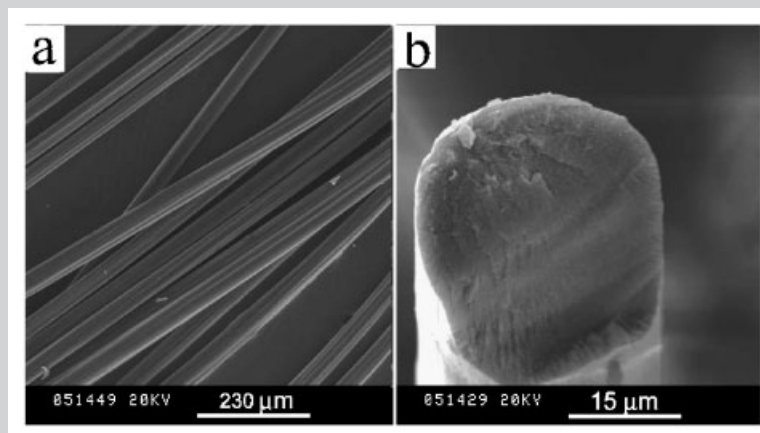


Summary: Cellulose was dissolved rapidly in 9.5 wt.-% NaOH and 4.5 wt.-% thiourea aqueous solution pre-cooled to -5°C to prepare a transparent solution. Novel cellulose multi-filament fibers were spun successfully, for the first time, from the cellulose dope on an extended laboratory scale. The results from ^{13}C NMR, scanning electron microscopy and wide angle X-ray

diffraction (WAXD) patterns indicated that the fibers exhibited cellulose II character and possessed a circular cross-section and smooth surface. The tensile strength of the novel fibers reached $1.9\text{--}2.2\text{ cN}\cdot\text{dteX}^{-1}$. 2D WAXD and SAXS patterns revealed that, with a drawing progress, the orientation factor increased and mechanical properties were improved.



SEM micrographs of the novel multi-filament fibers spun from cellulose solution in a NaOH/thiourea aqueous system pre-cooled to -5°C on an extended laboratory scale.

A Rapid Process for Producing Cellulose Multi-Filament Fibers from a NaOH/Thiourea Solvent System^a

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Introduction

Cellulose is a promising chemical material in the 21st century, and has attracted much recent attention in a wide range of applications, such as functionalized materials, nanoscience and nanotechnology.^[1–4] However, the cellulose industry faces a tremendous challenge with regard to

^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

providing a viable, economical and environmentally friendly chemical processing scheme.^[5] So far, the production of cellulose-regenerated materials has been based largely on the viscose technology, an undesirable process that is accompanied by hazardous byproducts (CS₂, H₂S, heavy metals).^[6,7] In this respect, there is a growing urgency to develop novel and environmentally friendly processes for fiber production in the cellulose industry. Recently, an environmentally friendly process of cellulose fiber spinning using a direct solvent system, such as *N*-methylmorpholine-*N*-oxide (NMMO), has been developed, leading to a new class of man-made cellulose fibers with the generic name of Lyocell. Lyocell fibers show better performance qualities, and have a less ordered layered structure that tends to hinder fibrillation by the dry-jet wet spinning process with a two stage precipitation of fibers via alcohol into the water bath.^[8–10]

In a previous work, we developed another novel solvent system for cellulose, i.e., a NaOH/thiourea aqueous solution pre-cooled to -8 to -5 °C, in which the “dissolution” of cellulose could be achieved within short time periods.^[11,12] An industrial application would require the process to be scaled up first on an extended laboratory scale and pilot plant level. This article represents a first attempt at preparing wet-spun regenerated cellulose fibers from cellulose in the NaOH/thiourea aqueous system on an extended laboratory scale via a pilot machine. Moreover, the structure and properties of the fibers produced, as well as the effects of drawing and polymer concentration on properties, are presented and discussed. It is our intention that the results may contribute toward a meaningful pathway that can help us to develop the production of regenerated cellulose materials including fibers, functional fiber, non-woven fabric and blended nanomaterials more simply.

Experimental Part

The cellulose (cotton linter pulp) with an α -cellulose content of more than 95% was provided by the Hubei Chemical Fiber Group Ltd. (Xiangfan, China). The viscosity-average molecular weights (M_{η}) of the two kinds of cellulose samples were 10.1×10^4 g · mol⁻¹ and 7.1×10^4 g · mol⁻¹ (degree of polymerization, $\overline{DP} = 620$ and 440), respectively. Unless otherwise noted, all other chemical reagents were purchased from commercial sources in China. Na₂SO₄, H₂SO₄, NaOH and thiourea were of analytical grade and industrial grade (noted as “i” in the sample code).

A mixture of solutions with a NaOH:thiourea:H₂O ratio of 9.5:4.5:86 by weight was pre-cooled to -5 °C. Then, 0.2 kg of dried cellulose was immediately dispersed in 4 kg of the solvent system under vigorous stirring at an ambient temperature (below 20 °C) for about 15 min to form a transparent cellulose dope. The resulting cellulose dope was filtered through 250 pore meshes and degassed in a vacuum oven for 6 h at 15 °C. The wet spinning process was carried out on an extended laboratory scale via a preliminary pilot-scale machine (see Supplementary Informa-

tion) which was constructed by the Hubei Chemical Fiber Company in China. The spinning apparatus was equipped with three pairs of Nelson-type rollers (I, II and III) and the wound spool. The wet spinning process was performed through two baths, and was coupled with drawing stages at ambient temperature. A 9–12 wt.-% H₂SO₄/10–15 wt.-% Na₂SO₄ aqueous solution was adopted as the first coagulant, and 5–6 wt.-% H₂SO₄ aqueous solution was used as the second coagulant for the spinning of a cellulose dope. The spinning dope was given a pressure of 0.15 MPa to extrude through a filtration pack, and then extruded through a platinum spinneret into the coagulation bath. To wash out the residual salts and acid, the resultant multi-filament fibers underwent a water bath at 60 °C until the pH value of the fibers was about 7, before plasticization. Finally, the fibers were dried by a heated roller (surface temperature 60–90 °C) and wound on a spool to obtain multi-filament fibers.

Scanning electron micrographs were obtained on a Hitachi X-650 scanning electron microscope. The fibers collected from 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 under a vacuum, then observed and photographed. Solid-state ¹³C NMR spectra of the cellulose were recorded on an Infinity Plus-400 spectrometer (Varian, Inc., USA; magnetic field = 9.4 T; ¹³C frequency = 100.12 MHz) with a cross polarization/magic angle spinning (CP/MAS) unit at ambient temperature. Two-dimensional flat plate wide-angle X-ray diffraction (2D WAXD) measurements of the cellulose fibers were performed on a WAXD diffractometer (D/MAX-1200, Rigaku Denki, Japan). The 2D synchrotron wide-angle X-ray diffraction (WAXD) measurements were carried out at Beamline X27 C (NSLS, BNL) using a 2D Mar CCD detector (MarUSA, Inc) with a pixel size of 158 μ m, and were then corrected for air scattering.^[13] The tensile strength (σ_b) and the elongation at break (ϵ_b) of the dried fiber without moisture content were measured on a universal tensile tester (XQ-1, Shanghai Textile University, China). The σ_b and ϵ_b values represented averages of 10 measurements.

Results and Discussion

We have successfully spun the multifilament fibers from cellulose dope in the NaOH/thiourea aqueous solvent system, for the first time, on an extended laboratory scale (Figure 1). Therefore, it is anticipated that the new cellulose dope can provide an alternative, promising and viable pathway to produce regenerated cellulose fibers and their function fibers. It is particularly interesting to note that the production cycle of the novel fibers is much shorter than that of the viscose technology. It is believed that the whole process, including dissolving cellulose, filtration, degassing, and employing the dope to spinning, may take less than 10 h on an industrial scale, whereas the production cycle of viscose technology is about 8 d in the Hubei Chemical Fiber Co. Ltd, Xiangfan in China. Moreover, the sulfate content in our multifilament fibers was determined to be essentially zero, whereas viscose rayon contains about 8 mg/100 g multi-filaments. Thus, the new cellulose multifilament fibers are also safer materials.

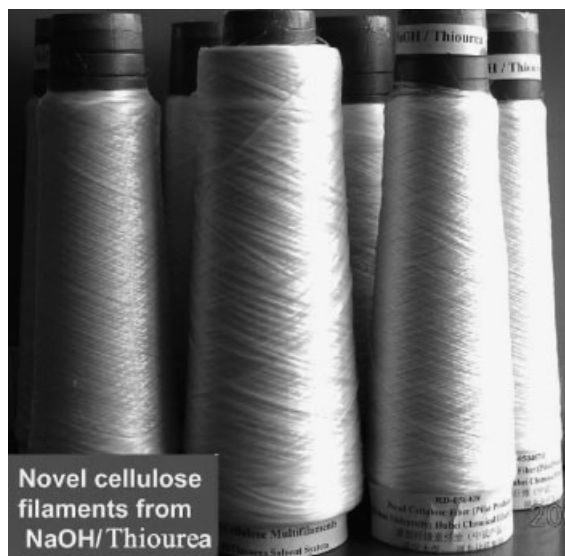


Figure 1. Photos of novel fibers spun on an extended laboratory scale via a pilot machine.

Figure 2 shows SEM images of the surfaces and cross-sections of the multifilament fibers (SU-2) produced at different stages of drawing/coagulation. The novel fibers have a circular cross section, which is similar to that of Lyocell fibers and cuprammonium rayon.^[14] It should be noted that the fibers were regenerated directly from cellulose solutions in a quasi-gel state formed mainly by

physical cross-linking and residual hydrogen bonds.^[15] The fibers exhibit a smooth surface structure, indicating that the wet-spun cellulose fibers started as a kind of coagulated gel, being markedly different from that of viscose fibers (lobulate skin-core structure)^[12] that are determined by chemical reaction. With drawing during the coagulation process, the fiber (and implicitly the cellulose chain) orientation along the drawing axis increased.

The results from 2D WAXD patterns (see Supplementary Information) indicate that the orientation degree of SU-1 is higher than that of NF-1 prepared in the laboratory. In order to further elucidate the structure formation of the novel fibers, we investigated the initially wet (never dried) fibers (SU-1) at different steps, as well as the drying process as the final step in the fiber formation using synchrotron X-ray scattering. In situ WAXS measurements on the running fibers after precipitation showed a poor equatorial scattering curve with only one broad reflection of the (110)/(020) lattice planes at around 20° in 2θ (see Supplementary Information). The typical cellulose II peak at about 12° was very weak.^[13] This indicates that the supramolecular ordering process was not finished in the initially wet fibers without drawing. However, the X-ray flat film photograph scattering curve became narrow and clear with increasing draw ratio and drying process, suggesting an increase in orientation of the novel fibers.^[16] In the cellulose fibers, the orientation plays an important role in the improvement of the mechanical properties. Hermans' orientation factors ($\bar{P}_{2,g}$), calculated from the (020) reflection in the 2D WAXD

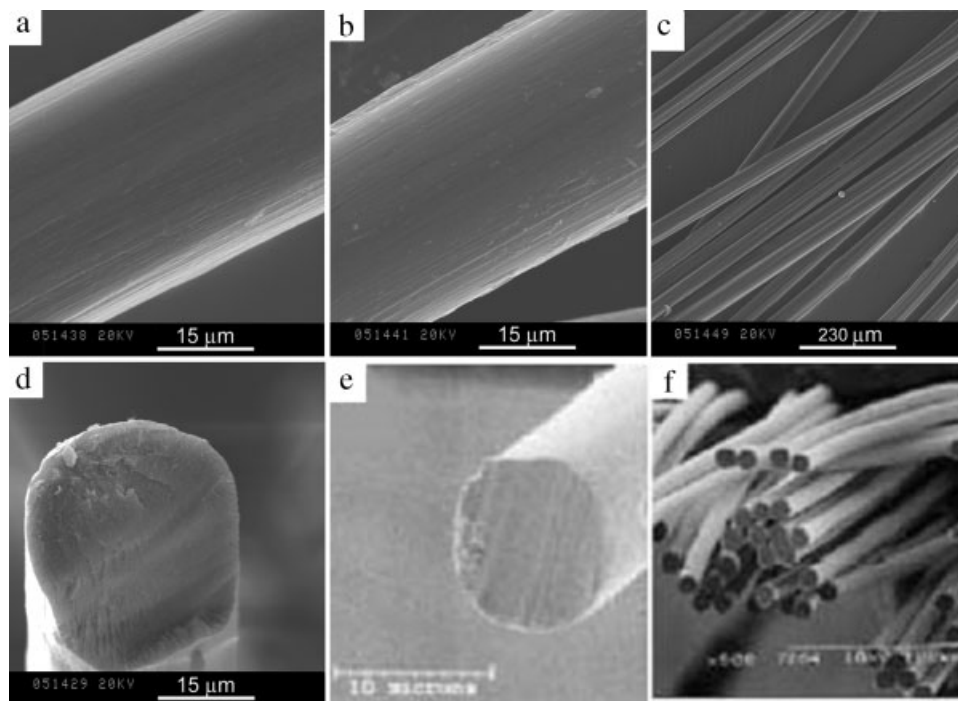


Figure 2. SEM images of the surface and cross-sections of SU-2 fibers on (a) Nelson-type roller I, (b) Nelson-type roller II, (c) and (d) heated roller III, (e) Lyocell fiber and (f) cuprammonium rayon.

Table 1. Structure and mechanical properties of the novel cellulose multifilament fibers and other fibers.

Sample	Cellulose concentration	Total crystallinity	Hermans' orientation parameter	\overline{DP}	Tensile Strength	Titer	Elongation at break ϵ_b
	wt.-%	%			$\text{cN} \cdot \text{dtex}^{-1}$	dtex	%
SU-1	4.8	62	0.59	590	1.4	11.3	3.6
SU-2	4.8	63	0.60	590	1.4	13.3	5.5
SU-3	5.6	60	0.63	420	2.2	–	2.1
SU-4-i	5.6	56	0.62	420	2.1	–	2.0
NF-2(in laboratory) ^[12]	5.0	61	0.50	590	0.9	6.6	15.2
Viscose rayon	8.0	49	0.68	350	2.0–2.5	–	16.3

patterns of the fibers, are listed in Table 1. The results from 2D WAXD patterns indicated that the $P_{2,g}$ values of the novel cellulose fibers spun from the NaOH/thiourea solution on the spinning machine remain lower than those of the viscose rayon fibers. Therefore, giving special attention to the enhancement of chain orientation is being considered in the pilot machine modification. By using the cellulose sample with a $\overline{DP} = 440$, we could derive cellulose solution with a higher concentration. We derived a solution with a cellulose concentration of 5.6 wt.-%, and obtained multi-filament fibers which were coded as SU-3 (analytical grade agents) and SU-4-i (industrial grade agents). Their $P_{2,g}$ values increased to 0.62 and 0.63. Figure 3 shows 2D-WAXD and SAXS patterns of the two kinds of the multifilaments, showing only the diffraction peaks from cellulose II. All of the SAXS patterns had sharp and long equatorial streaks and very short meridional peaks, indicating the presence of needle-shaped voids or a fibrillar structure aligned parallel to the fiber direction and with a periodic lamellar arrangement of crystalline and amorphous cellulose regions. The SAXS patterns of the

regenerated cellulose fibers in this study are still different from those of the commercial rayon.

Figure 4 shows the CP/MAS ^{13}C NMR spectra of the SU-2 fibers with different degrees of drawing and original cellulose. All of the fibers of the regenerated cellulose exhibit four main peaks at 105.6, 88.0, 75.2 (77.0, 73.5) ppm, assigned to the C1, C4, C5 (C3, C2), as well as the C6 peak which lies at 63.1 ppm, which is assigned to cellulose II. The results strongly indicate that the cellulose dope did transform into regenerated cellulose II when the cellulose gel was regenerated in the coagulation bath, leading to the transformation of the crystalline structure. Moreover, it further confirmed that the native cellulose could be dissolved essentially completely in the solvent system presented. The signals of C4 at around 88 ppm and its shoulder peak at 84.0 ppm are related to the status of carbons located in either the crystalline or the amorphous regions,^[17] respectively. The shoulder peak at 84 ppm of C4 for the cellulose fibers could be related to the degree of anisotropy. Obviously, the C4 shoulder becomes higher for SU-2 filaments from (b) to (d), reflecting an increase in the

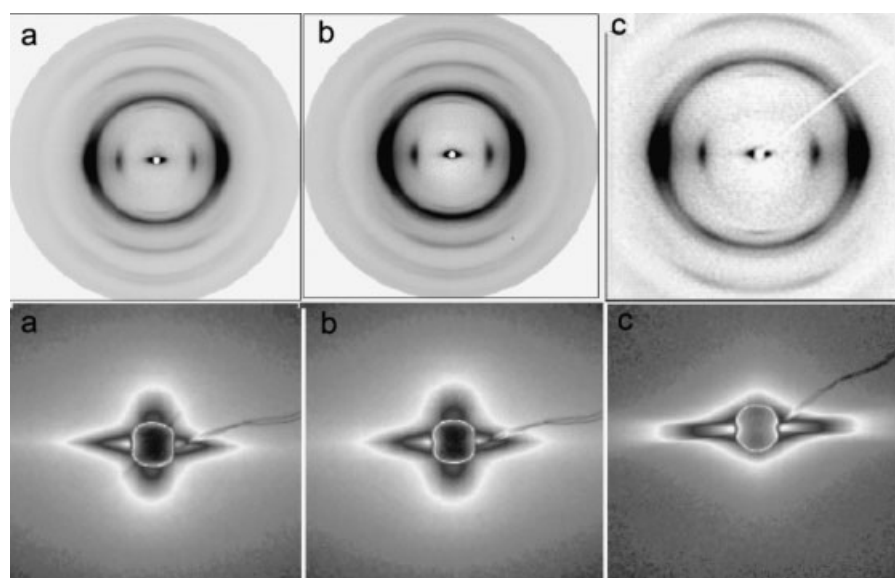


Figure 3. 2D Synchrotron WAXD patterns (top) and SAXS patterns (bottom) of (a) SU-3 fibers, (b) SU-4-i fibers and (c) commercial viscose rayon.

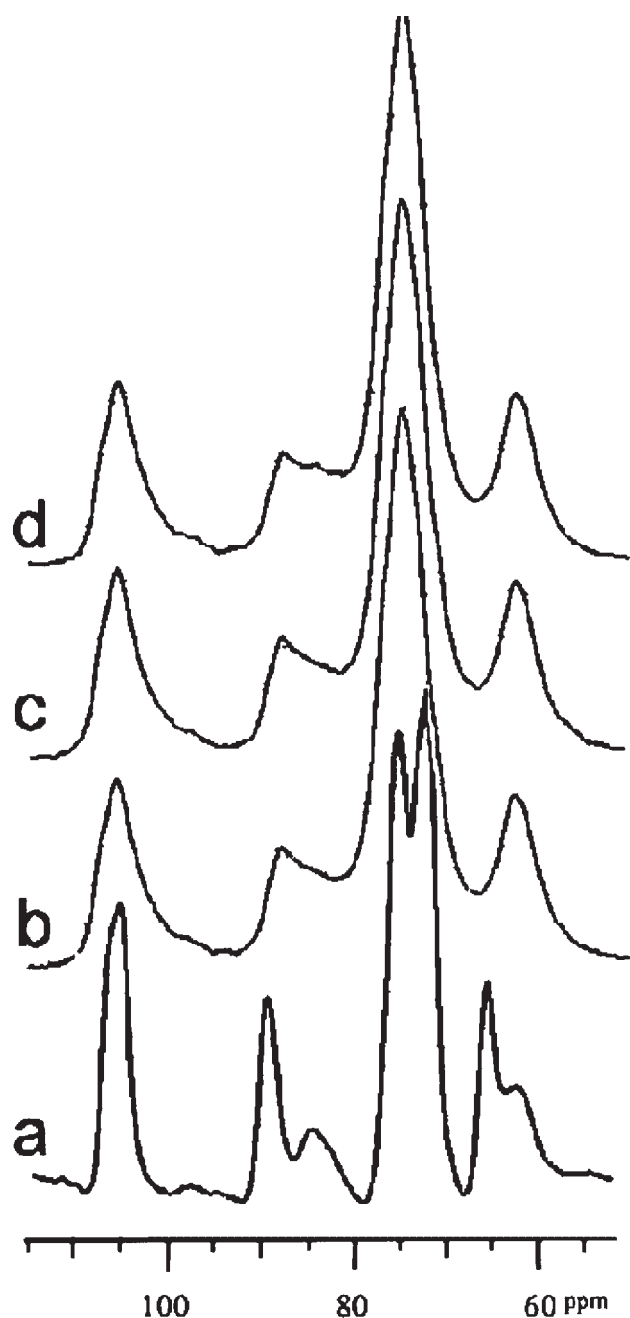


Figure 4. CP/MAS ^{13}C NMR spectra of SU-2 fibers with increasing drawing from (b) to (d) and original cellulose (a).

degree of anisotropy, i.e., an increase in chain orientation as a result of the drawing of fibers.

Data for the current produced multifilament fibers are summarized in Table 1. It is noted that the \overline{DP} values of the produced fibers determined are 590 for SU-1 and SU-2, and 420 for SU-3 and SU-4-i, close to that of the original cotton linter pulp, indicating that no obvious degradation of cellulose occurred in the dissolution and regeneration process. The orientation of SU-1 and SU-2 was not sufficient, so they exhibited a slightly low tensile strength. Under controlled humidity conditions, the titer, tensile strength and elongation

at break of a single fiber for SU-1 were 6.03 dtex , $1.1 \text{ cN} \cdot \text{dtex}^{-1}$ and 14.7% , respectively. Interestingly, using the cellulose sample with $\overline{DP} = 440$, we prepared $5.0\text{--}5.6\%$ cellulose solution, and spun good fibers, which possessed relatively high tensile strength ($1.9\text{--}2.2 \text{ cN} \cdot \text{dtex}^{-1}$) in the dry state. Moreover, the tensile strength of SU-4-i spun from industrial reagents reached $2.1 \text{ cN} \cdot \text{dtex}^{-1}$, that is, it has mechanical properties coming closer to commercial specifications. In view of the above results, the mechanical properties of the cellulose fibers are enhanced with increasing of crystallinity index, drawing orientation and cellulose concentration. Therefore, it is anticipated that the mechanical properties of the novel fibers will be improved significantly in an improved spinning pilot instrument and with the enhancement of the cellulose concentration. Moreover, many functional materials from cellulose with chitin,^[18] nanoparticles,^[19] soybean protein^[20] etc. in the NaOH/thiourea aqueous system have been prepared. Therefore, this work provides a new pathway for the preparation of novel functional cellulose fibers and materials. It is worth noting that the process of producing cellulose fibers is very simple and rapid, and allows in situ synthesis of nanofibers and other functional materials.

Conclusion

Novel cellulose multi-filament fibers have been successfully spun, for the first time, on an extended laboratory scale via a pilot machine, from a cellulose dope in $9.5 \text{ wt.}\% \text{ NaOH}/4.5 \text{ wt.}\% \text{ thiourea}$ aqueous solution that was pre-cooled to -5°C . This was a simple and rapid process for the production of cellulose fibers with a circular cross-sectional shape and a smooth surface. The native cellulose I was regenerated completely to form cellulose II in the fibers during the coagulation process. The tensile strength of the novel fibers from industrial grade agents reached $2.1 \text{ cN} \cdot \text{dtex}^{-1}$, coming closer to those of the viscose rayon. With a drawing progress and an increase in cellulose concentration, the structure and properties of the multi-filament fibers were improved significantly. This new approach offers great potential for cellulose fiber, functional fibers and nanomaterial production on an industrial scale.

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