

DISSOLVED STATE AND VISCOSITY PROPERTIES OF CELLULOSE IN A NaOH COMPLEX SOLVENT

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Cellulose may be quickly dissolved in a NaOH complex solvent (NaOH/urea/thiourea/H₂O). A detailed investigation on the effects of solvent composition and temperature on cellulose solubility has been presented. Optical microscopy and wide-angle X-ray diffraction (WAXD) were used to study the process of dissolution. The highest solubility of cellulose was recorded in NaOH/urea/thiourea/H₂O with an 8/8/6.5/77.5 composition, at -10 °C, although the components of this solvent cannot dissolve cellulose on their own, even at a low temperature. CP MAS ¹³C NMR spectra proved that, during regeneration, cellulose I (cotton linters) first changed to amorphous cellulose chains in solution and then to cellulose II. The intrinsic viscosity [η] of the cellulose solutions revealed that the cellulose complex occurs as flexible coil chains in the NaOH/urea/thiourea aqueous system, the chain stiffness of cellulose being higher than that of normal synthetic polymers, in a good solvent. According to relative viscosity measurements, the cellulose solution was stable during the storage stage.

Keywords: cellulose dissolution, NaOH complex, low temperature, viscosity

INTRODUCTION

Cellulose is the most important renewable resource on the earth. However, the dissolution of cellulose without chemical modification or derivatization is difficult to achieve because of the molecule stiffness and close chain packing caused by the numerous inter- and intra-molecular hydrogen bonds present in cellulose.¹ For this reason, cellulose needs to be “activated” or made “accessible” to dissolution, even though these notions are not clearly defined. Cellulose crystals are difficult to dissolve; even worse, the production of cellulose derivatives with heavy use of alkali may cause serious pollution problems and involve high costs.

Traditionally, the production of regenerated cellulose fibres and films was largely based on the viscose technology, whose main problem is environmental pollu-

tion. Moreover, the process of producing man-made cellulose fibres, using cuprammonium to dissolve the cellulose, generates heavy metal residues difficult to dispose of.² Thus, it is environmentally sound to identify new spinning systems for the cellulose industries to avoid such environmental problems.

The solvents generally known to dissolve cellulose contain metal complexes, such as cuoxam, cuen and cadoxen. Also lithium chloride/N, N-dimethylacetamide (LiCl/DMAc),³ N₂O₄/N, N-dimethylformamide (DMF)⁴ and N-methylmorpholine-N-oxide monohydrate (NMMO)⁵ can be used. However, limitations such as volatility, toxicity and high cost still exist. Among the solvents identified, the NMMO/H₂O system seems to be the most powerful cellulose sol-

vent; the product has been commercialized as Tencel or Lyocell. The advantage of this solvent is its ability to attain an exceedingly high cellulose concentration. However, the NMMO/H₂O system has some disadvantages, such as the high temperature required for dissolution, degradation of cellulose, side reactions of the solvent itself without an antioxidant and the high costs, which does not recommend it for completely replacing the viscose technology.

Recently, Zhang⁶⁻⁸ investigated the influence of the NaOH/urea and NaOH/thiourea solvent composition on cotton linter dissolution, the optimal ratios found out for NaOH/urea/H₂O and NaOH/thiourea/H₂O to dissolve cellulose being of 6/4/90 and 9.5/4.5/86, respectively. Both solvent systems were inexpensive and less toxic, and cellulose fibres could be prepared by a simple technology.

Previous works⁹ demonstrated that cellulose could be dissolved directly and quickly in a NaOH/urea/thiourea aqueous solvent. The dissolution mechanism was investigated by SEM, WAXD and ¹³C NMR. The new solvent, more powerful in dissolving cellulose, could be used to prepare a more stable spinning solution with a higher concentration of cellulose, compared to the NaOH/urea (or NaOH/thiourea) aqueous solvent system.

Basic understanding of the rapid dissolution of cellulose in this system is essential for the successful development and application of the cellulosic resources. The present work attempts at clarifying the dissolution behaviour and solubility of cellulose in NaOH/thiourea/urea aqueous solutions. A comparison between the behaviour of cellulose-NaOH/urea/thiourea and that of cellulose/NaOH/urea was also performed by viscosity methods. The solvent system evidenced a higher solubility capacity for cellulose, the prepared cellulose solution being rather stable.

EXPERIMENTAL

Materials

The cotton linter pulps (coded as C520, C620 and C1400, respectively, according to their degree of polymerization) were supplied by Xinxiang Bailu Chemical Fibers Co. Ltd. (Henan, China). All cellulose samples were ground into powder

and dried in a vacuum-oven at 70 °C, for 24 h, before use. No activation treatment was required. All other chemicals, of analytical grade, were used as received. Unless otherwise stated, C520 was used in the experiments.

Cellulose treatment

To investigate the effects of NaOH, thiourea and urea on cellulose dissolution, aqueous solutions of NaOH (8 wt%), thiourea (6.5 wt%), urea (8 wt%) and NaOH/urea/thiourea (8/8/6.5 wt%) were used to treat the cellulose fibres at ambient temperature (25 °C). The three different cellulose samples obtained were coded as NaC, TC, UC and NaUTC, respectively. The features of the treated fibres were observed on a polarized optical microscope.

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 K α ($\lambda = 0.15406$ nm), 40 kV, 100 mA, $2\theta = 5-60^\circ$, scan rate 10°/min, reflection mode.

Viscosity measurement

To compare the viscosity properties of the cellulose solution prepared by dissolving cellulose in NaOH/thiourea/urea, 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 data⁶⁻⁸ and preliminary experiments.

The intrinsic viscosity $[\eta]$ of each cellulose solution was measured at 25 ± 0.1 °C, with an Ubbelohde capillary viscometer. The kinetic energy correction was always negligible. Huggins' equation was used to estimate the $[\eta]$ value by extrapolating concentration (c) to be zero, as follows:

$$\eta_{sp} / c = [\eta] + k_H [\eta]^2 c$$

where k_H is a constant for a given polymer at a given temperature in a given solvent, η_{sp}/c is the reduced specific viscosity and η_r (equaling $\eta_{sp} + 1$) is the relative viscosity, defined as the ratio between the solution and the solvent viscosities, used to characterize the viscosity properties of the cellulose solutions involved in the present investigation.

Cellulose solubility test

Generally, solubility (S_a) characterizes the dissolution properties of cellulose in a solvent. During regeneration, S_a was obtained according to $S_a = [W_1/(W_1 + W_2)]$, where W_1 was the mass of the dissolved cellulose and W_2 was the combined

mass of the gel and insoluble cellulose isolated by centrifugation.

The direct dissolution of cellulose could be observed with a polarized optical microscope, because of the high crystallinity of the cotton linters. A 10 g sample of C520, C620 or C1400 was dispersed into 200 g of NaOH/urea/thiourea aqueous solution pre-cooled to $-10\text{ }^{\circ}\text{C}$ and vigorously stirred for 3 min. The solution temperature was then controlled between -2 and $0\text{ }^{\circ}\text{C}$, using a salt-ice bath, after which the cellulose solution was vigorously stirred. After stirring time periods of 0, 20, 30 and 100 s, the samples of the cellulose solution (coded as Cell-0, Cell-20, Cell-30, Cell-100) were removed and divided into two. One part was photographed with a polarized microscope (Olympus RX51-P, Japan) and the other was immediately regenerated using 3% H_2SO_4 , washed five times with excess water and then dried at $70\text{ }^{\circ}\text{C}$ under vacuum, overnight. The raw cellulose (coded as Cell-raw) and the three cellulose samples obtained (R-Cell-20, R-Cell-30, R-Cell-100) were characterized by solid-state ^{13}C NMR using a CP/MAS unit, at room temperature.

RESULTS AND DISCUSSION

Cellulose stability in an alkali hydroxide/urea/thiourea aqueous solution

By changing the NaOH (C_{NaOH}), urea (C_{urea}) and thiourea (C_{thiourea}) concentration, a series of NaOH/urea/thiourea aqueous

solutions were tested.

Cellulose solubility in solvents with different compositions was measured (Table 1); it was found that it changed with the composition, reaching the highest value (0.84) when the NaOH/urea/thiourea composition was set at 8/8/6.5. Thus, the solvent for the set composition was used. A comparison of cellulose solubility in different aqueous systems (Table 2) showed that the NaOH/urea/thiourea aqueous system was more powerful than the other solvent systems. Moreover, it was observed that the superiority of cellulose solubility in NaOH/urea/thiourea aqueous solvents over that in other NaOH complex systems became more remarkable as the DP of the dissolved cellulose increased.

The results indicate that, at ambient temperature, the single-component aqueous solutions or the solvent could only swell cellulose, no crystalline transformations occurring at any specific concentration, as they do not appear as good solvents of cellulose under such conditions, which agrees with the results obtained by Kunze and Fink.¹⁰

Table 1
Cellulose solubility in solvents with different composition

NaOH (wt %)	Urea (wt %)	Thiourea (wt %)	Solubility (S_a)
7	12	4.5	0.49
7.5	10	5	0.66
8	8	6.5	0.84
8.5	6	5.5	0.80
9.0	4	5.5	0.80
9.5	0	4.5	0.63
10	2	5.5	0.75

Table 2
Comparison of cellulose solubility in different aqueous systems

Samples	Solubility (in 100 g solvent)		
	NaOH/urea/thiourea (g)	NaOH/thiourea (g)	NaOH/urea (g)
C520	7.6	6.7	5.4
C620	6.5	4.8	4.3
C1400	3.2	1.4	0.8

Many researchers have found out that, when decreasing temperature, the solvent quality of different NaOH aqueous systems increased strongly.^{1,6-9} During the dissolution process, it was also discovered that the pre-cooled temperature of the solvent considerably influenced cellulose solubility. As seen in Figure 3, cellulose solubility in a NaOH/thiourea/urea aqueous solution at +20 °C was much lower than that obtained in solvents at 0, -5 and -10 °C. It should be also observed that, when decreasing the temperature of the solvent, its quality increased. Particularly, the solvent pre-cooled to -10 °C showed the highest solubility for cellulose.

Figure 4 shows that crystal precipitation occurs during pre-cooling. It was interesting that the long, needle-like crystal separated out from the solvent at the optimum pre-cooled temperature (-10 °C), while the precipitation was thiourea, not urea or NaOH or any of their mixture. The solvent would become solid ice-block when the temperature

reached -15 °C, and could not be used to dissolve cellulose anymore.

The effect of the low temperature was also tested by treating cellulose with NaOH, thiourea, urea and NaOH/urea/thiourea aqueous solution at -10 °C. A peakfit software was used to separate the peaks, and cellulose crystallinity was determined according to the usual area method.¹⁰ The apparent crystal size (ACS) was calculated according to Scherrer's equation.¹¹ The crystalline parameters for the raw and treated celluloses are listed in Table 3. The results obtained showed that untreated cellulose possessed the highest crystallinity, which indicated that NaOH, urea and thiourea destroyed more or less the hydrogen bonds in cellulose at -10 °C. In addition, the highest decrease in crystallinity and increase in ACS for the sample treated by NaOH aqueous solution at -10 °C suggest that NaOH plays a leading role during cellulose dissolution in a NaOH/thiourea/urea aqueous solution.

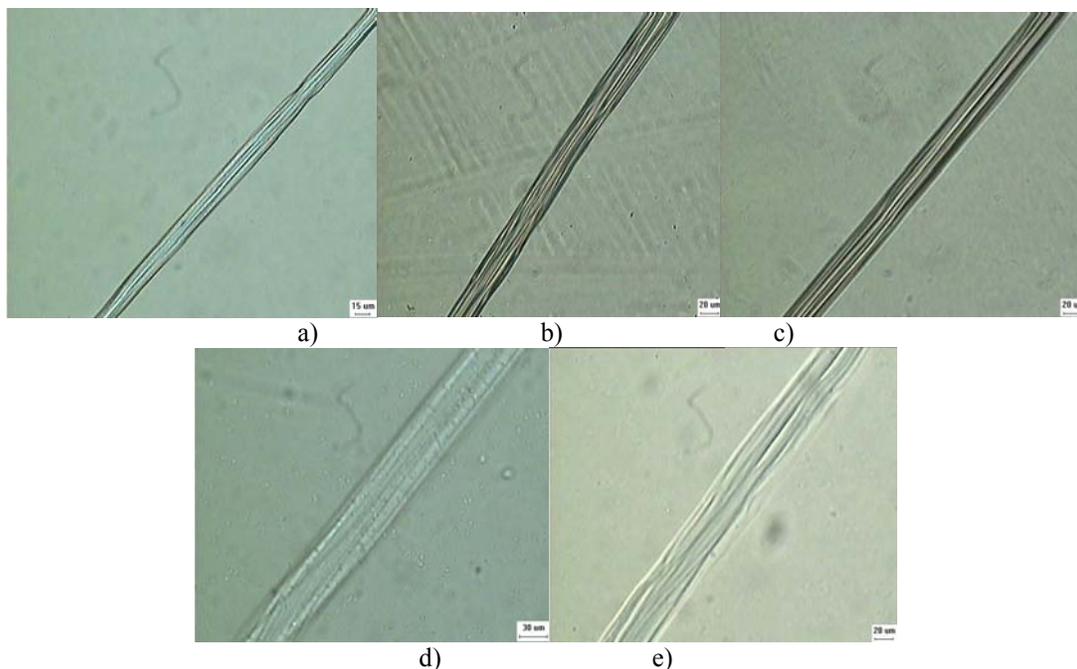


Figure 1: Polarized optical images of: a) C520; b) NaC; c) TC; d) UC; e) NaUTC

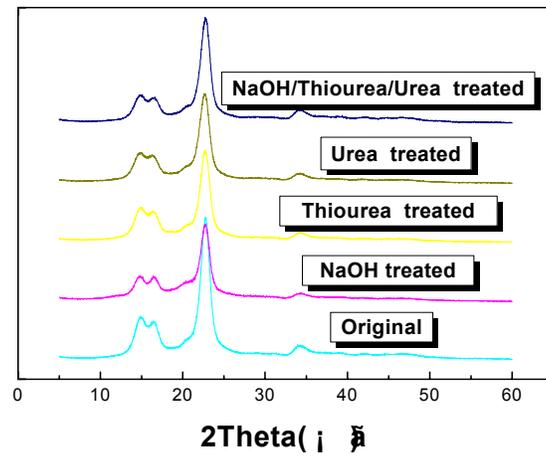


Figure 2: WAXD patterns for C520, NaC, TC, UC and NaUTC

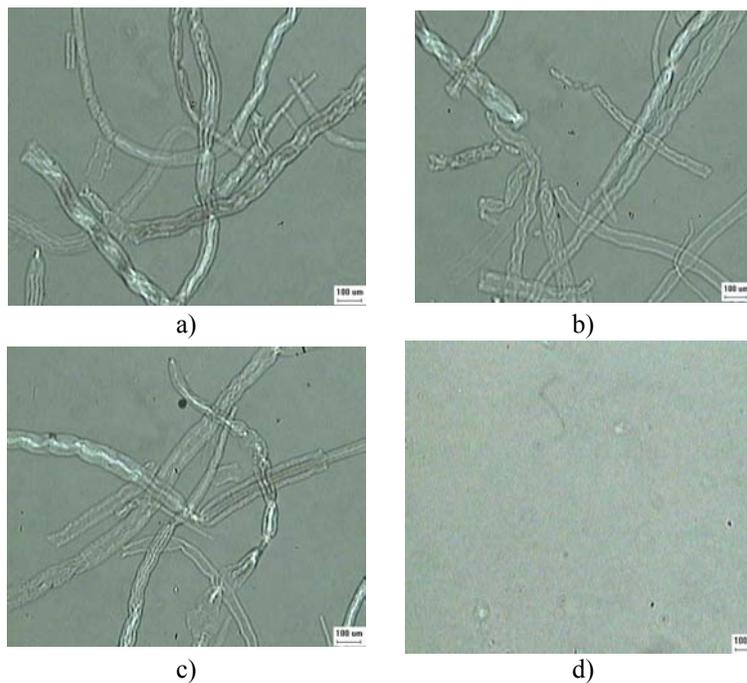
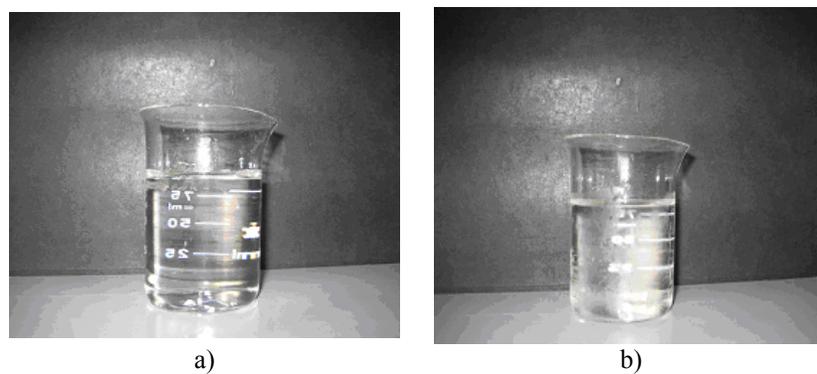


Figure 3: Optical images of cellulose dissolved in a NaOH/urea/thiourea aqueous solution, at different temperatures: a) +20; b) 0; c) -5; d) -10 °C



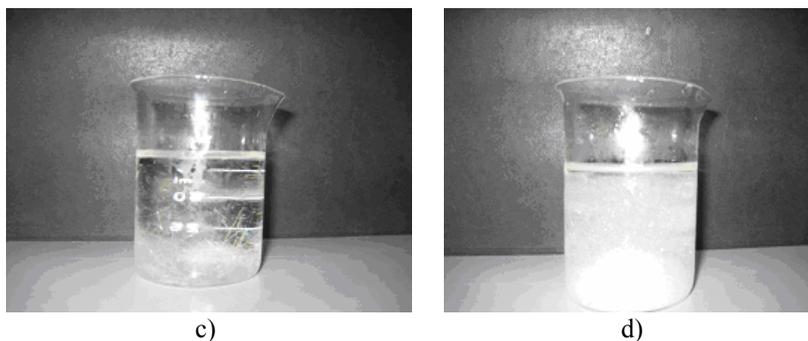


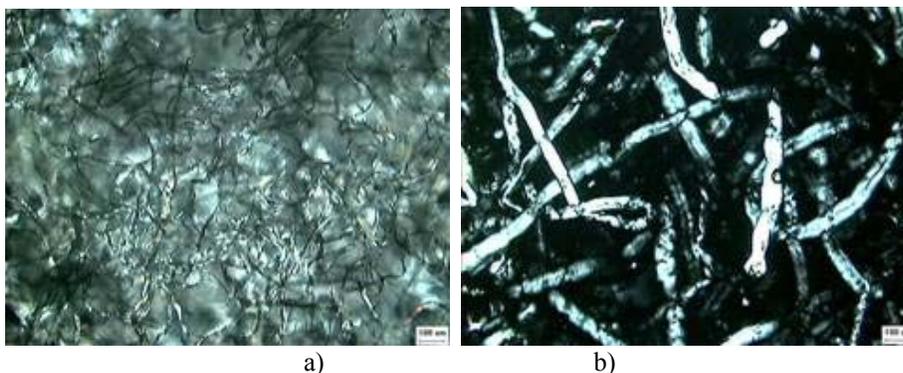
Figure 4: Solvent structure at different temperatures: a) +20; b) -5; c) -10; d) -15 °C

Figure 5 shows polarized optical microscope images of cellulose in a NaOH/urea/thiourea aqueous solution pre-cooled to -10 °C for different time periods. Clearly, cellulose dissolution in the solvent pre-cooled to -10 °C occurred rapidly, while solubility

increased when increasing the dissolution time from 0 to 100 s, that is, a transparent cellulose solution was formed above 100 s, indicating a rapid dissolution of cellulose in the NaOH/urea/thiourea aqueous solution at -10 °C.

Table 3
Crystalline parameters of raw and treated cellulose

Samples	Parameters	Crystallinity (%)	Apparent crystal size (Å)		
			(101)	(10 $\bar{1}$)	(002)
Original C520		89	50.1	55.9	63.3
C520 treated by NaOH aqueous solution at -10 °C		69	55.1	72.5	67.2
C520 treated by thiourea aqueous solution at -10 °C		80	40.0	67.5	45.8
C520 treated by urea aqueous solution at -10 °C		80	40.5	62.1	58.2
C520 treated by NaOH/urea/thiourea aqueous solution at 20 °C		85	50.9	52.3	61.3



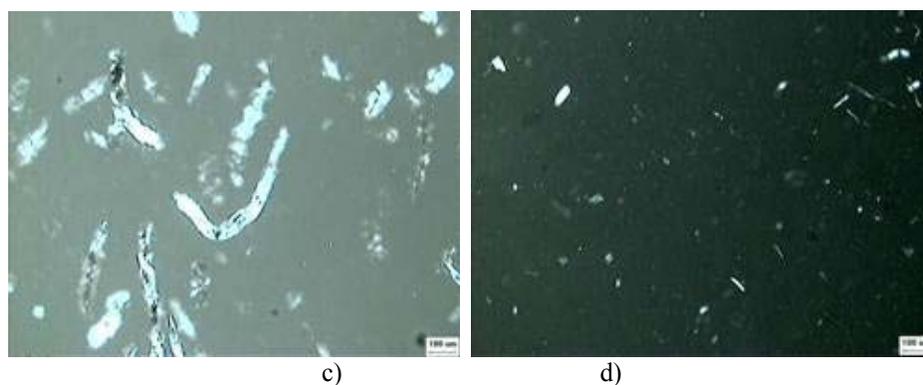


Figure 5: Polarized optical images of: a) Cell-0; b) Cell-20; c) Cell-30 and d) Cell-100

Figure 6 shows the corresponding NMR spectra for both raw cellulose and regenerated cellulose (Cell-20, Cell-30 and Cell-100 regenerated using 3% H_2SO_4). Considerable differences were evident in the corresponding ^{13}C NMR spectra. The C-4 resonance showed a sharp peak (88.9 ppm) and a shoulder (84.7 ppm) that could be assigned to the crystalline and amorphous regions, respectively.¹² The sharp peak became broader and less intense after 20 s, which indicated the destruction of the hydrogen bonds. In addition, only a small peak for the C-6 resonance at 64.7 ppm was observed, while the C-6 main peak (65.0 ppm for Cell-raw) shifted to a higher magnetic field (62.3 ppm for 20 s), suggesting that the *tg* conformation of CH_2OH shifted to a *gt* conformation, and also that intermolecular O-6-H \cdots O-2' hydrogen bonds had been formed.¹³

After 30 s, most of the cellulose was dissolved, according to the optical image, the corresponding NMR spectrum indicating that the conformation of most of the cellulose had changed from cellulose I to cellulose II. Optical images and ^{13}C NMR spectra indicated that complete dissolution had occurred by 100 s. Moreover, it was obvious that the following cellulose structural changes occur during dissolution and regeneration: cellulose I (cotton linters) changes to amorphous cellulose (in solution), and then to cellulose II.

Viscosity properties of cellulose in a NaOH/thiourea/urea aqueous system

Figure 7 displays the Huggins and Kraemer plots for cellulose in NaOH/

urea/thiourea, NaOH/thiourea and NaOH/urea, respectively, at 25 °C. The $[\eta]$ and k_H values could be estimated from the intercept and slope of the plots. For the same cellulose sample, the values of k_H in 8 wt% NaOH/8 wt% urea/6.5 wt% thiourea aqueous solution were apparently larger than those in NaOH/thiourea and NaOH/urea, suggesting that the cellulose molecules in the new solvent were more extended than in NaOH/thiourea and NaOH/urea. The $[\eta]$ value in the NaOH/urea/thiourea system was higher than that of cellulose, having the same viscosity-average molecular weights \overline{M}_h in NaOH/thiourea and NaOH/urea aqueous solution (as a semistiff chain conformation),^{8,14} yet similar to that of flexible polysaccharide in an aqueous solution.¹⁵

The value of $[\eta]$ was used as a measure of the hydrodynamic volume of an isolated polymer molecule. In dilute solutions, polymer chains were separated, intrinsic viscosity depending only on the dimensions of the polymer chain.

Therefore, the value of $[\eta]$ could reflect the size of the polymer chains, which was another piece of evidence that the cellulose complex existed as flexible coil chains in the NaOH/urea/thiourea aqueous system and also that the chain stiffness of cellulose was higher than that of normal synthetic polymers in a good solvent. Figure 8 plots the relative viscosity (η_r) of the cellulose solution as a function of time. A loss in viscosity of about 15% was observed after 30 days, for a cellulose solution maintained at 25 °C.

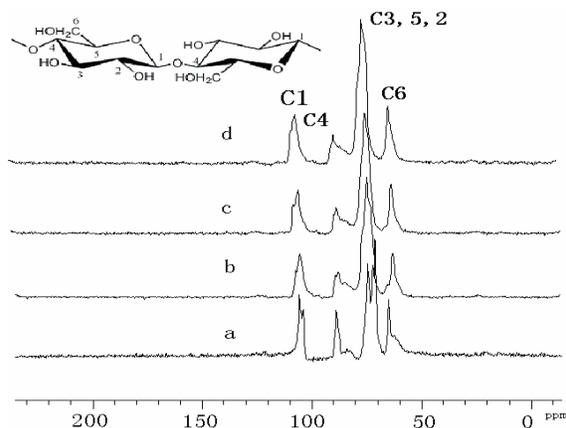


Figure 6: Solid-state ^{13}C NMR spectra of: a) Cell-raw; b) R-Cell-20; c) R-Cell-30; d) R-Cell-100

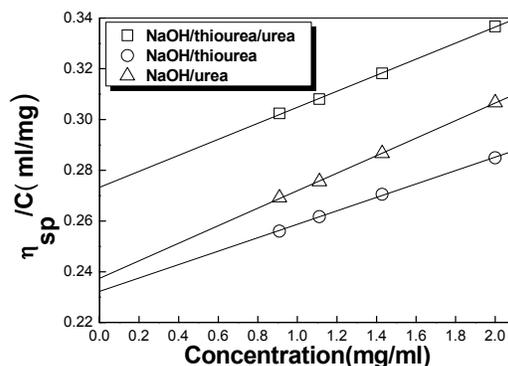


Figure 7: Comparison of the viscosity properties (η_{sp}/c dependence of c) of cellulose dissolved in different aqueous systems

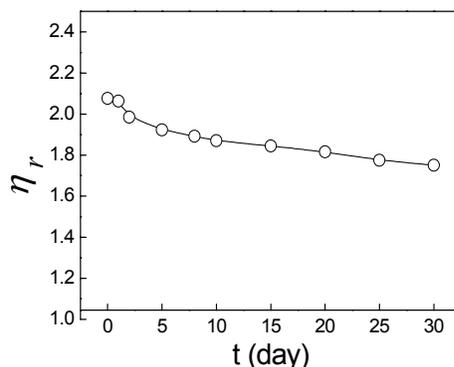


Figure 8: Relative viscosity *versus* time of cellulose solution storage at +25 °C

To investigate the influence of degradation on molecular mass, cellulose was recovered by precipitation from the cellulose solution stored for 30 days. The \overline{M}_h value of the prepared cellulose solution decreased slightly from 8.42×10^4 to 8.04×10^4 , indicating no significant influence on the molecular mass of cellulose during storage.

CONCLUSIONS

Cellulose was rapidly dissolved in a NaOH complex solvent at $-10\text{ }^\circ\text{C}$, forming a colourless transparent solution. The results showed that the highest solubility of cellulose was attained in the pre-cooled NaOH/urea/thiourea/ H_2O solvent with an 8/8/6.5/77.5 composition, while cellulose could not be dissolved in the same solvent mixture without prior cooling. Moreover, single components of this solvent system with any concentration

did not dissolve cellulose at low temperature. The process of cellulose dissolution in the new solvent was investigated by optical microscopy and WAXD, the complete dissolution of cellulose in this solvent requiring only 100 s. The NMR spectrum demonstrated that, during dissolution and regeneration, cellulose I (cotton linters) changed to amorphous cellulose (in solution), and then to cellulose II. It was also proved that the new dissolution method was more effective, leading to a stable cellulose solution. Although several components (NaOH, urea, thiourea as well as cellulose) are involved in the prepared cellulose solution, they are all non-toxic and inexpensive chemical products and can be easily recycled from the coagulation bath, either by chemical separation or by recrystallization, after the fibre or the film

was regenerated from the bath.

In conclusion, this simple, cheap and environmentally friendly technology can be used to prepare regenerated films and fibres, appearing as a promising perspective for substituting the viscose technology which involves hazardous by-products.

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