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Multifilament Fibers Based on Dissolution of Cellulose in NaOH/Urea Aqueous Solution: Structure and Properties**

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In the 21st century, science and technology have moved toward renewable raw materials and more environmentally friendly and sustainable resources and processes.[1] The Technology Road Map sponsored by the U.S. Department of Energy (DOE) has targeted to achieve 10 % of basic chemical building blocks arising from plant-derived renewable sources by 2020.[2] Cellulose is the most abundant renewable organic material and can be converted into cellulose derivatives (ethers and esters) and regenerated materials (fibers, films, food casings, membranes, and sponges, among others).[3] Moreover, numerous new functional materials of cellulose are being developed over a broad range of applications.[1a,4] It is noted that the traditional viscose route for producing regenerated cellulose fibers, films, and nonwoven fabrics still dominates the current processing route.[1a] The viscose route is technologically complex and requires additional facilities to treat the gaseous and aqueous waste emissions (end-of-pipe technology), which makes it a growing urgency to develop a new pathway to avoid the complicated current routes and hazardous byproducts. An more environmentally friendly process of cellulose-fiber spinning using a direct solvent system, *N*-methylmorpholine-*N*-oxide (NMMO), has been developed, leading to a new class of man-made cellulose fibers with the generic name of Lyocell.[5] Lyocell fibers show better performance qualities, but the Lyocell process suffers from 1) uncontrolled thermal stability of the system NMMO–cellulose–H_2O (a runaway reaction), 2) high evaporation costs (energy costs), and 3) high tendency of fibrillation of the Lyocell fiber.[3,5]

Faced with the serious pollution produced by the viscose method in China, India, and other countries, we hope to realize a dream of producing regenerated cellulose materials using the new route by using low-cost chemical reagents and a simple wet-spinning process that yields essentially nontoxic byproducts. In previous work, we developed a novel solvent system for cellulose, that is, an NaOH/urea aqueous solution precooled to –12 °C, in which the dissolution of cellulose could be achieved rapidly at ambient temperatures (below 20 °C).[6] Interestingly, cellulose with a relatively high molecular weight could not be dissolved in the solvent without being precooled to –12 °C or without urea being added. The addition of urea and the low temperature play an important role in the improvement of the cellulose dissolution, because low temperature creates a large inclusion complex associated with cellulose, NaOH, urea, and H_2O clusters, which bring cellulose into aqueous solution, even at relatively high cellulose concentrations. Moreover, the cellulose dope could remain in a liquid state for a long time period at about 0 to 5 °C.[7] It has motivated us to develop a more economical and environmentally friendly cellulose-fiber-fabrication process on an industrial scale in order to demonstrate the utility of this solvent system. Here, we present a first attempt to prepare the wet-spinning of cellulose multifilaments from the cellulose solution using a pilot machine, and to study the drawing process in terms of the structure and properties of the produced filaments.

The multifilament fibers produced from the new solvent system using a pilot machine is shown in Figure 1. Our process differed from the viscose rayon process in which the decomposition of cellulose xanthate was accompanied by the xanthation reaction with an unavoidable evolution of toxic gases. Furthermore, the production cycle of the current process was much shorter than that of the viscose technology, as a result of the formation of the cellulose dope being rapid (< 0.5 h). It differed also from the CarbaCell process,[8] in which the cellulose reacted with urea to yield cellulose carbamate in soda solution, accompanying the derivatization and by product—the cellulose carbamate was then dissolved in a certain amount of NaOH aqueous solution below 0 °C. Moreover, the sulfate content in our multifilament fibers was determined to be essentially zero, whereas viscose rayon could contain about 8 mg/100 g multifilaments. Thus, the new cellulose multifilaments provide a potential application for when a sulfate-free product is very important.

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Figure 1. Photograph of multifilament fibers produced by a pilot machine from cellulose dope using industrial (front) and analytical (back) grades of NaOH and urea.

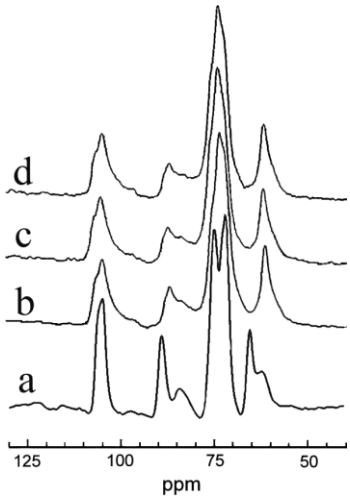

Figure 2. Cross polarization/magic-angle spinning (CP/MAS) ^{13}C NMR spectrum of cellulose (cotton linter pulp) (a) and filaments along the spinning process at each stage: U-2-I (b), U-2-II (c), and U-2-III (d).

Figure 2 shows cross polarization/magic-angle spinning CP/MAS ^{13}C NMR spectra of cellulose and the multifilaments coded as U-2 at different degrees of drawing and orientation. The multifilament fibers along the spinning process at each stage of roller I, II, and III, respectively, were coded as U-2-I, U-2-II and U-2-III. The spectrum of the multifilament fibers exhibited four main peaks at 105.6, 87.6, 75.0 (77.0, 73.0) ppm, assigned to the C1, C4, C5 (C3, C2), as well as C6 peak lines at 62.4 ppm, which were assigned to cellulose II (i.e., multifilament cellulose fibers). The results strongly indicate that the native cellulose could be dissolved in the present solvent system. Moreover, it confirmed that the cellulose dope did transform into regenerated cellulose II when the cellulose gel was regenerated in the coagulation bath. The C4 signal at around 88 ppm and its shoulder peak at 84.0 ppm depended on the status of carbons located in either the crystalline or amorphous regions, respectively.[9] For the U-2 multifilaments, the C4 peaks located at 87.6 ppm shifted to higher magnetic fields than the native cellulose (89.3 ppm), and the intensity was significantly lower, suggesting a decrease in crystallinity, as a result of the regeneration of the cellulose molecules during the coagulation process. The shoulder peak of C4 for the filaments could be related to the degree of anisotropy.[10] With the drawing process, the C4 shoulder became higher for U-2 filaments (from (b) to (d)), reflecting an increase in the degree of anisotropy, that is, an increase in chain orientation.

Figure 3 shows scanning electron microscopy (SEM) images of the surface (top) and cross-section (bottom) of the U-2 multifilaments under different drawing conditions. The new cellulose filaments had a circular cross section, which was

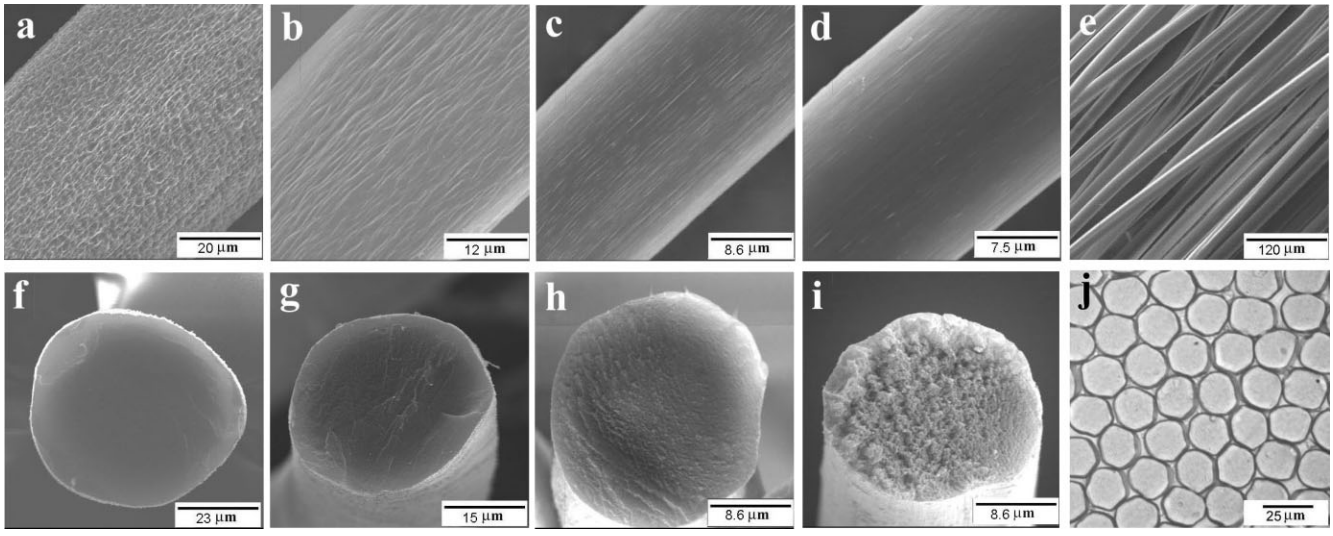

Figure 3. SEM images of the surface (top) and cross section (bottom) of the U-2 filaments at each stage from the Nelson-type roller I (a) to the take-up device (d). A bundle of filaments on the take-up device was observed by using SEM (e) and by using optical microscopy (j).

markedly different from the lobulate shape of the viscose rayon, but similar to cuprammonium rayon (Bemberg) and Lyocell fibers.[5] In our situation, the novel filaments were regenerated directly from cellulose 'solution' in a quasi-gel state formed mainly by physical crosslinking and residual hydrogen-bonds.[7] The cellulose filaments were influenced by the gelation, regeneration, and drawing, and the cellulose solution showed a unique gelation behavior, which was very sensitive to temperature, cellulose concentration, and molecular weight.[7] By changing them, therefore, the cellulose structure during the regeneration process would be improved.

As shown in Figure 3, the cellulose-fiber diameter could be varied from 60 to 20 μm by drawing, while still maintaining its circular shape (Fig. 3f–i). The first orientation of the cellulose could occur in the spinneret. The molecular orientation was partially maintained in the coagulation bath because of the rapid cellulose precipitation. The fibers exhibited a homogenous network structure with small voids of pore sizes of about 100 nm on the surface (Fig. 3a), resembling the formation of voids in concrete fibers on wet-spinning.[11] With drawing of the concrete fibers, the fibrils of the filaments could be oriented along the axis of the fibers (Fig. 3b). Moreover, with the drawing process, the cellulose multifilaments from the take-up device exhibited a more uniform and denser structure (Fig. 3d, e, i, and j). In contrast to the fibrillation of Lyocell,[5] our filaments spun from the NaOH/urea aqueous solution had a homogenous surface structure without fibrillation, and could be regarded approximately as a fine uniform cylinder as a result of the cellulose dope in the form of a physically crosslinked gel.

Figure 4 shows 2D wide-angle X-Ray diffraction (WAXD) patterns of the U-2 multifilaments under different drawing conditions, together with the original cellulose, commercial viscose rayon, and Lyocell. It was seen that all other samples showed the diffraction peaks from cellulose II, except for the original cellulose. Table 1 lists the calculated crystallinity and Hermans' orientation parameter ($\bar{P}_{2,g}$, see Experimental for more details). The U-2-III, U-3-i, and U-4-i fibers had a relatively high orientation, but lower than that of the commercial viscose rayon (Fig. 4e). Both the orientation and the crystallinity of U-2-I and U-2-II were lower than those of U-2-III, suggesting that the draw-processing step in the third roller and the take-up device could be redesigned to improve the final cellulose structure dramatically.

Table 1. Crystallinity, orientation parameter, and mechanical properties of multifilament fibers. See Experimental for more details.

Sample	Total crystallinity [%]	Orientation parameter, π	Hermans' orientation parameter	$\overline{DP}$	Tensile Strength [cN/dtex]	Elongation at break, e_b [%]
U-1	62	0.81	–	590	1.8	13
U-2-I	57	0.76	0.56	590	1.3	18
U-2-II	59	0.79	0.57	590	1.6	15
U-2-III	61	0.81	0.64	590	1.7	9
U-3-i	57	–	0.62	420	1.9	2
U-4-i	56	–	0.61	420	1.7	2

Figure 5 shows small-angle X-ray scattering (SAXS) patterns of our regenerated cellulose filaments and commercial viscose rayon. 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 multifilaments in this study are still different from those of the commercial viscose rayon. The meridional peaks of U-2-III were a little bit stronger than those of U-2-I and U-2-II, indicating that the higher draw ratio could induce stronger lamellar arrangements. Supplementary, typical SAXS intensity profiles (not shown) of multifilament fibers in the meridian direction showed that the lamella long period was higher than 100 nm for all of the regenerated cellulose fibers.

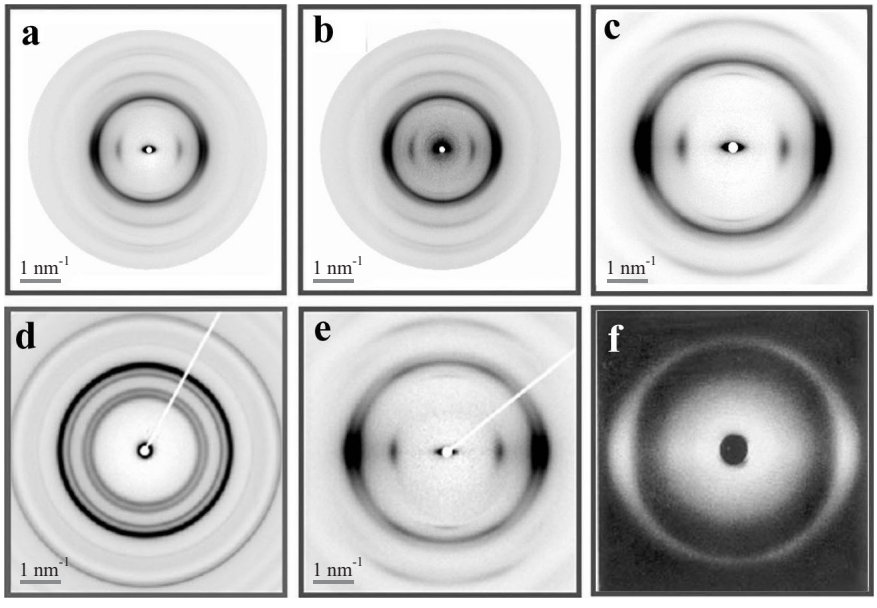

Figure 4. 2D WAXD patterns of U-2-I (a), U-2-II (b), and U-2-III (c) multifilament fibers. 2D WAXD patterns of the cotton linter pulp (d), the commercial viscose rayon (e), and the Lyocell [3] (f) are also shown.

Mechanical properties of the current produced fibers are summarized in Table 1. The degree of polymerization (DP) values of the produced fibers were about 590 for U-1 and U-2, and 420 for U-3-i and U-4-i, close to that

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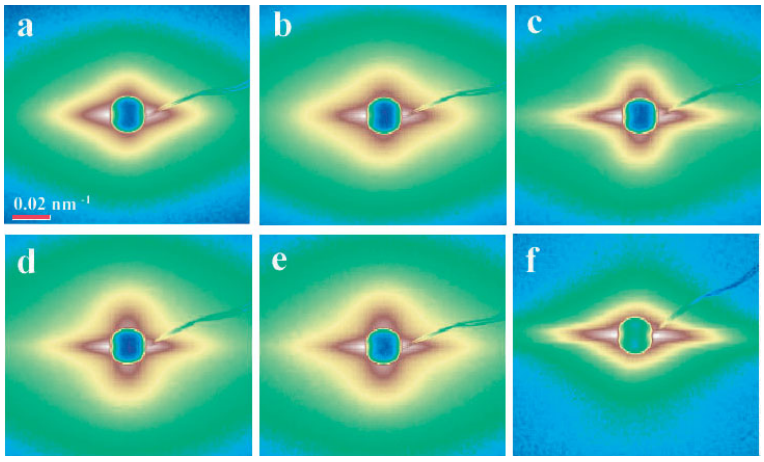

Figure 5. SAXS patterns of U-2-I (a), U-2-II (b), U-2-III (c), U-3-i (d), and U-4-i (e) filaments and the commercial viscose rayon (f).

of the original cellulose, indicating that no obvious degradation of cellulose occurred in the dissolution (or solvation) and regeneration processes. The novel filaments spun using the preliminary pilot machine possessed relatively high tensile strength (1.7 to 1.9 cN/dtex), with the mechanical properties being close to the commercial viscose rayon. The U-3-i and U-4-i filaments were obtained from the cellulose dope using industrial grades of NaOH and urea. This test further demonstrated the industrial potential of the new approach. The lower cost and much less toxic nature of the NaOH/urea solvent system, and the relative ease for wet-spinning clearly suggests a promising potential for the development of a more economical and environmentally friendly process for cellulose-fiber production. The current cellulose filaments have a larger crystallinity index and a higher molecular weight or *DP* than those of the viscose rayon (40 %, $DP = 250–300$).[3] Moreover, in view of the results from Table 1 and Figure 3, the mechanical properties of the novel cellulose filaments could obviously be increased with a drawing process. The orientation of the U-2 multifilaments was weaker than that of viscose rayon ($\bar{P}_{2,g} = 0.68$), as a result of using a preliminary pilot apparatus. It is anticipated that the orientation and the mechanical properties of the fibers could be improved significantly after further optimization of the spinning process with special attention to the details of the spinneret design and the conditions for the multistage draw process. In addition, the concentration of cellulose in the novel solvent system could be increased to 8 % as the *DP* of the cellulose was being decreased, being similar to that of viscose rayon. Thus, this new pathway offers great potential for producing high-quality cellulose multifilaments by using a relatively low-cost, simple, and essentially nonpolluting process, in contrast to the viscose method with hazardous byproducts.

In Summary, 7 wt % NaOH and 12 wt % urea aqueous solution precooled to –12 °C could rapidly dissolve cellulose at ambient temperature. From the cellulose dope, high-quality cellulose multifilaments were spun successfully using a pilot machine, for the first time, by using a low-cost, simple, and environmentally friendly process. The cellulose crystals were completely transformed from cellulose I (cotton linter pulp) to II (multifilament fibers) during these processes. The multifilament fibers had a circular cross-sectional shape and a smooth surface as well as good mechanical properties. With a drawing progress, the orientation factor increased and tensile strength of the multifilament fibers were significantly improved. Particularly, the new multifilaments provide a potential application, where A sulfate-free product is very important. The new solvent system and the multifilament wet-spinning process will be important for numerous new developments of cellulose derivatives, regenerated cellulose fibers, films, nonwoven fabrics, as well as functional materials.

Experimental

The cellulose (cotton linter pulp) with an α-cellulose content of more than 95 % was provided by the Hubei Chemical Fiber Co. Ltd. (Xiangfan, China). The viscosity-average molecular weight (M_w) of two kinds of cellulose samples were determined to be 10.1×10^4 and 7.1×10^4 g mol^{-1} ($\overline{DP} = 620$ and 440), respectively. NaOH and urea of analytical grade and industrial grade (noted as i in the sample code) were used. A mixture solution with NaOH/urea/H_2O of 7:12:81 by weight was precooled to –12 °C. Then the cellulose sample in the desired amount was immediately dispersed into the solvent system (6 L) under vigorous stirring for 30 min at ambient temperature to obtain a transparent cellulose dope with concentrations of 4.0 to 4.5 wt %. The wet-spinning process was carried out on an extended laboratory scale using a preliminary pilot apparatus that was constructed by the Hubei Chemical Fiber Co. Ltd. (Xiangfan, China). The multidrawing processes through the Nelson-type rollers I, II, and III, respectively, which extruded the cellulose dope into coagulants with two baths, were used. A 8 wt % H_2SO_4/12 wt % Na_2SO_4 aqueous solution was adopted as the first coagulants in the first bath, and a 4 wt % H_2SO_4 aqueous solution was used as the second coagulant at 10 to 20 °C with no evolution of gas during coagulation.

Morphology of the cross section of the filaments was observed on an optical polarizing microscope (Leica DMLP, Germany). The surface and cross section of the fibers were observed by using a scanning electron microscope (SEM, Hitachi, S-570, Japan). Solid-state ^{13}C NMR spectra of the cellulose were recorded on an Infinity Plus-400 spectrometer (Varian, Inc., USA; magnetic field = 9.4 T; ^{13}C frequency = 100 MHz) with a (CP/MAS) unit. X-ray diffraction measurements were basically performed according to the previous report [12]. WAXD photographs were taken on flat films using nickel-filtered CuKR radiation produced by a Rigaku RINT-2500HF X-ray generator at 40 kV and 40 mA. Synchrotron X-ray measurements were carried out at the Advanced Polymers Beamline (X27C), National Synchrotron Light Source (NSLS), Brookhaven National Laboratory

(BNL). A typical collection time was 45 s and the sample-to-detector distance was 107.5 mm for WAXD, and 1847.0 mm for SAXS. The crystallinity was estimated from the WAXD pattern. The Hermans' orientation parameter ($\bar{P}_{2,g}$) from the (020) reflections in the 2D WAXD pattern was calculated according to ref. [13]. The tensile strength (σ_b) and the elongation at break (ε_b) of the dried fibers were measured on a universal tensile tester (XQ-1, Shanghai Textile University, China). The S element contents were measured on an elemental analyzer (Heraeus Co., Germany).

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