

Effect of Stirring Conditions on Cellulose Dissolution in NaOH/Urea Aqueous Solution at Low Temperature

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ABSTRACT: Cellulose can be dissolved in precooled (-12°C) 7 wt % NaOH/12 wt % urea aqueous solution within 2 min as a result of a dynamic self-assembly process among solvent molecules (NaOH, urea, and water) and cellulose macromolecules. The dispersion condition of cellulose could play an important role on the formation of cellulose inclusion complex, leading to good dissolution (Cai et al., *Macromolecules* 2008, 41, 9345). Therefore, the stirring conditions on the cellulose dissolution in NaOH/urea were studied in this work. The results from solubility experiments, optical microscope images, and rheology experiments suggested that larger stirring blade area, longer stirring time, and higher stirring rate could improve the saturated solubility value (C_{max}) of cellulose. How-

ever, when C_{max} value reached a maximum, it changed hardly with further increasing stirring time and rates, which could be regarded as complete dissolution of cellulose in NaOH/urea. Moreover, a schematic diagram of the cellulose solubility had been made, as an instruction of cellulose dissolution in NaOH/urea. The DLS experiments displayed a similar rule. On the other hand, the C_{max} values could be significantly enhanced by decreasing the stirring environment temperature, and the favorable environment temperature range was from -10 to -5°C . © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: cellulose; NaOH/urea; stirring

INTRODUCTION

Cellulose, as a biomass-based “green” material, attracted much attention for its high performance, economical, and environmental friendly characteristics.^{1–7} However, the strong inter- and intra-molecular hydrogen bonds of the cellulose have made the dissolution of cellulose a difficult process in most common solvents.^{8–10} Research and development of cellulose are focused on new solvents such as *N*-methylmorpholine-*N*-oxide (NMMO),¹¹ lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc),¹² ionic liquids,^{13,14} and NaOH solution.^{15,16} There is a growing urgency

to develop a novel, green, low-cost solvent for cellulose.

In our laboratory, we have developed a series of novel cellulose solvent system such as NaOH/urea, NaOH/thiourea, and LiOH/urea aqueous solutions.^{17–20} Cellulose can be dissolved in 7 wt % NaOH/12 wt % urea aqueous solution precooled to -12°C in 2 min. It is a “green” system and has no environmentally hazardous byproducts involved in the dissolution and regeneration process. In this system, the NaOH “hydrates” could be more easily attracted to cellulose chains through the formation of new hydrogen-bonded networks at low temperature, whereas the urea hydrates could be self-assembled at the surface of the NaOH hydrogen-bonded cellulose to form an inclusion complex (IC) at a low temperature. A new hydrogen-bonded network structure consisted of cellulose and the solvent small molecules (NaOH, urea, and water) exists in the system, and it is at a stable state at 0 – 10°C . The formation of IC is hosted by urea, and cellulose chain associated with NaOH hydrates as guest.²¹ With the cellulose dope in NaOH/urea, derivative, cellulose fibers, membrane, hydrogels, and microspheres with good mechanical properties and different functions have been successfully prepared.^{22–25}

It is well-known that dissolution of normal polymers includes a slow diffusion based on the interchangeability of solvent and polymer and needs a

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long time. Obviously, our finding differs from the traditional dissolution process.²¹ Cellulose dissolution is a dynamic self-assembly process among solvent molecules and cellulose macromolecules in NaOH/urea aqueous solution. The cellulose solution is relatively unstable, and sensitive to many factors, such as temperature, cellulose concentration, and so on.¹⁹ On the other hand, the solubility of cellulose strongly depends on the temperature and molecular weight in NaOH/urea aqueous solution.²⁶ However, the influences of stirring conditions on the cellulose dissolution in 7 wt % NaOH/12 wt % urea aqueous solution have been reported scarcely. In the present work, the effects of agitators, stirring time, and the stirring rate on cellulose dissolution in 7 wt % NaOH/12 wt % urea aqueous solution were investigated. We hope that this research may seek us a favorable approach for cellulose dissolution, and furthermore, an industrial scale trial to use this green system.

EXPERIMENTAL

Materials

Cellulose (cotton linter pulps) with an α -cellulose content of more than 95% was supplied by Hubei Chemical Fiber (Xiangfan, China). Its weight-average molecular weights (M_w) was determined in 4.6 wt % LiOH/15.0 wt % urea aqueous solution precooled to -10° with laser light scattering to be 9.4×10^4 g/mol.¹⁷ The cellulose sample was vacuum-dried at 55°C for 24 h to remove any moisture before use. NaOH and urea of analytical grade (Shanghai Chemical Reagent, China) were used without further purification.

Cellulose solution preparation

Solvent (100 g) was prepared as a mixed solution of NaOH/urea/ H_2O (7 : 12 : 81, by weight). A desired amount of cellulose was immersed into the solvent and stirred by different agitators (teflon and steel stirring rod) at various time and rates. Both of the two stirring rod were designed to a propeller type with the same thickness. Teflon stirring rod has a larger diameter of stirring blade about 1.4 cm than the steel rod (about 1.2 cm). The cellulose solution stirred by the agitator with teflon (T) and steel (S) stirring rod at the rates were coded as TX and SX ($X = 300, 600, 1200, 1500, 2000$ rpm). The influence of stirring environment temperature was undertaken by stirring the precooled solvent in a low-temperature thermostat water tank, in which the temperature can be controlled.

Solubility test

The resultant cellulose solution was centrifuged at 8000 rpm at 5°C for 10 min to obtain a transparent

cellulose solution. The remaining undissolved fractions were isolated and then washed using water and acetone, respectively, and finally dried at 60°C for 24 h in a vacuum oven. Thus, the saturated solubility of cellulose (C_{max}) value of cellulose in NaOH/urea aqueous solution was calculated by

$$C_{\text{max}} = \frac{(W_0 - W_1)}{(100 + W_0 - W_1)} \quad (1)$$

where W_0 is weight of original cellulose, and W_1 is weight of the undissolved fraction.²⁷

Characterization

Optical microscope (Axiovert 200M, ZEISS, Germany) was used to observe the morphological change of cellulose in precooled NaOH/urea aqueous solution at ambient temperature. To observe the dissolution process, the cellulose solutions were taken out at different time and revolutions during the dissolution, and were pressed between two glass slides directly, and then sealed by paraffin to be observed and photographed.

The rheology experiment was carried out on an ARES-RFS III rheometer (TA instrument Inc., New Castle, USA). A doubleconcentric cylinder geometry with a gap of 2 mm was used to measure dynamic viscoelastic parameters such as the shear storage modulus (G') and loss modulus (G'') as functions of angular frequency (ω). The cellulose solution degassed was transferred from a glass bottle to the rheometer.

Dynamic light scattering (DLS) was used to determine the hydrodynamic radius (R_h) of cellulose in 7 wt % NaOH/12 wt % urea aqueous solution at 25°C . The cellulose solution was prepared at different agitators (with teflon stirring rod and steel stirring rod) with constant revolutions for some times. A modified commercial light scattering spectrometer (ALV/SP-125, ALV, Germany) equipped with an ALV-5000/E multi-t digital time correlator and a He-Ne laser (at $\lambda = 632.8$ nm) was used at scattering angles $\theta = 90^\circ$. All of the test solutions were prepared at a concentration of 2.1×10^{-4} g/mL and made optically clean by filtration through 0.45 μm millipore filters. The precisely measured intensity-intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode can be related to the normalized field-field autocorrelation function $g^{(1)}(q,t)$ via the Siegert relation as^{28,29}

$$G^{(2)}(q, \tau) = A \left[1 + \beta |g^{(1)}(q, \tau)|^2 \right] \quad (2)$$

where A is the measured baseline and β is a constant related to the coherence of the detected optics. For a polydisperse system, $g^{(1)}(q,t)$ is related

to the distribution of the characteristic line width $G(G)$ by^{30,31}

$$|g^{(1)}(q, \tau)| = \int_0^\infty G(\Gamma) e^{-\Gamma\tau} d\Gamma \quad (3)$$

Thus, $g^{(1)}(q, t)$ can be converted to a line-width distribution $G(G)$ by the CONTIN Laplace inversion algorithm in the correlator according to eq. (2). For a pure diffusive relaxation, G is related to the translational diffusion coefficient (D), and $G(G)$ can be converted to a translation diffusion coefficient distribution $G(D)$ by

$$\Gamma = Dq^2 \quad (4)$$

and a hydrodynamic radius distribution, $f(R_h)$, by the Stokes–Einstein equation

$$R_h = \frac{K_B T}{6\pi\eta_0 D} \quad (5)$$

where R_h , K_B , T , and η_0 denote the hydrodynamic radius, Boltzmann constant, absolute temperature, and the solvent viscosity, respectively.

RESULTS AND DISCUSSION

Effect of stirring time

The dependence of the C_{\max} values and optical microscopic images ($\times 40$ magnification) of cellulose dissolved at a revolution of 1200 rpm on stirring time are shown in Figure 1. It is clear that the C_{\max} values of cellulose stirred with both stirring rods increased rapidly with the stirring time, but after 240 s, they showed a slight increase and reached a maximum. In the short stirring regime (less than 50 s), the C_{\max} of both rods did not differ much. The optical microscopic observation indicated cellulose only swelled in the solvent, showing lots of fiber with diameter of 20–30 μm . The C_{\max} values increased with an increase of the dissolution time from 50 to 300 s. The C_{\max} of cellulose stirred with teflon rod exhibited a larger C_{\max} than the steel rod. The optical microscopic observation revealed that the swelling degree of the cellulose fiber increased, which strongly supported the results of the solubility test. When stirring longer than 300 s, both the teflon and steel rod had the same C_{\max} values, indicating a complete dissolution and transparent cellulose solution occurred.

In our previous work, rapid dissolution of cellulose in precooled (-12°C) NaOH/urea aqueous solution could be described as two parts: first, the cellulose was immersed in the precooled solvent and dispersed by mechanical stirring as cellulose chains;

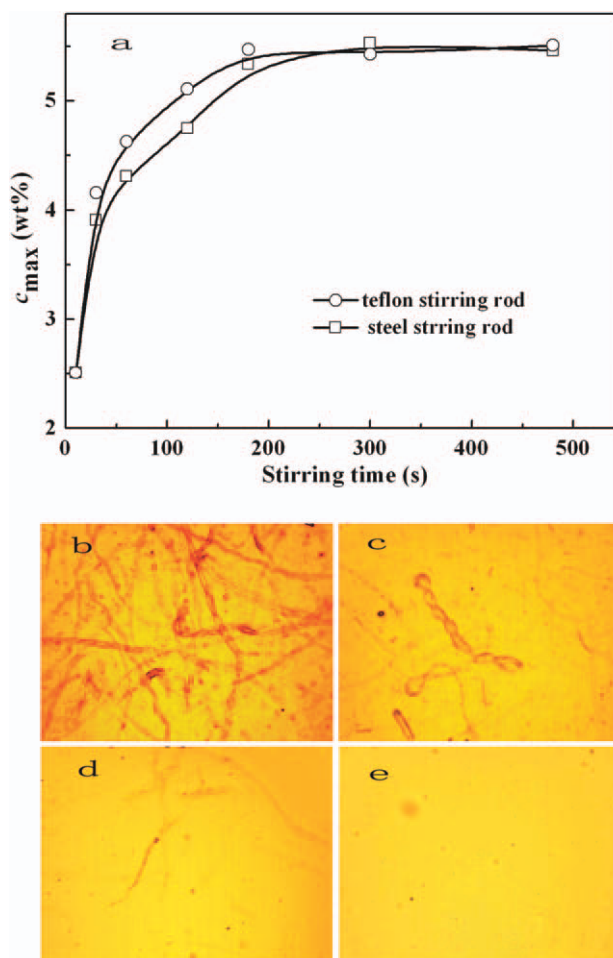


Figure 1 The dependence of the solubility values (a) and optical microscopic images ($40\times$ magnification) of cellulose stirred for 10 s (b), 120 s (c), 300 s (e) with teflon stirring rod and stirred for 120 s (d) with steel stirring rod at stirring rate of 1200 rpm at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

second, NaOH “hydrates” could be attracted to the dispersed cellulose chains through the formation of new hydrogen-bonded networks at low temperatures, the urea hydrates could be self-assembled at the surface of the NaOH hydrogen-bonded cellulose to form an IC.²¹ Short stirring time was not favorable for the dispersion of cellulose, leading to few differences between cellulose dissolution stirred with teflon and steel rod. With increasing stirring time, the teflon rod improved the solubility of cellulose obviously, since the teflon rod had a larger stirring blade area than the steel rod. The C_{\max} of cellulose solution reached a maximum when stirred more than 300 s, regardless of agitator types, indicating a complete dissolution had been reached.

A lower stirring rate (300 rpm) was applied to the cellulose in NaOH/urea aqueous solution. Figure 2 shows the dependence of the solubility values (C_{\max}) of cellulose on the stirring time at 300 rpm at room

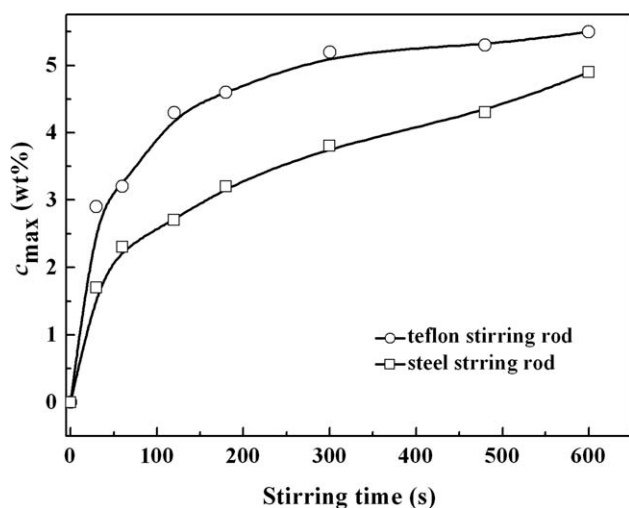


Figure 2 The dependence of the solubility values (C_{\max}) of cellulose on the stirring time at 300 rpm at room temperature.

temperature. Under lower stirring rate, the C_{\max} values of the cellulose stirred with both agitators increased all with the extending stirring time. However, the C_{\max} values of cellulose stirred with the teflon rod were higher than the steel rod in the time range from 60 s to 480 s. The larger shear area and the longer stirring time could improve the cellulose dispersion and dissolution. The results demonstrated that the complete dissolution of cellulose should occur at a higher rate and longer time. However, the teflon rod promoted the cellulose dispersion because of a larger stirring blade area.

To investigate the effect of stirring time on the solution properties, the rheology measurement was applied to evaluate the rheological properties of the cellulose solution stirred with teflon stirring rod at room temperature. Figure 3 shows the G' and G'' curves as a function of angular frequency (ω) for the cellulose solution for different stirring time at 1200 rpm. The data are shifted along the vertical axis by 10^a to avoid overlapping. The G' curves of cellulose solution stirred with the teflon stirring rod presented a plateau-like behavior in the range of low frequency at 10 s, and the difference between the G' and G'' values was small, which was a sign of chain aggregates and entanglements of cellulose in NaOH/urea aqueous solution.^{32,33} This could be explained that at relatively short time, the molecular chain could not disperse enough and the original three dimensional networks still remained, which showed much elasticity. For the cellulose solution stirred for 2–5 min, the G'' values became larger than G' for the entire frequency with increasing stirring time, indicating a liquid-like behavior.³⁴ The results indicated that the increasing stirring time could improve the cellulose dissolution in NaOH/urea.

Effect of stirring rate

The dependence of C_{\max} values of cellulose and optical microscopic images of the cellulose in NaOH/urea aqueous solution on the revolutions of the agitator stirred for 180 s is shown in Figure 4. The C_{\max} values displayed a similar rule with Figure 1. The C_{\max} curves increased sharply and then became flat at more than 1200 rpm. The C_{\max} values of the cellulose solution with teflon stirring rod increased more quickly than the steel rod in the range from 0 rpm to 1200 rpm, and then the C_{\max} values of cellulose solution stirred by both stirring rods reached a maximum at higher revolutions. This indicated that the increase of shearing force of the stirring rod of agitators and the rates could enhance the dispersion and solubility. The optical microscopic image of the cellulose solution stirred with steel stirring rod at 300 rpm (S300) showed the swelling cellulose. However, the optical image of the cellulose solution stirred by the agitator with teflon stirring rod at the same rate exhibited less dissolved and swollen fiber, suggesting that its higher solubility contributed to the larger stirring blade area. At the rate of 1700 rpm, both optical microscopic images displayed transparent solution. The results indicated intuitively that the solubility of cellulose in NaOH/urea solution could be improved significantly by the relatively high revolutions. When the stirring rates were higher than 1700 rpm, both the teflon and steel rod had the same C_{\max} value, indicating a completed dissolution.

Figure 5 is the dependence of the C_{\max} of cellulose stirred for 60 s on the stirring rates. The C_{\max} values of cellulose stirred with teflon and steel rod increased sharply first and then increased slowly. At shorter stirring time, the C_{\max} values of the cellulose

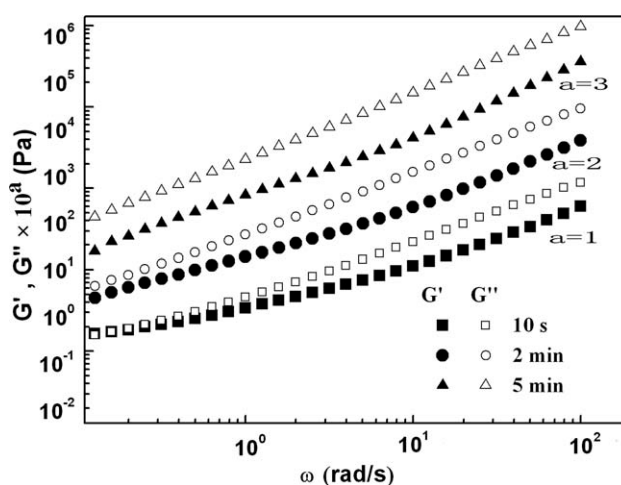


Figure 3 Dependence of G' and G'' on the frequency (ω) for the cellulose solutions stirred with teflon stirring rod for various time at 1200 rpm at room temperature. The data are shifted along the vertical axis by 10^a to avoid overlapping.

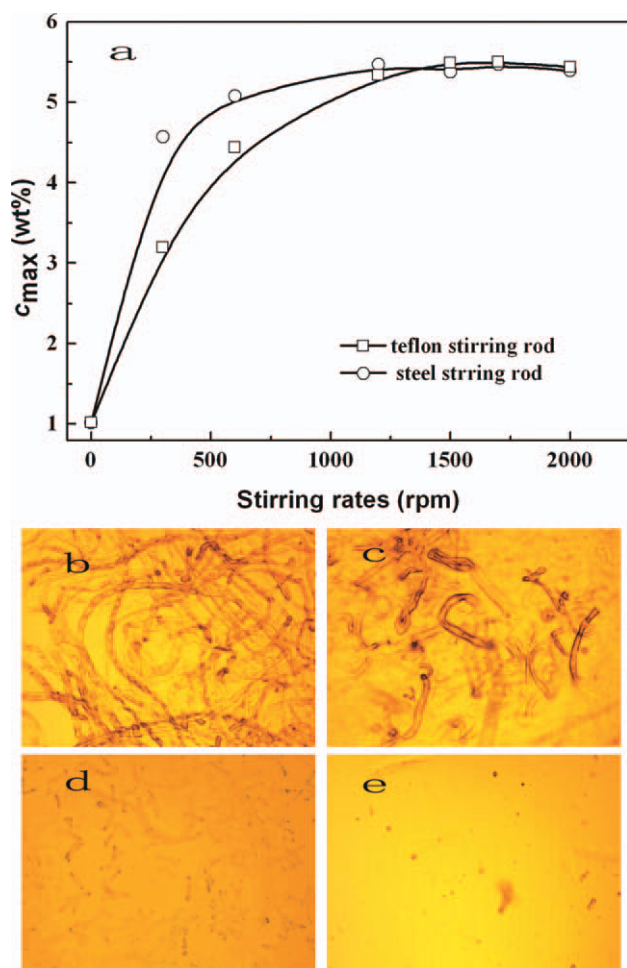


Figure 4 The dependence of the C_{\max} (a), and optical microscopic images ($40\times$ magnification) of cellulose at 0 rpm (b), 300 rpm (c) with steel stirring rod and at 300 rpm (d), 1200 rpm (e) with teflon stirring rod stirred for 180 s on the stirring rates at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stirred with teflon rod were higher than the one stirred with steel stirring rod. It suggested that the stirring blade area played an important role in the process of dissolution. Higher rate could accelerate the dispersion of cellulose, and the teflon stirring rod with a larger stirring blade area could enhance cellulose dispersion into the solvent for shorter stirring time.

Dependence of G' and G'' on the frequency (ω) of the cellulose solutions stirred with teflon stirring rod for various rates for 180 s are shown in Figure 6. The data are shifted along the vertical axis by 10^a with the given a value to avoid overlapping. To clarify the influence of the stirring rates, the angular frequency dependence of G' and G'' curves of the cellulose solution with different rate is discussed as follows. At low rate of 300 rpm, the G' values for cellulose solution are larger than G'' at lower frequencies, suggesting an elastic behavior. It suggested

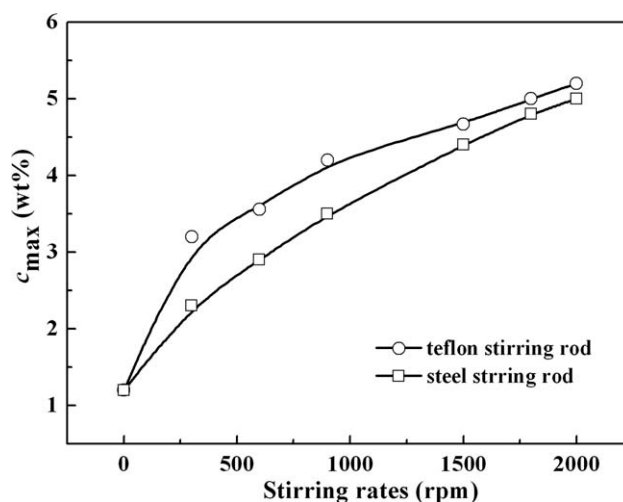


Figure 5 The dependence of the C_{\max} of cellulose stirred for 60 s on the stirring rates at room temperature.

that the cellulose dissolved incompletely, leading to the occasional aggregation. G'' exceeded G' at high frequency indicating that network of occasional aggregation was broken. At stirring high rates more than 600 rpm, the difference between the G' and G'' was small at low frequency. Cellulose solution behaved as a viscous fluid. The results illustrated that a homogeneous solution was obtained when stirred at high rates. It supported the solubility experiments above.

To inspect the effect of stirring time and rate on the immersing of cellulose in NaOH/urea, schematic diagram of the solubility of cellulose in NaOH/urea, which prepared cellulose stirred with teflon rod at different time and rate, I, complete dissolution area; II, partial dissolution area was summarized in Figure 7. Here the maximum C_{\max} values, corresponding to completed cellulose dissolution, at the plateau in

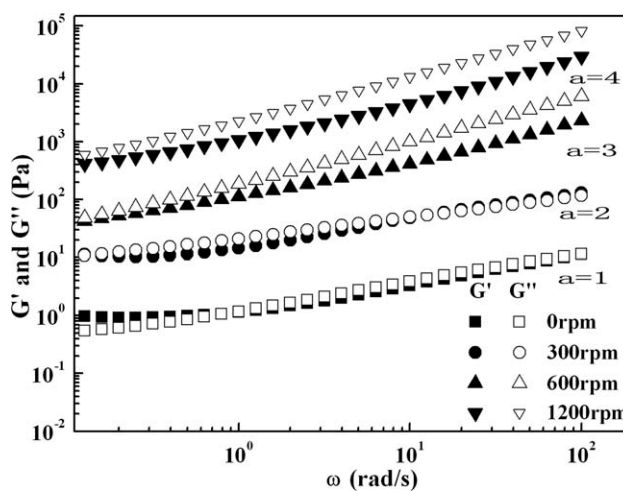


Figure 6 Dependence of G' and G'' on the frequency (ω) for the cellulose solutions stirred with teflon stirring rod at various rates for 180 s at room temperature. The data are shifted along the vertical axis by 10^a to avoid overlapping.

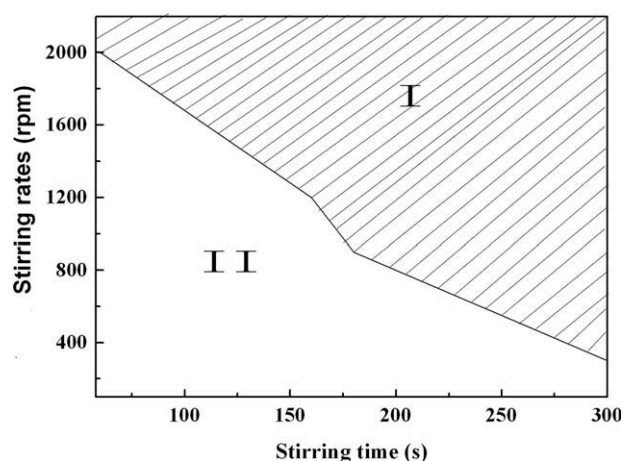


Figure 7 Schematic diagram of the cellulose solubility in NaOH/urea, which prepared cellulose stirred with teflon rod at different time and rates at room temperature: I, complete dissolution area; II, partial dissolution area.

Figures 1 and 3 had been used as a division of complete and uncompleted dissolution of cellulose in NaOH/urea at room temperature. Both stirring time and rates could accelerate the dispersion of cellulose, and completed dispersion could be achieved with relatively higher rate and lower time, or lower rate and higher time. For the short stirring time or low rates, the dispersion of cellulose was not sufficient, and the cellulose could only be dissolved partially (Fig. 7, area II).

DLS experiments were applied on the cellulose solution in NaOH/urea stirred with different rods of agitator, to clarify the effect of shearing force on the formation of IC. Figure 8 shows the $\langle R_h \rangle_{app}$ distributions of cellulose in NaOH/urea ($c = 2.1 \times 10^{-4}$ g/mL) stirred by various rates with teflon and steel stirring rod for 60 s at $\theta = 90^\circ$ (CONTIN analysis). The peak with lower hydrodynamic radius ($\langle R_h \rangle_{app}$) could rep-

resent individual cellulose chains, whereas that with a higher $\langle R_h \rangle_{app}$ value could be attributed to its aggregates.²¹ With an increase of stirring rates, the two overlapping peaks became sharper and separate, and the two peaks of cellulose solution stirred with both rods at higher rate corresponding to the individual chains and their aggregates were well-separated.³⁵ It revealed that the individual chains increased because of a rather good dispersion of cellulose with the increase rate. And the proportion of IC aggregates of cellulose solution stirred with teflon rod decreased more obviously than the steel one, indicating the single ICs gradually increased, as a result of the much larger area share of the teflon rod.

Effect of environment temperature on cellulose solution

The dissolution of cellulose in NaOH/urea aqueous solution is sensitive to temperature. The dependence of the C_{max} values of cellulose stirred at 2000 rpm for 3 min on the environment temperature is shown in Figure 9. In the temperature range from 40 to 45°C, C_{max} maintained a low and constant value (about 3 wt %), indicating that only a small fraction of cellulose with low molecular weight could be dissolved. However, as the temperature decreased from 25 to -10°C , the C_{max} value of cellulose increased rapidly, and cellulose could be dissolved in the range from 25 to -10°C . Interestingly, in the range from -10 to -5°C , cellulose solution reached the concentration of 6.3–6.5 wt %, indicating a considerable enhancement in the cellulose solubility in the NaOH/urea system at low environment temperature.

According to Marson and El Seoud³⁶ and Wang and Deng,³⁷ the total enthalpy of cellulose dissolution at lower temperatures can be analyzed as follows:

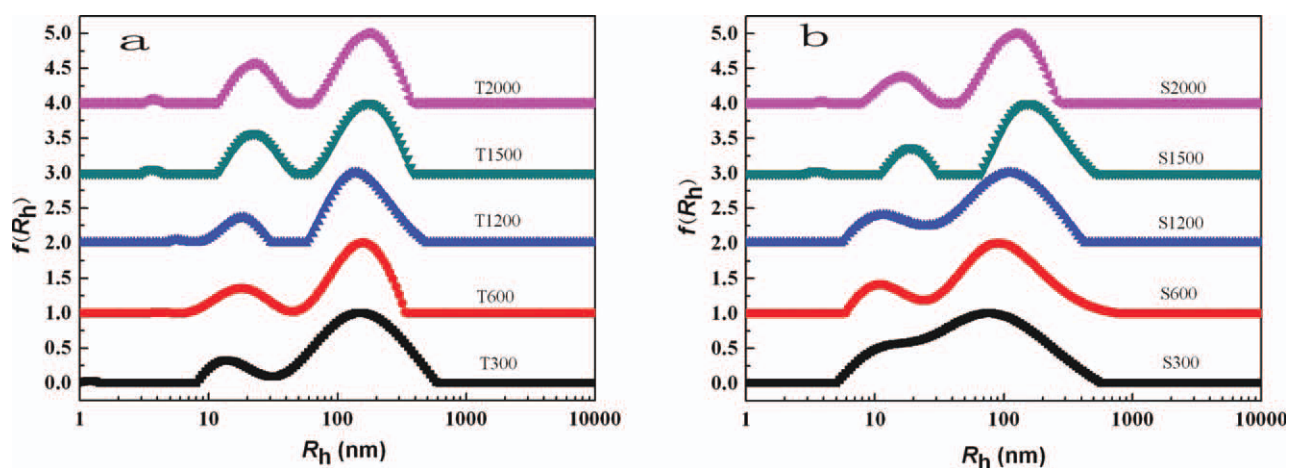


Figure 8 The corresponding hydrodynamic radius distributions (angle $\theta = 90^\circ$) of cellulose solution in NaOH/urea with $c = 2.1 \times 10^{-4}$ g/mL, (a) stirred by different rates with teflon stirring rod for 60 s at room temperature, (b) stirred by different rates with steel stirring rod for 60 s at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

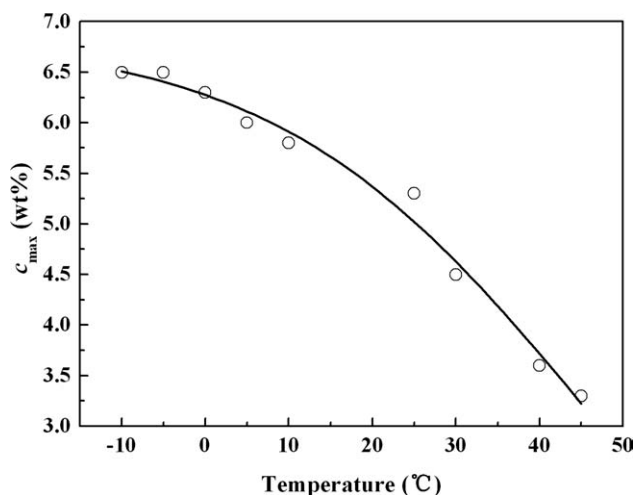


Figure 9 Dissolubility of cellulose under different environment temperature at 2000 rpm for 180 s.

$$\Delta H_{\text{dissolution}} = \Delta H_{\text{fusion}} + \Delta H_{\text{transition}} + \Delta H_{\text{interaction}} + \Delta H_{\text{mixing}} \quad (6)$$

In this dissolution process, the disintegration of the crystalline regions (ΔH_{fusion}) is the only endothermic term in the equation, transition of the amorphous regions from a vitreous to a highly elastic state ($\Delta H_{\text{transition}}$), the solvation of the polymer molecules ($\Delta H_{\text{interaction}}$), and the mixing of the solvation of the polymer molecules to give an infinitely diluted solution (ΔH_{mixing}) are exothermic. The overall process of cellulose dissolution is exothermic and is favored by lower temperature. Therefore, the lower environment temperature which decreases the heat exchanging between system and environment could advance the dissolution.

Effect of different stirring rods, various stirring time, and rates as well as stirring environment temperature on dissolution of cellulose in 7 wt % NaOH/12 wt % urea aqueous solution precooled to -12°C . The dissolution of cellulose in NaOH/urea was divided into the immersing of cellulose and the formation of IC. The results indicated that the stirring conditions played an important role on the immersing of cellulose when the cellulose dispersed incompletely. When the solubility value reached a maximum, the effect of stirring rod, time, and rate were slight. A high solubility value could be obtained at the stirring environment temperature from -5°C to -10°C , with the increase of the stirring environment temperature, the solubility value decreased.

CONCLUSION

In this work, the influence of the stirring blade area, stirring time, stirring rates, and environment temperature on the solubility values of cellulose in NaOH/

urea had been studied comprehensively. Lager stirring blade area, longer stirring time, and higher stirring rate could enhance the C_{max} values of cellulose when the cellulose was dissolved incompletely. When the C_{max} values reached a maximum, the increase of stirring time and rates promoted the dissolution hardly, indicating a completed dissolution. Moreover, a schematic diagram of the cellulose solubility had been made, as an instruction of cellulose dissolution in NaOH/urea. The results from DLS experiments manifested that increase of rates could advance the dispersion and dissolution of cellulose. On the other hand, the C_{max} values could be significantly improved by decreasing the stirring environment temperature, and the favorable environment temperature range was from -5 to -10°C . Therefore, the increase of stirring time, rates, and decrease of the environment could be applied to improve the dissolution of cellulose.

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