Effective Preparation of Bamboo Cellulose Fibers in Quaternary Ammonium/DMSO Solvent

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A novel, efficient, and direct blend of solvents, tetrabutylammonium acetate/dimethyl sulfoxide (TBAA/DMSO), was used for the dissolution and regeneration of bamboo pulp. Regenerated fibers were successfully prepared by a wet spinning process. The bamboo pulp without any pretreatment was readily soluble in the solvent under mild conditions. The dissolution process was observed using a confocal laser scanning microscope (CLSM). Rheological properties of the cellulose solutions at various concentrations were investigated. The regenerated fibers prepared by coagulation in ethanol were characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and an electronic tensile tester. The SEM images showed that the regenerated fibers possessed a smooth surface and circular cross-section, and the XRD and FT-IR results revealed that the fibers exhibited a cellulose II structure. The thermostability and mechanical properties of the fibers was also investigated.

Keywords: Cellulose fibers; Bamboo; TBAA; DMSO

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INTRODUCTION

Renewable resources are of importance in our modern society because of their positive effects on agriculture, the environment, and the economy. Because of the limited existing quantities of fossil supplies and the recent environmental conservation regulations, biopolymers being used as renewable materials are gaining considerable importance. Cellulose, the most abundant renewable polymer available, is produced by nature at an annual rate of 10^{11} to 10^{12} tons (Hae-ri *et al*. 2014). It is a homopolysaccharide that is formed from linearly connecting D-glucose units condensed through the $\beta(1-4)$ glycosidic bonds (Nishiyama *et al.* 2002; Van de Vyver *et al*. 2011). This natural polymer has a 2-fold screw axis along the chain direction. The degree of polymerization (DP) of the macromolecule can vary from 100 to 20,000 depending on the sources (Zhang *et al*. 2006). Lignocellulose, which refers to the chemical composition of plant-based material, occupies an important position as a raw material for papermaking, viscose fibers, bio-ethanol, *etc*.

Among natural plants, bamboo is rapidly grown, an early harvested vegetable, and has a high adaptability, unlike trees that suffer insect infestation. Bamboo is a renewable natural bioresource that is abundant in many parts of the world. After being grown for three years, bamboo can be felled every year within several decades to 100 years (He *et al*. 2007). It has several advantages, including small environmental load, rapid growth, renewability, relatively high strength, and good flexibility (Liu *et al.* 2010). Bamboo is considered an important biopolymer with useful applications in various fields, including textiles (Teli and

Sheikh 2012). Thus, it has been utilized for a long time and applied in different fields (Bassam 1998). If bamboo cellulose can be efficiently converted to fibers by various processes, it can better compete with cotton or other lignocellulosics and play an important role in meeting future textiles needs.

Regenerated bamboo fibers have been manufactured since 2002 by Hebei Jigao Chemical Fibers Co. Ltd. in China (Liu *et al*. 2004), using a viscose process. However, the conventional viscose process causes serious environmental problems that restrict the further development of regenerated bamboo fibers. Because of the high pollution and low efficiency of the traditional processes, it is imperative to explore a new and more productive way to utilize these "green" resources (Argyropoulos 2007).

To find new spinning systems that solve environmental problems, numerous new solvents for cellulose have been investigated. Among these, ionic liquids (ILs) are viewed as promising cellulose solvents. Ionic liquids are a group of organic salts that exist as liquids at a relatively low temperature (< 100 °C). It was reported in 2002 that cellulose can be directly dissolved in imidazolium-based ILs without any pretreatment, and the dissolved cellulose can be easily regenerated by precipitation upon addition of water or other common solvents (Swatloski *et al*. 2002). Since then, many kinds of ILs have been reported to act as cellulose solvents (Wu *et al*. 2004; Liu *et al*. 2011; Tan *et al*. 2011; Zhao *et al*. 2012). Ionic liquids such as 1-butyl-3-methylimidazoliumchloride ([BMIM][Cl]), 1-ethyl-3-methylimidazoliumacetate ([EMIM][Ac]), and 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) have been used for homogeneous esterification of cellulose as well as for the formation of films and fibers. Although significant progress has been made in the study of ILs, some problems, such as slow dissolution rate, high dissolution temperature, and high viscosity of the dissolution systems, have yet to be resolved. Thus, advances toward improved processes for the dissolution of cellulose are still necessary.

Recently, a new solvent system, tetrabutylammonium acetate/dimethyl sulfoxide (TBAA/DMSO) solution, has been used to dissolve cellulose in our laboratory (Miao *et al.* 2014). Compared with the existing cellulose solvents, the new cellulose dissolving system has the advantages of high efficiency, low energy, and no pollution. Compared with previously reported ILs, the dissolution temperature is lower (≤60℃) and the dissolution rate is more rapid (≤1h). Furthermore, both TBAA and DMSO can be recycled. Currently, the dissolution mechanism of TBAA/DMSO is being studied and has not been fully elucidated. We deduce that the dissolution mechanism of this new solvent is similar to that of tetrabutylammonium fluoride trihydrate/DMSO. According to previous research, the fluoride salt is the only halide salt of tetrabutylammonium ion (TBA^+) capable of rendering cellulose soluble in DMSO (Heinze *et al*. 2000). TBAA is a kind of IL that melts at 95 to 98 °C. DMSO cannot dissolve cellulose alone, although it is a good swelling agent for polymers because of its polarity. In addition, some researchers believe that DMSO can effectively reduce the viscosity of cellulose/ILs solutions, leading to an increase in the solution rate (Gericke *et al*. 2011).

The main purpose of the present study is to provide an environmentally friendly and low-energy method for the preparation of regenerated bamboo cellulose fibers from renewable bamboo pulp, replacing traditional high-grade dissolving pulp. In this paper, fibers were prepared from bamboo pulp. The pulp was dissolved and regenerated with TBAA/DMSO as a solvent, and the fibers were spun from the resulting solution. The details of the dissolution process of the bamboo pulp in the new solvent were observed.

The rheological behavior of cellulose solutions was evaluated, and the morphology, structure, and thermostability of the fibers were characterized.

EXPERIMENTAL

Materials

Bamboo cellulose pulp with an α-cellulose content of more than 90% was supplied by the Shandong Rizhao Senbo Pulp Paper Co., Ltd., China. The viscosity-average molecular weight (M_w) of the bamboo pulp sample was determined to be 1.2×10^5g•mol^{-1} (DP = 760) by viscometry. The bamboo pulp was vacuum-dried for 24 h at 60 °C to remove moisture before use. TBAA was purchased from TCI, Shanghai. Other chemicals used were analytical reagents and used without further purification.

Preparation of Cellulose solutions

Tetrabutylammonium acetate and DMSO were added to a 50-mL serum bottle with a mass ratio of 1:4 at 50 °C. Then, an appropriate amount of dried bamboo pulp sample was added to the bottle and the mixture was stirred continually for 1 h at 50 °C. Pulp solutions of 4 wt.%, 5 wt.%, and 6 wt.% in the new solvent were obtained. A high-vacuum pump was used to remove air bubbles in the solutions at 50 °C for 2 h. The resulting cellulose solutions were analytically characterized and used in a further spinning process.

Preparation of Regenerated Cellulose

The cellulose solutions (5 wt.%) were cast onto a glass plate at a thickness of approximately 1 mm; air bubbles were extracted in a vacuum oven, and the samples were then immediately coagulated in ethanol to obtain regenerated cellulose.

Preparation of Regenerated Fibers

A simple wet spinning device (Fig. 1), which consisted of a micro-syringe pump system, a glass syringe (inner diameter, 10 mmΦ) with a needle (length, 35 mm; inner diameter, 0.355 mmΦ) as a spinneret, a coagulating bath, a turning round godet roller, and a winding device, was used for the spinning. The cellulose solutions (5 wt.%) obtained earlier were introduced into the glass syringe with a precise drive. The extrusion speed was 0.8 mL/min. The winding speed was controlled at 15 mL/min. Ethanol was the coagulation and cleanout fluid, and the solution temperature was changed by the heating cylinder. The temperature of the cellulose solutions and coagulating bath was kept at 20 °C.

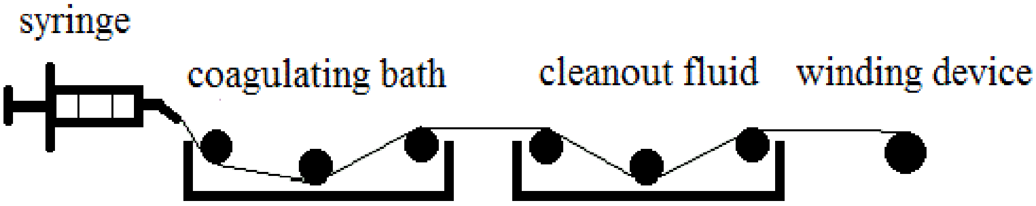

Fig. 1. Simple spinning device

Methods

DP characterization

The viscosity-average degree of polymerization (DP) of the bamboo pulp was characterized with reference to intrinsic viscosities [η] in copper(II) ethylenediamine (Cuen) according to DIN 54270, Part 2 (1977). DP was determined in Cuen using an Ubbelohde type viscometer (1835A, ZONWON, China) at 25 °C. The DP was calculated according to the following equation:

$$DP^{0.905} = 0.75[\eta] \tag{1}$$

Content of α-cellulose

The content of α-cellulose in the used pulp was determined as the remaining cellulose that was not dissolved in a 17.5 wt.% NaOH aqueous solution at 25 °C.

Dissolution of bamboo pulp in TBAA/DMSO

The dissolution process of cellulose in TBAA/DMSO was observed by confocal laser scanning microscope (CLSM) (Leica TCS SP5, Germany) with a hot stage and a multicolor digital camera. A small quantity of pulp and TBAA/DMSO solvent were sandwiched between two pieces of cover glasses at room temperature.

Rheological characterization of cellulose solutions

Rheological properties of the cellulose solutions were determined using a rheometer (Bohlin CVO-100-901, Malvern, UK) equipped with a PP20 plate measuring system for both viscometry and oscillatory measurements.

Scanning electron microscope (SEM) characterization

The surfaces and cross sections of fibers spun from the pulp concentration of 5% (wt.) were observed using a scanning electron microscope (S-3400N, Hitachi, Japan). The fibers were frozen in liquid nitrogen, immediately snapped, and then vacuum-dried. The samples were sputtered with gold using a sputter coater (SBC-12, KYKY, China) before being observed and photographed.

X-ray diffraction (XRD) characterization

X-ray diffraction measurements of the samples were performed on an XRD diffractometer (Shimadzu XRD-6000, Japan). Samples were vacuum-dried for 24 h before measurement and ground into powders to negate the influence of the crystalline orientation of each fiber sample (Yamane *et al*. 1996). The patterns were measured with Cu Kα radiation (λ = 0.154 nm) at 40 kV and 30 mA. The powder samples were scanned from 5 to 40° at a rate of 2°/ min. And crystallinity value was calculated by MDI jade 5.0.

Fourier transform infrared spectroscopy (FTIR) characterization

The samples were ground to powder and dried in a vacuum for 24 h. The IR spectra of samples were recorded using an FTIR spectrometer (VERTEX 70/70v FTIR Spectrometer, Germany). All the test specimens were prepared with the KBr-disk method.

Thermal gravimetric analyzer (TGA) characterization

The thermostability of samples was studied by TGA (STA 449 F3 Jupiter, Netzsch, Germany) in the range of 50 to 500 °C at a rate of 10 °C /min under a nitrogen flow. The samples were evenly and loosely distributed in an open sample pan 6.4 mm in diameter and 3.2 mm deep with an initial sample amount of 8 to 10 mg.

The mechanical properties characterization of the regenerated fibers

Denier of fibers was estimated assuming that the cross-section of the fiber is a true circle, by weighting the dried fiber with 100 cm in length. The tensile strength and elongation at break of the dried fibers were measured on an electronic tensile tester (Instron 5848, Germany). The sample length was 20 mm. Each specimen was tested for 30 times, and the average was obtained.

RESULTS AND DISCUSSION

The Dissolution Process

The dissolving process of pulp in the new solvent was observed by CLSM. As shown in Fig. 2, the pulp samples could dissolve in the TBAA/DMSO within 15 min at room temperature. The dissolution velocity in the novel solvent at room temperature for pulp was rapid, and similar velocities have only been reported for the TBAF.3H_2O /DMSO solvent system (Heinze *et al*. 2000). For neat IL solvents such as [AMIM][Cl] solvent, with temperatures above 100 °C, the cellulose began to dissociate and dissolved gradually (Fukaya *et al.* 2006). The low dissolution temperature and the rapid velocity indicates this technology is promising for industrialization, and it is note-worthy that the pulp dissolved in TBAA/DMSO rapidly without any pretreatment or activation at room temperature.

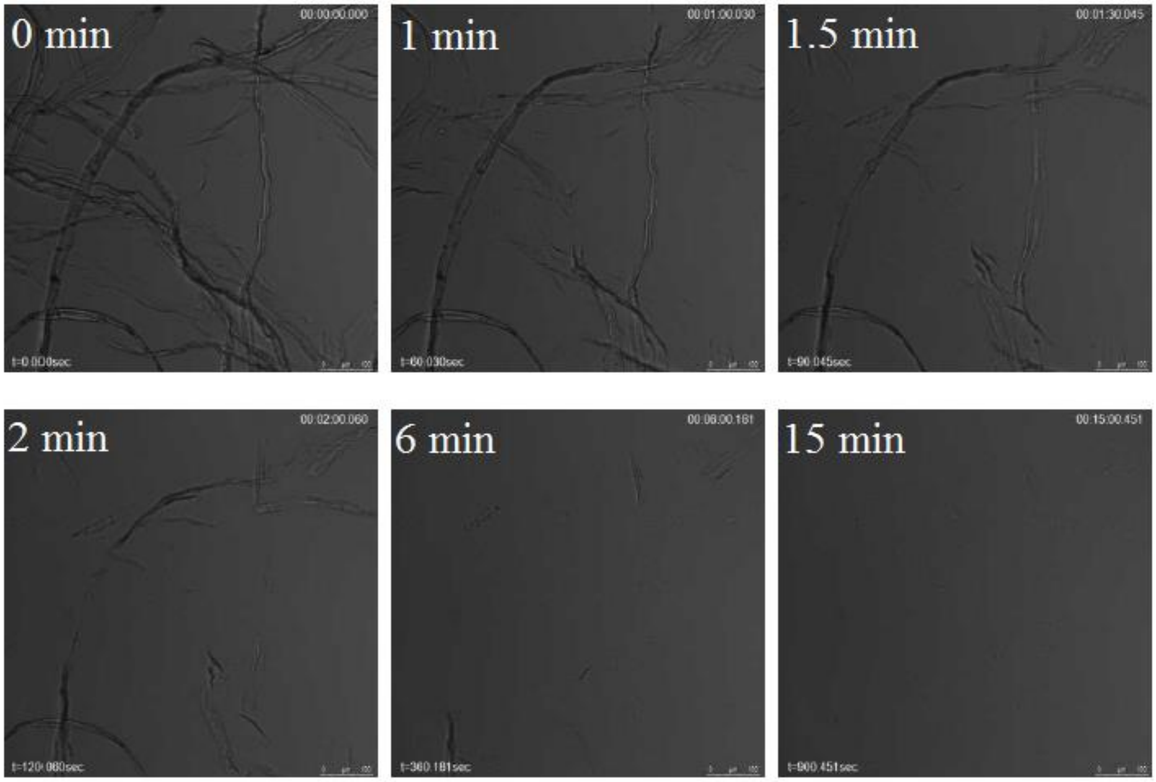

Fig. 2. CLSM images of pulp dissolution in TBAA/DMSO at 0, 1, 1.5, 2, 6, and 15 min

Viscosity of Cellulose/TBAA/DMSO Solutions

The nature of the regenerated fibers is believed to be related intimately to the viscosity of the cellulose solutions. As shown in Fig. 3, the solutions exhibited a typical shear-thinning behavior with varying shear rate. The shear thinning behavior of the solution resulted from both shear-induced reduction of the number of entanglements and the desolvation of macromolecules by the high shear rate (Chen *et al.* 2009). This behavior is similar to that of other cellulose solutions, such as in NMMO (Chae *et al*. 2002). However, the viscosity of NMMO/cellulose solutions was much higher; at 90 °C with a cellulose (DP = 670) concentration of 6%, the viscosity was almost 10 times that of the present solution (Collier *et al*. 2000).

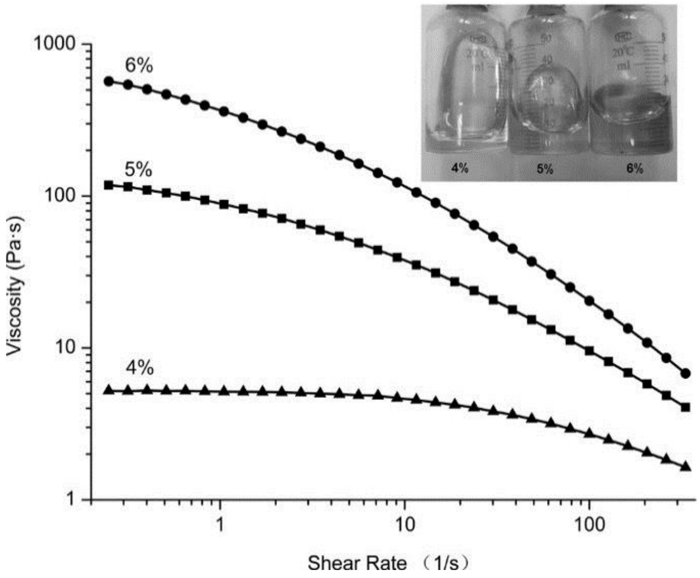

Fig. 3. Steady shear rheological curves for the pulp/TBAA/DMSO solution at 50 °C

Figure 3 also shows that with increasing concentration of cellulose solutions, the zero-shear viscosity increased. To investigate this phenomenon, the capped bottles filled with 20-mL solutions of various pulp concentrations at room temperature were tipped to induce flow, and the low-concentration solution behaved better fluidity. This phenomenon may be caused by the increase in chain entanglements of cellulose as the pulp concentration increased. The high concentration also led to a critical shear rate of non-Newtonian flow transition, which are shifted to lower shear rates with increasing concentration. This is quite similar to reports for many solutions of neutral polymers (Graessley 1974; Kulicke and Kniewske 1984) and for many other studies of cellulose in ILs (Sammons *et al*. 2008; Collier *et al*. 2009; Gericke *et al*. 2009; Le *et al.* 2012).

Dynamic Oscillation Behavior of Cellulose/TBAA/DMSO Solutions

The relationship between storage modulus *G′* and loss modulus *G″* could provide more information about the interaction between cellulose molecules and solvent. As long as *G″* is larger than *G′*, liquidity takes a dominant position in the system, while the opposite is true for a semisolid such as a gel (Olsson and Westman 2013). Figure 4 shows *G′* and *G″* curves as a function of angular frequency for cellulose solutions. The *G′* and *G″* values all tend to become larger with increasing pulp concentration from 4% to 6%. At low deformation rates, the novel solution behaves most likely as a viscous liquid (loss modulus being larger than storage modulus), but at high angular velocities, elastic properties develop. The ability of temporary networks was enhanced by an increase in cellulose concentration. This could be related to the increase in segment density and number of entanglement points. In this situation, the $G' < G''$ behavior occurs at low frequencies. This can be explained by the fact that at low concentrations, the cellulose chains have room to avoid the externally imposed deformation. The deformation takes place so slowly in cellulose solution that the majority of the energy is dissipated by the viscous flow. With increasing frequency, G' increases more sharply than does G'', and the two domains of viscoelastic behavior have finally been separated by the so-called crossover point. As the pulp concentration increases, the crossover point $G'(w) = G''(w)$, shifts to the low-angular frequency region. These results show that the ability of the entanglement networks was enhanced with increasing polymer concentration, which can be attributed to the increase in segment density of cellulose chains at high pulp concentrations.

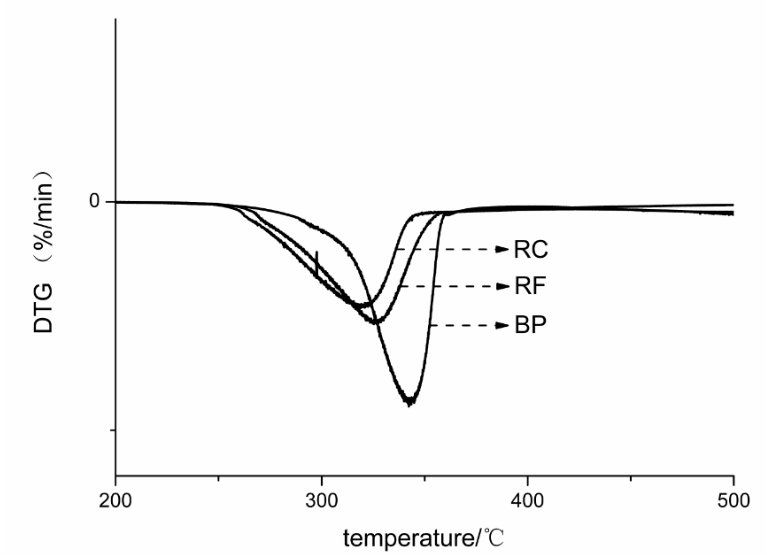

Fig. 4. Modulus of pulp/TBAA/DMSO solutions with different concentration at 50 °C

Morphology of the Fibers

Figure 5 shows SEM images of the surface and cross sections of the bamboo fibers. The fibers exhibited a dense and homogenous structure with pores in which no undissolved original cellulose could be detected. It was determined that TBAA/DMSO is a good solvent for cellulose, and the solution was homogeneous.

The cross-section of fibers was circular, and the smooth surface might be due to the fact that in the spinning process, the cellulose solution suffered quick permeation of coagulation bath, which resulted in uniform coagulation. These results indicate that regenerated fibers were formed as a result of coagulation of gels containing a large amount of solvent, and there was no porosity and no cracks in the fibers. The regenerated fibers always contained some coagulating solution, giving a porous structure after freeze-drying using liquid nitrogen. This phenomenon was attributed mainly to the fact that the cellulose molecules were completely dissolved in the solvent. The solvent was a good solvent for cellulose and the solution was highly homogeneous. When phase inversion happened during the spinning process, the homogeneity of solution was retained and the regenerated fibers had a dense and homogenous structure.

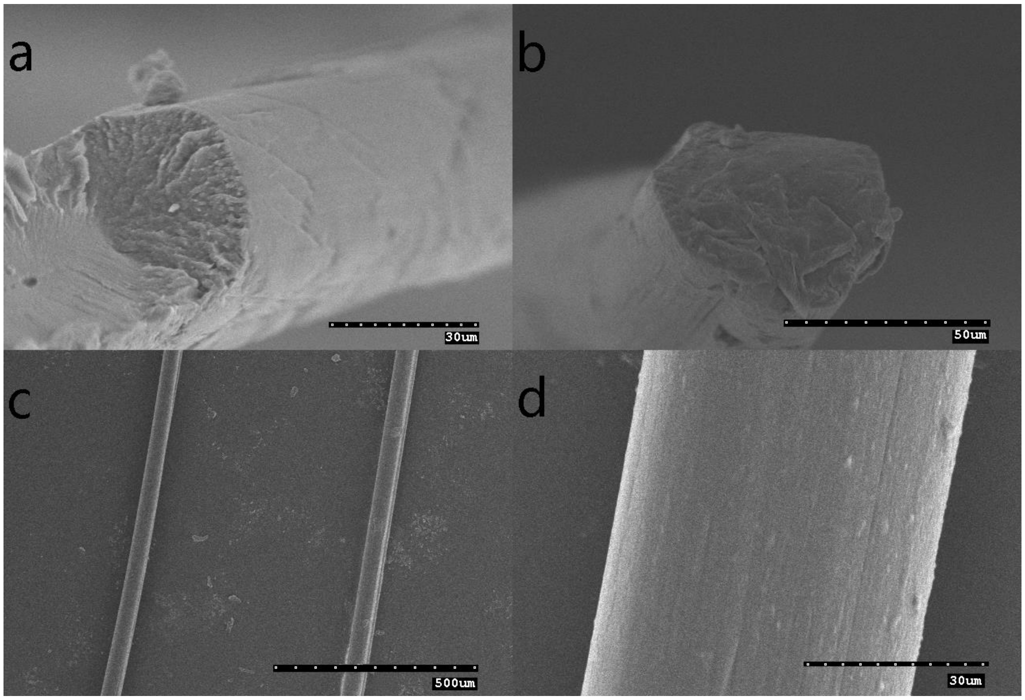

Fig. 5. Scanning electron microscopy photographs of cross sections (a, b) and surfaces (c, d) of the regenerated fibers

Crystal Structure of the Fibers

There were two obvious crystal peaks for the bamboo pulp (BP) sample, at 2θ = 15.4°, and 22.1° in Fig. 6, assigned to the crystal planes (110) and (020) of cellulose I, respectively (Kaplan 1998). However, in the curves of regenerated fibers (RF) and regenerated cellulose (RC), two crystal peaks appeared, at 17.9° and 21.6°, assigned to the crystal planes (110) and (020) of cellulose II (Isogai *et al*. 1989).

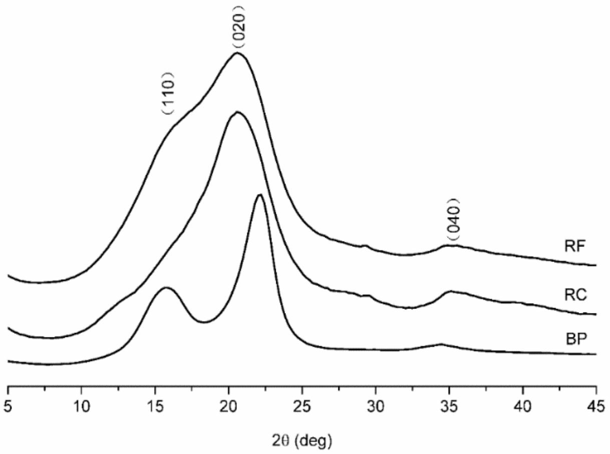

Fig. 6. X-ray diffraction patterns of bamboo pulp (BP), regenerated fibers (RF), and regenerated cellulose (RC)

The results reveal that the crystal structure of the fibers regenerated from the solution had been transformed from cellulose I to cellulose II. The crystallinity values of RF and RC were 35.54% and 15.61%, respectively. The crystallinity of RF was similar to that of BP (39.60%). The results showed that the crystalline values of the regenerated cellulose slightly decreased. Moreover, the crystallinity values of RF were much higher than RC; this phenomenon could be explained by the spinning process, which improved the orientation degree of cellulose molecules.

FTIR Analysis

The FTIR spectra of bamboo pulp (BP) and regenerated fibers (RF) are shown in Fig. 7. The FTIR curves can provide more information about the fiber's structure. Some of the characteristic bands related to the physical and chemical changes are the O-H bending vibrations at 4000 to 2950 cm^{-1}, the C-H stretching at 2900 cm^{-1}, the H-C-H and O-C-H in-plane bending vibrations at 1430 cm^{-1}, the C-H deformation vibration at 1375 cm^{-1}, and the C-O-C, C-C-O, and C-C-H deformation modes and stretching vibrations in which the motions of the C-5 and C-6 atoms are at 900 cm^{-1} (Proniewicz *et al*. 2001). Bands at 4000 to 2995 cm^{-1}, 2900 cm^{-1}, 1430 cm^{-1}, 1375 cm^{-1}, and 900 cm^{-1} are especially sensitive to the state of the crystalline and amorphous regions. The peak at 1437 cm^{-1} in BP, attributed to the cellulose I crystal, disappeared in the RF, indicating that the crystal structure of the fibers regenerated from the new solvent had already changed to cellulose II. In addition, the strong absorption peak in the range of 3000 to 3500 cm^{-1} represented the O-H vibrations of cellulose. Compared with the original cellulose, the peak intensity of the O-H vibration of the regenerated fibers increased. This may have occurred due to the hydroxyl groups of cellulose that are less associated with either intra- or inter-molecular hydrogen bonding (Zhang *et al.* 2005).

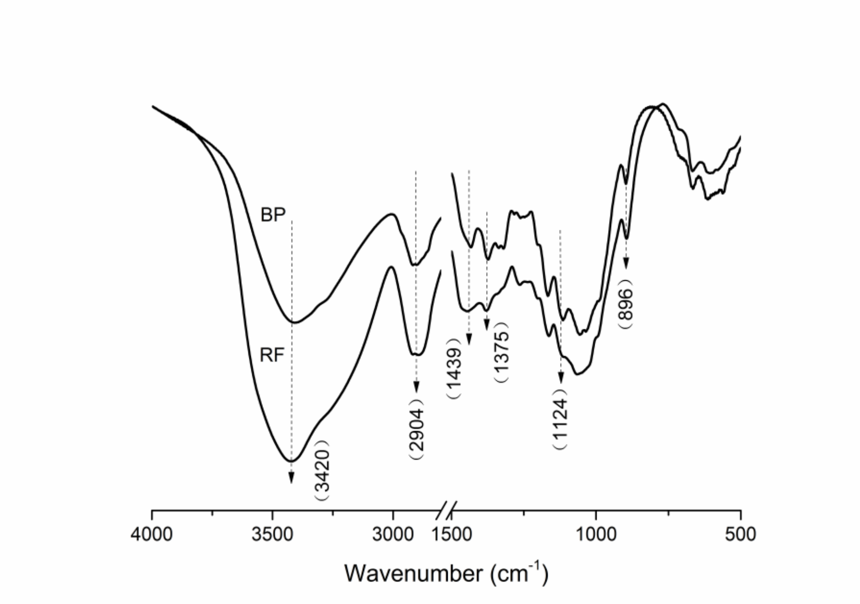

Fig. 7. FTIR spectral of bamboo pulp (BP) and regenerated fibers (RF)

Thermogravimetric Analysis

TGA analyses of the samples (Fig. 8) indicated that the pyrolysis of samples includes three stages: initial, main, and char decomposition. The corresponding temperature, speed, and weight loss of every stage can be found from the TGA curves. In the initial stage, the most important changes of the samples were some physical properties and a little weight loss. Here, the damage of the cellulose occurred mostly in the amorphous region of the polymers. The onset decomposition temperatures of the RC, RF, and BP were

258, 266, and 277 °C, respectively. The onset temperature of the BP thermal decomposition process was 8 °C higher than the onset temperature for RC. In this process, higher onset temperatures were associated with higher thermal stability.

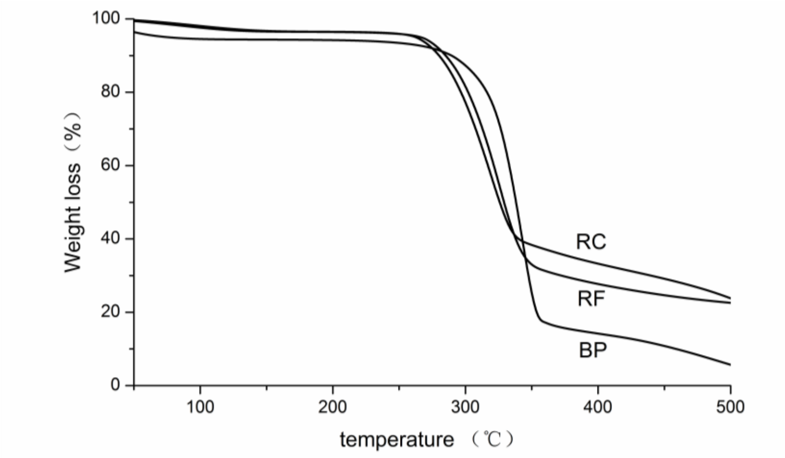

Fig. 8. TG scans of bamboo pulp (BP), regenerated cellulose (RC) and regenerated fibers (RF)

From the DTA curves (Fig. 9), the corresponding temperatures of maximum decomposition rate for RC, RF, and BP were 318, 327, and 342 °C, respectively. The temperature of maximum decomposition rate for RC was lower than that for BP and RF. Based on the TGA and DTA curves, it can be concluded that RF was more thermally stable than RC. The aforementioned shear rheological data showed that the cellulose solution was a shear-thinned fluid. And during the spinning process the cellulose solution was fast-flowing. It follows that fluid flow may have increased the molecular orientation. When the flowing solution was immersed in coagulating bath, the molecular orientation was retained. Besides, the subsequent drawing could effectively increase the fiber orientation degree. The RF was more thermally stable than RC, which could be related to the high crystallinity degree as well as the high orientation of samples obtained by the spinning process, as increases in either property are associated with increases in their thermal resistance (Carrillo *et al.* 2004).

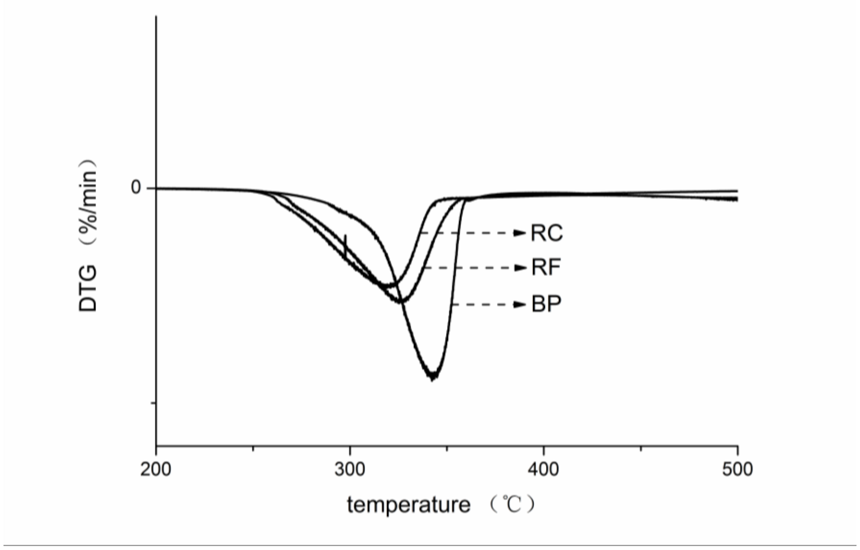

Fig. 9. DTA curves of bamboo pulp (BP), regenerated fibers (RF), and regenerated cellulose (RC)

Properties of the Regenerated Fibers

The tensile strength, elongation at break of the regenerated fibers are summarized in Table 1. The tensile strength of RF was slightly lower than Lyocell fiber, but was better than viscose fiber. This could be because of concentration of spinning solution used in the experiment was lower than lyocell (10 to 12 wt.%), and the high concentration of solution also led to the segment density rising and the number of entanglement points increasing with the increase of cellulose concentration. So the RF embodied a slightly lower tensile strength than lyocell. We speculated that under the same concentration RF would have a similar performance to that of lyocell.

Table 1. Mechanical Properties of the Regenerated Fibers

Sample	Dry tensile strength (cN/dtex)	Wet tensile strength (cN/dtex)	Elongation at break (%)
RF	3.85	3.21	11.9
Lyocell	4.0-4.2	3.4-3.6	17-19
Viscose fiber	2.2-2.6	1.3-1.6	18-24

CONCLUSIONS

1. A new cellulose solvent blend, TBAA/DMSO, was successfully used to dissolve bamboo pulp under mild conditions. The regenerated bamboo cellulose fibers were successfully prepared from the cellulose solution with wet spinning equipment.
2. The cellulose solutions exhibited typical shear thinning behavior with varying shear rates. Their viscosities were much lower than other cellulose solutions, such as cellulose/NMMO.
3. The generated fibers had a smooth surface and a round and compact structure; XRD and FTIR indicated the fiber was a kind of cellulose II fiber and its mechanical properties was slightly lower than Lyocell.
4. As a result of the spinning process, the regenerated fibers with higher crystallinity values embodied a better thermostability.
5. The new solvent could provide a new method for preparation of bamboo fibers, which could be a new kind of environmentally friendly fiber.

ACKNOWLEDGMENTS

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