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Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution

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Abstract—Untreated cellulose was directly and quickly dissolved in NaOH/thiourea/urea aqueous solution. The mechanism of dissolution was investigated by SEM, WXRD and ^{13}C NMR. The components of this solvent cannot dissolve cellulose on their own, and the interactions between NaOH and urea, as well as between NaOH and thiourea, play an important role in improving the dissolution of cellulose. Moreover, ^{13}C NMR spectra proved that NaOH, thiourea, and urea were bound to cellulose molecules, which brings cellulose molecules into aqueous solution to a certain extent and prevents cellulose macromolecules from associating. ^{13}C NMR spectra of the cellulose solution show that this novel mixture is a direct solvent. Optical microscopy and CP MAS ^{13}C NMR were used to study the process of dissolution. The results reveal that cellulose is dissolved completely and that cellulose I (cotton linter) first changes to amorphous cellulose chains in solution, and then to cellulose II during regeneration. Moreover, a new, more effective dissolution method is proposed, as confirmed by dynamic rheology measurements.

Keywords: Aqueous solution; Cellulose; Direct dissolution; Dissolution mechanism

1. Introduction

Cellulose, as the most abundant renewable biopolymer in the world, has attracted much attention because of its outstanding properties. Cellulose is composed of β-(1→4)-linked D-glucopyranosyl units with three hydroxyl groups, which can form complex inter- and intramolecular hydrogen bonds.[1] Thus, cellulose cannot be dissolved in common solvents and does not melt before thermal degradation. Many efforts have been made to identify solvents for cellulose. Traditionally, production of regenerated cellulose fibers and films was largely based on viscose technology, which requires the use of harmful CS_2 and produces H_2S.[2] Another traditional technique used to prepare cellulose products is the cuprammonium technology, which generates heavy metal residues that are difficult to dispose of.[3] Thus, it is imperative to identify new spinning systems for cellulose industries that can solve these environmental problems.

To date, many derivative and non-derivative solvents for cellulose have been found, such as N_2O_4/*N*,*N*-dimethylformamide (DMF),[4] SO_2/amine,[5] Me_2SO/paraformaldehyde (PF),[6–8] LiCl/*N*,*N*-dimethylacetamide (DMAc),[9–11] *N*-methyl-morpholine-*N*-oxide (NMMO),[12–14] and molten salt hydrates such as $LiSCN\cdot 2H_2O$[15] and NaSCN/KSCN/LiSCN/water.[16] However, limitations such as volatility, toxicity and high cost still exist. Among the solvents identified, the NMMO/water system seems to be the most powerful cellulose solvent and has been used to prepare Lyocell fibers, which possess some excellent properties. However this innovative technology also produces considerable amounts of byproducts and requires effective recovery of the expensive solvent, and thus it is not suitable for replacing viscose technology completely.[12]

More recently, Zhang and co-workers found that NaOH/urea and NaOH/thiourea aqueous solutions can dissolve cellulose directly and quickly. Both solvent systems are inexpensive and less toxic, and good cellulose fibers can be prepared using simple technology.[17–19] However, spinning solutions containing high concentrations

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of cellulose in these two solvents are unstable, which is a disadvantage in industrial applications. Moreover, the dissolution mechanism for cellulose in these ternary solvent systems is not clear. Recently, we identified a NaOH/thiourea/urea aqueous solution that can dissolve cellulose quickly. The most important finding is that the new solvent is more powerful in dissolving cellulose, and can be used to prepare more stable spinning solutions containing higher concentrations of cellulose than NaOH/urea (or NaOH/thiourea) aqueous solution systems, as registered in our patent.[20]

In this paper, we present the process for dissolution of cellulose and discuss the mechanism involved in these solvent systems. Furthermore, a more favorable dissolution method is proposed here in detail.

2. Experimental

2.1. Materials and sample preparation

Three different cellulose samples were used. Two types of cotton linter cellulose pulp sheets (coded as C520 and C620 according to their degree of polymerization) were supplied by Shanghai Cellulose Pulp Factory, China. Another cotton linter cellulose pulp sheet (coded as C1400 according to its degree of polymerization) was obtained from Dandong Chemical Fiber Factory, China. All cellulose samples were shredded into powder, and dried in a vacuum oven at 70 °C for 24 h before use. No activation treatment is required. Unless otherwise stated, the cellulose used was C520. All other chemicals were of analytic grade and were used as received.

The degree of polymerization was determined using a standard procedure, as follows. Cellulose was dissolved in cadoxen, and the intrinsic viscosity of a dilute solution was measured using an Ubbelodhe capillary viscometer. The viscosity-average molecular weight ($\overline{M}_\eta$) can be calculated according to the equation: $[\eta] = 3.85 \times 10^{-2} \times \overline{M}_w^{0.76}$.[21] The degree of polymerization (DP) of cellulose can be obtained from the equation: $\overline{M} = \mathrm{DP} \times M$, where M is the molecular weight of the glucopyranosyl unit of cellulose.

2.2. Cellulose solubility tests

To compare the dissolution power of the NaOH/thiourea/urea (coded as NS), NaOH/thiourea and NaOH/urea aqueous systems, the solubility of cellulose in these systems was measured. Each solvent system was prepared using a specific composition according to the ability of the individual solvents to dissolve cellulose, based on literature data[17,18] and preliminary experiments.

For C520 and C620, various weights of cellulose were dispersed into 100 g of solvent precooled to −10 to −12 °C, followed by vigorous stirring for 3 min at room temperature. After 3 min, the temperature of the solution was controlled to −2 to 0 °C using a salt–ice bath and the mixture was vigorously stirred for 27 min. The resulting solutions were observed by polarized optical microscopy. The cellulose was considered to have dissolved completely if no cellulose fragment was observed. The solubility was expressed as the maximum weight of cellulose dissolved in 100 g of solvent. Transparent cellulose solutions (5 g of C520 or C620) in the NaOH/thiourea/urea aqueous system were neutralized with 5% H_2SO_4, washed with water and then acetone, and dried at 70 °C for 24 h. DP values for two types of regenerated cellulose were determined using an Ubbelodhe capillary viscometer.

For C1400, 2.5 g of cellulose was dispersed in 100 g of solvent precooled to −10 to −12 °C and dissolved according to the method described above. The dissolved, gel, and insoluble fractions of the cellulose were isolated by centrifugation at 4800 rpm for 30 min. The gel and insoluble cellulose fractions were poured into 5% H_2SO_4 for neutralization, and the regenerated celluloses thus formed was isolated by filtration, washed with water and acetone, and dried under vacuum at 70 °C to constant weight. Dry regenerated cellulose from the dissolved cellulose fraction was obtained using the same procedure. The cellulose solubility (S_a) was calculated according to $S_a = [W_1/(W_1 + W_2)] \times 100\%$, where W_1 is the weight of the dissolved cellulose and W_2 is the combined weight of the gel and insoluble cellulose.[22] To reduce errors, these tests were repeated three times and the average value was considered as S_a.

2.3. Treatment of cellulose

To investigate the effects of NaOH, thiourea, and urea on the dissolution of cellulose, aqueous solutions of NaOH (8% w/w), thiourea (6.5% w/w) and urea (8% w/w) were each precooled to −12 °C. Then 5 g of cellulose was dispersed into each solution and stirred vigorously for 3 min and the solutions were placed in a refrigerator at 0 °C for 24 h. The treated cellulose was then washed five times with excess water and dried at 70 °C under vacuum overnight. The three different cellulose samples obtained were coded as NaC, TC, and UC, respectively.

2.4. Characterization

Dried NaC, TC, and UC samples and C520 were observed by scanning electron microscopy (SEM; JSM-5600LV, Japan). The samples were sputtered with gold, followed by observation and photography. Wide-angle X-ray diffraction measurements (D/max-2250PC, Japan) were used to investigate the crystal structure of the samples. The measurement conditions were as

follows: Cu Kα ($\lambda = 0.15406$ nm), 40 kV, 100 mA, $2\theta = 5$–40°, scan rate 10°/min, reflection mode.

The solvent for ^{13}C NMR measurements (8% NaOH/6.5% thiourea/8% urea/D_2O solution, coded as S1) was prepared in a 5-mL tube. Solutions with a cellulose concentration of 6 wt % for ^{13}C NMR (Bruker AV 400, Switzerland, magnetic field 9.4 T) measurements were prepared by dispersing the required amount of C520 into S1 at 0 °C with vigorous stirring for 10 min in a 5-mL tube. The solvent and solution were injected into NMR tubes using syringes and ^{13}C NMR measurements were carried out at room temperature.

The process of direct dissolution of cellulose can be observed using a polarized optical microscope because of the high crystallinity of cotton linters. A sample of 11.6 g of C520 was dispersed into 200 g of NS precooled to −12 °C and vigorously stirred for 3 min. The temperature of the solution was then controlled at −2 to 0 °C using a salt–ice bath and the cellulose solution was stirred vigorously. After stirring times of 20 s, 30 s and 20 min, samples of the cellulose solution were removed and divided into two parts. One part was photographed under a polarized microscope (Olympus RX51-P, Japan) and the other part was immediately regenerated using 3% H_2SO_4, washed five times with excess water and then dried at 70 °C under vacuum overnight. Raw cellulose (coded as Cell-0) and the three cellulose samples obtained (Cell-1, Cell-2, Cell-3) were characterized by solid-state ^{13}C NMR using a CP/MAS unit at room temperature.

Cellulose solutions for dynamic rheological measurements were prepared as follows: 8 g of C520 was dispersed into 200 g of NS precooled to −12 °C and vigorously stirred for 3 min at room temperature. The as-prepared solution was degassed by centrifugation at 4800 rpm for 5 min at room temperature. Dynamic rheology measurements were carried out on an ARES rheometer (ARES-RFS, TA Instruments, USA). Degassed cellulose solutions were heated or cooled to the required temperature directly in the sample chamber. The temperature was controlled within ±0.3 °C using a circulating thermobath with a cooling liquid (mixture of water and propylene glycol). Dynamic rheology experiments were performed until the required temperature was reached. The elastic modulus was measured as a function of time.

3. Results and discussion

3.1. Comparison of the dissolution power of the three solvents

The solubility of the three types of cellulose in the solvents is shown in Table 1. The results show that C520 and C620 can be dissolved completely, but only part of C1400 can be dissolved in these solvents. It is obvious that the NaOH/thiourea/urea aqueous system is more powerful than the other solvent systems. Moreover, cellulose is more stable in the NaOH/thiourea/urea aqueous system, which will be discussed in detail in a future paper. The DP values for cellulose regenerated from the NaOH/thiourea/urea aqueous system are also shown in Table 1. The DP value for regenerated cellulose C1400 could not be measured since it was not completely dissolved. It is interesting that the decrease in DP for regenerated cellulose is negligible, since mechanical destruction usually occurs on vigorous stirring. Thus, the dissolution process does not involve degradation at low temperature.

Table 1. Comparison of the solubility of cellulose in different aqueous systems and DP values for cellulose regenerated from the NaOH/thiourea/urea aqueous system

Sample	Solubility			DP
	NaOH/thiourea/urea	NaOH/thiourea	NaOH/urea	NaOH/thiourea/urea
C520	7.6 g	6.7 g	5.4 g	510
C620	6.5 g	5.5 g	4.5 g	605
C1400	83%	65%	55%	—

3.2. Effects of NaOH, thiourea, and urea on cellulose dissolution

Figure 1 shows SEM images of C520 and cellulose treated with NaOH, thiourea, and urea aqueous solutions. Compared with C520, all the treated celluloses show slight swelling, but with little breakage of the structure. In addition, no distinct differences are evident among the NaC, TC, and UC samples. Further research was carried out by WXRD. Figure 2 shows that the XRD patterns for C520, NaC, TC and UC are similar, with each spectrum displaying sharp 2θ peaks at approximately 14.8°, 16.5°, and 22.8°, which are characteristic of the cellulose I family and can be assigned to crystal planes $(1\bar{1}0)$, (110) and (200).The definition of crystal planes is based on the unit cell model suggested by French et al.[23] Peakfit software was used to separate the peaks. The amorphous peak at 18° can also be attributed to cellulose I[24] and the cellulose crystallinity is determined according to the usual area method.[25] The apparent crystal size (ACS) was calculated according to Scherrer's equation.[26] The crystalline parameters for the raw and treated celluloses are listed in Table 2. Result shows that untreated cellulose possesses the highest crystallinity, which indicates that NaOH, thiourea, and urea more or less destroyed hydrogen bonds in the cellulose. In addition, the greatest decrease in crystallinity and increase in ACS for the NaC sample suggest that NaOH plays a leading role during the dissolution of cellulose in NaOH/thiourea/urea aqueous

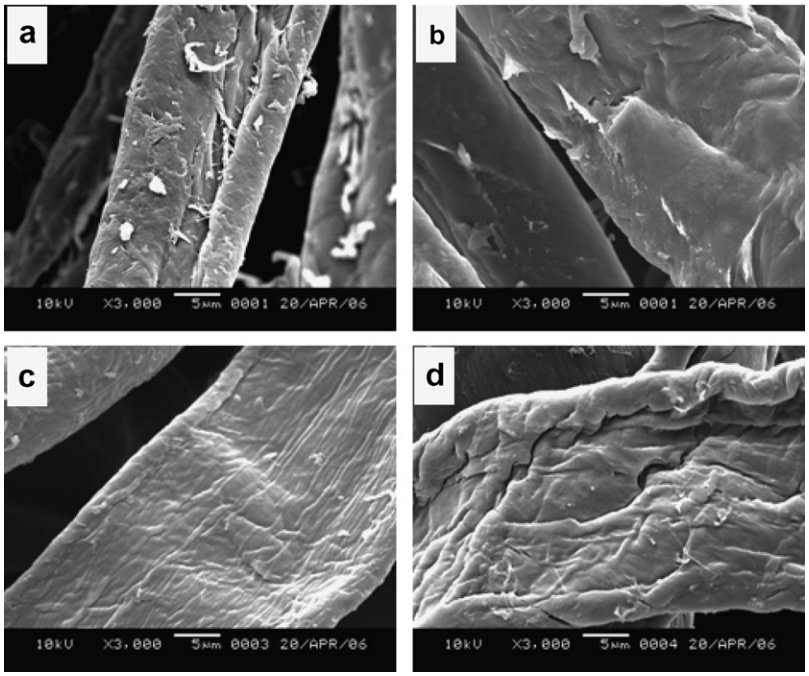

Figure 1. SEM images of (a) C520, (b) NaC, (c) TC and (d) UC cellulose samples.

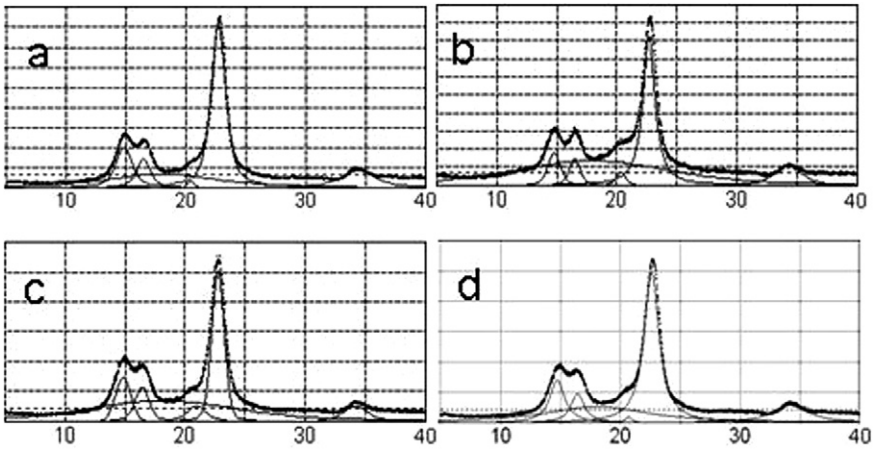

Figure 2. WXRD patterns for (a) C520, (b) NaC, (c) TC and (d) UC cellulose samples.

Table 2. Crystalline parameters for raw and treated cellulose

Sample	Crystallinity (%)	Apparent crystal size (nm)		
		$1\bar{1}0$	110	200
C520	76.3	5.08	6.10	5.82
NaC	51.62	6.74	7.60	7.32
TC	55.61	5.49	6.10	7.07
UC	70.23	6.19	6.10	5.82

solution. The SEM and XRD results indicate that the single-component aqueous solutions can only swell cellulose and no crystalline transformations occur at any specific concentration, which is similar to the results reported by Kunze and Fink.[27]

The structure and properties of the solvents in this complex system are not known, but some helpful information can be obtained from their ^{13}C NMR spectra shown in Figure 3. The NMR spectra of the solvent exhibits two singlets at 181.2 and 163.0 ppm, assigned to C=S and C=O, respectively, which are similar to the values (183.5 and 163.4 ppm) reported for thiourea and urea in polysol by Sadtler Research Laboratories.[28] The differences in chemical shift values indicate some interactions among NaOH, thiourea, and urea. The chemical shift for C=O in the NaOH/urea/D_2O system is 162.5 ppm according to Zhou et al.,[29] indicating a shift to higher magnetic field compared to C=O for urea in polysol, suggesting an interaction between NaOH and

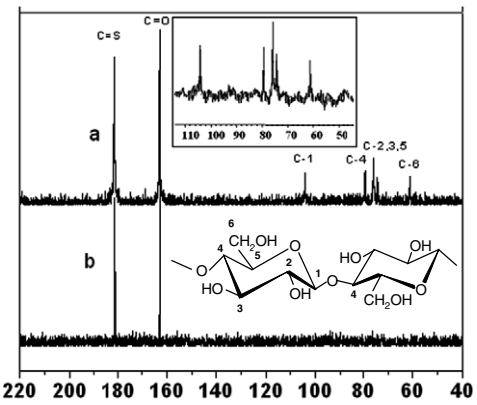

Figure 3. ^{13}C NMR spectra of (a) 6 wt % cellulose solution and (b) solvent. The inset shows a magnification of (b) between 110 and 50 ppm.

urea. Some researchers have demonstrated that Na^+, OH^-, and urea can form hydrates in aqueous media.[30,31] Thus, the interaction between NaOH and urea is in fact between Na^+ hydrates, OH^- hydrates and urea hydrates, which involves ionic and electron donor–acceptor interactions. In addition, the chemical shift for C=O in the NaOH/urea/D_2O system shifts to higher magnetic field by 0.5 ppm compared with that for C=O in the NaOH/thiourea/urea/D_2O system, which indicates an interaction between thiourea and urea. This conclusion is also confirmed by the fact that the solubility of thiourea in water increased on addition of urea to the water. The difference in chemical shifts for C=S of thiourea between polysol and NaOH/thiourea/urea/D_2O can mostly be attributed to an interaction between NaOH and thiourea; the similar chemical structure of urea and thiourea implies a similar interaction with NaOH. Obviously, interactions between NaOH and urea, and between NaOH and thiourea play an important role in the dissolution of cellulose, since no single component of this solvent system can dissolve untreated cellulose. It is interesting that the chemical shifts for C=O and C=S in the solvent (NaOH/thiourea/urea/D_2O) and in solution (cellulose in NaOH/thiourea/urea/D_2O) show only slight differences, suggesting a similar interaction among NaOH, urea, thiourea and water in the solvent and the cellulose solution. In other words, the structure of the solvent does not change when cellulose is dispersed in this system. On the other hand, the slight difference indicates that urea and thiourea hydrates interact to a certain degree with cellulose, which brings cellulose molecules into aqueous solution which means that urea and thiourea hydrates are bound to cellulose. Moreover, many studies have confirmed that NaOH hydrates can bind to cellulose.[31,32] These molecules bound to cellulose form a protective layer that prevents the association of cellulose macromolecules.

Figure 3 shows a ^{13}C NMR spectrum of a 6 wt % cellulose solution, displaying five sharp peaks at 104.1, 79.4, 75.8, 74.3, and 61.2 ppm, assigned to C-1, C-4, C-3, C-5, C-2, and C-6 atoms of cellulose, respectively. The C-4 chemical shift for raw cellulose (Fig. 5) is located at 88.9 ppm, which is assigned to intra-molecular hydrogen bonds (C-3–H···O-5′).[22] It is obvious that the chemical shift of the C-4 peak shifts upfield compared

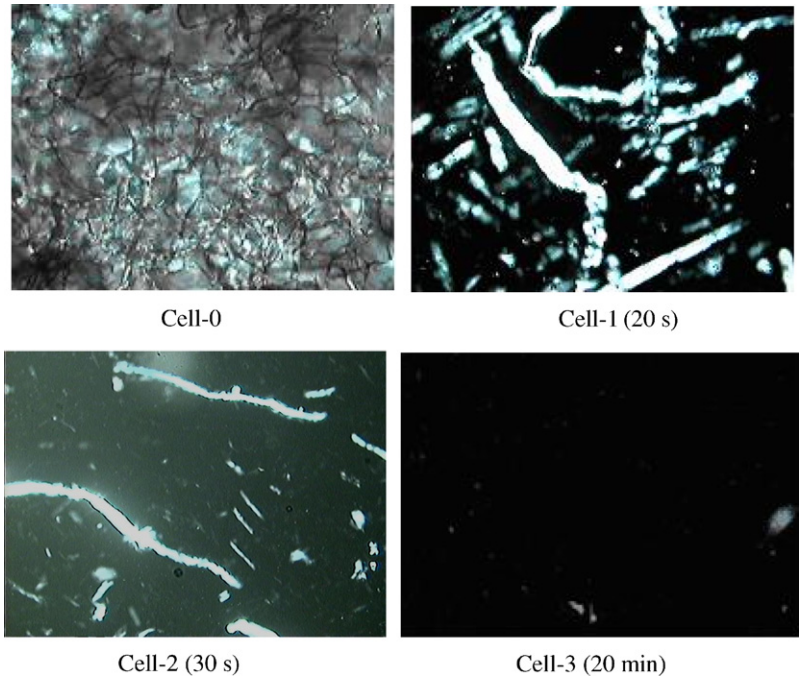

Figure 4. Polarized optical images of Cell-0, Cell-1, Cell-2, and Cell-3.

with that for raw cellulose, which indicates that the intra-molecular hydrogen bonds of cellulose have been destroyed. The chemical shifts of these peaks are very similar to those for some true solvents of cellulose, such as sodium hydroxide solution,[33] LiCl–DMAC,[34] and BMIMCl.[35] Moreover, the ^{13}C NMR spectrum does not show any new peak, which indicates that the NaOH/thiourea/urea aqueous solution is a direct solvent.

3.3. Dissolution process for cellulose in NaOH/thiourea/urea aqueous solution

During the dissolution process, the cellulose morphology in solvents was observed by polarized optical microscopy, and the structure of raw and regenerated celluloses was investigated by solid-state ^{13}C NMR spectroscopy. Figures 4 and 5 show optical images and the corresponding NMR spectra for raw cellulose (Cell-0), Cell-1, Cell-2 and Cell-3, with NMR data listed in Table 3.

The optical images indicate that swelling has occurred, based on the change in diameter of cellulose after 20 s. Considerable differences are evident in the corresponding ^{13}C NMR spectra. The C-4 resonance shows a sharp peak (88.9 ppm) and a shoulder (84.7 ppm) that can be assigned to crystalline and amorphous regions, respectively.[36] The sharp peak becomes broader and less intense after 20 s, which indicates destruction of hydrogen bonds. In addition, only a small peak for the C-6 resonance at 64.7 ppm was observed, and the C-6 main peak (65.0 ppm for Cell-0) shifts to a higher magnetic field (62.3 ppm for 20 s), which suggests that the *tg* conformation of CH_2OH shifts to a *gt* conformation, and that intermolecular O-6–H···O-2′

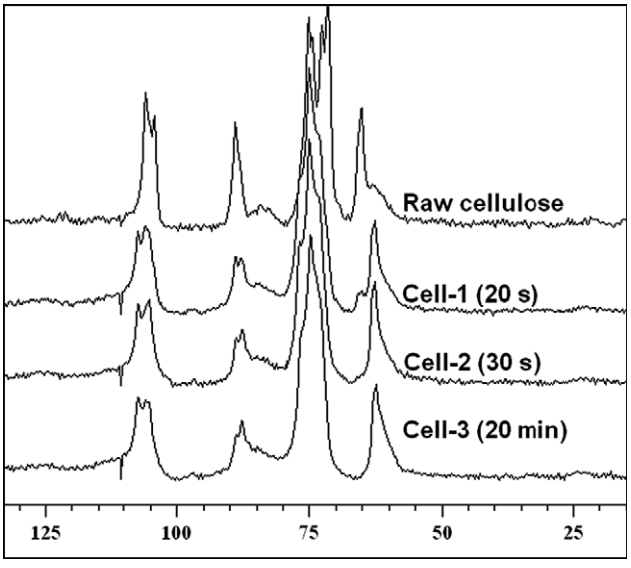

Figure 5. Solid-state ^{13}C NMR spectra of Cell-0, Cell-1, Cell-2, and Cell-3.

Table 3. Solid-state ^{13}C NMR data for raw cellulose and regenerated cellulose sampled at different times

Sample	δ (ppm)				
	C1	C4	C3, C5	C2	C6
Cell-1	105.7	88.9	75.0	71.5	65.0
Cell-1 (20 s)	107.2, 105.7	88.9, 87.9	74.7	74.7	65.0, 62.3
Cell-2 (30 s)	107.2, 105.0	88.6, 87.6	74.7	74.7	62.3
Cell-3 (20 min)	107.2, 105.0	87.6	74.7	74.7	62.3

hydrogen bonds have been formed.[37] After 30 s, most of the cellulose was dissolved according to the optical image, and the corresponding NMR spectrum indicates that the conformation of most of the cellulose has changed from cellulose I to cellulose II. The optical images and ^{13}C NMR spectra indicate that complete dissolution has occurred by 20 min. Moreover, it is obvious that the following cellulose structural changes occur during dissolution and regeneration: cellulose I (cotton linters) changes to amorphous cellulose (in solution), and then cellulose II.

3.4. Improvement of the dissolution process

In the NaOH/urea and NaOH/thiourea aqueous systems, cellulose was dissolved in solvents precooled to −12 to −10 °C for 5 min at room temperature. Most of the cellulose was dissolved within 1 min. However, some cellulose cannot be dissolved completely, even after 5 min, since it is difficult for the solvent to enter into the fibers surrounded by viscous cellulose solution. Thus, it is disadvantageous for filtration and spinning. These solvents can dissolve cellulose at −16 to 4 °C, with the greatest dissolution power at −12 to −8 °C according to our patent. The cellulose solution is most stable at 0 °C, and shows gelation at higher temperature and if held at lower temperature for a longer time. To improve the dissolution process, the following procedure was carried out. Cellulose was dispersed in solvents precooled to −12 °C, followed by vigorous stirring for 3 min at room temperature. After 3 min, most of the cellulose was dissolved and the temperature of the solution increased to approximately 0 °C. Further dissolution was conducted for 17 min at a temperature of −2 to 0 °C, which was monitored by a salt–ice bath. The as-prepared solution is more transparent and rather easy to filter compared with solution dissolved at room temperature, even for 30 min. The new dissolution method is very effective, as shown by dynamic rheological measurements. Figure 6 shows that G' (elastic modulus) decreases with time at temperature settings of −5 and 0 °C and increases at 30 °C, with the actual solution temperature well controlled and varying only slightly for each temperature setting. Moreover, the curves for G' versus

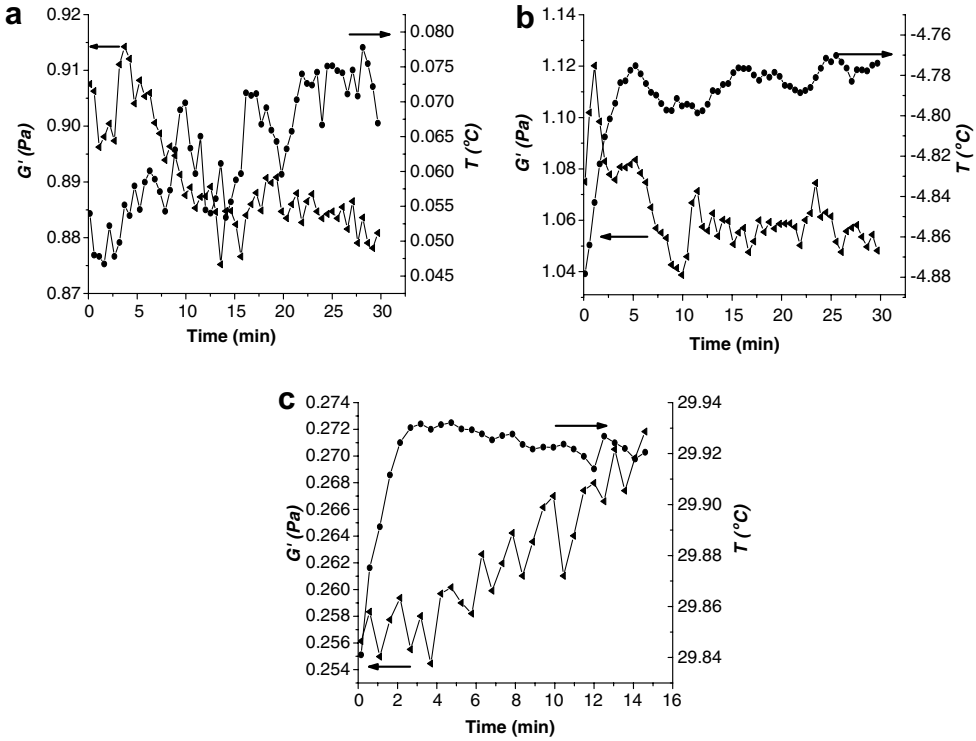

Figure 6. G' (Elastic modulus) of 4% cellulose solution and the actual solution temperature as functions of time at different temperature settings: (a) −5, (b) 0, and (c) 30 °C.

time show some obvious differences at different temperature settings, which indicates that G' is strongly affected by temperature. To eliminate the effect of temperature, G'/T was plotted as a function of time (Fig. 7). It is interesting that G'/T increases with time at temperature settings of −5 and 30 °C, while it decreases at 0 °C on

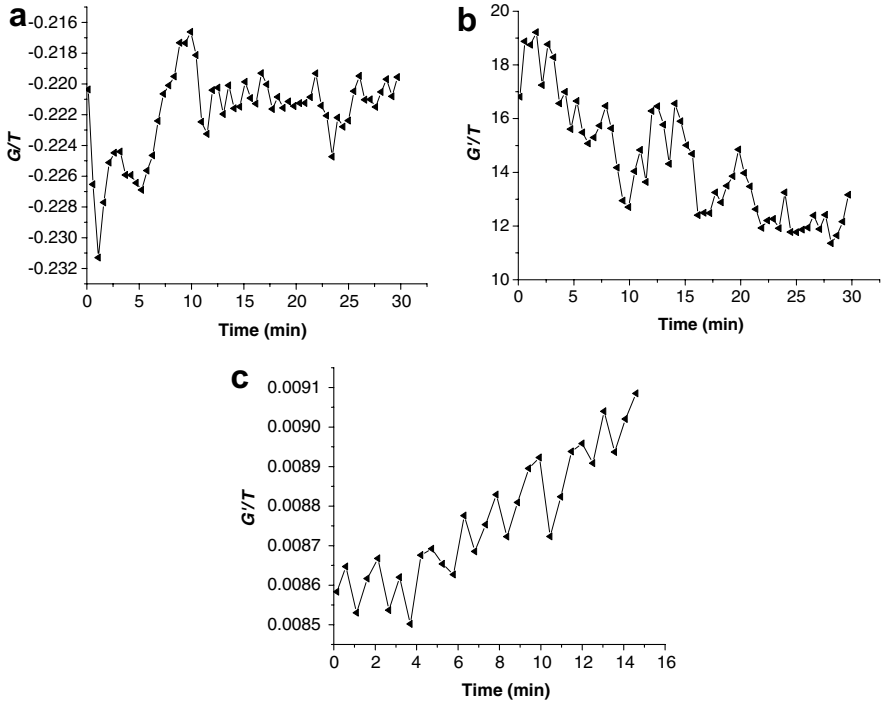

Figure 7. G'/T as a function of time at different temperature settings: (a) −5 °C, (b) 0 °C, and (c) 30 °C.

the whole. This indicates that cellulose molecules in solution are disentangled and structural units are partly destroyed at 0 °C, leading to more complete dissolution, while the cellulose solution forms a more complex network because of aggregation of cellulose molecules via hydrogen bonds at −5 and 30 °C. The results are consistent with the fact the cellulose solution is most stable at 0 °C, although the NS solvent system is the most powerful at −8 °C. Visual observation of the transparency of the solution also confirmed that the new dissolution method is very effective. In particular, the new dissolution method proposed here is very suitable for preparation of more concentrated cellulose solutions.

4. Conclusions

Untreated or nonactivated cellulose can be dissolved directly and quickly in an NaOH/thiourea/urea aqueous solution. The solvent system is of low toxicity and possesses higher solubility capacity for cellulose compared with NaOH/thiourea and NaOH/urea aqueous solutions. The mechanism for dissolution of cellulose in the novel solvent was investigated by SEM, WXRD, and ^{13}C NMR. The results show that single components of this solvent system cannot dissolve untreated cellulose, implying that interactions between NaOH and urea, and NaOH and thiourea play an important role in improving the dissolution of cellulose. Moreover, ^{13}C NMR spectra proved that NaOH, thiourea, and urea were bound to cellulose molecules, which brings cellulose molecules into the aqueous solution to a greater extent and prevents cellulose macromolecules from associating. Moreover, NMR spectra of cellulose solutions show that the novel system is a direct solvent. During dissolution and regeneration, cellulose I changes to amorphous cellulose in solution, and then to cellulose II. Dynamic rheological measurements showed that the new dissolution method is more effective, leading to a good cellulose solution. This simple technology is cheap and environmentally friendly, and can be used to prepare regenerated films and fibers, which is promising for substitution of the viscose technology that involves hazardous byproducts. Moreover, the novel solvent provides a medium for preparing cellulose derivatives homogeneously.

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