# Structure and Properties of Cellulose Fibers from Ionic Liquids

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**ABSTRACT:** 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) was used as a solvent for cellulose, the rheological behavior of the cellulose/[BMIM]Cl solution was studied, and the fibers were spun with a dry-jet–wet-spinning process. In addition, the structure and properties of the prepared cellulose fibers were investigated and compared with those of lyocell fibers. The results showed that the cellulose/[BMIM]Cl solution was a typical shear-thinning fluid, and the temperature had little influence on the apparent viscosity of the solution when the shear rate was higher than 100 $s^{-1}$. In addition, the prepared fibers had a cellulose II crystal structure just like that of lyocell fibers, and the orientation and crystallinity of the fibers increased with the draw ratio increasing, so the mechanical properties of the fibers improved. Fibers with a tenacity of 4.28cN/dtex and a modulus of 56.8 cN/dtex were prepared. Moreover, the fibers had a smooth surface as well as a round and compact structure, and the dyeing and antifibrillation properties of the fibers were similar to those of lyocell fibers; however, the color of these dyed fibers was brighter than that of lyocell fibers. Therefore, these fibers could be a new kind of environmentally friendly cellulose fiber following lyocell fibers.  J Appl Polym Sci 115: 1047–1053, 2010

**Key words:** fibers; mechanical properties; structure

## INTRODUCTION

Cellulose is the most abundant renewable resource; it has a wide range of applications in plastics, films, fibers, and so forth. Cellulose has been used as a raw material for making fibers with well-established technology for a long time. Cellulose consists of linear glucose polymer chains that form hydrogen-bonded supramolecular structures, which make cellulose insoluble in most common organic liquids. Along with the increasing exhaustion of petroleum reserves, the willingness to develop cellulosic materials has increased. Up to now, the technologies used in cellulose processing have been mostly non-green. For example, viscose rayon is prepared from cellulose xanthate with carbon disulfide as both the reagent and solvent. At the end of the last century, a new processing technology using a more environmentally friendly solvent, *N*-methylmorpholine-*N*-oxide, was commercialized. However, this new process developed very slowly because of the complexity of the dissolution and solvent recycling processes.

In recent years, scientists have paid more and more attention to developing a new way of processing cellulose by using a new kind of green cellulose solvent: an ionic liquid.[1–5] Ionic liquids are a group of new organic salts that exist as liquids at a relatively low temperature (100°C). They have many attractive properties, such as chemical and thermal stability, nonflammability, immeasurably low vapor pressure, excellent dissolving capability, and recyclability.[6] Therefore, ionic liquids are considered desirable green solvents.[7]

Swatloski et al.[1] studied the solubility of cellulose in ionic liquids containing different anions and cations, and they found that chloride-containing ionic liquids such as 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) appear to be the most effective solvents. Zhang and coworkers[3,8,9] also conducted extensive research in this field, but they focused on 1-allyl-3-methylimidazolium chloride. In addition, there are a few reports on the spinning of cellulose/ionic liquid solutions. The Thuringian Institute of Textile and Plastic Research has studied the dissolution of cellulose in different ionic liquids and prepared regenerated cellulose fibers by a dry–wet-spinning process.[10] The Institute for Textile

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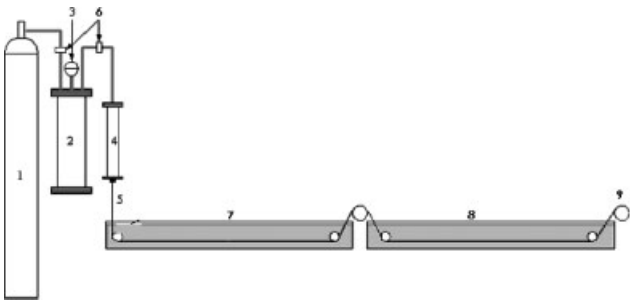


**Figure 1** Schematic drawing of the single-filament spinning equipment: (1) nitrogen, (2) surge flask, (3) pressure gauge, (4) spinning tank, (5) air gap, (6) needle valve, (7) coagulation bath, (8) washing bath, and (9) take-up.

Chemistry and Chemical Fibers has manufactured cellulose fibers by a wet-spinning process using 1-ethyl-3-methylimidazolium acetate as the direct solvent.[11] However, the properties of cellulose fibers from ionic liquids, including the mechanical, dyeing, and antifibrillation properties, have not been discussed in detail.

Because ionic liquids are direct solvents for cellulose, the processing is environmentally friendly; it is similar to the lyocell process. Therefore, cellulose fibers from ionic liquids may be a new kind of environmentally friendly fiber following lyocell fibers.

In this study, a typical ionic liquid, [BMIM]Cl, was used as the solvent, and the rheological behavior of the cellulose/[BMIM]Cl solution was examined. Then, the fibers were dry–wet-spun from the spinning dope; and the structure and properties of the prepared cellulose fibers were compared with those of lyocell fibers.

## EXPERIMENTAL

### Materials

The wood pulp [DP (degree of polymerization) = 722, α-cellulose content = 91%] used in this work was provided by Alaska Pulp Corp. (Sitka, AK). [BMIM]Cl was purchased from BASF (Ludwigshafen, Germany). Two reactive dyes, Blue FN-R and Yellow 6-GS, were provided by Cibacron (Uppsala, Sweden).

Lyocell fibers were prepared in our laboratory under similar process conditions.[12]

The simple single-filament spinning equipment without a metering pump shown in Figure 1 was used in the spinning process.

### Dissolution and spinning

The preparation of the cellulose solution was carried out as follows. A certain amount of [BMIM]Cl was put into a three-necked flask, and the flask was heated to 100°C. Then, a certain amount of dried cellulose was added to the flask, and the mixture was stirred continually for 3 h *in vacuo* at 100–105°C. The mixture gradually turned into a homogeneous solution, and solutions of 8 wt % cellulose in [BMIM]Cl were obtained.

Each obtained solution was transferred to a spinning tank, for which the temperature was set at 85°C. The spinning solution was extruded through a spinneret orifice with a diameter of 0.145 mm and then passed through a 50-mm-long air gap and immersed in a coagulation bath of water to precipitate cellulose into a filament form. The filaments were washed with water, wound, and dried.

### Rheological measurements

The rheological measurements were made on an RS150L rheometer (Thermo Haake, Karlsruhe, Germany), and a cone plate (Ti, 35/1°) was used. The rheological properties of the cellulose/[BMIM]Cl solution were determined at 70, 80, 90, 100, and 110°C, respectively. The data analysis was performed with Rheowin Pro Data Manager software.

### Birefringence measurements

Birefringence measurements of fibers were performed on an Olympus Co. (Tokyo, Japan) XP51 optical polarized light microscope with the aid of an Olympus CTB Berek compensator.

### Wide-angle X-ray diffraction (WAXD) measurements

WAXD measurements of the fibers were performed on a D/MAX-2500PC diffractometer (Rigaku, Tokyo, Japan; Cu Kα, wavelength = 0.154 nm) at 40 kV and 35 mA. The powder samples were scanned from 5 to 60°, and the data were analyzed with Peakfit software (version 4.12, Seasolve Co., San Jose, CA); then, the crystallinity could be calculated according to the method reported in the literature.[13] Furthermore, according to the azimuthal intensity distribution of X-ray diffraction, at a fixed azimuthal angle of 21.9° for parallel fiber bundle samples, the Hermans

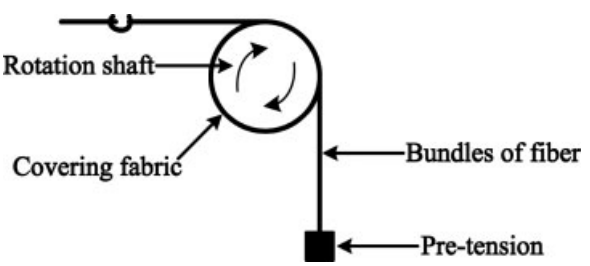


**Figure 2** Schematic wet-abrasion test.

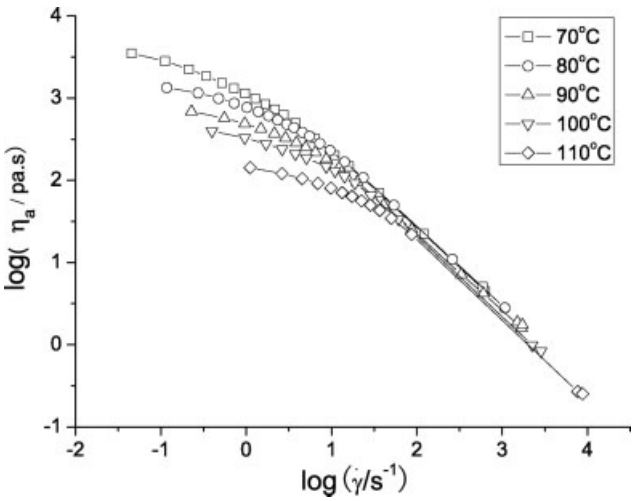


**Figure 3** Flow curves of 8% cellulose/[BMIM]Cl solutions at different temperatures.

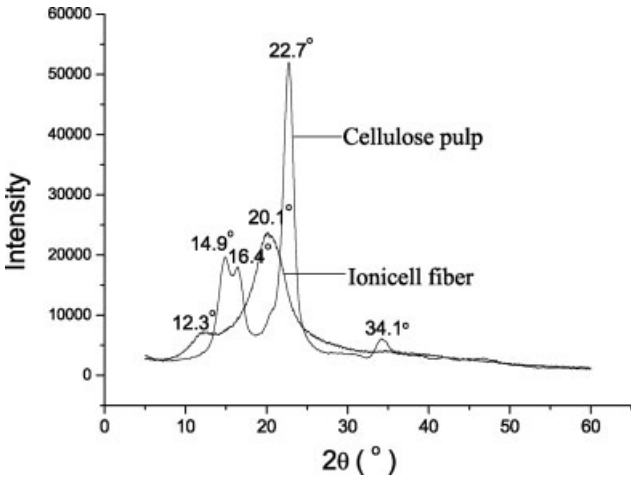


**Figure 4** Powder WAXD patterns of the original cellulose pulp and ionicell fibers.

crystalline orientation factor could be calculated.[13] Moreover, the amorphous orientation factor could be calculated with the Stein equation:

$$\Delta n = \alpha f_c \Delta n_{co} + (1 - \alpha) f_a \Delta n_{ao} \quad (1)$$

where $\Delta n$ is the total fiber birefringence; $\alpha$ is the crystallinity; $f_c$ is the crystalline orientation factor; $f_a$ is the amorphous orientation factor; and $\Delta n_{co}$ and $\Delta n_{ao}$ are the characteristic birefringences of the crystal phase and amorphous phase in the fibers, respectively. Here, it is assumed that $\Delta n_{co} = \Delta n_{ao} = 0.05$.[14]

### Measurements of the mechanical properties of the fibers

The mechanical properties of the fibers were measured with an XQ-1 tensile tester (China Textile University, Shanghai, China). The sample length was 20 mm, and the extension rate was set at 4 mm/min. The statistical results came from more than 25 measurements for each specimen. All measurements were performed at 20°C and 65% relative humidity.

### Morphological characterization

The surfaces and cross sections of the fibers were observed with a JSM-5600LV scanning electron microscope (JEOL Co., Tokyo, Japan).

### Measurement of the fibrillation resistance of the fibers

The fibrillation resistance of the fibers was determined with the wet-abrasion value, which increases nonlinearly as the fibrillation resistance increases.[15,16] The schematic wet-abrasion test is shown in Figure 2.

The wet-abrasion value was measured as follows.[15,16] The rotor speed was 6 m/min, and the pretension was $9.54 \times 10^{-3}$ cN/dtex. A poplin cotton Ne 60 × 60 fabric was used to cover the rotating shaft, and water was dropped onto the fabric continuously. The wet-abrasion value was the mean of 20 measurements for each specimen.

### Measurement of the dyeing properties of the fibers

The fibers were dyed according to the standard dyeing method (GB 2391-80) of the People's Republic of China.[17]

The dye exhaustion ratio [$E$ (%)] was calculated as follows:

$$X = \frac{B \times 100}{A \times n} \quad (2)$$

$$E = 100 - X \quad (3)$$

where $X$ is the dye content in the dye residual solution (%), $A$ is the absorbance value of the diluted

**TABLE I**
**Crystallinity and Orientation of the Ionicell Fibers**

| Sample | Draw ratio | Crystallinity (%) | Crystalline orientation factor | Birefringence | Amorphous orientation factor |
|---|---|---|---|---|---|
| 1 | 2.4 | 51.69 | 0.788 | 0.02636 | 0.247 |
| 2 | 3.5 | 54.21 | 0.831 | 0.02867 | 0.267 |

**TABLE II**
**Mechanical Properties of the Ionicell Fibers**

| Sample | Draw ratio | Tensile strength (cN/dtex) | Initial modulus (cN/dtex) | Elongation at break (%) |
|---|---|---|---|---|
| 1 | 2.4 | 2.64 ± 0.17 | 35.0 ± 2.44 | 8.0 ± 1.28 |
| 2 | 3.5 | 2.93 ± 0.18 | 40.3 ± 3.65 | 7.0 ± 0.85 |

dye standard solution, $B$ is the absorbance value of the diluted dye residual solution, and $n$ is the diluted ratio of the dye standard solution to the dye residual solution.

Moreover, the dye fixing ratio [$F$ (%)] was obtained according to the following equation:

$$Y = \frac{D \times 100}{C \times n} \tag{4}$$

$$F = E - Y \tag{5}$$

where $Y$ is the unfixed dye content in the soaping residual solution (%), $C$ is the absorbance value of the diluted soaping standard solution, $D$ is the absorbance value of the diluted soaping residual solution, and $n$ is the diluted ratio of the soaping standard solution to the soaping residual solution.

All absorbance values were measured with a UV-3000 spectrophotometer (Shimadzu, Kyoto, Japan). The higher the dye exhaustion ratio and the dye fixing ratio were, the better the dyeing properties of the fibers were.

The dyeing quality of the fibers was evaluated with a color yield parameter ($K/S$). The determination of $K/S$ values of the dyed samples was carried out on a Datacolor SF600 computer color matching system (Datacolor International, USA).

## RESULTS AND DISCUSSION

### Rheological behavior of the cellulose/[BMIM]Cl solution

Figure 3 illustrates lg $\eta_a$–lg $\dot{\gamma}$ flow curves of 8% cellulose/[BMIM]Cl solutions at different temperatures ($\dot{\gamma}$ is the shear rate, and $\eta_a$ is the apparent viscosity). The viscosity of the solution obviously decreased with an increase in $\dot{\gamma}$, and this shows typical shear-

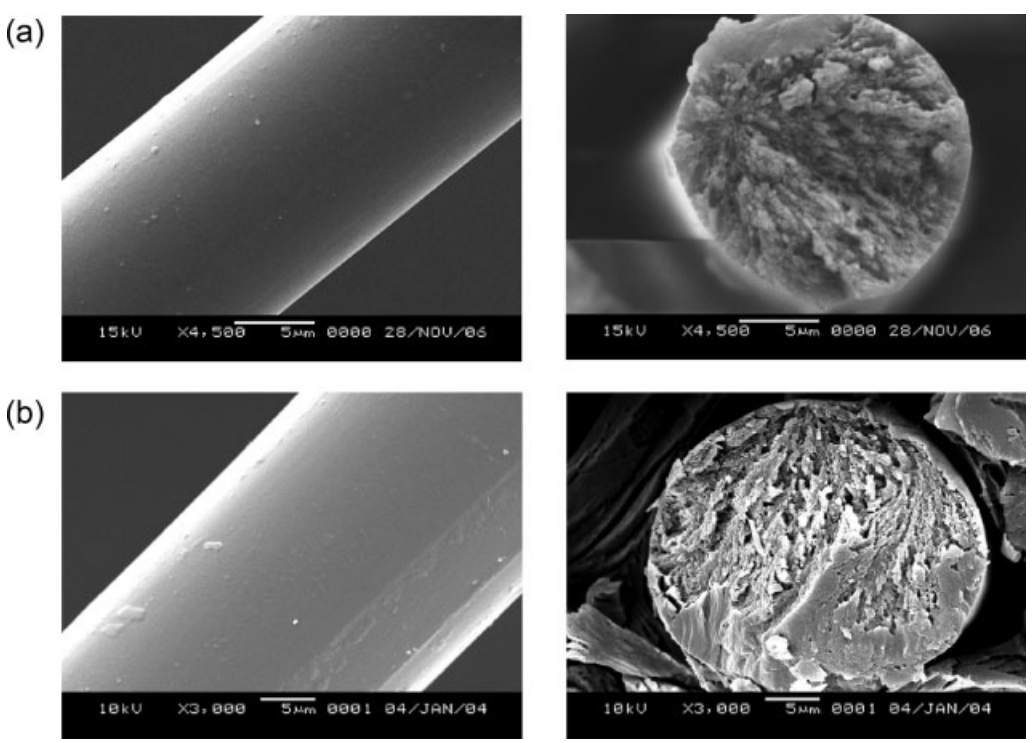


**Figure 5** Scanning electron microscopy photographs of surfaces and cross sections of (a) ionicell fibers and (b) lyocell fibers.

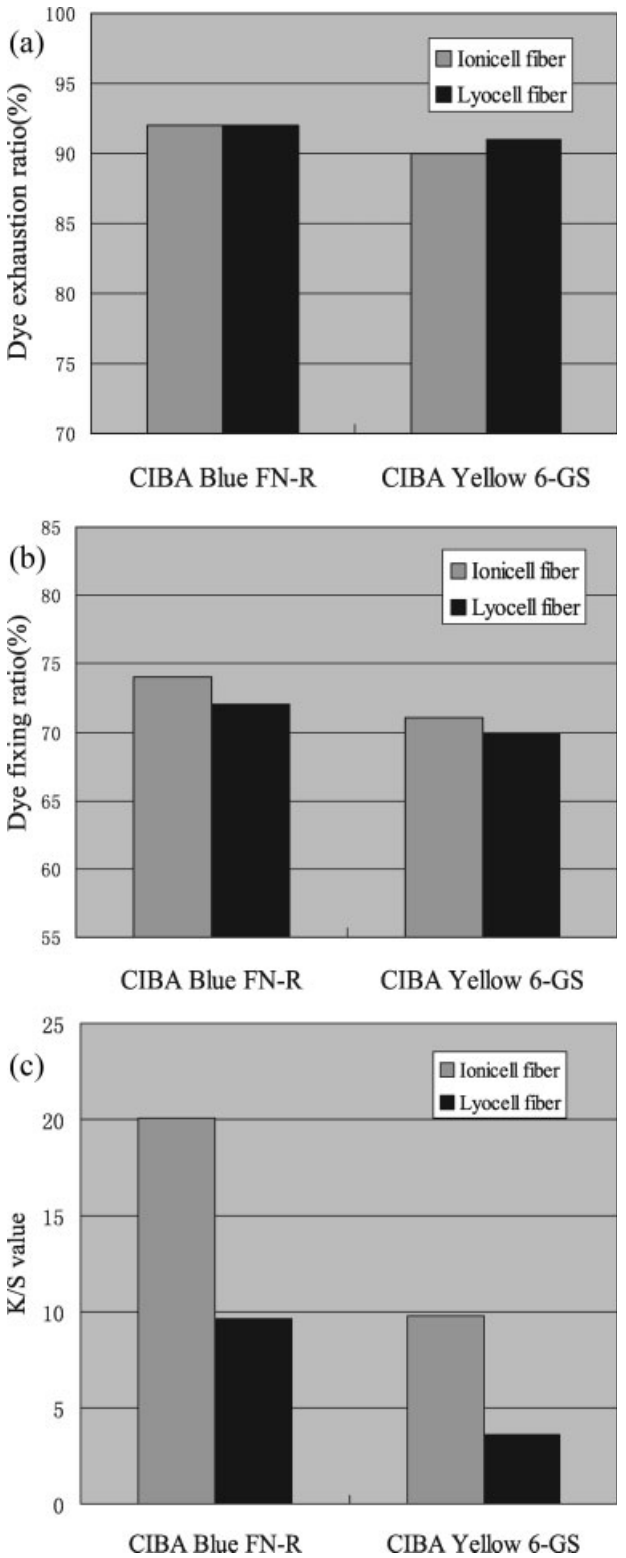


**Figure 6** Comparison of the dyeing properties of the ionicell fibers and lyocell fibers: (a) dye exhaustion ratio, (b) dye fixing ratio, and (c) *K/S* value.

thinning behavior. Moreover, with the temperature increasing, the flow curve of the solution descended, and $\eta_a$ showed a tendency to decline. In addition, Figure 3 shows that when lg $\dot{\gamma}$ was greater than 2, the lg $\eta_a$–lg $\dot{\gamma}$ flow curves of the solution at different temperatures almost overlapped; that is, the temperature had little influence on $\eta_a$ of the solution when $\dot{\gamma}$ was more than 100 $s^{-1}$. This means that the system could be spun at a lower temperature without the spinning temperature being increased if $\dot{\gamma}$ of the spinning dope at the spinneret is higher than 100 $s^{-1}$; this is helpful for optimizing the process parameters. In the experiments of this study, $\dot{\gamma}$ was greater than $10^3$ $s^{-1}$, so the spinning temperature was set at 85°C after comprehensive consideration.

### Crystal structure of the fibers

Figure 4 shows powder WAXD patterns of the original cellulose pulp and the cellulose fibers regenerated from cellulose/[BMIM]Cl solutions (ionicell fibers). The original cellulose pulp had a cellulose I crystal structure, as indicated by the typical diffraction peaks at 2θ values of 14.9, 16.4, and 22.7°. However, after dissolution and subsequent coagulation, the regenerated ionicell fibers exhibited diffraction patterns typical of a cellulose II structure. These results indicate that the transformation from cellulose I to cellulose II occurred after the dissolution and spinning; this is similar to the transformation of the cellulose crystal structure in the lyocell process.

### Crystallinity and orientation of the fibers

In this study, two fiber samples were prepared from 8% cellulose/[BMIM]Cl solutions with different draw ratios, and the crystallinity and orientation of the ionicell fibers are listed in Table I. The crystallinity, birefringence, crystalline orientation factor, and amorphous orientation factor of the ionicell fibers increased with the draw ratio increasing. The reason is that with the draw ratio increasing, the spinning tension in the spinning line improved, the macromolecules gradually aligned in an orderly fashion along the direction of drawing, and then the orientation of the fibers increased. At the same time, the crystallinity of the fibers increased because of the crystallization induced by the orientation.

### Mechanical properties of the fibers

The mechanical properties of the ionicell fibers are listed in Table II. With an increase in the draw ratio,

**TABLE III**
**Comparison of the Antifibrillation Properties for the Ionicell Fibers and Lyocell Fibers**

| Sample | Wet-abrasion value (s) |
|---|---|
| Ionicell fibers | 55.60 ± 2.32 |
| Lyocell fibers | 55.34 ± 2.89 |

the tensile strength and initial modulus of the ionicell fibers improved, whereas the elongation at break decreased. It is known that the tenacity of fibers mainly relies on the orientation of the amorphous phase, and the modulus depends on the crystallinity and the crystal orientation. Therefore, the mechanical properties of the ionicell fibers corresponded with the crystallinity and orientation of the ionicell fibers listed in Table I.

Table II shows that the ionicell fibers had better mechanical properties that were similar to those of lyocell fibers prepared under similar spinning conditions on the same spinning equipment.[12] To obtain fibers with better mechanical properties, spinning equipment with a metering pump and a smaller orifice spinneret were used, and ionicell fibers with a tenacity of 4.28cN/dtex and a modulus of 56.8cN/dtex were prepared. Further work is being carried out to optimize the spinning parameters and fiber properties.

### Morphology of the fibers

Figure 5 shows scanning electron microscopy photographs of ionicell fibers and lyocell fibers. We can clearly see that the surfaces of the two fibers were all smooth without any obvious crevices or flaws. In addition, the cross section of the ionicell fiber was as round as that of the lyocell fiber. Moreover, a comparison of the cross-section photographs shows that there were many voids in the cross section of the lyocell fibers, whereas the ionicell fibers had a compact structure, and almost no voids could be found.

### Dyeing properties of the fibers

The dyeing properties of the fibers were estimated with the dye exhaustion ratio, dye fixing ratio, and *K/S* value (Fig. 6). Figure 6(a,b) compares the dye exhaustion ratio and dye fixing ratio of the ionicell fibers and lyocell fibers, respectively. The greater the dye exhaustion ratio and the dye fixing ratio were, the better the dyeing properties were of the fibers. The dye exhaustion ratios of the ionicell fibers and lyocell fibers were similar, whereas the dye fixing ratio of the ionicell fibers was slightly higher than that of the lyocell fibers. Therefore, reactive dyes suitable for the lyocell fibers were also usable for the ionicell fibers.

Figure 6(c) compares the *K/S* values for the ionicell fibers and lyocell fibers. The higher the *K/S* value of the fibers was, the brighter the color of the dyed fibers was. The *K/S* values of the ionicell fibers were much higher than those of the lyocell fibers. Therefore, the color of the dyed ionicell fibers was brighter than that of the lyocell fibers.

On the basis of these results, it could be concluded that the ionicell fibers had better dyeing properties than the lyocell fibers.

### Antifibrillation properties of the fibers

The fibrillation phenomenon is the formation of microfibrils on the surface of cellulosic fibers, particularly in a wet state. Generally, all cellulosic fibers have a fibrillation tendency, whereas the fibrillation degree differs according to the different processes and materials. In this study, the antifibrillation properties of the fibers were determined with the wet-abrasion values. The greater the wet-abrasion value was, the better the antifibrillation properties of the fibers were. Table III compares the antifibrillation properties of the ionicell fibers and lyocell fibers. The wet-abrasion value of the ionicell fibers was similar to that of the lyocell fibers, and this means that the ionicell fibers and lyocell fibers had similar antifibrillation properties.

## CONCLUSIONS

In this study, a typical ionic liquid, [BMIM]Cl, was used as a solvent for cellulose; the rheological behavior of the cellulose/[BMIM]Cl solution was investigated, and the regenerated cellulose fibers were prepared by a dry–wet-spinning method. The results showed that the cellulose/[BMIM]Cl solution was a typical shear-thinning fluid, and the temperature had little influence on $\eta_a$ of the solution when $\dot{\gamma}$ was higher than 100 $s^{-1}$; this indicated that the spinning temperature could be decreased to avoid further degradation of cellulose if a high $\dot{\gamma}$ value was applied in the spinning process. In addition, the prepared fibers had a cellulose II crystal structure, just like lyocell fibers, and the orientation and crystallinity of the fibers increased with the draw ratio increasing, so the mechanical properties of the fibers improved. In this study, fibers with a tenacity of 4.28cN/dtex and a modulus of 56.8cN/dtex were prepared successfully. Moreover, the fibers had a smooth surface as well as a round and compact structure; the dyeing and antifibrillation properties of the fibers were similar to those of lyocell fibers. Therefore, cellulose fibers from the ionic liquid [BMIM]Cl could be a new kind of environment friendly cellulose fiber following lyocell fibers.

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