

Effects of Coagulation Conditions on Properties of Multifilament Fibers Based on Dissolution of Cellulose in NaOH/Urea Aqueous Solution

Yuan Mao,^{*,†,‡} Lina Zhang,^{*,†} Jie Cai,[†] Jinping Zhou,[†] and Tetsuo Kondo[§]

Department of Chemistry, Wuhan University, Wuhan 430072, China, and Biomaterial Design, Laboratory, Bio-Architecture Center and Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, Japan

Effects of coagulation temperature, coagulants, and wet-spinning methods on structure and properties of novel regenerated cellulose (RC) fibers prepared from cellulose in 7.5 wt % NaOH/11 wt % urea aqueous solution on pilot scale spinning machine by one- and two-stage coagulation were investigated by tensile testing, optical microscopy, scanning electron micrograph, and wide-angle X-ray diffraction. The results indicated that H₂SO₄/Na₂SO₄ and H₂SO₄ aqueous solutions are potential coagulants for NaOH/urea system and fibers wet-spun from the two-stage coagulation obviously exhibited the better mechanical properties than those from the one-stage coagulation. The optimal coagulation conditions for two-stage coagulation are 10 wt % H₂SO₄/15 wt % Na₂SO₄ for the first coagulation bath and 5 wt % H₂SO₄ for the second bath or 5 wt % H₂SO₄/15 wt % Na₂SO₄ for the first coagulation bath and 10 wt % H₂SO₄ for the second bath. Moreover, the tensile strength of novel fibers increased with a drop in coagulation temperature. The diffusion rate between the coagulant and solvent plays a major role in determining the mechanical properties of the cellulose fibers. Our spinning process was quite different from that of the viscose process, in which orientation and coagulation proceed more or less simultaneously. The production method of this fiber wet-spun could be suitable in the wide range of coagulation conditions, compared to the viscose one.

Introduction

Cellulose as an environmentally friendly material can be widely used to yield various useful products because of its renewability, biodegradability, and derivatizability.¹ Utilizing cellulose to spin fibers has a long history in the evolution of humankind.² Nowadays, regenerated cellulose fibers have developed a series of application for apparel, functional materials, nanometer technology, microwave technology, etc.^{3–7} It is noted that yielding fibers in each application require different physical properties such as textile fibers which should have a low modulus and tenacity but high elongation at break and fibers for technical applications such as tire yarns which should have an intermediate modulus and strength.^{3,8} Usually, the physical properties of fibers are intimately related to the coagulation condition, spinning procedure, and the resulting morphological characteristics such as pore sizes and cross-sectional shapes.⁹ Rayon fibers based on the traditional viscose method, as the oldest regenerated cellulose (RC) man-made fibers, can be date back to the early 1900s.¹⁰ Fibers prepared from the wet-spinning process generally exhibit a skin–core structure with larger voids (around 25–150 nm) in the core region and a densified skin layer with pores of about 5–25 nm; the thickness of the skin is mainly controlled by the concentration of Zn²⁺.^{11,12} Moreover, different physical properties and cross-sectional shapes of fibers can be obtained by choosing the proper coagulation conditions and wet-spinning method such as 13 wt % H₂SO₄/25 wt % Na₂SO₄/2 wt % ZnSO₄ at 50 °C for multifilaments with the

lobulate shape and two-stage coagulation with 0.4 wt % H₂SO₄/15 wt % Na₂SO₄/5 wt % ZnSO₄ at 40 °C and 4 wt % H₂SO₄ at 70 °C for high-tenacity fibers with the near-circle shape. Recently, an environmentally friendly process of cellulose fiber spinning using the direct solvent system such as *N*-methylmorpholine-*N*-oxide (NMMO) has been rapidly developed, leading to a new class of man-made cellulosic fiber with the generic name lyocell.^{11,13} The commercial lyocell fiber can be characterized by good tensile properties as compared with viscose, by a circular cross-section, a dense structure with high crystallinity, and a tendency of fibrillation in the wet state. Two-stage precipitation (alcohol–water) in dry-jet wet-spinning results in a lyocell-type fiber with low fibrillation tendency due to a skin–core structure with a nonfibrillating skin and the usual high tenacity core.¹¹ This process provides a new promising alternative method to the viscose process with hazardous byproducts.¹⁴

In our laboratory, another cheap and nonpolluting direct solvent of cellulose, NaOH/urea aqueous solution, has been developed and studied.^{15–19} Cellulose could be completely dissolved to obtain transparent solution within 2 min in laboratory at the ambient temperature below 20 °C when 7.5 wt % NaOH/11 wt % urea aqueous solution was precooled to –10 to –12 °C.¹⁸ In the previous work, the effects of coagulants and coagulation conditions on physical properties and resulting structure and morphology of RC membranes were systematically investigated.²⁰ The RC membranes showed the one-phase homogeneous porous structure with better physical properties and larger pore size than commercially available cellophane in the wide range of the coagulation conditions.^{20–22} Moreover, the RC fibers were successfully prepared by a wet-spinning method both from a simple homemade and pilot scale spinning machines, showing the higher tensile strength than that of the viscose fiber and circular shape in the cross-section.^{19,23,24} In this work, we prepared the wet-spun RC fibers from cellulose/NaOH/urea system via pilot plant by two-stage coagulation to

* To whom correspondence should be addressed. E-mail: ym07@fsu.edu (Y.M.); lnzhang@public.wh.hb.cn (L.Z.). Phone: 850-644-1098(Y.M.); +86-27-87219274(L.Z.). Fax: 850-644-1366 (Y.M.); +86-27-68756661 (L.Z.).

† Wuhan University.

‡ Current address: National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, FL 32310-3706.

§ Kyushu University.

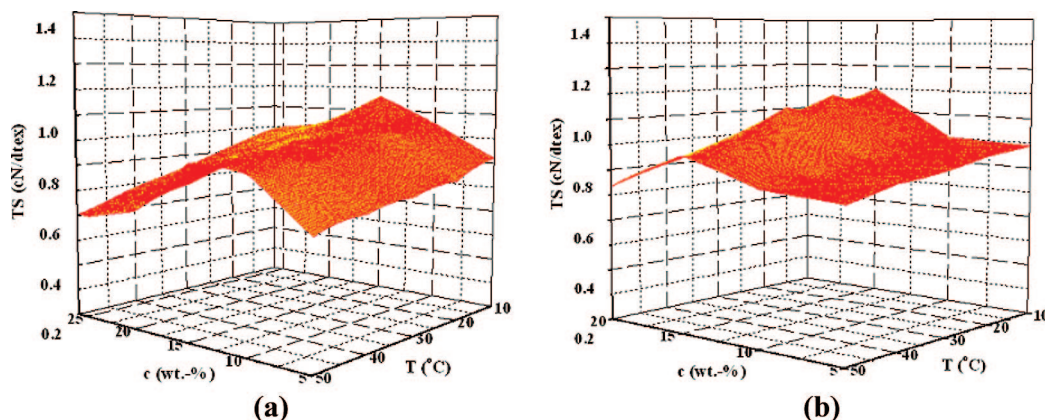


Figure 1. Effects of coagulation temperature and coagulant concentration on tensile strength of novel fibers coagulated from (a) H_2SO_4 aqueous solution and (b) 10% $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ aqueous solution.

Table 1. Spinning Parameters and Coagulation Conditions for Regenerated Novel Fibers by One-Stage Wet-Spinning

coagulation bath	T (°C)	flow speed at spinneret (m/min)	flow speed		
			v_{I} (m/min)/SDR _I ^a	v_{II} (m/min)/SDR _{II}	v_{III} (m/min)/SDR _{III}
15% Na_2SO_4	10–50	94.8			
5–20% HOAc	10	94.8	40.3/0.43		
5–20% $(\text{NH}_4)_2\text{SO}_4$	10	94.8	40.3/0.43	42.6/1.06	
5–25% H_2SO_4	10–50	94.8	40.3/0.43	42.6/1.06	44.9/1.05
10% $\text{H}_2\text{SO}_4/$ 5–25% Na_2SO_4	10–50	94.8	40.3/0.43	42.6/1.06	44.9/1.05

^a Spin draw ratio.

Table 2. Mechanical Properties and Spinnability of Novel Fibers Spun from One-Stage Coagulation^a

sample	coagulation bath	tensile Strength (cN/dtex)/standard error		elongation at break (ϵ_b %)/standard error		$\overline{\text{DP}}$	spinnability
		dennier (dtex)					
F-1	15% Na_2SO_4					590	×
F-2	15% HOAc	0.71/0.010	6.23	12.2/0.915			Δ
F-3	12% $(\text{NH}_4)_2\text{SO}_4$	0.82/0.067	6.01	9.60/0.815			Δ
F-4	15% H_2SO_4	1.06/0.020	8.48	13.7/0.672			○
F-5	10% $\text{H}_2\text{SO}_4/$ 15% Na_2SO_4	1.10/0.029	4.02	10.3/0.647			○

^a (○) Proper coagulation and good spinnability; (Δ) weak coagulation but unstable spinning fiber; (×) too slow coagulation rate with no spinnability. The coagulation temperature is controlled at 10 °C.

drive the industrial interest. The coagulation conditions for wet-spinning and characteristic features of the novel fibers including structure and morphology were investigated and compared with other commercially available regenerated cellulose fibers.

Experimental Section

Materials. The cellulose (cotton linter pulp) was provided by Hubei Chemical Fiber Group Ltd. (Xiangfan, China), and the α -cellulose content was more than 95%. The cellulose was used without further purification. The viscosity-average molecular weight (\overline{M}_η) in cadoxen was determined using viscometry to be 10.1×10^4 (degree of polymerization, $\overline{\text{DP}} = 620$). The sheets of cellulose were shredded and dried for 8 h in a vacuum oven and stored in a desiccator prior to use. A small amount of plasticizer with 5 wt % Marpol FR-700 (lipid and pharmacy chamber) aqueous solution was used to finish the multifilament. NaOH and urea of analytical grade were used. Unless otherwise noted, all other chemical reagents were purchased from commercial resources in China and were of industrial grade.

Preparation of Concentrated Fiber Spinning Dopes. The cellulose solution in a NaOH/urea aqueous solution was prepared according to our innovative method.^{18,19} The solvent, NaOH/urea aqueous solution (7.5:11 in weight percent), was precooled to -12 °C. Then the cellulose in dry base was immediately dispersed in it under vigorous stirring at ambient temperature for 5 min. The dispersed cellulose was dissolved within 5 min with stirring at about 700 rpm to form transparent cellulose dope. To ensure the continuity at spinning, the resulting cellulose solution was filtered through 400 pores meshes to remove insoluble particles and degassed in a vacuum oven under reduced pressure for 10–25 h at 5 °C. The solution (4.0–4.8 wt %) thus obtained was immediately employed in wet-spinning of the cellulose fibers.

Wet-Spinning. Multifilament spinning of the cellulose solution was carried out on a pilot scale spinning apparatus (see Figure 1 in ref 25), constructed by the Hubei Chemical Fiber Group Ltd. Fiber extrusion proceeded by first transferring the spinning solution to the pressure cylinder cooled at 0–5 °C. The solution was first forced through a filtration pack and then extruded through a platinum spinneret (30 holes, 120 μm hole diameter) into the first coagulation bath. The coagulated filaments were rolled up at the Nelson-type roller, passed through the second coagulation bath, washed with a washing roller (water, 65 °C) until the pH value of the fibers was about 7, and then dipped through the finishing oil bath. Finally, the fibers were dried at the roller heater having a surface temperature of 90 °C and wound on a spool. The samples of fiber for coagulation conditions studies were obtained under the same extrusion conditions. The extrusion velocity, Nelson-type roller I, Nelson-type roller II, and roller heater speed were maintained at 94.8, 40.3, 42.6, and 44.9 m/min, respectively.

In order to explore the spinnability and select appropriate coagulation conditions for two-stage wet-spinning on a pilot scale, a series of aqueous solutions including H_2SO_4 , $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$, HOAc, $(\text{NH}_4)_2\text{SO}_4$, and Na_2SO_4 were first examined in a one-stage wet-spinning process. The composition and temperature of these coagulation baths were varied from 5–25 wt % and 10–50 °C, respectively. Resulting novel fiber samples were coded from F-1 to F-5 and stored in a desiccator until tested.

Characterizations. The \overline{M}_η values of the cellulose materials and the fiber samples were determined in cadoxen at 25 °C using a Ubbelohde viscometer and were calculated by the Mark–Houwink equation:²⁶

$$[\eta] = 3.85 \times 10^{-2} (\overline{M}_w)^{0.76} \text{ (mL/g)} \quad (1)$$

Table 3. Coagulation Conditions and Mechanical Properties of Novel Fibers Wet-Spun from the NaOH/Urea Solvent System on a Pilot Scale Spinning Machine with Two Coagulation Baths

cellulose conc (wt %)	first coagulation bath	T ($^{\circ}\text{C}$)	second coagulation bath	T ($^{\circ}\text{C}$)	TS (cN/dtex)/standard error	ET (%) /standard error
4	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10				
4	5% H ₂ SO ₄ /15% Na ₂ SO ₄	10	5% H ₂ SO ₄	10	1.16/0.012	10.2/0.509
4	5% H ₂ SO ₄ /15% Na ₂ SO ₄	10	10% H ₂ SO ₄	10	1.30/0.047	10.1/0.620
4	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	5% H ₂ SO ₄	10	1.33/0.025	9.20/0.358
4	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	10% H ₂ SO ₄	10	1.18/0.069	11.7/0.352
4.5	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	5% H ₂ SO ₄	10	1.49/0.041	9.70/0.374
4.5	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	10% H ₂ SO ₄	10	1.22/0.037	13.4/0.431
4.5	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	15% H ₂ SO ₄	10	1.20/0.033	10.6/0.356
4.8	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	5% H ₂ SO ₄	10	2.00/0.088	9.50/0.393
4.8	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	5% H ₂ SO ₄	20	1.61/0.048	10.2/0.623
4.8	10% H ₂ SO ₄ /15% Na ₂ SO ₄	10	5% H ₂ SO ₄	30	1.52/0.029	11.9/0.548

The crystalline measurement of regenerated cellulose fibers was performed with a reflection method on a wide-angle X-ray diffraction (WAXD) diffractometer (D/MAX-1200, Rigaku Denki, Japan). Samples were vacuum-dried for 24 h before measurement and cut into particle-like size so as to erase the influence from the crystalline orientation of each fiber sample.²⁷ The patterns with Cu K α radiation ($\lambda = 1.5406$) at 40 kV and 30 mA were recorded in the region of 2θ from 4° to 40° . The crystalline degree (χ_c) was calculated by peak areas responsible for the (110), (110), and (200) planes, separated with the Lorentz–Gaussian peak separation method.²⁸

X-ray diffraction measurements were basically performed according to a previous report.²⁹ WAXD photographs were taken on flat film using nickel-filtered Cu KR radiation produced by a Rigaku RINT-2500HF X-ray generator at 40 kV and 40

mA. The WAXD intensity curves with a scanning speed of $0.5^{\circ}/\text{min}$ were measured by a transmission method using a scintillation counter at 40 kV and 200 mA through the angular range 2θ for the equatorial and the meridional scan to the drawing direction; $2\theta = 5-35^{\circ}$ and $10-80^{\circ}$, respectively. Instrumental broadening was corrected using Si powder as a standard.

Morphology of the cross-section of the fibers was observed on an optical polarizing microscope (Leica DMLP, Germany). A bundle of fibers were embedded in celloidin and allowed to harden for about 5 min at 25°C . Cross-sections normal to the fiber axis of about 2 mm thickness were prepared using a Struers Accutom. The cross-sections were ground and polished down to a thickness between 10 and $40\ \mu\text{m}$ and cemented to a microscope glass slide with glycerol. A commercial product of viscose rayon provided by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China) was used in comparison with the novel fibers. Scanning electron micrographs (SEM) were taken on a Hitachi X-650 scanning electron microscope. The fibers on each roller were frozen in liquid nitrogen, immediately snapped, and then vacuum-dried. The surface and the cross-section of fibers were sputtered with gold, then observed and photographed.

The linear density of the cellulose fibers was estimated assuming that the cross-section of the fiber is a true circle, by weighting the dried fiber with 90 cm in length. The weight (milligram per meter) corresponds to 1 tex or 1/9 denier. Tensile strength (σ_b) and elongation at break (ϵ_b) of the dried fibers were measured on a universal tensile tester (XQ-1, Shanghai Textile University, China) according to ASTM method D2256-80. The fibers were first preconditioned for one day at 21°C and 65% relative humidity (RH); a test length of 50 mm was

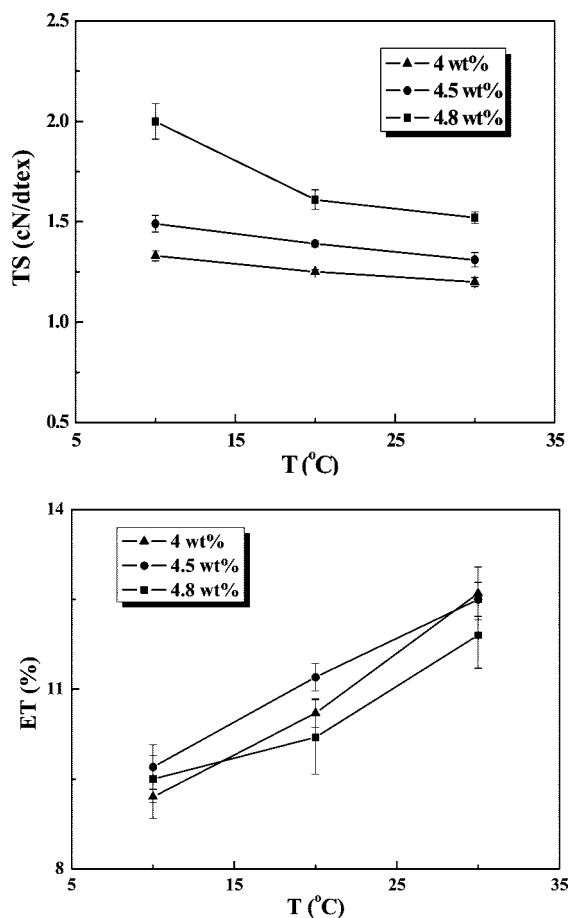


Figure 2. Effects of coagulation temperature and cellulose concentration on the tensile strength and elongation at break of novel fibers spun from two-stage coagulation (the first coagulation bath controlled at 10 wt % H₂SO₄/15 wt % Na₂SO₄, 10°C).

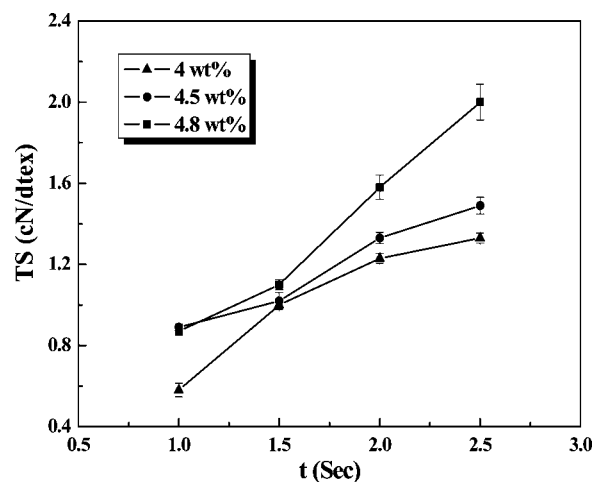


Figure 3. Effects of coagulation time and cellulose concentration on the tensile strength of novel fibers spun from the two-stage coagulation (the first coagulation bath controlled at 10 wt % H₂SO₄/15 wt % Na₂SO₄, 10°C).

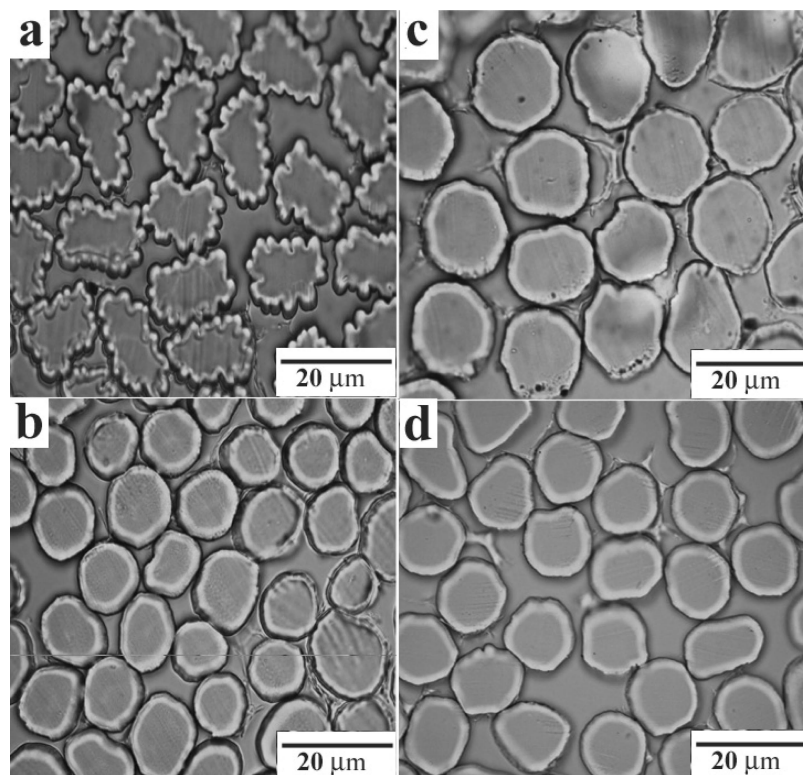


Figure 4. Cross-sectional shapes of (a) viscose filaments coagulated from $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4/\text{ZnSO}_4$ aqueous solution, (b) novel fibers coagulated from 15 wt % H_2SO_4 aqueous solution, (c) 10 wt % $\text{H}_2\text{SO}_4/15$ wt % Na_2SO_4 aqueous solution by one-stage coagulation, and (d) novel fibers coagulated from 10 wt % $\text{H}_2\text{SO}_4/15$ wt % Na_2SO_4 and 5 wt % H_2SO_4 by two-stage coagulation observed with optical microscopy.

used for fibers at a speed of 5 mm/min. The σ_b and ε_b values represented averages of the 20 strongest measurements of 50 multifilaments.

Results and Discussion

Preliminary Selection of Coagulation Conditions and Coagulants. Preliminary selection of coagulation conditions and coagulants was performed on the pilot scale spinning apparatus by one-stage wet-spinning. Table 1 summarizes the spinning parameters and coagulation conditions for regenerated novel fibers. Figure 1 shows the three-dimensional plots of σ_b-c-T for novel fibers wet-spun from H_2SO_4 and 10 wt % $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ aqueous solutions, respectively. Clearly, as coagulant concentration increases, the σ_b values of the fibers increase slightly at first, but as concentration further increases, σ_b decreases. The optimal coagulation conditions for the fibers are 15 wt % H_2SO_4 and 10 wt % $\text{H}_2\text{SO}_4/15$ wt % Na_2SO_4 , and the σ_b values achieve 1.06 and 1.10 cN/dtex, respectively. The results may indicate that coagulant in higher concentration increases the concentration gradient between nonsolvent and solvent in the cellulose dope, which produces coagulation that is too fast and thus causes serious condensing and frail, whereas a low concentration of coagulant interferes the coagulation rate, regeneration only occurs in the surface of the fibers, and the internal is still a semisolid cellulose gel, which consequently lead to a drop of the tensile strength of fibers.²³ In addition, coagulation temperature has a negative effect on the mechanical properties of fibers. The fibers wet-spun at relatively low temperature obviously possess higher tensile strength than that at relatively high temperature as shown in Figure 1, which can be explained by the fact that the higher temperature could accelerate the mobility of all components in the coagulation system and increase the coagulation rate. This rapid precipitation

gives the cellulose chains less time to pack themselves into an ordered structure, resulting in the lower mechanical properties.^{12,30,31} Therefore, highly improved fiber structure and properties could be obtained when a lower bath temperature is applied in our cellulose/NaOH/urea solution system. It is noted that the change of the σ_b values caused by coagulant concentration is more remarkable than that by coagulation temperature, suggesting that the coagulant concentration is the main factor determining the mechanical properties of the fibers.

Table 2 shows the mechanical properties and spinnability of novel fibers spun from different coagulants at proper concentration and lower temperature. It is clear that novel fibers exhibit different physical properties under different coagulant nature. Fibers wet-spun from weak acidic and salt coagulants obviously show the lower tensile strength than those from the wild acidic aqueous solution. During the wet-spinning process, it is even difficult to form stable fibers with 15 wt % Na_2SO_4 aqueous solution at the temperature range from 10 to 50 °C. However, the fibers through the Nelson-type roller I and II could be formed by coagulating with 15 wt % HOAc and 12 wt % $(\text{NH}_4)_2\text{SO}_4$ aqueous solution, respectively, but unstable wet-spinning. Interestingly, the stable fibers spun from 10 wt % $\text{H}_2\text{SO}_4/15$ wt % Na_2SO_4 and 15 wt % H_2SO_4 could be rolled up even on the Nelson-type roller III easily, resulting in the better physical properties. These results suggested that $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ and H_2SO_4 could be used as potential coagulants for wet-spinning in our NaOH/urea system.

Coagulation Conditions of Multidrawing Two-Stage Wet-Spinning. Multidrawing processes with two coagulation baths were used to further improve the mechanical properties of regenerated cellulose fibers with compact structure (and, thus, increase crystal orientation), and the optimal conditions of the second coagulation bath were explored. On the basis of the

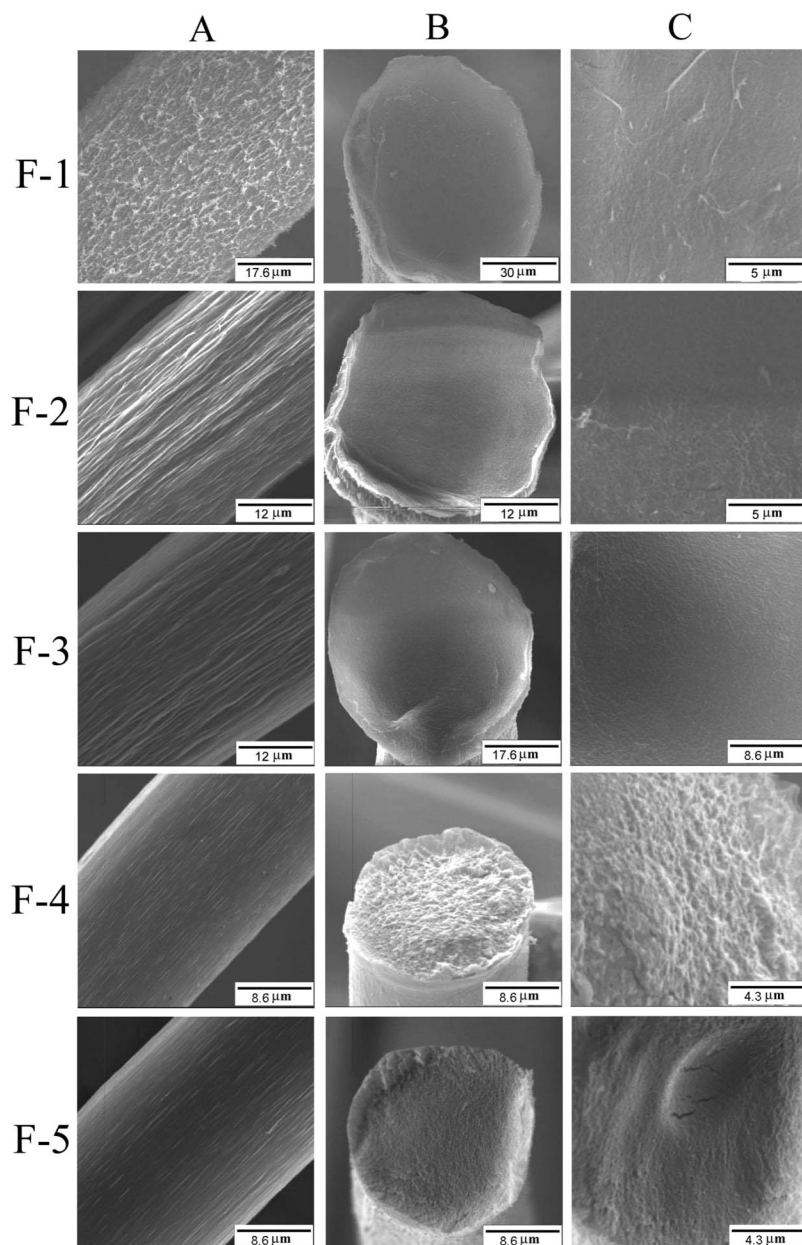


Figure 5. SEM images of the surface (A) and cross-section (B) and enlargement of the cross-section (C) for F-1–F-5 fibers, respectively.

above results, a 10 wt % H_2SO_4 /15 wt % Na_2SO_4 or 5 wt % H_2SO_4 /15 wt % Na_2SO_4 aqueous solution controlled at lower temperature 10 °C was adopted as the first coagulation bath and H_2SO_4 aqueous solution as the second coagulation bath. The composition and temperature for the second coagulation bath were studied and varied from 5–15 wt % and 10–50 °C, respectively. Table 3 shows the coagulation conditions and resulting mechanical properties of novel fibers. The fibers wet-spun by one-stage coagulation show the lower tensile strength and hardly roll up at the take-up device. On the contrary, the fibers wet-spun by two-stage coagulation obviously possess much higher tensile strength in the wide range of coagulation conditions, which lie in the range of 1.16–2.00 cN/dtex, nearly close to that of commercial available fiber products.^{12,14,31,32} It is reasonable to attribute this to the fact that the coagulation process for only the one-stage coagulation could be not full and fibers which emerged from the first coagulation bath could exhibit a highly elastic gel state because of the short coagulation time, while during the washing roller process to wash away inorganic ions, water actually acts to promote the regeneration

of cellulose fibers and the formation of the irregular inner structure of the fibers with the subsequently multiroller drawing. Interestingly, we found that novel fibers wet-spun from the two-stage coagulation with H_2SO_4 including the first and second coagulation bath at the 15 wt % critical value display relatively better mechanical properties than those wet-spun with H_2SO_4 concentrations higher or lower than this critical value, such that the optimal coagulation conditions are 10 wt % H_2SO_4 /15 wt % Na_2SO_4 for the first coagulation bath and 5 wt % H_2SO_4 for the second bath or 5 wt % H_2SO_4 /15 wt % Na_2SO_4 for the first coagulation bath and 10 wt % H_2SO_4 for the second bath.

As mentioned previously, the temperature of the coagulation bath has the same effect on the mechanical properties of fibers. Figure 2 shows the effects of coagulation temperature (T) and cellulose concentration on the tensile strength and elongation at break of novel fibers. An increase in the coagulation temperature from 10 to 30 °C leads to a decrease in tensile strength but an increase in breaking elongation of fibers irrespectively of the coagulant composition and cellulose content. It is noted that the elongation at break from 9.2% to

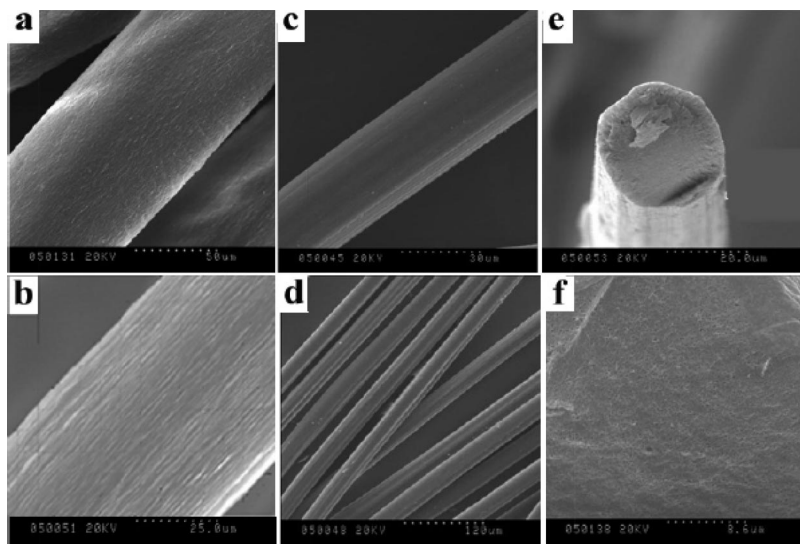


Figure 6. SEM micrographs of side surface sections for novel fibers on (a) Nelson-type roller I, (b) Nelson-type roller II, (c) roller heater, (d) take-up device, (e) cross-section for fibers, and (f) the enlargement of a cross-section.

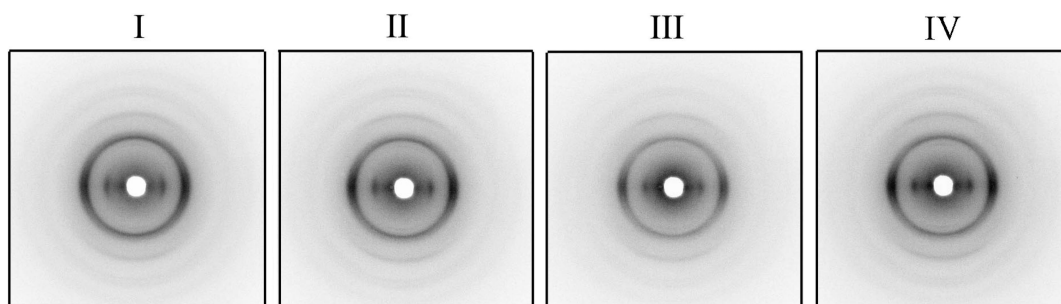


Figure 7. 2D WAXD flat plate images of novel fibers on the (I) Nelson-type roller I, (II) Nelson-type roller II, (III) roller heater, and (IV) take-up device.

Table 4. Physical Property Comparison between Novel Fibers and Other Commercial Regenerated Fibers

comparison	cross-section		crystallinity (%)	crystalline type	DP	tensile strength (cN/dtex)/standard error	elongation at break (%) / standard error	ref
	shape	morphology						
novel fibers	round/oval	homogeneous and dense	57–63	II	590	1.16/0.012–2.00/0.088	9.20 / 0.358–13.4/0.431	this work
cuprammonium fiber	round/oval	multilayers	ca. 43	II	ca. 500	2.05	9.10	11, 37
viscose rayon	lobuate	core/skin	ca. 29	II	ca. 300	2.00	15.0	11, 35
NMMO fibers	round/oval	homogeneous and dense	ca. 42	II	ca. 600	3.15	15.4	11, 14

13.4% is closer, even larger than that of the other fibers (5.0–15.4%), indicating the dissolution and regeneration process of cellulose in the NaOH/urea aqueous solution facilitated retaining the elastic properties of natural cellulose fibers.^{12,14,32,33}

Figure 3 clearly shows effects of coagulation time (t) and cellulose concentration on the novel fibers. As shown in Figure 3, 1.0, 1.5, 2.0 and 2.5 s time periods correspond to the time including the coagulation/regeneration and stretch process of the fiber from spinneret to the Nelson-type roller I, Nelson-type roller II, heater roller, and take-up device, respectively. The results indicated that the increase of coagulation/regeneration time during the spinning could be favored for the improvement of the tensile strength of novel fibers. The effect of the cellulose concentration on the mechanical properties was also investigated in this work, and it plays a very important role on mechanical properties of novel fibers. When the cellulose concentration is below 4.0 wt %, it is even hard to form a stable wet-spinning process, but when we increased the cellulose concentration from 4.0 to 4.8 wt %, mechanical properties of the resulting fibers also increased. Moreover, Laszkiewicz et al. have reported that the tensile strength of viscose fibers depends

not only on the cellulose concentration and coagulation conditions, but also on the draw ratio of fibers during the spinning.³² Therefore, the better mechanical properties of the novel fibers could also be due to the significant enhancement in the two-stage wet-spinning process with multiroller drawing.

Coagulation/Regeneration Process during Multidrawing Wet Spinning. Figure 4 shows the cross-sections of fibers wet-spun with the different coagulation conditions and wet-spinning methods observed by optical microscopy, along with that of viscose filaments for comparison. All the novel regenerated fibers show circular cross-sections irrespective of coagulant nature and wet-spinning method, which are markedly different from the lobulate shape of the viscose rayon and similar to cuprammonium rayon (Bemberg) and lyocell fibers.³⁴ This could be due to the difference in physical process and chemical reaction during the wet-spinning. The cross-sections of viscose filaments were approximately round for the fibers straight from spinneret but then shank as a result of acid–alkali neutralization and the reverse xanthation reaction, leading to the lobulate skin–core structure.³⁵ The thickness of the skin could be determined by the depth of penetration of Zn^{2+} into the filaments

before the xanthate groups are split off by the acid in the generation/coagulation bath.¹² However, in the NaOH/urea system, the diffusion rate between the coagulant and solvent plays a major role in determining morphologies and mechanical properties of fibers similar to those of the $\text{NH}_3/\text{NH}_4\text{SCN}$ and $\text{NMMO}/\text{H}_2\text{O}$ systems,^{11,30,31} which can be seen from the different surface morphologies of fibers wet-spun from different coagulants as shown in Figure 5. The SEM image of the F-1 fibers shows a rough surface without any orientation and a porous cross-section, which could attribute to the slower coagulated rate and incomplete regeneration of fibers in 15 wt % Na_2SO_4 aqueous solution. The surface of the F-2 and F-3 fibers shows orientation along the fiber axis to some extent, but with a loose arrangement of cellulose chains. In contrast to the F-2 and F-3 samples, the F-4 and F-5 fibers shows more ordered but compact arrangement on the surface and more regular circular and dense cross-sectional structure, which is also consistent with results of physical properties we discussed above. In view of these results, it is reasonable to believe that the wet-spinning is just a physical sol-gel transition process caused by the nonsolvent diffusion into and solvent out of the cellulose dope, and subsequently uniform physical regeneration of the fibers directly from cellulose "solution" in a quasi-gel state formed mainly by physical cross-linking and residual hydrogen bonds without an asymmetrical chemical reaction on the fibers, leading to the circular cross-section.³⁶

SEM images of the side surface sections and cross-sections of the novel fibers on each roller wet-spun from the pilot scale spinning machine with two-stage coagulation are shown in Figure 6. The fibers after multidrawing process exhibit a dense and homogeneous structure with small voids of pore size from 50 to 150 nm (see Figure 6f). Actually, this porous structure is commonly found in wet-spun fibers.³⁷ As reported in several literature references, the small, submicrometer voids in the fiber which developed during the coagulation stage are believed to be a result of the phase separation process, valid in other wet shaping processes.³⁸ In this case, the wet-spun cellulose fibers from the first coagulation bath are a kind of coagulation of gels containing a large amount of solvent. The concentration and composition changes of the cellulose dope caused by the diffusion between the nonsolvent and solvent during the coagulation lead to the two-phase separation of the cellulose-rich phase in the gel and the cellulose-lean phase in solution. A first nucleus of the cellulose molecules has formed for a lamella and gradually developed the fibrillar cellulose with II family crystal structure from the cellulose-rich phase (see Figure 6a), which is surrounded by the cellulose-lean phase composed of the nonsolvent and solvent extracted from the cellulose dope. The nucleus and growth of cellulose-lean phase in the second coagulation bath lead to the cellulose gels filled with water, resulting in the formation of the submicrometer voids spread in the fibrillar matrix. After drawing concentric fibers during the wet-spinning process, fibrilla of the fibers orient along the axis of the fibers and display denser structure in the surface as shown in Figure 6b and c. A bundle of fibers with a similar circular shape is seen in Figure 6d and e, indicating a smooth surface of homogeneous fibers, which further confirmed the uniform physical coagulation process in the system. With respect to this succession of structure formation steps, the wet-spinning process differs considerably from the viscose process, in which orientation and coagulation proceed more or less simultaneously.

X-ray diffraction has been often used to investigate the crystalline structure and molecular orientation of fiber materials. 2D WAXD patterns of novel fibers with multidrawing process

on each roller are shown in Figure 7. With an increase of the draw ratio, the novel fibers exhibited an increase of preferential orientation along the fiber axis. However, the width and intensity of the characteristic arcs in diffraction patterns tend to be broad and weak, respectively, indicating that the orientation of the novel fibers spun via the preliminary pilot plant is not excellent. But we can believe that there is a potential space to further improve the mechanical properties and final structure of our novel fibers by redesigning the draw-processing step in the Nelson-type rollers and the take-up device. The degree of crystallinity (χ_c) of the novel fibers on each roller were calculated to vary from 0.52 to 0.59. It is noted that despite this increase in draw ratio and in the orientation of the chains, the number of crystalline domains in the fibers did not increase significantly. This may perhaps be attributed to the three-dimensional network structure resulting from the intermolecular hydrogen bonds between chains which are maintained through the drawing process and which can hinder the crystallization of cellulose.²⁹

The comparison of the physical properties for the novel fibers with other commercial regenerated fibers is summarized in Table 4. Novel fibers exhibit higher degree of crystallinity, DP, values and more regular cross-sections than viscose and cuprammonium fibers but are close to those of the NMMO fibers, owing to the similar dissolution and regeneration nature during the wet-spinning.¹¹ It is worth noting that the whole production cycle of the current process (dissolution, filtration, degassing, and spinning) is a much shorter and easier than that of the viscose technology and could take less than 12 h. Byproducts of Na_2SO_4 /urea in the coagulation bath can also be easily separated and recycled by crystallization and flash evaporation because of the remarkable difference in solubility between them. Therefore, the lower cost and lesser toxicity of the NaOH/urea solvent system, and its relative ease for the wet-spinning and recovery process, exhibited some good promise for the development of a more economical and environmentally friendly process for cellulose fibers. However, after all, this solvent system is still relatively new, the mechanical properties of novel fibers shown in Table 4 are not excellent, and it is anticipated that the mechanical properties will be improved significantly by decreasing the molecular weight or crystallinity of cellulose to increase the cellulose concentration further or by an improved spinning pilot machine with special attention on a multistage draw process.

Conclusion

Coagulation temperature and coagulants of novel fibers prepared from NaOH/urea aqueous solution on a pilot scale spinning machine by one-stage and two-stage wet-spinning were studied. The fibers wet-spun from the two-stage coagulation obviously exhibited the better mechanical properties than those from the one-stage coagulation, which lie in the range of 1.16–2.00 cN/dtex for tensile strength and 9.2–13.4% for elongation at break. The optimal coagulation conditions for two-stage coagulation are 10 wt % H_2SO_4 /15 wt % Na_2SO_4 for the first coagulation bath and 5 wt % H_2SO_4 for the second bath or 5 wt % H_2SO_4 /15 wt % Na_2SO_4 for the first coagulation bath and 10 wt % H_2SO_4 for the second bath. The cellulose concentration plays a major role in governing the fibers' mechanical properties. Moreover, the lower temperature is more favorable for fibers with better mechanical properties compared with that of relatively high temperature. The results from optical microscopy and SEM indicated that the wet-spinning process is just a physical sol-gel transition, and subsequently uniform

physical regeneration of the fibers directly from cellulose "solution" in a quasi-gel state and orientation/coagulation proceed more or less simultaneously during the multidrawing process with two coagulation baths. This new approach offers great potential for cellulose fiber on an industrial scale with a cheap, nonpolluting, and shorter production cycle when compared with that of the viscose technology.

Acknowledgment

This work was supported by the National High Technology Research and Development Program of China (863 Program; 2003AA333040 and 2004AA649250), the National Natural Science Foundation of China (59933070 and 20204011), and the Laboratory of Cellulose and Lignocellulosic Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Science, China.

Literature Cited

- (1) Schurz, J. Trends in polymer science a bright future for cellulose. *Prog. Polym. Sci.* **1999**, *24* (4), 481.
- (2) Kobayashi, S.; Uyama, H. Biomacromolecules and bio-related macromolecules. *Macromol. Chem. Phys.* **2003**, *204* (2), 235.
- (3) Shin, Y.; Li, X. S.; Wang, C.; Coleman, J. R.; Exarhos, G. J. Synthesis of hierarchical titanium carbide from titania-coated cellulose paper. *Adv. Mater.* **2004**, *16* (14), 1212.
- (4) Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. Cellulose: fascinating biopolymer and sustainable raw material. *Angew. Chem., Int. Ed.* **2005**, *44* (22), 3358.
- (5) Zabetakis, D.; Dinderman, M.; Schoen, P. Metal-coated cellulose fibers for use in composites applicable to microwave technology. *Adv. Mater.* **2005**, *17* (6), 734.
- (6) Hirano, S.; Midorikawa, T. Novel method for the preparation of N-acylchitosan fiber and N-acylchitosan-cellulose fiber. *Biomaterials.* **1998**, *19* (1), 293.
- (7) Polarz, S.; Smarsly, B.; Schattka, J. H. Hierarchical porous carbon structures from cellulose acetate fibers. *Chem. Mater.* **2002**, *14* (7), 2940.
- (8) Ott, E. *Cellulose and Cellulose Derivatives*; Wiley: New York, 1971; Vol. 5.
- (9) Morton, W. E.; Hearle, J. W. S. *Physical Properties of Textile Fibers*; The Textile Institute: Manchester, 1978; p 12.
- (10) Cross, C. F.; Bevan, E. J.; Beadle, C. British Patent 8700, 1892.
- (11) Fink, H. P.; Weigel, P.; Purz, H. J.; Ganster, J. Structure formation of regenerated cellulose materials from NMMO-solutions. *Prog. Polym. Sci.* **2001**, *26* (9), 1473.
- (12) Liu, C.; Cuculo, J. A.; Allen, T. C.; Degroot, A. W. Fiber formation via solution spinning of the cellulose/ammonia/ammonium thiocyanate system. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29* (2), 181.
- (13) McCorsley, C. C. Akzona Inc., Invs. US 44,161,698, **1979**.
- (14) Niekrazewicz, B.; Czarnecki, P. Modified cellulose fibers prepared by the N-methylmorpholine-N-oxide (NMMO) process. *J. Appl. Polym. Sci.* **2002**, *86* (4), 907.
- (15) Zhou, J.; Zhang, L. Solubility of cellulose in NaOH/urea aqueous solution. *Polym. J.* **2000**, *32* (10), 866.
- (16) Zhang, L.; Zhou, J. *New solvent compounds of cellulose and its application*. Chinese Patent ZL00114486.3, October 2003.
- (17) Zhang, L.; Ruan, D.; Zhou, J. Structure and properties of regenerated cellulose films prepared from cotton linters in NaOH/urea aqueous solution. *Ind. Eng. Chem. Res.* **2001**, *40* (25), 5923.
- (18) Zhang, L.; Cai, J.; Zhou, J. A solvent compounds and its preparation and application. Chinese Patent ZL 03128386.1, 2005.
- (19) Cai, J.; Zhang, L.; Zhou, J.; Li, H.; Chen, H.; Jin, H. Novel fibers prepared from cellulose in NaOH/urea aqueous solution. *Macromol. Rapid Commun.* **2004**, *25* (17), 1558.
- (20) Cai, J.; Wang, L.; Zhang, L. Influence of coagulation temperature on pore size and properties of cellulose membranes prepared from NaOH-urea aqueous solution. *Cellulose.* **2007**, *14*, 205.
- (21) Zhang, L.; Mao, Y.; Zhou, J.; Cai, J. Effects of coagulation conditions on the properties of regenerated cellulose films prepared in NaOH/urea aqueous solution. *Ind. Eng. Chem. Res.* **2005**, *44* (3), 522.
- (22) Mao, Y.; Zhang, L.; Cai, J.; Zhou, J. Effects of coagulants on porous structure of membranes prepared from cellulose in NaOH/urea aqueous solution. *J. Membr. Sci.* **2006**, *279* (1-2), 246.
- (23) Ruan, D.; Zhang, L.; Zhou, J.; Jin, H.; Chen, H. Structure and properties of novel fibers spun from cellulose in NaOH/thiourea aqueous solution. *Macromol. Biosci.* **2004**, *4* (12), 1105.
- (24) Cai, J.; Zhang, L.; Zhou, J.; Qi, H.; Chen, H.; Kondo, T.; Chen, X.; Chu, B. Multifilament fibers based on dissolution of cellulose in NaOH/urea aqueous solution: structure and properties. *Adv. Mater.* **2007**, *19* (6), 821.
- (25) Chen, X.; Burger, C.; Fang, D.; Ruan, D.; Zhang, L.; Hsiao, B.; Chu, B. X-ray studies of regenerated cellulose fibers wet-spun from cotton linter pulp in NaOH/thiourea aqueous solutions. *Polymer* **2006**, *47* (8), 2839.
- (26) Brown, W.; Wiskstön, R. A viscosity-molecular weight relationship for cellulose in cadoxen and a hydro-dynamic interpretation. *Eur. Polym. J.* **1965**, *1*, 1.
- (27) Yamane, C.; Mori, M.; Saito, M.; Okajima, K. Structures and mechanical properties of cellulose filament spun from cellulose/NaOH solution system. *Polym. J.* **1996**, *28* (12), 1039.
- (28) Rabek, J. F. *Experimental Methods in Polymer Chemistry: Application of Wide-angle X-ray Diffraction (WAXS) to the Study of the Structure of Polymers*; Wiley Interscience: Chichester, 1980; p 505.
- (29) Togawa, E.; Kondo, T. Change of morphological properties in drawing water-swollen cellulose films prepared from organic solutions. a view of molecular orientation in the drawing process. *J. Polym. Sci., B: Polym. Phys.* **1999**, *37* (5), 451.
- (30) Cho, J. J.; Hudson, S. H.; Cuculo, J. A. The coagulation of cellulose from anisotropic solution in the NH₃/NH₄SCN solvent system. *J. Polym. Sci. Polym. Phys. Ed.* **1989**, *27*, 1699.
- (31) Liu, C.; Cuculo, J. A.; Smith, B. Diffusion competition between solvent and nonsolvent during the coagulation process of cellulose/ammonia/ammonium thiocyanate fiber spinning system. *J. Polym. Sci. Polym. Phys. Ed.* **1990**, *28*, 449.
- (32) Laszkiewicz, B.; Weislo, P.; Cuculo, J. A. Fibers made from concentrated viscose solutions. *J. Appl. Polym. Sci.* **1992**, *46*, 445.
- (33) Yamashiki, T.; Matsui, T.; Kowsaka, K.; Saitoh, M.; Okajima, K.; Kamide, K. New class of cellulose fiber spun from the novel solution of cellulose by wet-spinning method. *J. Appl. Polym. Sci.* **1992**, *44* (40), 691.
- (34) Woodings, C. *Regenerated Cellulose Fibres*; Woodhead Publishing Ltd: England, 2001.
- (35) Ziabicki, A. *Fundamentals of Fiber Formation*; Wiley: New York, 1976; p 328.
- (36) Cai, J.; Zhang, L. Unique gelation behavior of cellulose in NaOH/urea aqueous solution. *Biomacromolecules* **2006**, *7* (1), 183.
- (37) Schurz, J.; Lenz, J.; Wrentschur, E. Inner surface and void system of regenerated cellulose fibers. *Angew. Makromol. Chem.* **1995**, *229*, 175.
- (38) Altena, F. W.; Smolders, C. A. Calculation of liquid-liquid phase separation in a ternary system of a polymer in a mixture of a solvent and a nonsolvent. *Macromolecules* **1982**, *15*, 1491.

Received for review May 25, 2008

Revised manuscript received September 8, 2008

Accepted September 9, 2008

IE800833W