

Green Method for Production of Cellulose Multifilament from Cellulose Carbamate on a Pilot Scale

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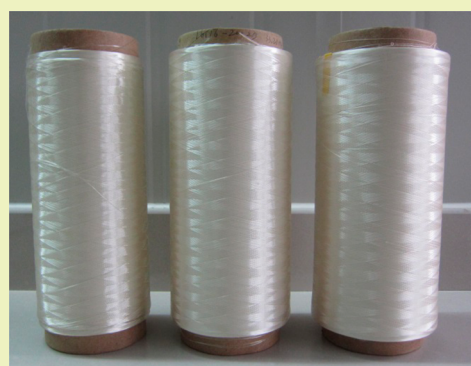
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ABSTRACT: In the cellulose industry, the viscose process is still occupying the leading position, although this process generates several environmentally hazardous byproducts. Here we report a novel method for the production of cellulose multifilament from cellulose carbamate (CC) on a pilot scale. In this method, CC was first prepared efficiently by microwave heating; it was then dissolved in NaOH/ZnO aqueous solutions through a freezing–thawing process. Wet spinning of the CC solution was performed on a pilot-scale machine. The cellulose multifilament displayed a dense circular microstructure and excellent physicochemical properties. The tensile strength and elongation at break of the multifilament in dry state were 2.58 cN/dtex and 12.1%, respectively. Moreover, the process could utilize most of the conventional equipment for the viscose method, which could have a great impact on the current cellulose industries.

KEYWORDS: Microwave-assisted synthesis, Fiber-spinning, Cellulose carbamate, NaOH/ZnO aqueous solution, Cellulose multifilament



INTRODUCTION

Recently, demands for biomass resources and renewable polymer products with a low carbon footprint have increased due to limited fossil resources, increasing energy demands, and global warming.¹ By 2025, the U.S. Department of Energy aims to replace 30% of petroleum transportation fuel with biofuels and 25% of industrial organic chemicals with biomass-derived chemicals.² As the most abundant form of terrestrial biomass, cellulose can be converted into monomers,³ derivatives,^{4,5} regenerated materials,^{6,7} and other functional materials.^{8–10} However, cellulose is insoluble in common solvents due to its fibril structure and intramolecular and intermolecular hydrogen bonds.^{6,7} As a result, the multistep viscose process has long been favored in the regenerated cellulose (RC) industry, although this process generates several environmentally hazardous byproducts including CS₂, H₂S, and heavy metals.^{6,7} In the past decade, global viscose fiber production has shown an average annual growth rate of about 5% with a production output of 3.392 million tons in 2011.¹¹ Approximately 60% of this was produced by China, while the aggregate output from the Association of Southeast Asian Nations region, Western Europe, and India was approximately 35%.¹¹ There is an urgent need for the development of an environmentally friendly method for the production of RC fibers.

In the last 30 years, several green cellulose solvent systems, including *N*-methylmorpholine-*N*-oxide (NMMO),^{12,13} ionic liquids,^{14–17} and NaOH/urea aqueous solution^{18,19} as well as

some uncommon methods,^{20–22} have been reported, and some progressive results have been achieved. NMMO hydrate has been identified as the most effectual solvent and has led to a new class of man-made cellulosic fibers with the generic name Lyocell.²³ However, the Lyocell technology, which holds some disadvantages, would benefit from further enhancement of improved consumer properties and reduced power consumption from solvent recycling and washing water.^{13,23} The CarbaCell process is advantageous in retaining the use of the viscose spinning technology while avoiding the use of hazardous sulfur-containing compounds for derivatization.^{6,24} During the patented CarbaCell process,²⁵ cellulose materials are first alkalinized and priripened with the occurrence of partial chain degradation. Cellulose carbamate (CC) is then obtained from the alkali cellulose in xylene (as a transfer medium) and result in being dissolved in NaOH solution. The prepared spinning dope is filtered and degassed before wet spinning in an acidic precipitation bath, followed by a salt-containing alkaline decomposition bath for hydrolysis of the carbamate groups at elevated temperature.^{6,7} Compared with the viscose process, the CarbaCell process is much more ecological and has high applicability for the production of high-absorbent nonwoven hollow fibers, sponges, and carpet cleaners.^{25–27} However, the

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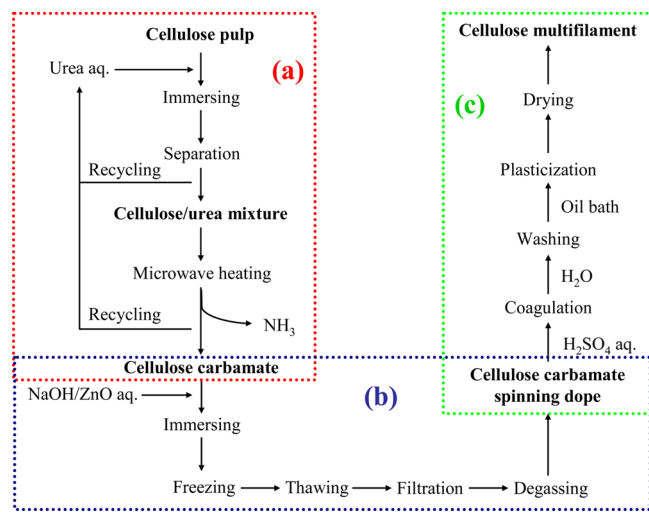
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CarbaCell process has not yet been established on the industry scale due to limitations presented by the catalyst, organic solvents, reaction time, and temperature in the synthesis stage.^{28–30} Moreover, the complete dissolution of CC requires complex pretreatment and an extended dissolution period.^{6,7,31,32}

In previous work, we presented a microwave-assisted synthesis of CC from native cellulose under catalyst-free and solvent-free conditions for the first time.^{33,34} The shortening of the reaction time from hours to minutes is of great importance in the method. Although we have done it successfully in our laboratory scale, a large-scale microwave-assisted synthesis of CC in an industrial microwave oven is essential for the successful industrialization of the new synthesis method. More recently, we found that the solubility and stability of CC in a NaOH solution could be improved significantly by adding a small amount of ZnO. 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 the microwave-assisted synthesis and the NaOH/ZnO solvent system. Herein, we present a novel pilot-scale process for the preparation of cellulose multifilament. As illustrated in Scheme 1, the method includes

Scheme 1. Green Method for Production of Cellulose Multifilament: (a) Microwave-Assisted Synthesis of CC, (b) Dissolution of CC in NaOH/ZnO Aqueous Solution, and (c) Preparation of Cellulose Multifilament from Spinning Dope



the microwave-assisted synthesis of CC, dissolution of CC in a NaOH/ZnO aqueous solution, and wet fiber-spinning. The trigger was transformation of native cellulose with urea into CC through microwave heating under catalyst-free and solvent-free conditions. The key in this process is to avoid the use of organic solvent transfer medium and to be capable of recycling any surplus urea solution. The prepared CC was then dispersed in a NaOH/ZnO aqueous solution prior to a freezing–thawing process that subsequently resulted in a concentrated spinning dope. Cellulose filaments, with exemption of sulfur and nitrogen, were directly spun from the CC–NaOH/ZnO solution by regeneration in a bath of acidic/salt solution. This offers advantages over previous viscose and CarbaCell processes by avoiding the need for expensive alkali treatments of cellulose during the derivative process. Furthermore, time-consuming stirring for dissolution and alkaline treatments for

decomposition of the carbamate groups, which are other disadvantages in the conventional process, were completely abandoned.

EXPERIMENTAL SECTION

Materials. Three cellulose samples (cotton linter pulps) with α -cellulose content of 93% were provided by Hubei Chemical Fiber Co., Ltd. (Xiangyang, China). The degree of polymerization (DP) of the cotton linter pulps was determined to be 430, 620, and 790. All of the cellulose samples were used for scale-up microwave-assisted synthesis of CC, and the prepared CC from the origin cellulose with DP = 430 and 790 were used to study the solubility of CC and the wet-spinning test, respectively. Analytical grade reagent (urea) and industrial grade reagents (Na_2SO_4 , H_2SO_4 , NaOH, ZnO, and urea) were used without further purification.

Synthesis of Cellulose Carbamate. Cellulose was immersed into a 45 wt % urea aqueous solution. The mixture then stood at 25 °C for 3 h, followed by filtration and oven drying at 40 °C. The obtained cellulose/urea mixture was subsequently heated in a microwave apparatus (Dibang Microwave Equipment Co., Ltd., Nanjing, China, 3000 W) under a temperature control mode for 10–15 min. Finally, the sample was washed with water and dried at 60 °C. The urea aqueous solution was recycled during the filtration and washing processes. Table 1 summarizes the data of the microwave-assisted synthesis of CC with different nitrogen content (N%) or degree of substitution (DS) on a pilot scale. The other CC samples were prepared according to the previous work.^{33,34}

Dissolution of Cellulose Carbamate. Aqueous solutions were prepared as the solvents of CC by directly mixing NaOH, ZnO, and distilled water. The contents of NaOH and ZnO were varied from 6 to 10 wt % and 0 to 2 wt %. The effects of NaOH and ZnO concentration on the solubility of CC were examined through the dispersion of CC-5 (DP = 400, 1.042 N%, DS = 0.124) in the desired NaOH/ZnO solutions, followed by cooling to –12 °C. The dissolved and insoluble parts were separated through centrifugation at 7200 rpm and 10 °C for 15 min. The solubility (S_a) of CC was calculated by

$$S_a = \frac{W_0 - W_1}{W_0} \times 100\%$$

where W_0 is the weight of original CC (g), and W_1 is the weight of the insoluble part (g). The effects of dissolved temperature and the nitrogen content of CC on the solubility were examined through variances in the dissolution temperature from 10 to –23 °C and changes in the nitrogen content of CC (DP = 660) from 0 to 4.405%. The concentration of CC was kept constant at 6.5 wt %.

In a typical pilot-scale test, 1.75 kg of CC-2 (DP = 660, 1.572 N%, DS = 0.191) was dispersed into 30 kg of 7 wt % NaOH/1.6 wt % ZnO solution. The mixture was cooled to –12 °C and then thawed at room temperature. The CC solution was obtained with a concentration of 5.5 wt %. The resulting solution was filtered through 350 and 450 pore meshes to remove impurities and then degassed under vacuum for 8 h at 25 °C in preparation for wet spinning.

The dependence of the nitrogen content of CC on the storage time was determined as follows: 4.0 wt % CC-2 (DP = 660, 1.572 N%, DS = 0.191) and 7 wt % NaOH/1.6 wt % ZnO solutions were stored at 25 °C for a desired time, followed by precipitating immediately in 3 wt % H_2SO_4 to obtain the recovered CC. The obtained CC was washed with distilled water and freeze-dried for nitrogen content analysis.

Fiber Spinning. The wet-spinning process was performed on an improved R535A viscose filament yarn spinning machine (Figure 1a). The obtained spinning dope was pushed from a sealed reservoir into a Zenith BPB-4391 gear pump (0.835 mL/rpm) using air pressure (0.4–0.6 MPa). The spinneret with 60 orifices (diameter: 0.08 mm) was directly immersed into the coagulation bath of 8 wt % H_2SO_4 /20 wt % Na_2SO_4 solution at 25 °C. The flow rate of the CC solution through the spinneret holes was 75 m/min. The multidrawing processes were achieved through Nelson-type rollers I and II and a heated roller. The fibers were washed with hot water (45 °C) until the pH reached 7 before plasticization. Finally, the fibers were dried by a

Table 1. Microwave-Assisted Synthesis of Cellulose Carbamates on a Pilot Scale^a

cellulose pulp	DP	790	790	620	620	430
	weight (kg)	2.0	2.0	2.0	2.0	2.0
urea aq	urea grade	analytical	industrial	industrial	industrial	recycled
	weight (kg)	18.5	18.5	18.5	18.5	18.5
	urea content (wt %)	45	45	45	45	45
immersing process	time (h)	3	3	3	3	3
	temperature (°C)	25	25	25	25	25
recycled urea aq	weight (g)	15.8	16.0	16.2	16.5	-
	urea content (wt %)	43	44	43	42	-
mixture of cellulose/urea	weight (kg)	3.38	3.31	3.26	3.35	3.10
	urea content (%)	41	40	39	40	35
microwave synthesis	reaction scale (kg)	0.6	0.6	0.6	0.6	0.6
	temperature (°C)	160–170	160–170	160–170	160–170	160–170
	time (min)	15	15	10	15	12
obtained CC	code	CC-1	CC-2	CC-3	CC-4	CC-5
	weight (kg)	2.0	1.92	1.96	1.91	1.96
	DP	642	660	535	540	400
	N%	1.785	1.572	1.185	1.391	1.042
	DS	0.218	0.191	0.142	0.168	0.124

^aDP, degree of polymerization; N%, nitrogen content; and DS, degree of substitution.

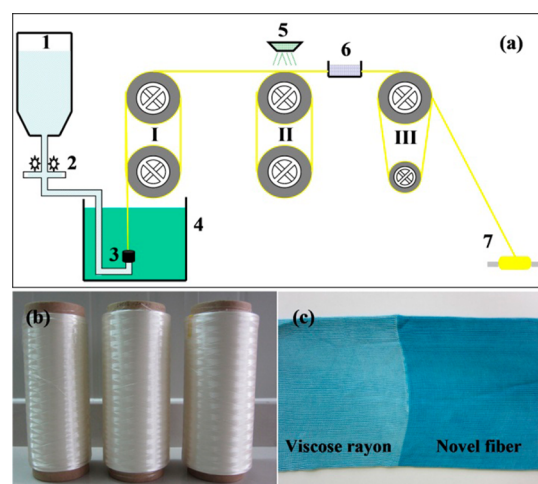


Figure 1. (a) Schematic illustration of the improved RS35A spinning apparatus: (1) stainless steel reservoir, (2) metering pump, (3) spinneret, (4) coagulation bath, (5) hot water washing, (6) plasticizing bath, (7) take-up roller, (I) Nelson-type roller, (II) Nelson-type roller, and (III) heated roller. Photographs of (b) the novel cellulose filaments and (c) the dyed textile prepared with the novel fiber (right) and viscose rayon (left).

heated roller (75 °C) and wound on a spool to obtain the multifilament. The speed of the take-up roller was 60 m/min.

Characterization. The intrinsic viscosities $[\eta]$ of cellulose, CC, and RC fibers were measured in cadoxen at 25 °C, and DP was calculated from $[\eta]$ by the following equation³⁵

$$[\eta] = 1.75 \times \text{DP}^{0.69} \text{ (mL g}^{-1}\text{)}$$

The nitrogen and sulfur contents of the samples were determined with an elemental analyzer (CHN-O-RAPID, Heraeus Co., Germany); the DS of CC was calculated from its nitrogen content. FT-IR spectra were recorded on a FT-IR spectroscopy (Nicolet 170SX, Thermo Electron Co., USA). Solid-state ¹³C CP/MAS NMR experiments were performed on a Bruker AVANCE III 400 WB spectrometer (Rheinstetten, Germany) with a (CP/MAS) unit. X-ray diffraction (XRD) was examined with an X-ray diffractometer (D8, BRUKER AXS, GmbH, Karlsruhe, Germany). Two-dimensional wide-angle X-ray diffraction (2D WAXD) measurements were performed on a

WAXD diffractometer (D/MAX-1200, Rigaku Denki, Japan). Hermans' orientation parameters (f) were calculated from the (020) reflections in the 2D WAXD pattern.³⁶

SEM images were taken on a VEGA 3 LMU (TESCAN, Czech) scanning electron microscope. The cross-section of RC filaments were observed on an optical polarizing microscope (Leica DMLP, Germany). Commercial viscose rayon provided by the Hubei Chemical Fiber Co., Ltd. (Xiangyang, China) was used for comparison purposes. The linear density was calculated in terms of tex and dtex, which are defined as the weight in grams per 1000 and 10,000 m of the fiber, respectively. The zinc content of the novel cellulose filaments was calculated by the means of an EDTA titration method in accordance with the National Standards of China (GJB 3940-2000).³⁷ Tenacity and elongation at break as well as initial modulus of the cellulose filaments in dry and wet state were measured on a universal tensile tester (XQ-1, Shanghai Textile University, China) according to ASTM method D2256-80. The dyeing property of the novel filaments was tested together with the viscose rayon. The dyeing, namely, KE-2B (C.I. Reactive Blue 160), at concentrations measured as 3% on weight of fiber (o.w.f.) was carried out in a laboratory-scale dyeing machine using a 50:1 liquor ratio at 90 °C for 1 h. The dyed samples were rinsed in cold tap water for 10 min and allowed to dry in the open air. The color strength (K/S) of the dyed samples was measured with computer color matching system (DCISF-600, Shenyang Research Institute of Chemical Industry, China).

RESULTS AND DISCUSSION

Microwave heating is often employed in synthetic chemistry due to overcoming conventional heating methods by non-contact heating, heightened control over the heating process, rapid heating, high reaction rate, high product yield, and so on.³⁸ As illustrated in Scheme 1 and Table 1, 2.0 kg of cellulose pulps with DP values of 430–790 were first immersed into 45 wt % urea solution to form a heterogeneous mixture and stood for 3 h. The excessive urea solution was recycled after filtration, and the recovery percent of urea was in the range of 82–85 wt % at this step. Then, the cellulose/urea mixtures with urea content of 35–41 wt % were dried in an oven and heated in a microwave oven at 160–170 °C for 10–15 min. The reaction products were washed, and the unreacted urea in the mixtures could also be recycled by water washing. The total recovery percent of urea was approximately 95% during the microwave synthesis process. After being oven-dried, about 2.0 kg of the

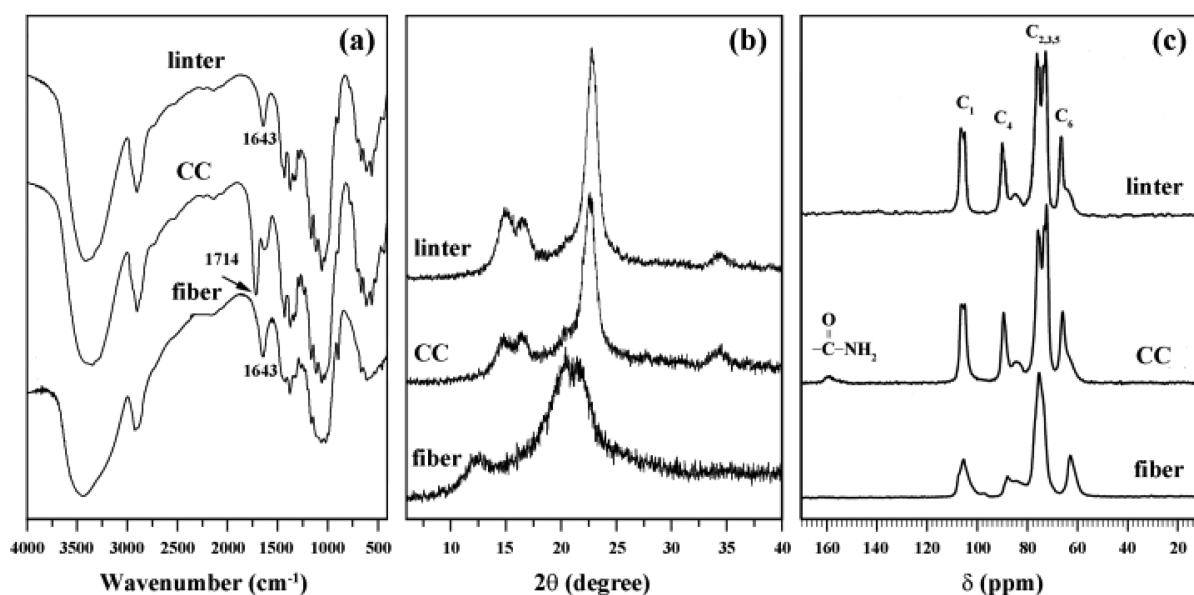


Figure 2. (a) IR spectra, (b) XRD patterns, and (c) solid-state CP/MAS ¹³C NMR spectra of the native cellulose (linter), CC (DP = 660, 1.572 N%, DS = 0.191) and the novel multifilament (fiber).

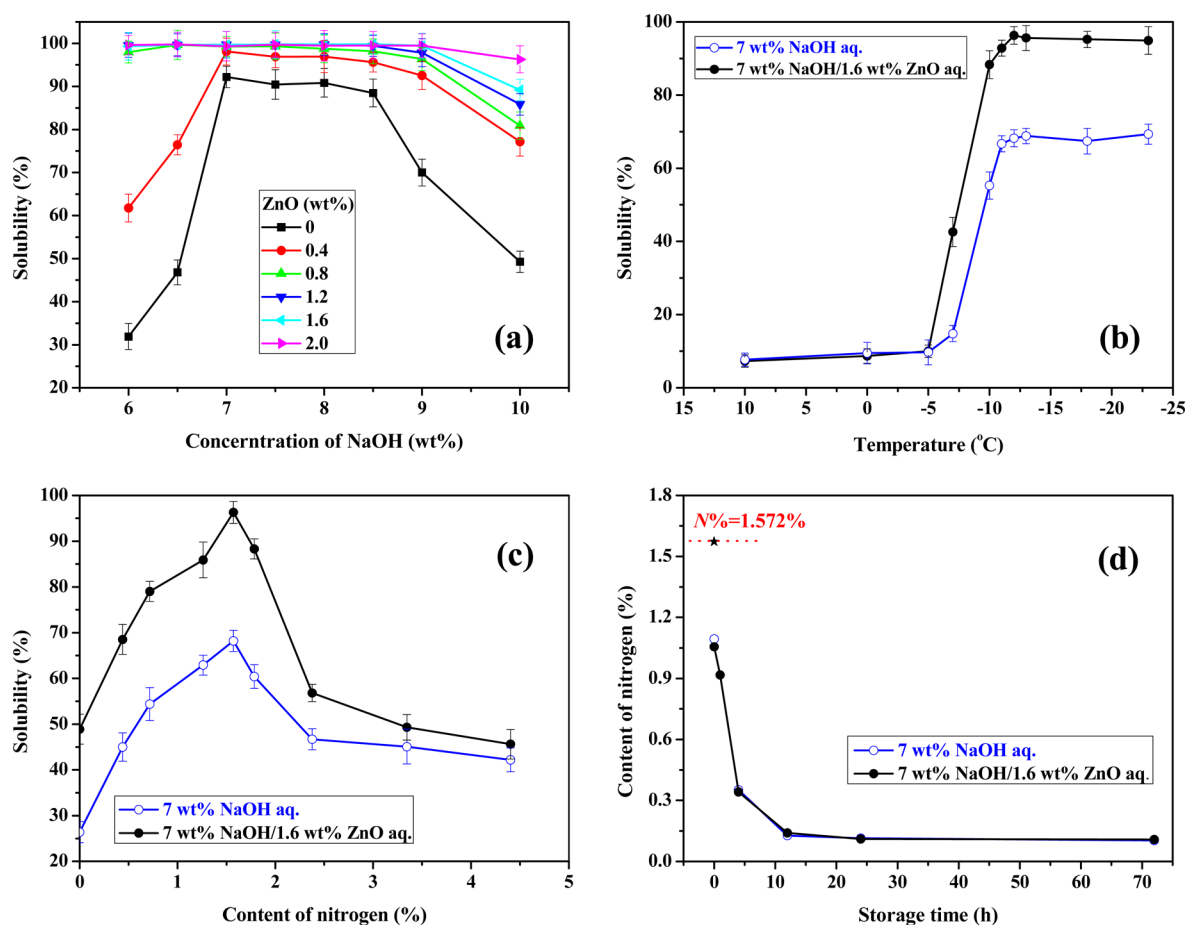


Figure 3. (a) Effects of solvent composition on the solubility of CC (DP = 400, 1.042 N%, DS = 0.124) in NaOH/ZnO aqueous solution. (b) Dependence of the solubility of CC (DP = 660, 1.572 N%, DS = 0.191) on the freezing temperature. (c) Dependence of the solubility of CC (DP = 660) on the nitrogen content of CC. (d) Dependence of the nitrogen content of CC (DP = 660, 1.572 N%, DS = 0.191) on the storage time of the spinning dope at 25 °C.

white or slight yellow CC samples with a preferable nitrogen content (1.042–1.785 N%, DS = 0.124–0.218) were obtained, indicating no obvious mass lost during the microwave-assisted

synthesis process. Compared to the previous work on a laboratory scale,^{33,34} the microwave heating process was well controlled by the temperature instead of the microwave power,

and the cross-linking and carbonization could be avoided. The industrial and recycled urea has also been used in the pilot-scale test. Moreover, there were neither organic transfer mediums (xylene) nor catalytic agents (sodium carbonate) used, and the energy savings was over 50% when compared to the conventional synthesis of CC. The small amount of NH_3 released in this process could be completely absorbed by dilute acid solution. Thus, the preliminary pilot test proved that the microwave-assisted method was a green and highly ecological process, which was available in industrialization.

Figure 2 shows spectroscopic data on the XRD, IR, and solid-state ^{13}C CP/MAS NMR measurements of CC in comparison to native cellulose. The IR spectrum of CC showed an obvious new absorption peak at 1714 cm^{-1} that was attributed to the stretching vibration of the carbonyl ($\text{C}=\text{O}$) in urethane groups.³⁹ It has been reported that some derivatization procedures led to the transformation of alkali cellulose with urea into similar structures as cellulose modifications II and IV.¹² In this process, CC displayed the same distinct peaks as native cellulose with 2θ values of 14.8, 16.3, and 22.6° corresponding to the (1 $\bar{1}$ 0), (110), and (020) planes of the cellulose I crystalline form.⁶ The results suggested that chemical modification did not change the crystalline form of cellulose. Furthermore, the degrees of crystallinity (χ_c) of the native cellulose and CC were determined to be 72% and 65%, respectively. With the reaction of cellulose and urea, the substitution of the hydroxyl groups might mainly occur in more accessible amorphous regions and on the surface of the elementary crystallites. These conditions led to the reduction of the density of hydrogen bonds and partially destroyed the crystalline structure of cellulose, which was beneficial for the dissolution of CC. The ^{13}C NMR spectra also verified the presence of the typical cellulose I crystal form of cellulose and CC. As shown in Figure 2c, the chemical shifts of carbon were determined as 105.9 ppm for C-1, 89.1 ppm for C-4, 74.6 ppm for C-2, C-3, and C-5, and 65.5 ppm for C-6.⁴⁰ With the exception of the chemical shifts of cellulose, CC displayed a remarkable signal at 159.0 ppm, which is a typical indicator of carbonyl carbon.⁶ Moreover, the shoulder of C6 in the spectra of CC tended to disappear when compared with that of the native cellulose. The reason could be attributed to C6 carbon atoms becoming less mobile after the substitution of C6 hydroxyls with the organic acid.⁴¹ The results further proved the partial introduction of carbamate groups into the cellulose backbone through microwave heating.

High concentration and stability of the CC solution was essential for wet-spinning and the industrial implementation of the carbamate technology. The CC dissolved in NaOH aqueous solution was found very sensitive to storage temperature, concentration, nitrogen content, and molecular weight of CC.⁴² More specifically, the CC/NaOH solution easily formed gel at room temperature, which was not conducive to the wet-spinning process. It has been reported that the solubility of cellulose in NaOH^{43,44} or the NaOH/urea solution^{45,46} could be improved with the addition of ZnO. On the basis of the results, we studied the solubility of CC in NaOH/ZnO solutions in terms of improving the properties of the spinning dope. As shown in Figure 3a, the solubility of CC in the NaOH/ZnO solution initially increased to reach the optimum NaOH concentration range between 7 and 8.5 wt %, followed by decreasing with increasing concentration of NaOH. The solubility of CC increased significantly even with the addition of 0.4 wt % ZnO to the NaOH solution. CC was completely

dissolved in the NaOH solution at more than 2.0 wt % of ZnO content, and thus, the solubility of CC in the NaOH solution could be significantly improved with the addition of a small amount of ZnO (0.4–2.0 wt %). However, the CC solution with high amounts of dissolved ZnO was found unstable. As a result, 7–8 wt % NaOH/0.4–1.6 wt % ZnO aqueous solution was selected as an optimum solvent for CC. The concentration of CC could be reached to 8–9 wt % as the DP of CC was about 400, which was similar to the levels of the viscose method.

The freezing temperature influenced the solubility of CC in both the NaOH and NaOH/ZnO solutions. As shown in Figure 3b, only a small fraction of CC with low molecular weight was dissolved under temperatures between 10 to -5°C . The solubility of CC rapidly increased as the temperature decreased from -5 to -23°C , saturated at -12°C or below in both solvents. The results indicated that lower freezing temperature was vital in achieving such an optimum CC dissolution. The nitrogen content of CC has also a great influence on the solubility of CC (Figure 3c). Solubility increased as the nitrogen content of CC increased from 0% to 1.572% (DS = 0.191) and then decreased until 4.405% (DS = 0.560). It was thus determined that a high degree of substitution was not necessarily significant for better dissolution, which could be achieved at CC nitrogen content between 1 and 2%. This could be attributed to the partial destruction of the hydrogen bonding and crystal structure with the introduction of the acylamino groups on the cellulose backbone, thus facilitating the dissolution of CC. However, carbonization and cross-linking induced by the side-reactions would occur in cellulose once a sufficient amount of carbamate groups had been formed and thereby decrease the solubility of CC. In addition, CC consistently demonstrated greater solubility in the NaOH/ZnO solution than in NaOH solution across different dissolution conditions, further establishing the advantages of the NaOH/ZnO aqueous solution. Figure 3d shows the dependence of the nitrogen content of CC in NaOH and NaOH/ZnO solutions on the storage time at 25°C . The nitrogen content of CC decreased from 1.572% (DS = 0.191) to about 1% (DS = 0.119) when the dissolving process was just completed and then decreased rapidly with increasing storage time. The carbamate groups were completely cleaved from the cellulose backbone as the storage time increased to 12 h. Attributing to the low nitrogen content of CC used, saponification, and hydrolysis of the carbamate groups in the dissolving and regeneration processes, pure cellulose fibers could be easily obtained.

Multifilament spinning of the CC dope was performed on a pilot scale with an improved R535 viscose filament yarn spinning machine (illustrated in Figure 1a). Compared with the conventional viscose process, the described method was advantageous in requiring just one coagulant bath, while avoiding the release of toxic gas during coagulation. With the optimized spinning test results in hand, more than 32 h of continuous spinning was achieved at a take-up speed of 60 m/min for the production of cellulose multifilament. The attainment of high stability and efficiency in the new method was essential for industrial-scale use. The whole production period only required a 48 h period, which covered the microwave-assisted synthesis of CC, CC dissolution, filtration, degassing, and fiber-spinning.

The multifilament fibers produced from the novel process are shown in Figure 1b. The linear density for the single filament

Table 2. Physical Properties of Novel Fibers and Other Regenerated Cellulose Fibers^a

fiber	DP	cross-section		mechanical properties			χ_c (%)	f	K/S	ref
		shape	morphology	tenacity (cN/dtex)	elongation (%)					
novel fiber	560	round	homogeneous and dense	2.58	12.1	55	0.82	39	this work	
cuprammonium	~500	round/oval	multilayers	1.5–2.0	10–20	43	–	–	12,	
viscose rayon	~300	lobate	core/skin	2.0–2.5	18–23	30	0.68–0.90	30	12, 36, 50	
NMMO	~600	round/oval	homogeneous and dense	4.0–4.2	15–17	55	0.96	20–25	12, 50, 51, 53	
NaOH/urea	420–590	round	homogeneous	1.3–1.9	2–18	56–62	0.56–0.64	~28–34	18, 52	
CarbaCell	–	round/oval	homogeneous	1.3–2.6	8–25	38–43	–	–	12, 50	
ionic liquids	722	round	homogeneous and dense	2.6–2.9	7–8	52–54	0.79–0.83	~10–20	49	

^aDP, degree of polymerization; χ_c , degree of crystallinity; f , Hermans' orientation parameter; and K/S , color strength.

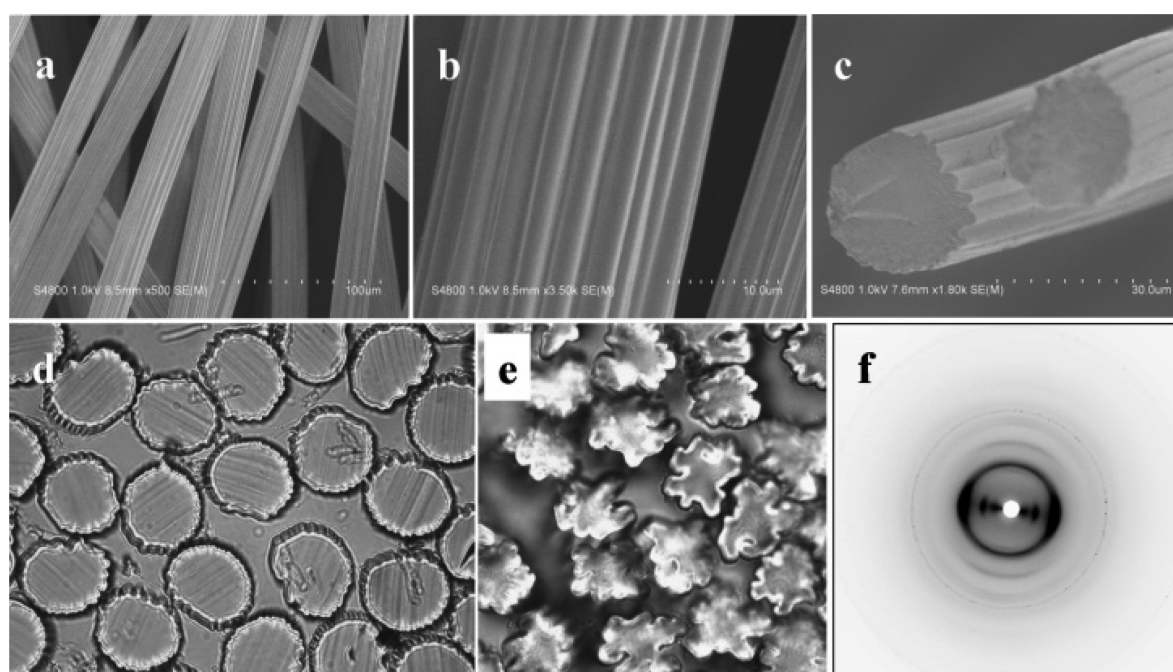


Figure 4. SEM images of (a, b) the surface and (c) cross-section of the novel cellulose filaments. Optical micrographs of the cross-section of (d) the novel cellulose filaments and (e) viscose rayon. (f) 2D WAXD pattern of the novel cellulose filaments.

and the yarn were 4.4 dtex and 26.5 tex, respectively. The fibers exhibited a bright surface with superior chromaticity to that of viscose rayon (Figure 1c). The color strength (K/S) value of the novel fiber reached to 39, which was higher than that of commercial viscose fibers and other regenerated cellulose fibers as shown in Table 2. Moreover, the element analysis proved that the novel fibers were free of sulfur and nitrogen, and the zinc content was determined to be zero, too. IR, XRD, and ^{13}C NMR spectra of the cellulose multifilament are shown in Figure 2. For the IR spectrum of the novel filaments, the peak at 1714 cm^{-1} assigned to the stretching vibration of the carbonyl disappeared. The broad peaks that appeared in the XRD pattern of the filaments at $2\theta = 12.4$, 20.2 , and 22.6° were attributed to the crystal planes (110), (110), and (020), respectively, indicating that the crystal structure of the fibers transformed to cellulose II.⁴⁷ Meanwhile, the ^{13}C NMR spectrum of the multifilament fibers exhibited four main peaks at 105.2, 87.8, 75.0, and 62.7 ppm, which were attributed to C1, C4, C5, and C6, respectively, as cases in viscose and

cuprammonium rayon.⁴⁷ Compared with the ^{13}C NMR spectrum of CC, the disappearance of the remarkable signal at 159.0 ppm further provided evidence for the complete hydrolysis of the carbamate groups through a one-step acidic precipitation.

Figure 4 shows the SEM images of the surface and cross-section of the novel cellulose multifilament. The fibers exhibited a small amount of shrink structure in the surface. However, this was less pronounced than that in regular viscose rayon. The new cellulose filaments demonstrated a quasi-circular cross section and homogeneous structure (Figure 4d), which was markedly different from the lobed shape of viscose rayon (Figure 4e), but similar to those of the NMMO fiber and ionic liquid fiber (Table 2). As stated by Ziabicki,²³ differences between the deformability in the thin surface layer and the core of the coagulating filament may produce noncircular shapes. The novel filaments were directly regenerated from the CC solution in a quasi-gel state, forming mainly through physical cross-linking and residual hydrogen bonds. A typical 2D

WAXD pattern of the cellulose filaments is shown in Figure 4f. The sample showed the diffraction peaks of cellulose II, and the reflection pattern appeared as short arcs. The degree of crystallinity (χ_c) of the filaments was determined to be 55%, which was lower than that of the used CC (65%) and obviously higher than those of the viscose rayon and CarbaCell fiber. The degree of orientation and Hermans' orientation parameter of the fibers were determined to be 79% and 0.82, respectively, which was close to those of the viscose rayon and the fibers prepared from ion liquids (Table 2). The orientation of the crystal proved vital in achieving enhanced mechanical properties in the cellulose fiber. The tenacity and elongation at break of the cellulose filaments in the dry state were determined to be 2.58 cN/dtex and 12.1%, respectively, which was comparable to the CarbaCell fiber and superior to those of the commercial viscose rayon and cuprammonium fiber and the fibers prepared from NaOH/urea aqueous solutions (Table 2). The tenacity of the filaments in the wet state was 0.80 cN/dtex, which was achieved in the range of the National Standard of China (GBT13758-2008) for viscose filament yarn (0.75 cN/dtex).⁴⁸ The initial modulus of our new filaments was tested to be 37.6 cN/dtex, which was very similar to that of cellulose fiber prepared from ionic liquid (35.0–45.3 cN/dtex).⁴⁹ Therefore, this new method has great potential for the production of high-quality cellulose fibers through a more economical and environmentally friendly process.

CONCLUSIONS

In summary, CC was efficiently synthesized on a large scale by microwave heating from cellulose and industrial urea under solvent-free and catalyst-free conditions. CC with low nitrogen content was dispersed in a NaOH/ZnO solution, which was then cooled to obtain a spinning dope in high concentration. A small amount of added ZnO could significantly improve the solubility and stability of CC in NaOH solution. High-quality cellulose filaments were successfully spun from the spinning dope on pilot equipment through an acid/salt coagulant bath. The filaments possessed a circular dense microstructure and excellent mechanical properties. The chromaticity of the novel fibers was found superior to that of viscose rayon. The novel method was intentionally similar to the existing viscose system, therefore allowing for cost-effective implementation in industry. In particular, the total cost for producing a ton of novel cellulose filaments was estimated to save 15–20% when compared to the conventional viscose method. This new and environmentally friendly method thus has great potential for easy application in the current cellulose industries.

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Notes

The authors declare no competing financial interest.

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