from Beijing Chemical Works.

**Preparation of CNC Suspensions in DMSO.** The CNCs were prepared by the Saito method.39 Specifically, approximately 5 g of needle wood pulp was suspended in deionized water (500 mL) containing TEMPO (0.1 g) and NaBr (0.5 g). The resulting mixture was homogenized by mechanical stirring at 200 rpm for 2 h. A 25 mM portion of aqueous NaClO (10 wt %) was slowly added to the suspension with mechanical stirring at 300 rpm to start the oxidization at room temperature. Throughout the reaction, the pH was maintained at 10.0–10.2 by addition of 0.5 M NaOH. When the pH stabilized, the reaction was quenched by addition of ethanol (20 mL). Then, 0.5 M HCl was slowly added to the mixture until the pH was neutral. The mixture was then transferred to a dialysis bag and dialyzed in deionized water for 72 h to remove residual small molecules. The resulting aqueous suspension was then subjected to solvent exchange in a DMSO dispersion by centrifugation. The suspension was then homogenized using an Ultra-Turrax (IKA) at 12 000 rpm for 15 min. Finally, the mixture was treated with a high-pressure viscolizer for 10 passes at 850 MPa to yield a CNC suspension in DMSO. Different concentrations of CNC suspensions (0.25, 0.50, 0.75, and 1.00 wt %) were obtained by diluting this suspension. The size distributions of the CNC/DMSO suspensions are shown in Figure 2; the equivalent grain size of the obtained CNC was 40–50 nm.

**Preparation of Well-Dispersed Cellulose/CNC Mixtures.** Transparent cellulose solutions were prepared by dissolving cellulose powder (8.0 wt %) in a 1:4 weight ratio TBAA/DMSO solvent mixture and then stirring at 60 °C for 8 h. Each of the above-described CNC suspensions was then mixed with the cellulose solution in a weight ratio of 0.8:1. The resulting mixtures were stirred for 30 min at room temperature to obtain cellulose/CNC solutions.

**Preparation of Composite Fibers.** Regenerated all-cellulose fibers were prepared by dry–wet spinning. Specifically, the above-prepared well-dispersed cellulose/CNC mixtures were spun into a coagulating bath at 25 °C. The spinneret needle inner diameter was 240 μm, and the extrusion velocity was 0.6 mL/min. The draw speed was 15 m/min. After the dry–wet spinning, the gel-like fibers were washed and dried with heat rollers at 120 °C to obtain dry fibers. The CNC contents of the fibers were controlled to be 2.5, 5.0, 7.5, and 10.0 wt %. The final composite fibers are denoted Cx, where x indicates the CNC content in wt %. For comparison, neat regenerated cellulose fibers with no CNC (denoted C0) were prepared under the same conditions.

**Characterization.** The rheological properties of the mixtures were determined from viscometry and oscillatory measurements, which were acquired using a rheometer (Bohlin CVO-100-901, Malvern, U.K.) equipped with a PP40 plate measuring system at 25 °C. Density determination was performed by aerometry with a 10 mL pycnometer filled with water at 25 °C. The initial sample weight, W1, was 2 g. The weight at 25 °C when water was added to the 10 mL pycnometer was recorded as W2. Samples were added to the pycnometer. The temperature was maintained for 24 h and water was added to the scale, and the final weight was defined as Wf. The fiber density was calculated by eq 1. The tensile strength and mechanical elongation of the fiber samples were measured at room temperature using an electronic tensile tester (Instron S848, Germany), with an extension rate of 1 cm/min. The sample length was 20 mm. The reported values for each sample were averages of 30 tests. The SEM images, XRD patterns, FT-
IR spectra, and TGA data were recorded by our early reported method.  
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\rho = \frac{W_2 \times \rho_{H_2O}}{W_1 + W_2 - W_3}
\]  
(1)

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03601.

Transmission electron microscopy image of a cellulose nanocrystal (Figure S1) (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: zhanglp418@163.com. Tel: +86 139-1186-8160.*

**ORCID**

Zeming Jiang: 0000-0002-7301-8768

**Notes**

The authors declare no competing financial interest.

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