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The dissolution of cellulose in NaOH-based aqueous system by two-step process

Haisong Qi · Quanling Yang · Lina Zhang ·
Tim Liebert · Thomas Heinze

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Abstract A new dissolution method, a two-step process, for cellulose in NaOH/urea aqueous system was investigated with ^{13}C NMR, wide X-ray diffraction (WXRD), and solubility test. The two steps were as follows: (1) formation and swelling of a cellulose–NaOH complex and (2) dissolution of the cellulose–NaOH complex in aqueous urea solution. The dissolution mechanism could be described as strong interaction between cellulose and NaOH occurring in the aqueous system to disrupt the chain packing of original cellulose through the formation of new hydrogen bonds between cellulose and NaOH hydrates, and surrounding the cellulose–NaOH complex with urea hydrates to reduce the aggregation of the cellulose molecules. This leads to the improvement in solubility of the polymer and stability of the cellulose solutions. By using this two-step process, cellulose can be dissolved at 0–5 °C in contrast to the known process that requires −12 °C. Regenerated cellulose (RC) films with good mechanical properties and excellent optical transmittance were prepared successfully from the cellulose solution.

Keywords NaOH-based aqueous system · Cellulose · Two-step dissolution process · Regenerated cellulose films

Introduction

Development of green technologies for cellulose processing is a topical problem in the field of sustainable chemistry. Some powerful non-derivatizing organic solvents for cellulose have been developed and used for preparing regenerated cellulose films and fibers during the last two decades, such as N-methylmorpholine-N-oxide (NMMO) (Schurz 1999; Fink et al. 2001) and ionic liquids (Swatloski et al. 2002; Turner et al. 2004).

In addition to solvents mentioned previously, NaOH-based aqueous systems have been one focus of cellulose solvents research because they can lead to environmentally friendly, simple, and economic processes. It is known that cellulose, such as microcrystalline cellulose (MCC), can be dissolved in aqueous NaOH in a narrow range of low temperatures and concentrations (from 7 to 10 wt% NaOH in water at −5 to −6 °C) (Sobue et al. 1939; Egal et al. 2007; Zhou and Zhang 2000; Isogai and Atalla 1998; Kuo and Hong 2005; Kamide et al. 1992; Roy et al. 2001).

H. Qi · Q. Yang · L. Zhang (✉)
Department of Chemistry, Wuhan University,
430072 Wuhan, People's Republic of China
e-mail: lnzhang@public.wh.hb.cn

H. Qi · T. Liebert · T. Heinze (✉)
Centre of Excellence for Polysaccharide Research,
Institute of Organic Chemistry and Macromolecular
Chemistry, Friedrich Schiller University of Jena,
Humboldtstraße 10, 07743 Jena, Germany
e-mail: thomas.heinze@uni-jena.de

However, it is difficult to dissolve substantially all cellulose having a high degree of polymerization (DP > 300) in an alkali aqueous solution having only a single alkali composition. Consequently, aqueous NaOH solutions are not suitable for technical applications (Egal et al. 2007). In contrast, several aqueous alkaline systems, such as aqueous NaOH/urea solution and aqueous NaOH/thiourea solution, can dissolve cellulose with relatively high DP (DP = 500–900) completely (Cai and Zhang 2005; Qi et al. 2008; Ruan et al. 2004). Although the compositions and dissolution conditions are different, all NaOH-based aqueous systems mentioned previously have similar NaOH concentrations (ranging from 6 to 10 wt%) and can only dissolve cellulose at low temperatures.

In this work, it will be demonstrated that cellulose can be dissolved in NaOH-based aqueous systems at 0–5 °C by applying higher NaOH concentrations and a new dissolution process. An attempt was made to prepare regenerated cellulose (RC) films from cellulose solutions prepared via this process. Such a procedure can lead a suitable technical process for cellulose processing with reduced power consumption.

Experimental part

Materials

Two kinds of cellulose samples, Avicel® (Fluka, degree of polymerization, DP 330) and cotton linters (supplied by Hubei Chemical Fiber Group Ltd., Xiangfan, China, DP 570), were used. The cellulose sample was dried at 60 °C for 24 h in a vacuum oven and stored in a desiccator until used. PEG (Poly (ethylene glycol), Fluka, DP 2000) and all other chemical reagents were of analytical grade.

Dissolution of cellulose in NaOH-based aqueous system

For a typical dissolution process, 4 g cellulose (cotton linters, DP 570) was dispersed in 48 g 14 wt% NaOH aqueous solution pre-cooled to 0 °C with stirring for 1 min. Then, 48 g 24 wt% urea aqueous solution pre-cooled to 0 °C was added immediately with stirring vigorously for 2 min. Within this time, a transparent cellulose solution without any native fibers was obtained. The quality of the solution was confirmed by optical microscopy.

Preparation of regenerated cellulose films from cellulose solution by two-step process

Regenerated cellulose films were prepared according to our previous work (Qi et al. 2009). Cotton linters were dissolved in NaOH-based aqueous solvents via the two-step process mentioned above. Subsequently, the cellulose solution was subjected to centrifugation at 166.66 Hz (10,000 rpm) for 10 min at 10 °C in order to carry out a degasification. The resulting transparent solution was immediately cast on a glass plate to give a thickness of 250 m for a gel sheet and then immersed into a coagulation bath with 5 wt% H_2SO_4 for 5 min at 25 °C to coagulate and regenerate. The resulting RC films were washed with running water and then with deionized water. The wet films were fixed on glass plate to prevent shrinkage and finally were air-dried at ambient temperature to obtain transparent films. The RC films prepared from the NaOH/urea aqueous system and NaOH/thiourea aqueous system were coded as RC-U and RC-T, respectively.

Characterization

The viscosity-average molecular weight (M_η) of cellulose films was determined in cadoxen at 25 °C by viscometry (Brown and Wikstrom 1965).

Wide-angle X-ray diffraction (WAXD) was measured with an X-ray diffractometer (D/MAX-1200, Rigaku Denki Co. Ltd., Japan). The X-ray radiation used was Ni-filtered Cu–K_α with a wavelength of 1.5406 Å. The voltage was set at 40 kV and the current was set at 30 mA. The samples were mounted on a solid circular holder, and the proportional counter detector was set to collect data at a rate of $2\theta = 1^\circ$/min over the 2θ range from 4° to 40°.

^{13}C NMR measurements of the cellulose solution in NaOH/urea/D_2O system prepared by two-step process were carried out on a Bruker 400 AMX NMR spectrometer at ambient temperature. The cellulose concentration was adjusted to be 4 wt%. Scanning electron micrographs (SEM) were taken on a Hitachi S-570 scanning electron microscope with 20 kV accelerating voltage and at a magnification of 3000. Optical transmittance (T_r) of the films was

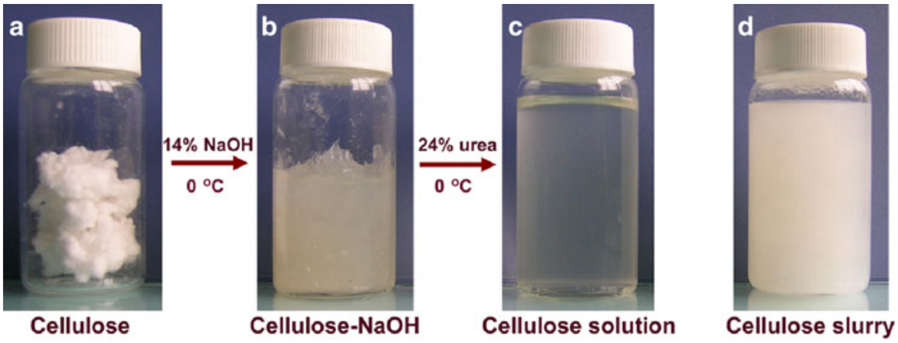

Fig. 1 Photos of the two-step dissolution process of cellulose: **a** Cellulose sample (cotton linter); **b** Cellulose–NaOH with 14 wt% NaOH; **c** Cellulose aqueous solution with 7 wt% NaOH and 12 wt% urea; **d** Swollen cellulose slurry by direct dispersing in 7 wt% NaOH/12 wt% urea aqueous solution at 0 °C

measured with a UV–vis spectrometer (Shimadzu UV-160A, Japan) at a wavelength of 800 nm. The tensile strength (σ_b) and elongation at break (ε_b) of the films were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) according to ISO 527-3, 1995 (E) at a speed of 5 mm min^{-1}.

Results and discussion

The new process for cellulose dissolution in NaOH-based solution

In a previous work, cellulose can be dissolved in NaOH/urea aqueous solution at −10 to −12 °C (Cai and Zhang 2005). To reduce the power consumption to achieve the low temperature required, a two-step process was investigated. An attempt to dissolve the cellulose in NaOH/urea aqueous solution at relatively high temperature (such as at 0 °C) was made, resulting in slurry-type mixtures (Fig. 1d). As shown in Fig. 1a–c, the cellulose was swollen in 14 wt% aqueous NaOH solution pre-cooled to 0 °C and then was dispersed and dissolved when 24 wt% aqueous urea solution pre-cooled to 0 °C was added. Finally, we obtained transparent cellulose solution through this process (Fig. 1c), with about 7 wt% NaOH and 12 wt% urea in the solution. This experimental phenomenon further supported the previous conclusion that NaOH "hydrates" can be more easily attracted to cellulose chains through the formation of new hydrogen-bonded networks, while urea hydrates can possibly be self-assembled at the surface of the NaOH hydrogen-bonded cellulose to form a transparent cellulose solution (Cai et al. 2008).

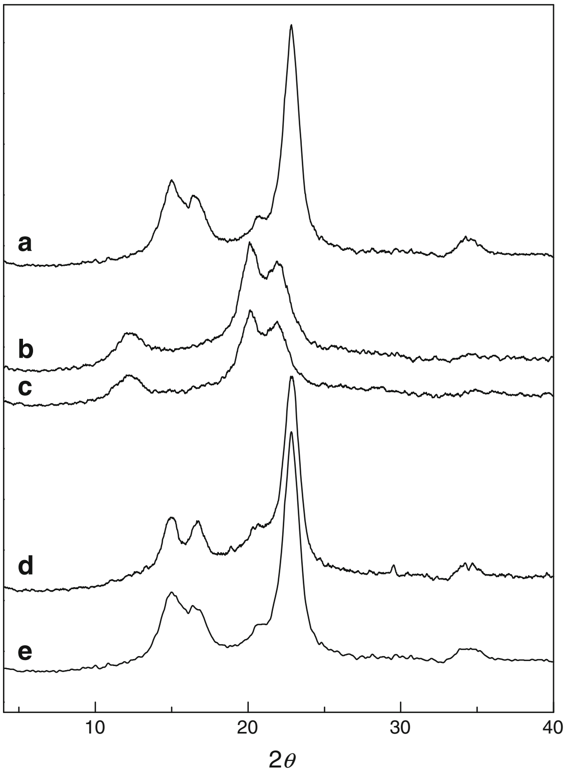

Fig. 2 X-ray diffractograms of initial cellulose (**a**), regenerated cellulose from cellulose solution in NaOH/urea aqueous system prepared by two-step process (**b**), cellulose regenerated from cellulose directly dispersed in 12 wt% NaOH at 0 °C (**c**), and cellulose regenerated from cellulose directly dispersed in 24 wt% urea at 0 °C (**d**), and cellulose regenerated from cellulose directly dispersed in 7 wt% NaOH/12 wt% urea at 0 °C (**e**)

Figure 2 shows the X-ray diffractograms of the initial cellulose and cellulose regenerated from systems treated with different methods. The initial cellulose has typical peaks of cellulose I (Fig. 2a), while the cellulose regenerated from the cellulose solution has typical peaks of cellulose II (Fig. 2b) (Kaplan 1998). This indicated that the crystal structure of the initial cellulose was destroyed completely and rearranged in this process. For comparison, there was no lattice conversion when cellulose was dispersed directly in 7 wt% NaOH/12 wt% urea aqueous solution at 0 °C (Fig. 2e).

Here, the structures of cellulose treated with only 14 wt% aqueous NaOH solution and/or only 24 wt% aqueous urea solution at 0 °C were also investigated. The regenerated polymer (Fig. 2c) exhibited typical peaks of cellulose II after interaction only with aqueous NaOH. However, the cellulose I crystal structure was maintained after exposure to aqueous urea (Fig. 2d). It has been indicated that the NaOH is the real agent that cleaves the inter- and intramolecular hydrogen bonds of cellulose. However, simply breaking the inter-strand hydrogen bonds is not sufficient; the active "single-strand" cellulose has to be blocked from contact with other strand in order to prevent aggregation. The addition of urea to the NaOH system can stabilize the solution by acting as blockers, as a result of the urea hydrates surrounding the cellulose–NaOH complex to reduce the aggregation of the cellulose molecules. The formation of the new hydrogen bond between the hydroxyl groups in cellulose bonded with NaOH and urea carbonyl and amino groups creates a water-dissoluble inclusion complex, leading to the good dissolution of cellulose (Cai et al. 2008). It is not hard to imagine that cellulose dissolution in NaOH/H_2O–urea/H_2O aqueous solutions involves two main steps: (1) the alkali hydrates and free water can penetrate the cellulose and destroy the intra- and inter-molecular hydrogen bonding of the cellulose, forming soluble cellulose–NaOH complex; and (2) the cellulose–NaOH complex disperses well in the urea aqueous solution to give transparent solution.

Figure 3 shows the ^{13}C NMR spectrum of cotton linters and Avicel in 7 wt% NaOH/12 wt% urea/D_2O solution prepared through two-step dissolution process. The six signals of the unmodified anhydroglucose unit appear clearly at 103.8 (C-1), 79.0 (C-4), 75.6 (C-3), 75.3 (C-5), 73.9 (C-2), and 60.7 ppm (C-6) for cotton linters and 103.8 (C-1), 79.0 (C-4), 75.5 (C-3), 75.3 (C-5), 73.9 (C-2), and 60.6 ppm (C-6) for Avicel, respectively. The signals of the carbon atoms C1–C6 are well resolved. And there is not any new peak for cellulose derivatives in ^{13}C NMR spectra, indicating an absence of derivatization. The ^{13}C NMR chemical shifts of cellulose solutions in various non-derivatizing solvent systems are summarized in Table 1. It is worth noting that the chemical shifts of C1–C6 for cellulose in NaOH/D_2O–urea/D_2O are almost the same as those for cellulose directly dissolved in NaOH/urea/D_2O. In addition, the chemical shifts of C1–C6 for cellulose in NaOH/D_2O–urea/D_2O are also similar to that in cadoxen (Nehls et al. 1994), AMIMCl (Zhang et al. 2005), DMAc/LiCl (McCormick et al. 1985), and DMSO/TBAF (Heinze et al. 2000), which are good solvents of cellulose. In view of these results, cellulose can dissolve in NaOH/H_2O–urea/H_2O aqueous solutions without derivatization by two-step dissolution process.

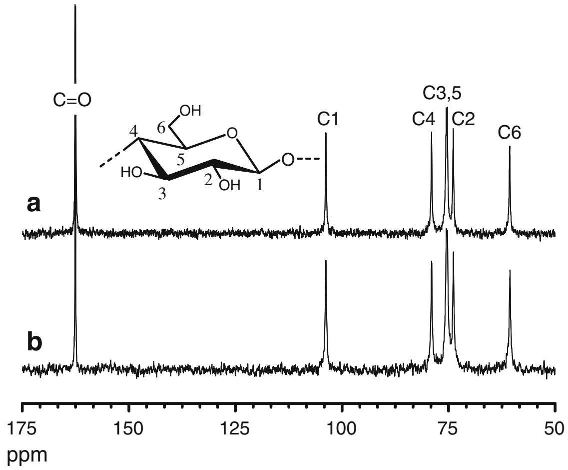

Fig. 3 ^{13}C NMR spectra of cotton linters (**a**) and Avicel (**b**) in 7 wt% NaOH/12 wt% urea/D_2O aqueous solution prepared through two-step dissolution process

The conditions to affect dissolution in two-step process

The influence of temperature and concentration on dissolution of cellulose in NaOH/H_2O–urea/H_2O aqueous solutions by two-step process was investigated. As mentioned earlier, the pathway from cellulose I to cellulose II solution goes through the forming of cellulose–NaOH complex. If cellulose I is treated with an alkali solution, the cellulose swells to various extents depending on the concentration of NaOH (c_{NaOH}) and temperature. Figure 4 shows the schematic diagram of the solubility of NaOH–cellulose complex, which was prepared from aqueous

Table 1 ^{13}C-NMR chemical shifts of cellulose in non-derivatizing solvent systems

Solvents	^{13}C-NMR chemical shift (ppm)						Source
	C1	C2	C3	C4	C5	C6	
NaOH/D_2O–urea/D_2O	103.8	73.9	75.6	79.0	75.6	60.7	This work[a]
NaOH/D_2O–urea/D_2O	103.8	73.9	75.6	79.0	75.5	60.6	This work[b]
NaOH/urea/D_2O	103.8	73.8	75.6	79.0	75.5	60.5	Cai and Zhang (2005)
LiOH/urea/D_2O	103.8	73.9	75.7	79.2	75.3	60.6	Cai and Zhang (2005)
NaOH/thiourea/D_2O	105.0	75.2	76.7	80.3	76.7	62.0	Ruan et al. (2004)
NaOH/PEG/D_2O	103.9	74.2	75.5	79.5	75.5	60.9	Yan and Gao (2008)
Cadoxen	103.8	74.9	76.6	78.9	76.4	61.8	Nehls et al. (1994)
AMIMCl	102.7	74.0	74.9	79.0	75.4	60.4	Zhang et al. (2005)
DMAc/LiCl	103.9	74.9	76.6	79.8	76.6	60.6	McCormick et al. (1985)
DMSO/TBAF	102.7	73.5	75.0	78.4	75.6	59.9	Heinze et al. (2000)

[a] Cotton linters

[b] Avicel

NaOH solution with different temperatures and concentrations, in 24 wt% aqueous urea solution pre-cooled to 0 °C. The diagram reveals that the NaOH–cellulose complex prepared from 12 to 18 wt% NaOH aqueous solution at –2 to 6 °C could be dissolved completely to obtain a cellulose solution, as shown in Fig. 4 area I. Otherwise, the cellulose could only be dissolved partially (Fig. 4, area II) or even could not be dissolved (Fig. 4, area III). Normally, high concentration of NaOH (c_{NaOH}) and low temperature are expected to disrupt the hydrogen bonds of cellulose. However, the insoluble Na-cellulose is also formed if c_{NaOH} is too high, such as above 14 wt% (Porro et al. 2007). And the insoluble Na-cellulose also found when the temperature is too low, such as below −5 °C.

At the same time, the dissolution of the cellulose–NaOH complex, which was formed from 14 wt% aqueous NaOH solution pre-cooled to 0 °C, in aqueous urea solution with different urea (c_{urea}) and temperature was also investigated (Fig. 5). For aqueous urea with too low or too high concentration, the cellulose could only be dissolved partially (Fig. 5, area II), or even could not be dissolved (Fig. 5, area III). The current cellulose–NaOH complex could only be dissolved completely in 14–28 wt% urea aqueous solution at −7 to 5 °C to obtain a cellulose solution, as shown in area I of Fig. 5.

The mass ratio of aqueous NaOH solution and aqueous urea solution in the dissolution process discussed previously was 1:1. In addition, we also investigated the solubility of cellulose in the two-step process with different solvent mass ratio (the mass ratio of aqueous NaOH solution and aqueous urea solution was in the range from 1:2 to 2:1). These dissolution experiments suggested that cellulose could be dissolved in 12–18 wt% aqueous NaOH solution and 14–28 wt% aqueous urea solution at −2 to 5 °C by this process. And the final cellulose solution

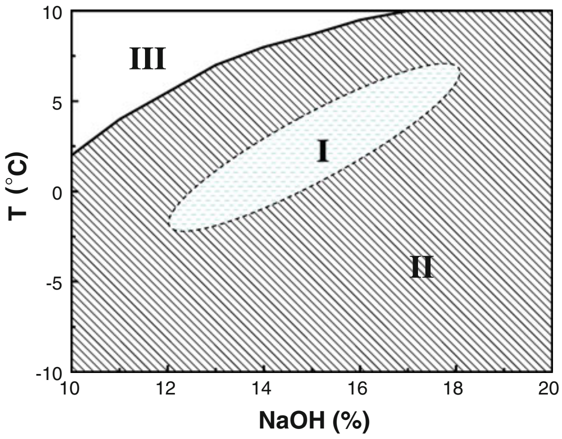

Fig. 4 Schematic diagram of the solubility of NaOH–cellulose complex, which prepared from aqueous NaOH solution with different temperature and concentration, in 24 wt% aqueous urea solution pre-cooled to 0 °C: *I* Complete dissolution area; *II* Partial dissolution area; *III* Non-dissolution area. (Mass ratio of aqueous NaOH solution and aqueous urea solution is 1:1.)

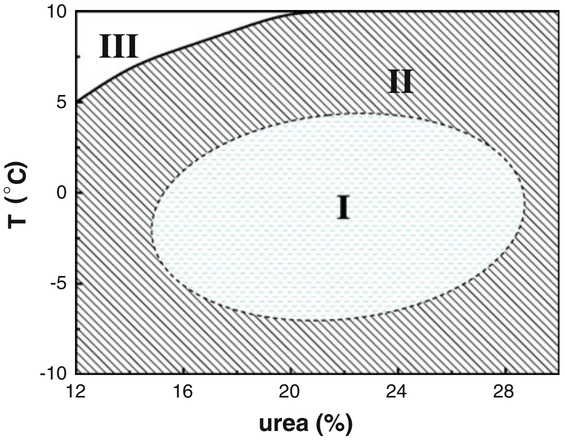

Fig. 5 Schematic diagram of the solubility of NaOH–cellulose complex, which prepared from 14 wt% aqueous NaOH solution pre-cooled to 0 °C, in aqueous urea solution with different temperature and concentration: *I* Complete dissolution area; *II* Partial dissolution area; *III* Non-dissolution area. (Mass ratio of aqueous NaOH solution and aqueous urea solution is 1:1.)

containing 6–8 wt% NaOH and 8–14 wt% urea was relatively stable when stored at room temperature.

Dissolution of cellulose in NaOH-based aqueous system

Several other kinds of NaOH-based aqueous solvents for cellulose had been reported, such as NaOH/thiourea aqueous system (Ruan et al. 2004; Zhang et al. 2002) and NaOH/PEG aqueous system (Yan and Gao 2008). With the similar structure, thiourea is also an additive for cellulose dissolution in the NaOH-based aqueous solution. Directly, cellulose can dissolved in 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution pre-cooled to about −4.5 °C. By using a two-step process, cellulose could also be dissolved in 12–18 wt% NaOH aqueous solution and 4–6 wt% thiourea aqueous solution (Table 2). Also, cellulose (Avicel) can be dissolved in 14–18 wt% NaOH aqueous solution and 2–4 wt% PEG aqueous solution by two-step dissolution process (Table 2). These results indicate that other agents such as thiourea and PEG can also be sufficient to act as blockers in NaOH-based cellulose aqueous system.

Some important investigations about dissolution of cellulose in NaOH-based aqueous systems are summarized in Table 2. They are all successful dissolution methods and conditions for cellulose. Table 2 reveals that NaOH/H_2O solution can only dissolve treated cellulose or cellulose with low DP such as MCC, whereas the NaOH/urea/H_2O and NaOH/thiourea/H_2O solution can dissolve cellulose with relatively high DP. Normally, it can be concluded that the dissolution of cellulose in NaOH-based aqueous systems is mainly determined by: (1) cellulose materials and DP, such as cotton linters

Table 2 Dissolution methods and conditions for cellulose in NaOH-based aqueous systems

Solvents	Method and condition	Cellulose	Source
8–10 wt% NaOH	Direct dissolution, 4 °C	Treated cellulose[a], DP = 330	Kamide et al. (1984)
7–9 wt% NaOH	Direct dissolution	Treated cellulose[b], DP = 300	Yamane et al. (1996)
8–9 wt% NaOH	Freeze–thaw	MCC, DP = 200	Isogai and Atalla (1998)
7.9–14.9 wt% NaOH	Freeze–thaw	MCC, DP = 250	Egal et al. (2008)
6 wt% NaOH/4 wt% urea	Freeze–thaw	Cotton linter, DP = 690	Zhou and Zhang (2000)
7 wt% NaOH/12 wt% urea	Direct dissolution, −10 °C	Cotton linter, DP = 700	Cai and Zhang (2005)
9.5 wt% NaOH/4.5 wt% thiourea	Direct dissolution, −4 to −5 °C	Cotton linter, DP = 620	Ruan et al. (2004)
9 wt% NaOH/1 wt% PEG	Freeze–thaw	Cellulose powder, DP = 810	Yan and Gao (2008)
12–18 wt% NaOH, 16–28 wt% urea	Two-step, −2 to 5 °C	Cotton linter, DP = 570	This work
12–18 wt% NaOH, 4–6 wt% thiourea	Two-step, −2 to 5 °C	Cotton linter, DP = 570	This work
14–18 wt% NaOH, 2–4 wt% PEG	Two-step, −2 to 5 °C	Avicel, DP = 570	This work

[a] Cellulose was regenerated from its cuprammonium solution

[b] Cellulose was treated by aqueous NaOH solution before dissolution

pulp, wood pulp, and MCC; (2) additives, such as urea, thiourea, and PEG; and (3) dissolution conditions, such as temperature, concentration, and time. Also, the amount of cellulose dissolved varies according to the process used. As known to us, there are mainly three processes to dissolve cellulose in NaOH-based aqueous system: (1) freeze–thaw; (2) direct dissolution in solvents; (3) two-step dissolution process. Usually, cellulose can be dissolved in NaOH aqueous systems with NaOH concentration ranging from 6 to 10 wt% by freeze–thaw and direct dissolution processes. We can broaden the cellulose dissolution scope using two-step dissolution process. In view of our experimental results and previous literature studies, a schematic diagram of the solubility of cellulose in NaOH-based aqueous systems depending on NaOH concentration and temperature was proposed in Fig. 6. We can dissolve cellulose completely in a wide range of 6–18 wt% NaOH by three processes mentioned above (Fig. 6, area I). Conditions for partial cellulose dissolution are indicated by area II in Fig. 6. Conditions where cellulose cannot be dissolved are indicated by area III in Fig. 6. Furthermore, the proper method for cellulose dissolution is determined by the NaOH concentration: (1) 6–10 wt% NaOH for freeze–thaw; (2) 6.5–10 wt% NaOH for direct dissolution; and (3) 10–18 wt% NaOH for two-step process. Whatever process is being used, however, the NaOH concentration in the final cellulose solution must be kept in a range of 6–10% to maintain the stability of the solution. Otherwise, the cellulose solution will gel easily when stored.

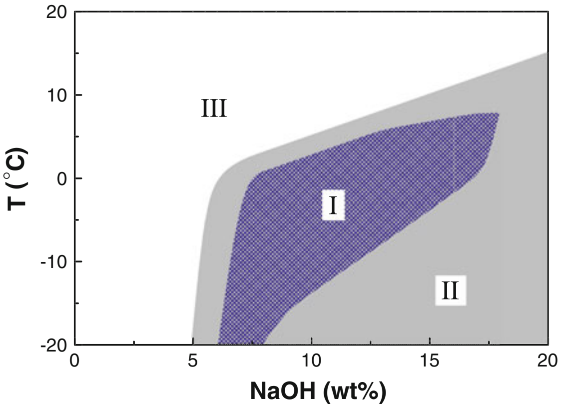

Fig. 6 Schematic diagram of the solubility of cellulose in NaOH-based aqueous systems depending on NaOH concentration and temperature: *I* Complete dissolution area; *II* Partial dissolution area; *III* Non-dissolution area

Regenerated cellulose films prepared from cellulose solution by two-step process

Cotton linters pulp dissolved well in NaOH-based aqueous solvents via the two-step process was transformed successfully to regenerated cellulose (RC) films during this process. The RC films prepared from the NaOH/urea aqueous system and NaOH/thiourea aqueous system were coded as RC-U and RC-T, respectively. The M_η values of RC-U and RC-T were determined to be 8.8×10^4 g/mol (DP = 540) and 8.1×10^4 g/mol (DP = 500) by viscometry, respectively. Compared with that of the original cellulose sample (DP = 570), almost no degradation of cellulose occurred in the dissolution and regeneration processes.

The X-ray diffraction patterns of the cellulose films are shown in Fig. 7. There were three peaks at $2\theta = 12.0°$, 19.9°, and 22.1°, corresponding to the (110), (10), and (200) planes, respectively, which are attributed to the typical cellulose II crystalline form. The regenerated films differed from the original materials, which had typical peaks of the cellulose I (see Fig. 2a). It was confirmed that the cellulose solution did transform into regenerated cellulose II when the cellulose gel was regenerated in the coagulation bath. Figure 8 shows the SEM images

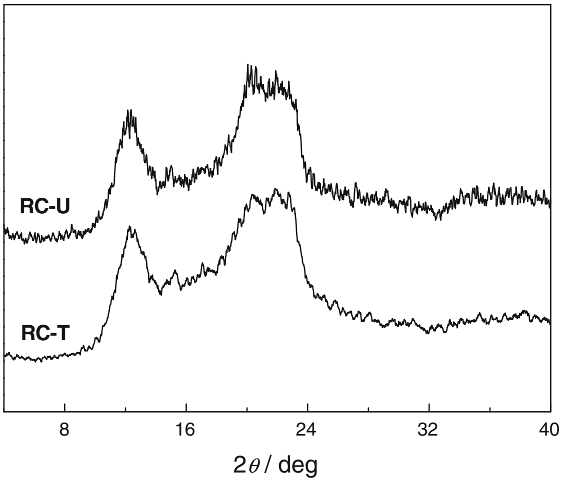

Fig. 7 X-ray diffractograms of RC films prepared from cellulose dissolution in NaOH-based systems via two-step process

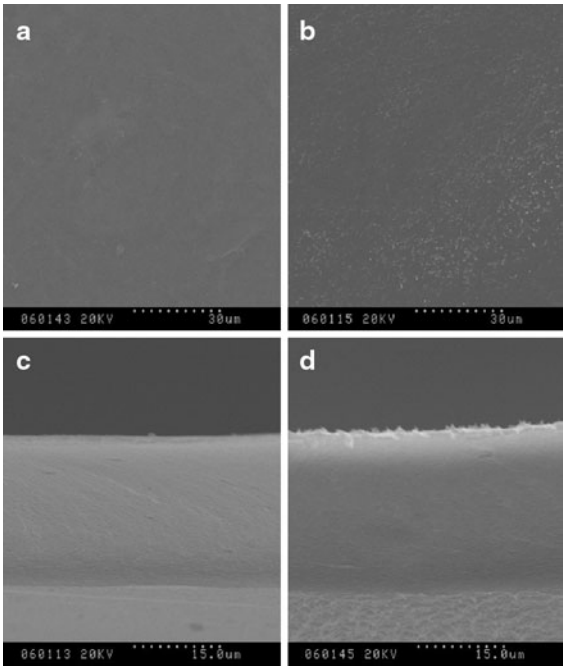

Fig. 8 SEM images of surface (**a**, **b**) and cross section (**c**, **d**) for RC films prepared from cellulose dissolution in NaOH-based systems via two-step process: **a**, **c**, RC-U; **b**, **d**, RC-T

of the RC films. Both of the RC films displayed highly uniform and dense surface and cross section. The tensile strength (σ_b) and the elongation at breaking value (ε_b) of the dry RC-U and RC-T were 94 MPa/8.9% and 89 MPa/9.2%, respectively. And the optical transmittance values (T_r) of the dry RC-U and RC-T films were 89 and 87%, respectively. The results revealed that the RC films exhibited structural homogeneity, good mechanical properties, and excellent optical transmittance. They were similar to that of the RC films prepared from NaOH/urea aqueous system by the direct dissolution process (Qi et al. 2009).

Conclusion

It was shown that the cellulose could be dissolved in NaOH-based aqueous system at 0–5 °C by a two-step process: the first step was formation of the cellulose–NaOH complex in aqueous NaOH solution; the second step was the dissolution of the cellulose–NaOH complex in aqueous urea solution. The cellulose solution with 6–8 wt% NaOH and 8–14 wt% urea was relatively stable at room temperature. Furthermore, the cellulose could be dissolved in 12–18 wt% NaOH to 4–6 wt% thiourea aqueous solution and 14–18 wt% NaOH to 2–4 wt% PEG aqueous solution by this same process. Thus, we could broaden the cellulose dissolution scope in NaOH-based aqueous system to a wide range from 6 to 18 wt%. Moreover, RC films with good mechanical properties and excellent optical transmittance were prepared successfully from the dissolved cellulose solution. The two-step process should result in economy of power consumption and a decrease in side reactions.

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