Effect of Solvent Exchange on the Structure and Rheological Properties of Cellulose in LiCl/DMAc

Yuping Wei, Fa Cheng

Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, People's Republic of China

Received 22 January 2007; accepted 14 May 2007
DOI 10.1002/app.26886

ABSTRACT: Effect of solvent exchange on the structure of cellulose was investigated by Fourier transform infrared spectroscopy, wide angle X-ray diffraction, and scanning electron microscopy analysis. The solvent exchange facilitated the dissolution of cellulose in LiCl/DMAc with no change of the crystalline structure of cellulose. In contrast, solvent exchange led to the fibrillation on the treated fiber surface and the trimmed rod-like particles, further confirming the occurrence of particle disintegration. The rheological properties of three cellulose samples with different degrees of polymerization (DP) and different concentrations were investigated. Results indicated that the cellulose LiCl/DMAc solutions were non-Newtonian fluids. At low deformation rates the cellulose solution behaved like a viscous liquid (loss modulus G'' being larger than storage modulus G'), but elastic properties developed at high angular frequency. The two domains of viscoelastic behavior were separated by the so-called crossover point for G' and G'', which was slightly shifted to lower frequencies as the testing temperature increased from 50 to 80°C. As the concentration and the average molecular weight (or DP) increased, the angular frequency at the crossover point increased also under the experimental conditions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3624–3630, 2007

Key words: cellulose; viscoelastic properties; rheology; FTIR; LiCl/DMAc

INTRODUCTION

Cellulose is one of the most important renewable and biodegradable macromolecules on earth. Every year, a great amount of cellulose is produced mainly by plants as parts of photosynthesis and part is generated by animals living in sea. Nevertheless, these abundantly produced resources have not been yet effectively utilized and several problems must be solved to increase its competitiveness with petroleum-based synthetic polymers.[1] Cellulose may be isolated from several sources including plants, marine organism, and bacteria. Furthermore, cellulose does not dissolve in common organic medium.

Cellulose derivatives, in particular, its esters, are industrially prepared by a two-phase process, in which cellulose reacts with liquid reaction medium. The amorphous regions, being more accessible, react faster than the crystalline ones. The scale of production and the increased importance of these products have prompted intense research aimed at eliminating some of the drawbacks of the heterogeneous process such as reaction rates, final degree of substitution (DS), and product heterogeneity. In 1979, McCormick discovered the utility of the combination of *N,N*-dimethylacetamide (DMAc) and lithium chloride (LiCl) as a solvent for cellulose.[2] In his article, cellulose dissolves in LiCl/DMAc molecularly without degradation. This feature makes the solvent system suitable for the processing, characterization, or derivatization of cellulose. Since derivatization is homogeneous, typically cellulose derivatives of any desired longer chain and DS are directly accessible. Homogeneous products tend to be soluble and processible.[3–6]

The dissolution of cellulose in LiCl/DMAc at room temperature requires a pretreatment of cellulose. Several different methods have been proposed.[7,8] One of them is a kind of solvent exchange that typically consists of sequential immersion of cellulose in water, methanol or acetone, and DMAc. The solvent exchange method for dissolution of cellulose has the advantage of less degradation of cellulose than other methods such as refluxing in DMAc. The mechanism with which the solvent exchange works for cellulose is still unknown. Some researchers have discussed it in terms of the changes in the supramolecular order of cellulose.[9–12] Others investigated the changes in nanometerscale heterogeneity and the molecular mobility of cellulose caused by the solvent exchange and the relation of these changes to the dissolution behavior of cellulose in LiCl/DMAc.[13]

Rheological properties of cellulose in LiCl/DMAc have also been reported.[11,12,14–17] Research is concentrated on the dependence of origin of cellulose on shear

---

Correspondence to: F. Cheng (ypwei@tju.edu.cn).
Contract grant sponsor: Tianjin Natural Science Foundation; contract grant number: 043602611.

Journal of Applied Polymer Science, Vol. 106, 3624–3630 (2007)

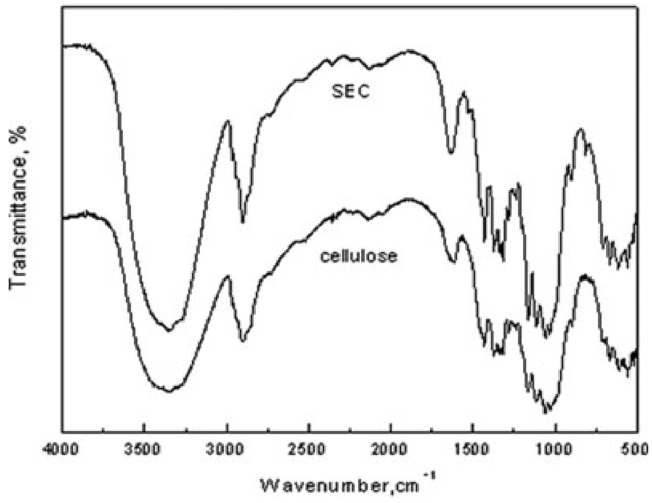

Figure 1 FTIR spectrum of cellulose and solvent-exchange cellulose.

TABLE I
IR-Band Assignments of Cellulose and SEC

Sample	Absorbing peak (cm^{-1})
Cellulose	3356.257 (O(3)—H···O(5) intramolecular hydrogen bond) 2898.956 ($\gamma_{s}CH_{2}$) 1371.887 (δCH_{2}) 1432.084 ($ICH_{2}OH$ of cellulose δCH_{2}) 1112.828 (γC—O)
SEC	3351.743 (O(3)—H···O(5) intramolecular hydrogen bond) 2902.090 ($\gamma_{s}CH_{2}$) 1430.346 (cellulose I $CH_{2}OH\delta CH_{2}$) 1372.416 (δCH_{2}) 1112.997 (γC—O)

viscosity and pretreatment of cellulose such as mercerization in terms of solution properties. And others elucidated the relation of molecular properties and structures of a single chain of celluloses to rheological properties. It is concluded that the differences of solution properties resulted from the difference of molecules structure and the difference in the relaxation process or mechanism in entanglement systems; however, details are still unclear.

Many other solution properties of cellulose in LiCl/DMAc, especially dynamic viscoelasticity, still remain hardly revealed. In this article, the rheological properties of three cellulose samples with different degrees of polymerization (DP) are investigated. Effects of solvent exchange on the structure of cellulose were also investigated by Fourier Transform infrared spectroscopy (FTIR), X-ray, and scanning electron microscopy (SEM) analysis.

EXPERIMENTAL

Materials and reagents

Three cellulose samples with different average DP_{Cuen}(280, 643, 850) employed in this study were purchased from Changshu Medial Supplements, Jiangshu Province, P.R. China. Cellulose with DP_{280} was Avicel PH-101 microcrystalline cellulose, another two were cotton linters. DMAc and LiCl were dried and purified before use. DP was determined (25°C) from the intrinsic viscosity of cellulose solution in Cuen solution.

Preparation of solvent-exchanged cellulose

Cellulose was pretreated as follows to facilitate dissolution: cellulose (50 g) was stirred overnight in 500 mL of deionized water. The mixture was vacuum filtered through coarse fritted glass. Cellulose was then added to 300 mL of reagent grade methanol. The resultant mixture was stirred for 6 h and filtered. Similar repetition with 300 mL DMAc completed the process. The concentration of cellulose per gram of swollen material was determined by drying 2.39 g samples in a vacuum oven at 80°C for 48 h. The average cellulose content for this material was thus determined to be 0.490 g/g of sample.

Preparation of cellulose solution

LiCI/DMAc solvent

Stock solutions of LiCl in DMAc (9%, w/w) were prepared by dissolving 4.2 g of reagent grade LiCl in 50 mL of DMAc at 80°C. Solvent mixtures for

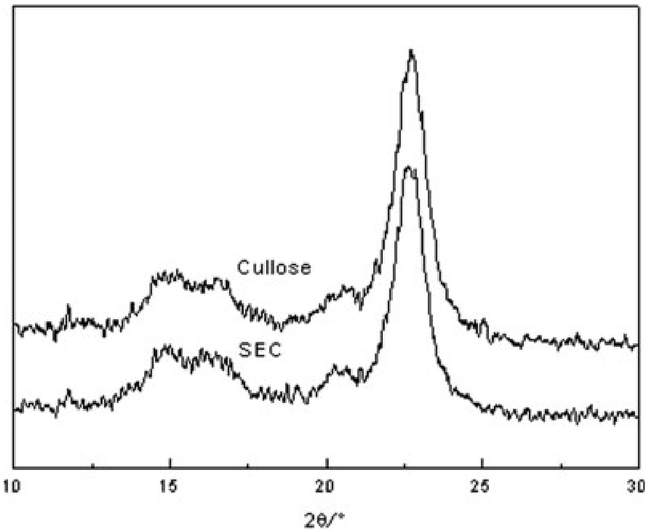

Figure 2 X-ray of cellulose and solvent-exchange cellulose.

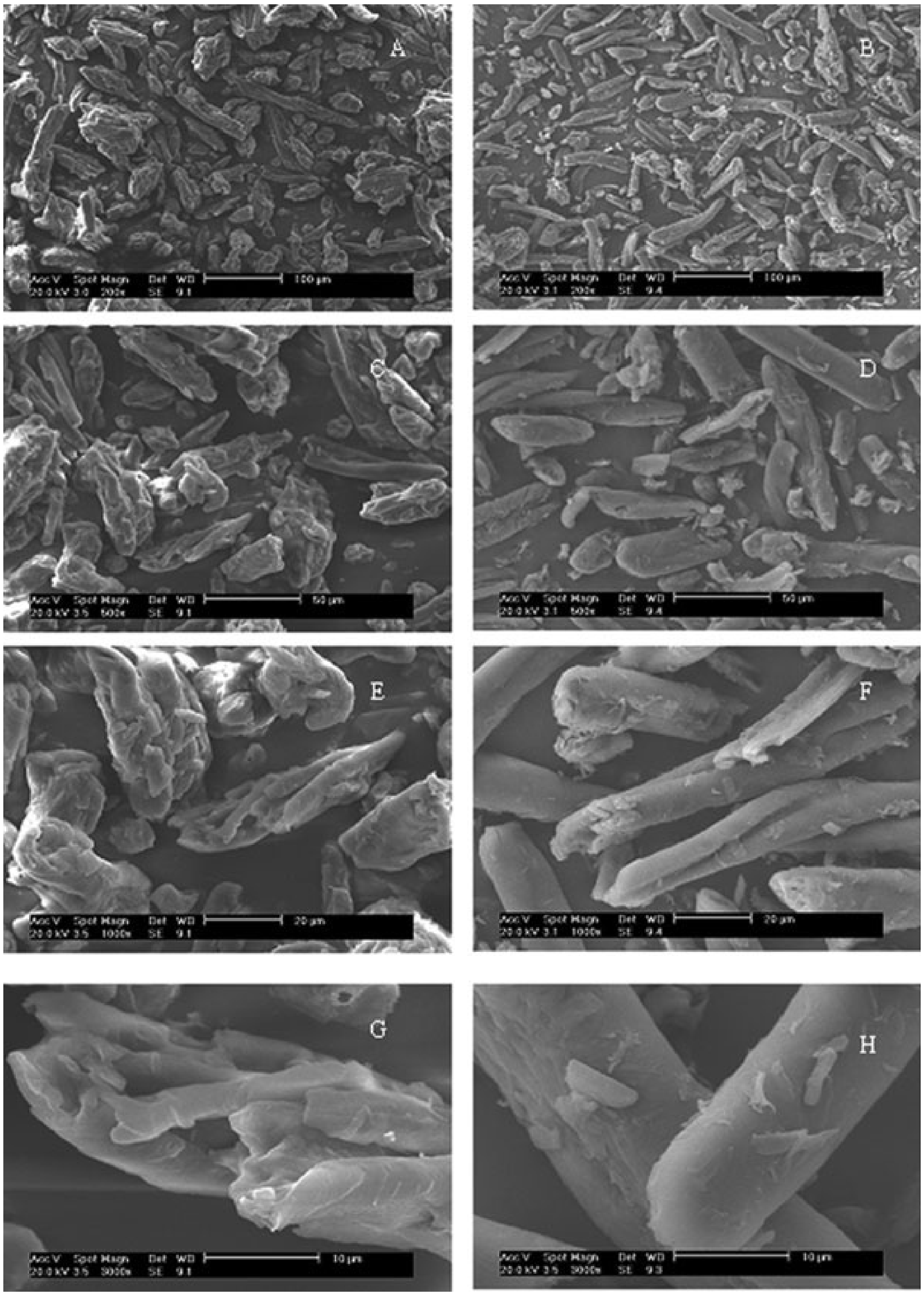

Figure 3 SEM images of cellulose (left) and SEC (right) with different magnification times.

each experiment were prepared immediately prior to use to minimize moisture uptake.

Cellulose dissolution

The solution of cellulose in LiCl/DMAc was accomplished by a known procedure.[18] Briefly, fresh LiCl/DMAc solvent was prepared as described earlier in a dry, 100-mL three-necked flask equipped with a dry nitrogen inlet/outlet, heating mantle, thermometer, and magnetic stirrer. After the temperature was allowed to reach 80°C, solvent-exchanged cellulose (SEC) was added to the heated solvent. The mixture was allowed to stir with nitrogen sparging while cooling to room temperature. The mixture was stirred at room temperature for DP 280 or 60°C for DP 643 and 850 until clear. Conveniently, cellulose solution with three different DP and concentration were defined as follows: 1# 2.5 wt % (DP 280), 2# 1.0 wt % (DP 280); 3# 1.0 wt % (DP 643); 4# 1.0 wt % (DP 850).

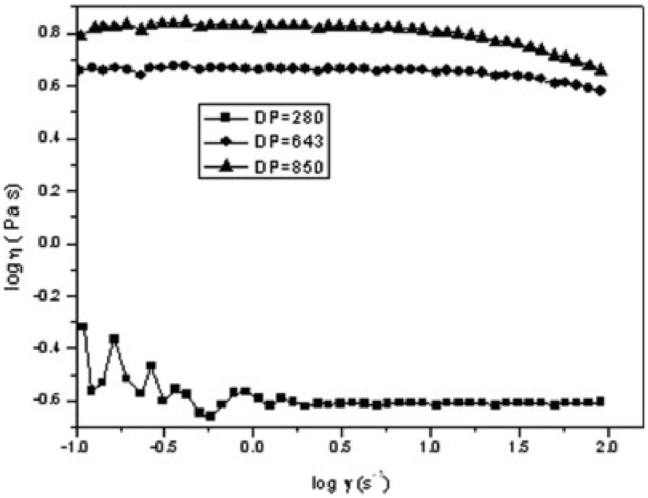

Figure 4 Dependence of shear viscosity on shear rate of cellulose solution with different DP.

Measurements

FTIR analysis

IR spectra were recorded on Fourier-transform infrared spectrometer (BIO-BAD EXALIBUR FTS3000) in KBr discs.

Wide angle X-ray diffraction

X-ray diffraction spectrometry was measured using a DMAX-RC powder diffraction meter with Cu radiation in the range 10–300θ at 40 kV and 30 mA.

Scanning electron microscopy

SEM images were observed on a Philips XL-3 scanning microscope. Each cellulose sample was suspended in a bottle in which there was a small amount of ethanol by ultrasonography. The sample was mounted on glass plates and dried for removal of the ethanol, followed by coating with a thin layer of gold in a vacuum before examination.

Rheological measurements

Dynamic viscoelasticity measurements were performed with a Bob/cup type rheometer Stress Tech-ETC2 (Reologica Instruments, Sweden). The diameter of the cup was 25 mm and the gap between them was 1 mm. The rheometer was equipped with a reservoir to prevent sample drying during the measurements. The dynamic viscoelasticity measurements were performed at 50 and 80°C, respectively.

RESULTS AND DISCUSSION

FTIR analysis

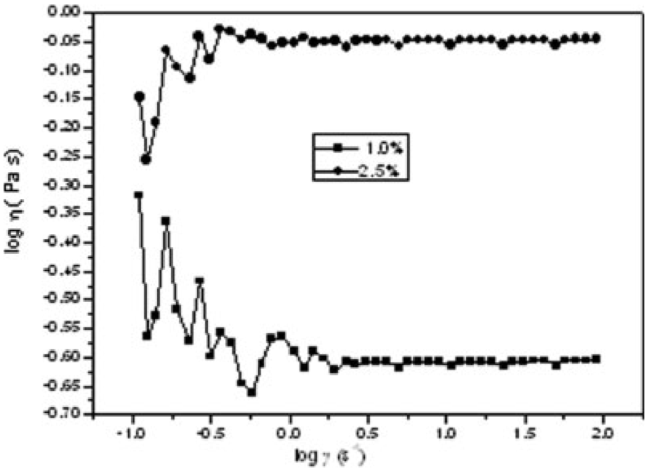

Figure 5 Dependence of shear viscosity on shear rate of cellulose with different concentrations.

Figure 1 and Table I show the FTIR spectrum of cellulose (DP 280) and SEC. As seen from Figure 1 and Table I, similar infrared spectrum was observed for cellulose and SEC. This indicated that solvent exchange facilitated the dissolution in LiCl/DMAc without damage on the cellulose structure.

Wide angle X-ray diffraction

Figure 2 shows the X-ray spectrum of cellulose (DP 280) and SEC. As shown in Figure 2, 10-ray spectrum of cellulose and SEC have similar profiles. This fact suggests that the solvent exchange has no effects on the crystallinity of cellulose, though it affects the dissolution of cellulose remarkably. Therefore, it can be deduced that there is almost no relation between the crystallinity evaluated by wide-angle X-ray diffraction and the dissolution of cellulose in LiCl/DMAc.

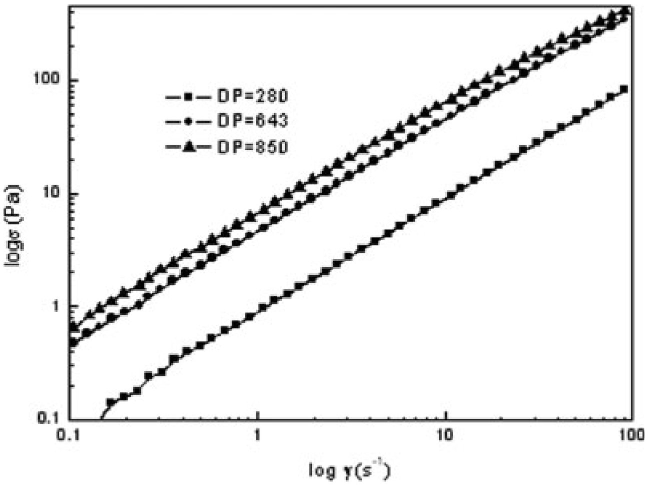

Figure 6 Dependence of stress on shear rate of cellulose solution with different DP.

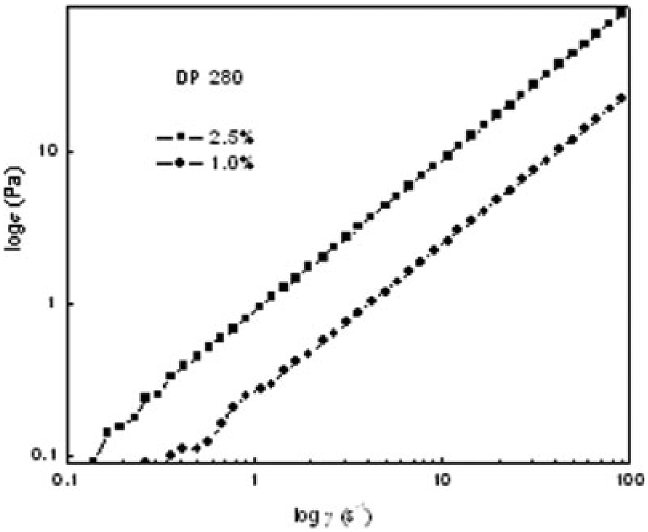

Figure 7 Dependence of stress on shear rate of cellulose solution with different concentrations.

Scanning electron microscopy

SEM was employed to evaluate the morphological structures of cellulose (DP 280) and SEC. Figure 3 shows the SEM micrographs of cellulose at four magnifications (panels A, C, E, and G) on the left side, as well as SEC (panels B, D, F, and H) on the right side. The micrographs of cellulose avicel clearly show its nonfibrous nature and the presence of pinholes on its surface. The SEC (as shown in Picture H with 3000 times) had a smoother fiber surface than the untreated cellulose (as shown in Picture G with 3000 times). It was concluded that solvent exchange led to the fibrillation on the treated fiber surface and the trimmed rod-like particles was observed after solvent exchange, further confirming the occurrence of particle disintegration. This disintegration consequently led to an increased specific surface area of cellulose, which could subsequently promote the cellulose solubilization in solvent.

Rheological measurement

Flow curves for the investigated solution are given in Figures 4–7. As shown in Figures 4–7, cellulose LiCl/DMAc solutions were non-Newtonian fluids and the shear-thinning behavior was not appreciable only when the shear rate is somewhere higher than 2 s^{-1} in the case of DP 850. The shear stress increased with the shear rate for all cellulose solu-

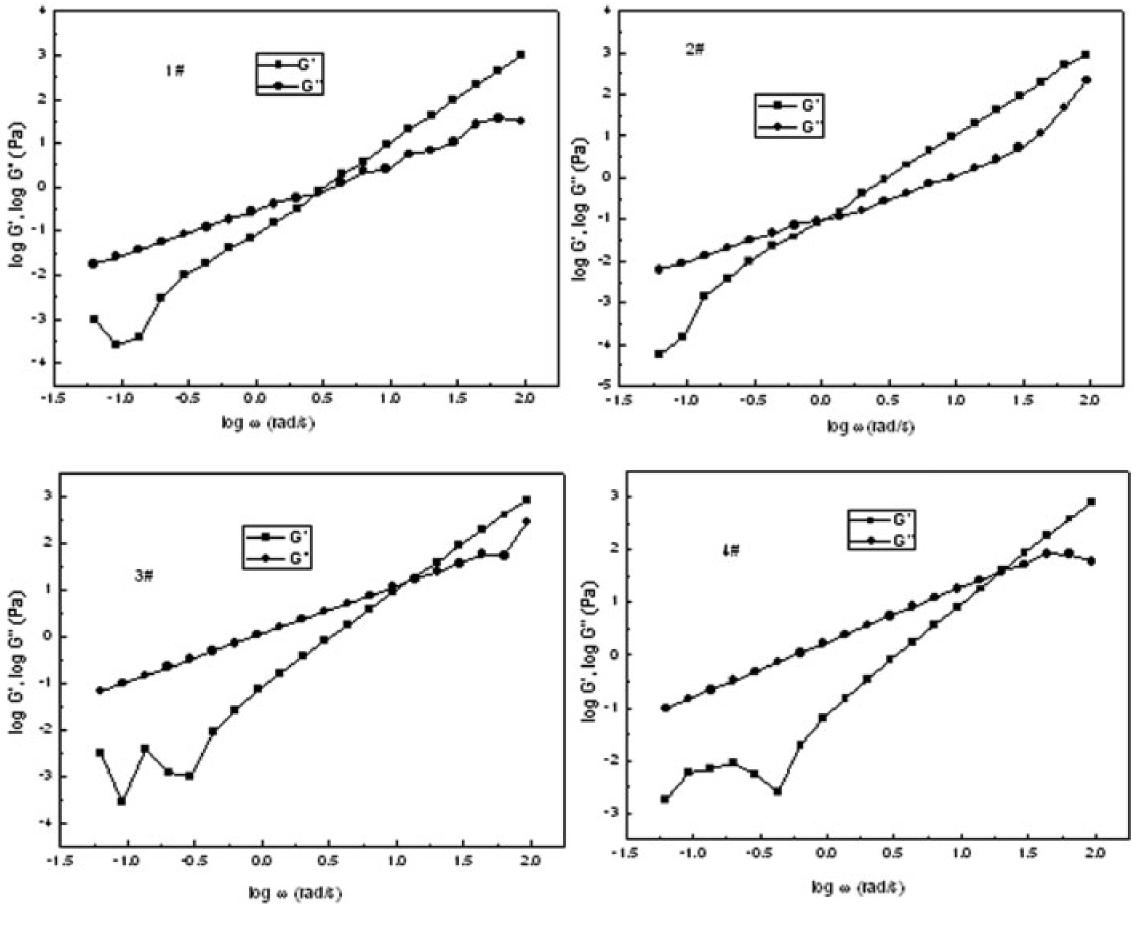

Figure 8 Dynamic moduli for cellulose solution at 50°C.

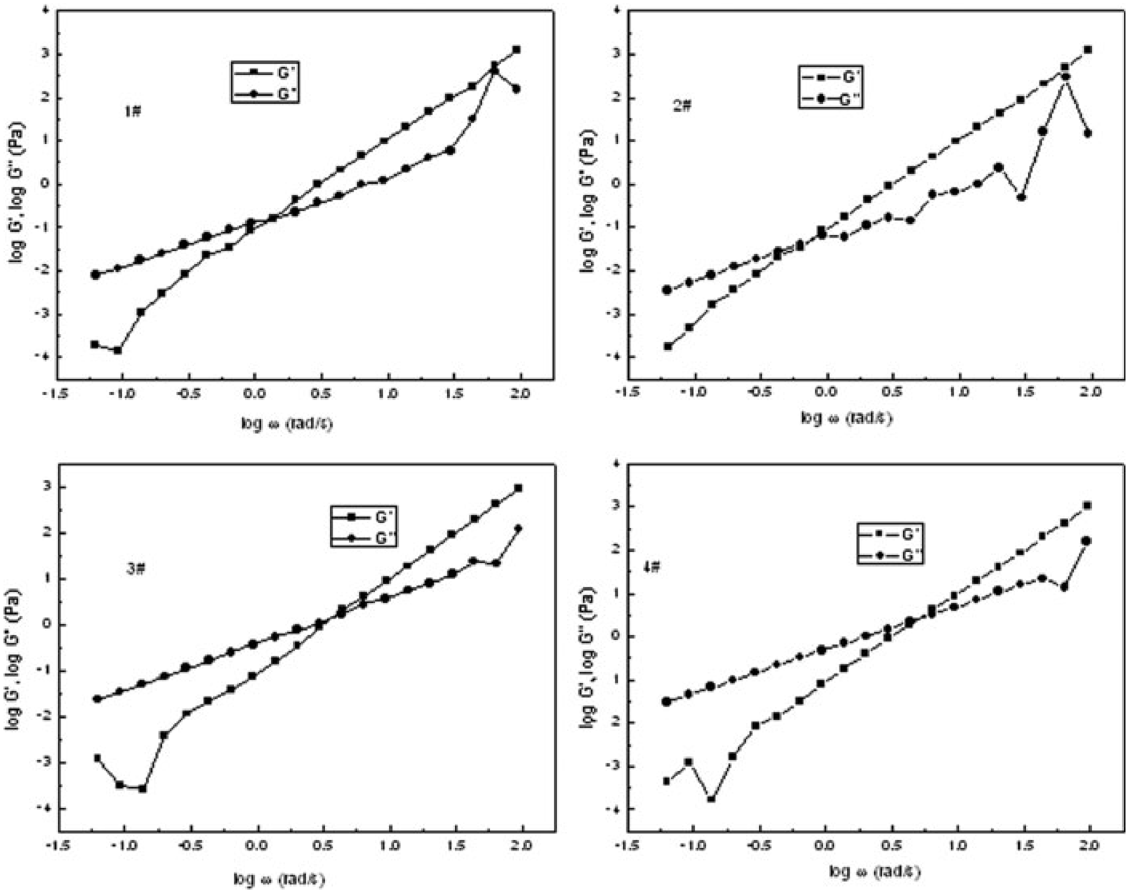

Figure 9 Dynamic moduli for cellulose solution at 80°C.

tions. At the same shear rate, cellulose solution with higher DP and solution concentration possess higher stress. This may be because that there exist hydrogen bonds through hydroxyl groups between cellulose macromolecules and solvent. Thus, the macromolecular chain entanglement can form easily, which makes the relative motion of cellulose macromolecules difficult. The entanglement crosslinks in the solution will be destroyed and rebuilt consistently and a dynamic equilibrium will be obtained under a certain condition; each entanglement only acts as a temporary crosslink when the shear rate increases, part of the entanglement crosslinks are destroyed, showing a decrease of shear viscosity. At the same time, the chain segment stress among entanglement crosslinks cannot relax and probably orientate along the flow field, which makes it less able to transport energy among flow layers. Thereafter, the drag force among flow fields decreases, which also could lead to the drop of the shear viscosity. As a higher DP and concentration lead to the increase of inner-molecular resistance, intermolecular action, and the crosslink, corresponding stress increases at the same shear rate.

The dependence of storage modulus, G', and loss modulus, G'', on angular frequency, ω, is shown in Figures 8 and 9 for cellulose solution with three average molecular weight (or DP) and two weight fraction of polymer (1 and 2.5 wt %) at 50 and 80°C, respectively. As presented in Figures 8 and 9, almost the same pattern for all temperatures and concentrations were observed. At low deformation rates the cellulose solution behaves like a viscous liquid (loss modulus G'' being larger than storage modulus G'), but elastic properties develop at high angular velocities. The two domains of viscoelastic behavior are separated by the so-called crossover point for G' and G'', which slowly shifted as the testing temperature and concentration changed. Data for dynamic moduli were summarized in Tables II and III.

As presented in Figures 8 and 9, the angular frequency at the crossover point of all samples decreased

TABLE II
Characteristic Modulus and Frequency for All Samples (50°C)

Samples	log G_c (Pa)	log ω_c (rad/s)
1#	5.13	5.23
2#	4.43	4.12
3#	7.04	6.89
4#	7.27	7.54

TABLE III
Characteristic Modulus and Frequency for All Samples (80°C)

Samples	log G_c (Pa)	log ω_c (rad/s)
1#	4.31	4.33
2#	3.76	3.70
3#	5.75	5.45
4#	5.81	5.88

when the testing temperature increased from 50 to 80°C. This behavior can be attributed to the basis that the retardation and relaxation times which constitute the viscoelastic spectra decrease with increasing temperature.[19] But the angular frequency at the crossover point increased at experimental testing temperature when the concentration of cellulose solution (DP 280) increased from 1.0 to 2.5 wt % and the average molecular weight (or DP) increased from 280 to 850. The crossover point for G' and G'' was defined as G_c, which is related to the molecule weight distribution. But the angular velocity at the crossover point (ω_c) is related to the relaxation time of cellulose from solution, which, in turn, is related to the average molecular weight (or DP) of cellulose.[20] Also, the viscoelastic response of polymer solutions is a combination of the contributions from the polymer and the solvent. Therefore, since the solvent is typical much less elastic (and, in fact, often only viscous and not viscoelastic), a lower polymer concentration, and hence higher solvent content, causes the viscous response to dominate up to higher crossover strain rates. But under our experimental conditions, LiCl/DMAc was solvent for cellulose dissolution and hydroxyl protons of anhydroglucose units are associated with the chloride anion by hydrogen bonding (according to the proposed mechanism[7]). Cellulose in LiCl/DMAc is a complicated system; it is difficult to make clear such transitional change in the viscoelastic behavior only from the change of the average molecular weight (or DP). And further research on this topic is under way in our lab.

CONCLUSIONS

In the present work, cellulose with three average DP (280, 643, 850) was employed to dissolve in LiCl/DMAc. Results showed that the solvent exchange facilitated the dissolution of cellulose in LiCl/DMAc with no change of the crystalline structure of cellulose. In contrast, the fibrillation on the treated fiber surface and the trimmed rod-like particles were observed after solvent exchange, further confirming the occurrence of particle disintegration. Rheological measurements can be used to characterize the behavior of cellulose solution with different average DP and different concentrations in LiCl/DMAc. Almost the same pattern for all temperatures and concentrations were observed. At low deformation rates the cellulose solution behaves most likely as a viscous liquid (loss modulus G'' being larger than storage modulus G'), but at high angular velocities elastic properties develop. The two domains of viscoelastic behavior are separated by the so-called crossover point for G' and G'', which is slightly shifted to lower frequencies as the testing temperature increased from 50 to 80°C. As the concentration and the average molecular weight (or DP) increased, the angular frequency at the crossover point increased also. Due to the complexity of the system of cellulose in LiCl/DMAc, the results of such transitional changes in the viscoelastic behavior are still unclear under the experimental conditions.

References

1. Schurz, J. Prog Polym Sci 1999, 24, 481.
2. McCormick, C. L.; Lithatowich, D. K. J Polym Sci Polym Lett Ed 1979, 17, 479.
3. McCormick, C. L.; Callais, P. A. Polymer 1987, 28, 2317.
4. Edgar, K. J.; Pecorini, T. J.; Glasser, W. G. In Cellulose Derivatives: Modification, Characterization, and Nanostructures (ACS Symposium Series 688); Heinze, T.; Glasser, W. G., Eds.; American Chemical Society: Washington, DC, 1998; p 38.
5. Sealey, J. E.; Samaranayake, G.; Todd, J. G.; Glasser, W. G. J Polym Sci Part B: Polym Phys 1996, 34, 1613.
6. Samaranayake, G.; Glasser, W. G. Carbohydr Polym 1993, 22, 1.
7. McCormick, C.; Callais, P.; Hutchinson, B. Macromolecules 1985, 18, 2394.
8. Röder, T.; Morgenstern, B.; Schelosky, N.; Glatter, O. Polymer 2001, 42, 6765.
9. Johnson, D. C. In Cellulose Chemistry and Its Applications; Nevell, T. P.; Zeronian, S. H., Eds.; Ellis Horwood: Chichester, UK, 1985; p 185.
10. Klemm, D.; Philipp, B.; Heinze, T.; Heinze U.; Wagenknecht, W. In Comprehensive Cellulose Chemistry, Vol. 1; Wiley-VCH: Weinheim, Germany, 2001; p 150.
11. Ramos, L. A.; Assaf, J. M.; El Seoud, O. A.; Frollini, E. Biomacromolecules 2005, 6, 2638.
12. Aono, H.; Tatsumi, D.; Matsumoto, T. Biomacromolecules 2006, 7, 1311.
13. Ishii, D.; Tatsumi, D.; Matsumoto, T. Biomacromolecules 2003, 4, 1238.
14. Matsumoto, T.; Tatsumi, D.; Tamai, N.; Takaki, T. Cellulose 2001, 8, 275.
15. Aono, H.; Tatsumi, D.; Matsumoto, T. J Polym Sci Part B: Polym Phys 2006, 44, 2155.
16. Zhang, H. H.; Zhang, Y. P.; Shao, H. L.; Hu, X. C. J Appl Polym Sci 2004, 94, 598.
17. Ishii, D.; Tatsumi, D.; Matsumoto, T.; Murata, K.; Hayashi, H.; Yoshitani, H. Macromol Biosci 2006, 6, 293.
18. Dawsey, T. R.; McCormick, C. L. J Macromol Sci Rev Macromol Chem Phys 1990, C30, 405.
19. Ferry, J. D. Viscoelastic Properties of Polymers, 3rd ed.; Wiley: New York, 1980; Chapter 11.
20. Petrovan, S.; Collier, J. R.; Negulescu, I. I. J Appl Polym Sci 2001, 79, 396.