Rheological Characterization of Cellulose Solutions in *N*-Methyl Morpholine *N*-Oxide Monohydrate

Dong Wook Chae,[1] Byoung Chul Kim,[1] Wha Seop Lee[2]

[1] *Division of Chemical Engineering, Hanyang University, 17 Haengdang, Seongdong. Seoul 133-791, Korea*
[2] *Polymer Hybrid Center, Korea Institute of Science and Technology, P. O. Box 131, Cheongryang, Seoul 136-791, Korea*

ABSTRACT: Three different modes of rheological properties were measured on 11 and 13 wt % solutions of cellulose in *N*-methyl morpholine *N*-oxide (NMMO) monohydrate, in which concentration range lyocell fibers of much reduced fibrillation are preferably produced. The dynamic rheological responses revealed that the Cox–Merz rule did not hold for these cellulose solutions. Both cellulose solutions showed a shear thinning behavior over the shear rate measured at 85, 95, 105, and 115°C. However, 13 wt % solution gave rise to yield behavior at 85°C. The power law index ranged from 0.36 to 0.58. First normal stress difference (N_1) was increased with lowering temperature and with increasing concentration as expected. Plotting N_1 vs shear stress (τ_ω) gave almost a master curve independent of temperature and concentration, whose slope was about 0.93 for both cellulose solutions over the shear rate range observed ($\tau_\omega > 500$ Pa). In addition, the cellulose solutions gave high values of recoverable shear strain (S_R), ranging from 60 to 100. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 216–222, 2002

Key words: solution properties; shear; rheology

INTRODUCTION

Cellulose is a semirigid chain polymer with high glass transition temperature (T_g). Further the hydroxyl groups make cellulose molecule highly polar, leading to inter- and intrahydrogen bonding. Consequently, the solvent that can directly dissolve cellulose requires formation of a physical complex.[1] Lots of attempts have been made to find out direct solvent systems of cellulose. Among them *N*-methyl morpholine *N*-oxide (NMMO) proved most versatile and commercially successful. Franks and Varga[2,3] first reported that concentrated solutions of cellulose were obtained in the aqueous NMMO. Several reports on other effective solvent systems for cellulose were also disclosed.[4–6] The lyocell fibers by direct dissolution of cellulose have been commercialized by some companies.[7–11]

The cellulose solutions produce different phases mainly depending on the hydration number (*n*) of NMMO hydrate together with cellulose concentration and temperature.[12–14] Recently Kim et al.[13] modified the phase diagram of cellulose solutions in NMMO hydrates indicating the critical concentration for producing mesophase is much lower than the value previously reported. Chanzy et al.[14] reported the physical properties of mesomorphic phase cellulose solutions in NMMO hydrates. Up to now, however, most rheological analyses focus on dynamic rheological properties because of experimental convenience. The oscillatory shear rheology does not provide practical engineering data applicable to the actual fabrication processes. Particularly with cellulose solutions of mesophase frequently encountered in lyocell spinning, the rheological data would exhibit poor reproducibility because of long relaxation spectra. That is, accumulation of residual stresses during dynamic rheological measurements might give incredible data. This may hold true even for the rotational-type steady shear rheometers as well.

Comprehension of steady shear properties of cellulose solutions in NMMO hydrates is essential to determine the optimum spinning conditions of lyocell. In spite of the commercial success, however, there is little paper devoted to steady shear rheology of cellulose solutions in NMMO hydrates. However, little literature on the steady shear rheological properties for the cellulose solutions is available, which have practical importance in lyocell spinning. In addition, it is desirable to use a cellulose solution in NMMO monohydrate in the fiber spinning process to obtain lyocell fibers with lower fibrillation and higher flexibility. We investigated the dynamic and steady shear rheological properties of 11 and 13 wt % solutions of cellulose in NMMO monohydrate whose concentration proved effective in producing lyocell fibers with suppressed undesirable fibrillation.[15]
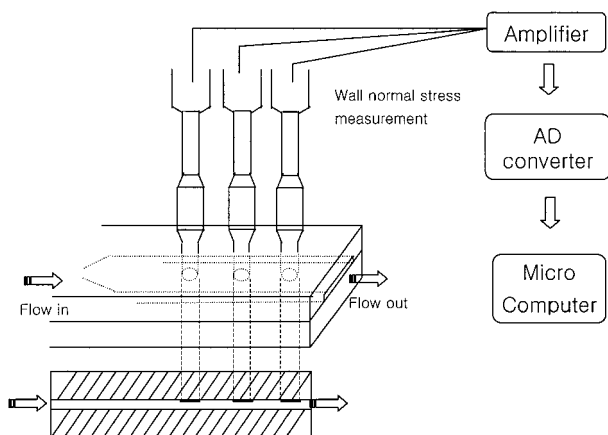

Figure 1 Specially designed apparatus installed for rheological measurement of cellulose solutions in NMMO hydrates.

EXPERIMENTAL

Materials

Cellulose was an ITT Rayonier (U.S.A.) product, whose weight-average degree of polymerization (DPw) was 800. It was dried at 80°C for 24 h prior to use. The NMMO monohydrate was prepared by evaporating excess water from dilute aqueous NMMO purchased from Aldrich. The water content in the condensed NMMO was confirmed by 200 MHz ^{1}H nuclear magnetic resonance (^{1}H-NMR) (Varian). As an antioxidant n-propyl gallate (PG) was used (0.01 wt % to cellulose).[1] The formulated recipes of cellulose, PG, and NMMO monohydrate were mixed in the static rotary mixer at 120°C for 10 minutes to yield 11 and 13 wt % cellulose solutions. The cellulose solutions for rheological measurements were defoamed by stirring them at 130°C for 40 min under vacuum. The density of the solutions was 1.15 g/cm³.

Rheological Measurement

A slit rheometer was specially designed to measure the rheological properties of melt-like cellulose solutions in NMMO hydrates. The slit rheometer makes it possible to obtain steady shear viscosity (denoted as η_{ss}), shear stress (τ_ω), and first normal stress difference (N_1) at high shear rate ($\dot\gamma$), which have real significance in lyocell spinning. The overall apparatus is schematically illustrated in Figure 1, and the detailed layouts of die section are given in Figure 2. A tapered hemispherical reservoir was adopted to eliminate the dead space, in which thermal degradation may be initiated. The cellulose solutions were fed into the ram-type extruder equipped with a slit rheometer. After the extrusion temperature was adjusted, a preliminary extrusion was carried out to get a steady state. The steady pressure gradient ($\partial P/\partial Z$) along the slit die for a given volumetric flow rate (Q) was measured at 85, 95, 105, and 115°C but at 115°C for 13 wt % cellulose solution because the solution is explosive at that condition. The mass flowed down for 1 min at given temperature was measured as well.

Temperature was precisely controlled by three independently operated controllers. Both of the reservoir and die section were highly insulated to prevent heat loss, and temperature was controlled to within ±1°C by a proportional-integral-derivative (PID)-type heating system. The pressure transducer and amplifier system were strain gauged type pressure transducer (Dynisco TPT 432A) and μPR690 (Dynisco), respectively. Pressure transducers were calibrated to give outputs repeatable to within ±1% of the measured value at operating temperature. A microcomputer system was employed for the continuous measurement of the pressure at the wall through A/D converter. The pressure at the wall, i.e., the radial normal stress at wall, was measured with pressure transducers flush-
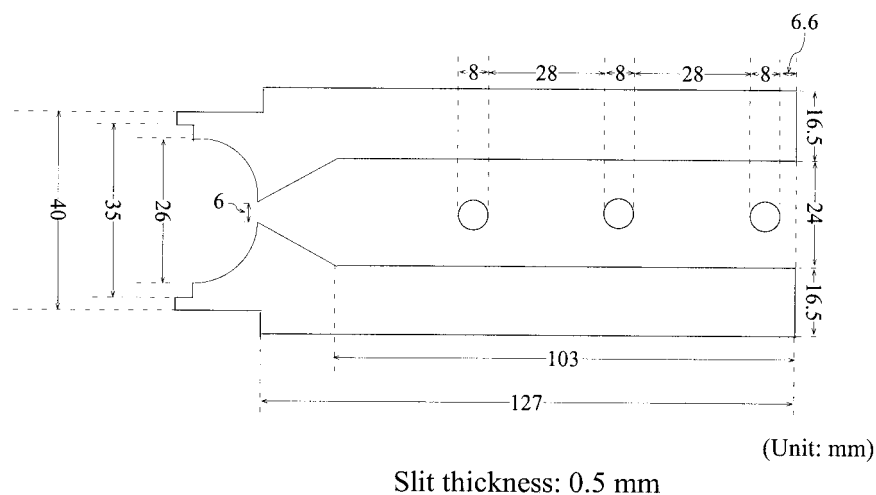

(Unit: mm)

Slit thickness: 0.5 mm

Figure 2 Detailed layouts of the reservoir and die sections specially designed for melt-like cellulose solutions in NMMO hydrates.

(a)

(b)

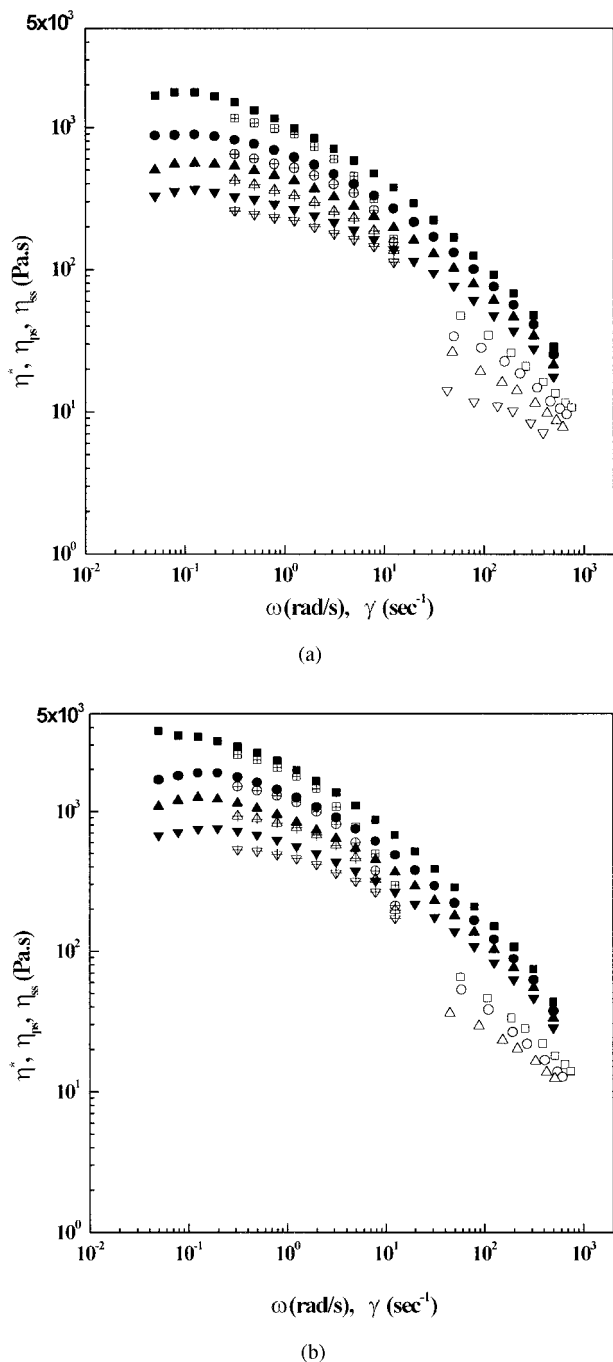**Figure 3** Viscosity curves of (a) 11 and (b) 13 wt % solutions of cellulose in NMMO monohydrate: solid (η^*) and crossed (η_{ps}) symbols from a parallel plate rheometer; open symbols (η_{ss}) from a slit rheometer. (■, ⊞, □) 85°C; (●, ⊕, ○) 95°C; (▲, ⬕, △) 105°C; (▼, ⩔, ▽) 115°C.

The Advanced Rheometric Expansion System (ARES) (Rheometric Scientific, Inc.) was also employed to measure rheological properties; the steady shear mode gave steady shear viscosity (denoted as η_{ps} to differentiate it from steady shear viscosity measured by slit die) over the shear rate range 0.1–50 s^{-1} and the dynamic shear mode gave complex viscosity (η^*), dynamic loss modulus (G''), and dynamic storage modulus (G') over the angular frequency (ω) range 0.05–500 rad/s. The parallel plates of diameter 50 mm were used, whose gap was 1 mm. To avoid water uptake by the sample while running the experiment, the edges of the specimen sandwiched between the plates were covered with a thin layer of silicon oil.

RESULTS AND DISCUSSION

Viscosity behavior

Figure 3 presents logarithmic plots of η^* vs ω and η_{ps} vs $\dot{\gamma}$ measured by parallel plate rheometer for 11 and 13 wt % cellulose solutions. For comparison, logarithmic plots of η_{ss} vs $\dot{\gamma}$ measured by slit rheometer for the solutions are also shown in Figure 3. The values of η_{ps} are somewhat lower than those of η^* at $\dot{\gamma} = \omega$, while the values of η_{ss} are much lower than those of η^*. For many polymer solutions, the frequency dependence of η^* measured in oscillatory shear and the steady shear rate dependence of η are observed to be closely superposable, when the same numerical values of ω and $\dot{\gamma}$ are compared. This empirical correlation, often called the Cox–Merz rule, does not hold for the cellulose solutions. The 11 wt % cellulose solution gives greater difference than the 13 wt % solution at low shear rate, less than 5 s^{-1}. This difference in the values between η^* and η_{ps} seems to result from the rigid chain properties of cellulose molecule. Researchers also found that there are also a few exceptions to the Cox–Merz rule and they ascribed the reason to occurrence of weak gel system or stiffness of chain profiles.[16] The relatively small differences between η^* and η_{ps} seem to suggest that the morphological state of highly concentrated cellulose solution might not have changed much at low shear rate during shear flow.[17] In addition, a big difference between η^* and η_{ss} may be caused by the elongational flow to occur in the slit die during shear flow. That is, elongational flow-induced orientation plays a role in reducing the steady shear viscosity at high shear rate.

mounted along the die length. The electrical outputs in millivolts (0–33 mv) were amplified to voltages (0–10 v) and they were digitized by 12-bit A/D converter. The wall pressure measurement was performed 5 times a second for 40 s and their average was taken as data to minimize the error by mechanical fluctuations.

TABLE I
Power Law Index (*n*) of 11 and 13 wt % Solutions of Cellulose in NMMO Monohydrate

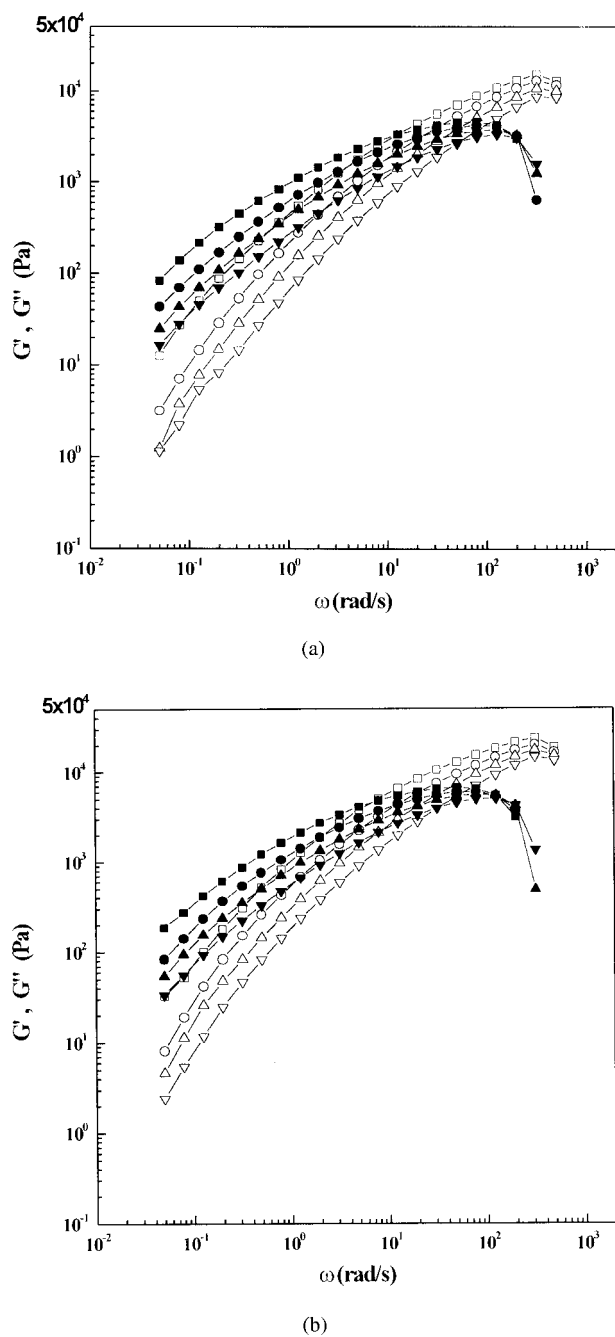| n	85°C	95°C	105°C	115°C
11 wt %	0.364	0.394	0.488	0.584
13 wt %	0.367	0.370	0.479	—

(a)

(b)

Figure 4 Dynamic moduli curves of (a) 11 and (b) 13 wt % solutions of cellulose in NMMO monohydrate: solid symbols (G″) and open symbols (G′): (■, □) 85°C; (●, ○) 95°C; (▲, △); 105°C (▼, ▽) 115°C.

The viscosity curves of cellulose solutions in Figure 3 show lower Newtonian flow region over the range of shear rates and temperatures except for 13 wt % solution at 85°C. This indicates that a phase transition from heterogeneous to homogeneous takes place in the solution between 85 and 95°C. Disappearance of lower Newtonian flow region is an indication of heterogeneity, which is frequently encountered in the liquid crystalline phase of rigid chain polymers. The heterogene-

ity of 13 wt % cellulose solution at 85°C seems to result from rigidity of cellulose molecules and hydrogen bonding by hydroxyl groups on the molecules. That is, cellulose molecules exhibit semirigid chain characteristics particularly when the cyclic rings of the cellulose molecule take the chair conformation. Thus the cellulose molecules may produce the mesophase through physical interactions at the concentration.[18,19]

The power-law index (n) of the cellulose solutions is given in Table I. The value of n approximately ranges from 0.36 to 0.58, indicative of pseudoplasticity. The value of n is increased with raising temperature and with lowering concentration, which may offer favorable conditions for reduction of the polar intermolecular interactions of hydrogen bonding.

Elastic properties

As shown in Figure 4, dynamic moduli show almost the same trend at all temperatures measured. At low deformation rate, both cellulose solutions behave most likely as a viscose liquid: loss modulus (G'') is larger than storage modulus (G'). However, at high angular frequency the elastic properties exceed the viscose properties. The two domains of viscoelastic behavior are separated by the so-called crossover point, which is shifted to higher angular frequency with increasing testing temperature or with decreasing concentration as summarized in Table II. This means that at higher temperature or lower concentration the cellulose solution behaves as a viscose liquid over the broader range of the tested angular frequency. In addition, the angular frequency of the crossover point is very dependent upon testing temperature in contrast to the moduli of the crossover.[20]

It is recognized that yield behavior of heterogeneous systems is well characterized by adopting the Casson plot defined by

$$G''^{1/2} = G_y'^{1/2} + K\omega^{1/2} \qquad (1)$$

in which G''_y stands for yield stress and K is constant. The Casson plot reveals a nonzero positive intercept only for the 13 wt % cellulose solutions at 85°C, which corresponds to yield stress, 19.62 Pa, as shown in

TABLE II
Crossover Point (G_c) on G′ and G″ Curves and the Angular Frequency (ω) at the Crossover Point

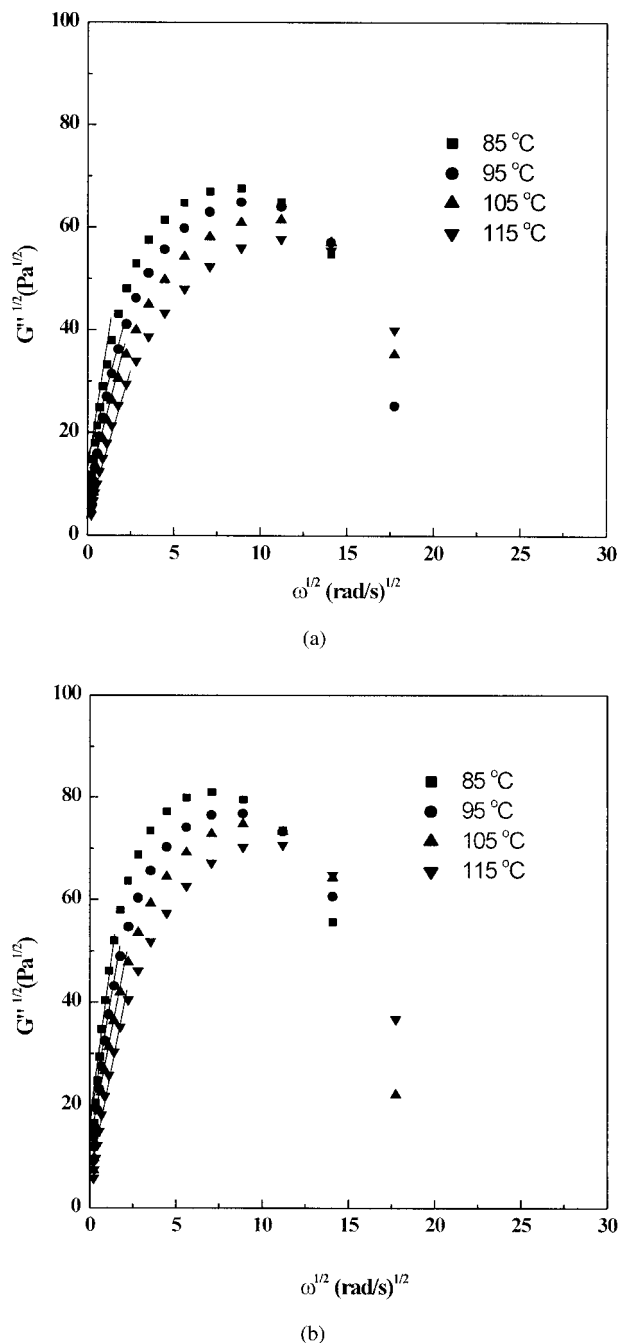| Concentration	11 wt %		13 wt %	
	ω	G_c	ω	G_c
85°C	12.058	3257.7	6.687	4485.6
95°C	22.496	3223.0	12.422	4293.1
105°C	35.950	3064.3	21.449	4257.4
115°C	54.085	2818.6	33.085	3992.4

(a)

(b)

Figure 5 Casson plots of (a) 11 and (b) 13 wt % solutions of cellulose in NMMO monohydrate.

Figure 5. This ascertains aforementioned suggestion that a phase transition from heterogeneous to homogeneous takes place in the vicinity of 85°C.

The first normal stress difference (N_1) obtained from the slit rheometer is plotted against shear rate for two cellulose solutions in NMMO monohydrate in Figure 6. N_1 is a quantitative measure of elasticity of a fluid caused by disentangling–recoiling process of polymer chains, which has real significance in designing fabrication process. Values of N_1 are increased with increasing concentration and with lowering temperature

as expected. Owing to chain rigidity, the cellulose molecules are predicted to be easily oriented, leading to ordering of molecules like liquid crystalline polymers. The higher cellulose concentration gives rises to increase of rigidity of the cellulose molecules and leads to higher ordering in the solutions due to increased intermolecular interactions.[21] As a result, the 13 wt % cellulose solutions give higher value of N_1 at the same temperature.

It is recognized that plotting elastic parameters of polymeric materials against shear stress gives a master
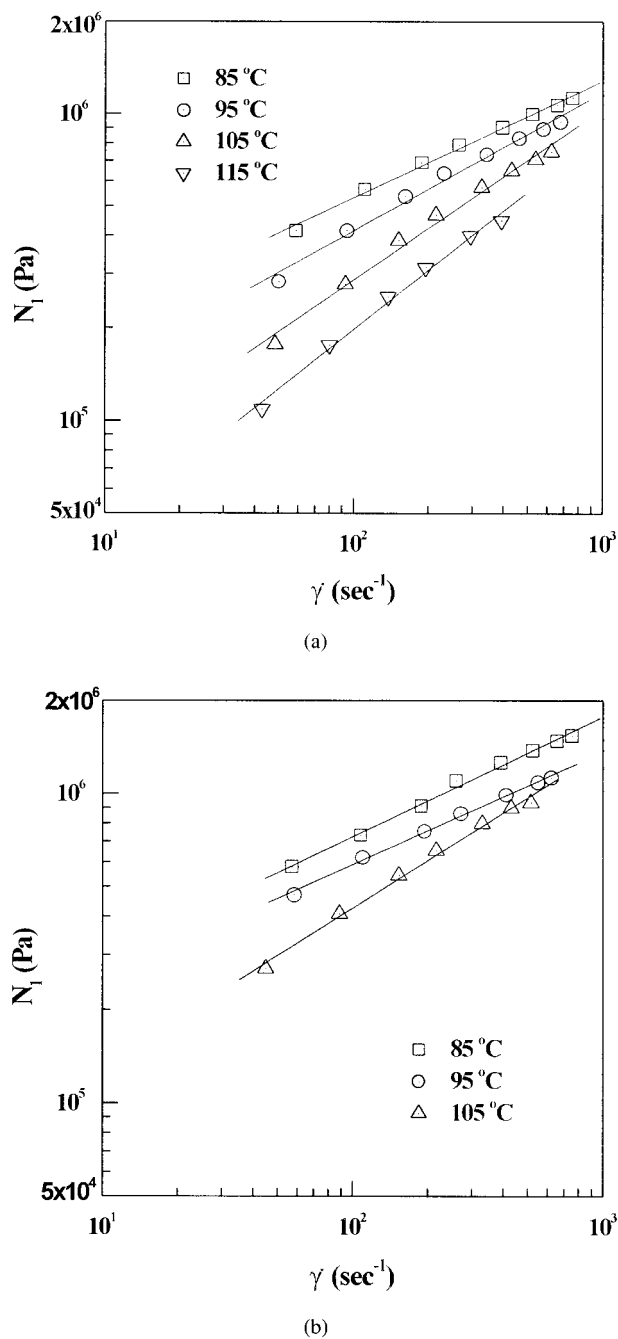

(a)

(b)

Figure 6 Plots of first normal stress difference (N_1) vs shear rate ($\dot{\gamma}$) for (a) 11 and (b) 13 wt % solutions of cellulose in NMMO monohydrate.
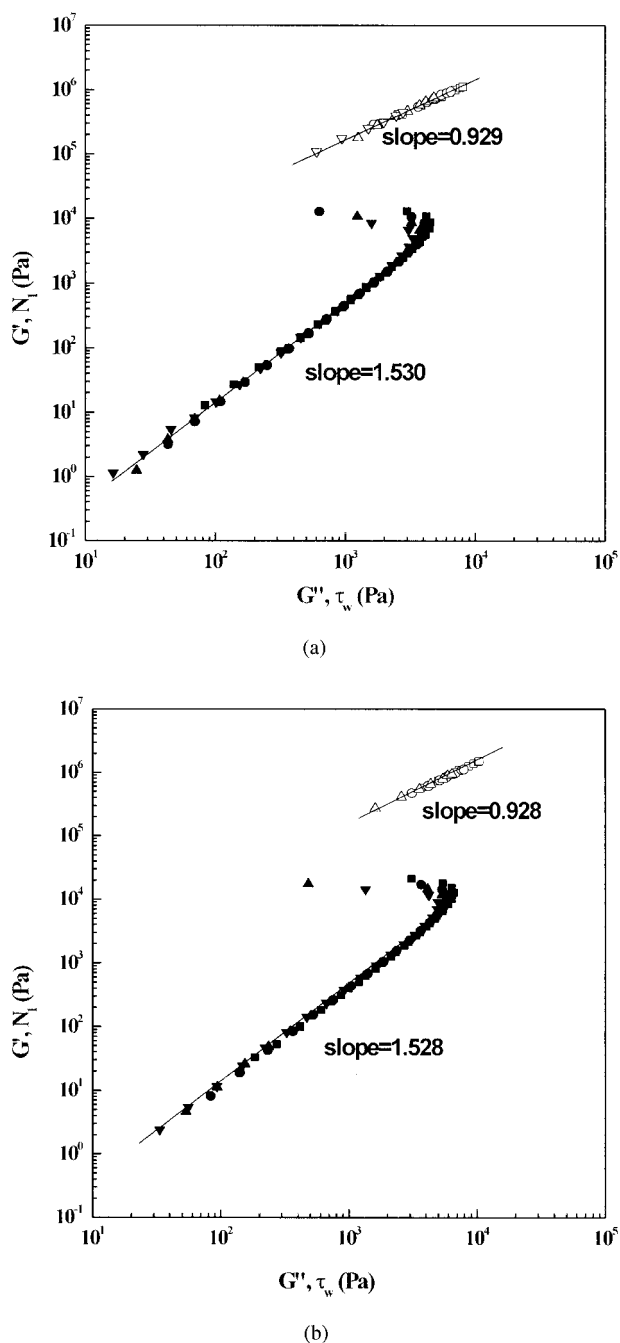
(a)

(b)

Figure 7 Plots of first normal stress difference (N_1) vs shear stress (τ_ω) and storage modulus (G') vs loss modulus (G'') for (a) 11 and (b) 13 wt % solutions of cellulose in NMMO monohydrate: solid symbols for plot of log G' vs log G'' and open symbols for log N_1 vs log τ_ω: (■, □) 85°C; (●, ○) 95°C;(▲, △) 105°C; (▼, ▽) 115°C .

monohydrate is plotted against G'' and N_1 is also plotted against shear stress ($\tau_\omega > 500$ Pa) in Figure 7. Least square fitting of data over the shear rate range gives respective master curves for 11 and 13 wt % cellulose solutions. In the case of plotting G' vs G'' the slopes of straight lines for 11 and 13 wt % cellulose solutions are 1.530 and 1.528, respectively. On the other hand, plotting N_1 vs τ_ω for the two solutions gives slopes of 0.929 and 0.928, respectively. The slopes obtained from the slit rheometer are much smaller than those obtained from the parallel plate rheometer. It is because of a big
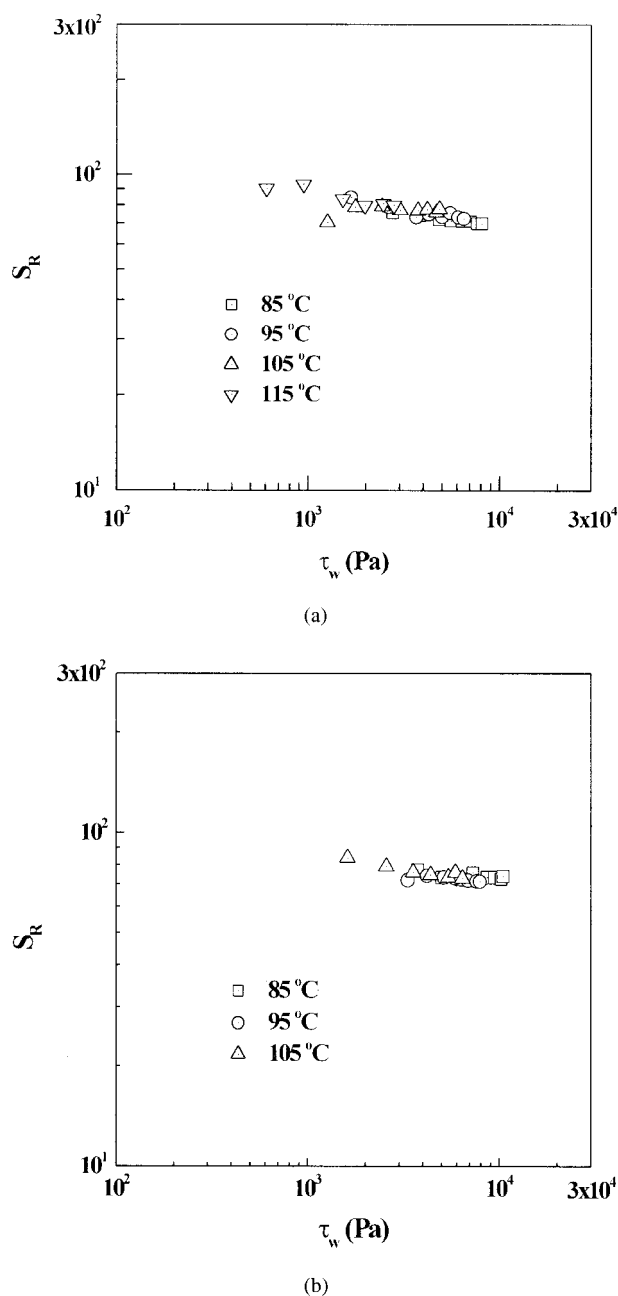

(a)

(b)

Figure 8 Plots of recoverable shear strain (S_R) vs shear stress (τ_ω) for (a) 11 and (b) 13 wt % solutions of cellulose in NMMO monohydrate.

curve independent of measured temperature. The so-called Cole–Cole plot shows a temperature-independent master curve whose slope is 2 theoretically if the polymer system is isotropic and homogeneous.[22] Thus, the deviation of slope from 2 indicates the degree of microheterogeneity of the solution system. The G' of 11 and 13 wt % cellulose solutions in NMMO

difference in shear rate applied in rheological measurements. That is, much higher shear rate was applied in the steady state rheological measurement by slit die. Anyway, both cellulose solutions give slopes smaller than 2, suggesting occurrence of some permanent deformation during rheological measurement resulting from slow relaxation rate of semirigid cellulose molecules.

Another convenient way of expressing fluid elasticity is to define recoverable shear strain (S_R), which is calculated from the following expression:.

$$S_R = \frac{N_1}{2\tau_\omega} \qquad (2)$$

The S_R is plotted against shear stress for 11 and 13 wt % solutions of cellulose in NMMO monohydrate in Figure 8(a) and (b), respectively. The S_R obtained at several different temperatures exhibits a good proportionality to the shear stress with little temperature effect. The cellulose solutions tested give the values of S_R in the range of 60 ~ 100, which are comparable with the values 3 ~8 for the high-density polyethylene melt at 200°C and 0.4 ~ 2 for the polypropylene melt at 200°C in the corresponding shear stress range.[23] Thus, the cellulose solutions have S_R values much higher than the flexible-chain polymer melt by 10 times although the latter has shear viscosity higher than the former by almost 10 times.

CONCLUSIONS

Dynamic and steady shear rheological properties of 11 and 13 wt % solutions of cellulose in NMMO monohydrate revealed that the solution systems gave a shear thinning behavior over the whole deformation rate. Particularly with 13 wt % solutions, yield behavior was observed between 85 and 95°C, indicating a transition from mesophase to isotropic phase. On the Cole–Cole plot, two cellulose solutions gave temperature and concentration-independent master curves.

However, there was a difference in the slope of the master curves between the slit rheometer and the parallel plate rheometer. In addition, the cellulose solutions in NMMO monohydrate exhibited much higher S_R than HDPE and PP melts in spite of much lower viscosity. This result may be helpful to the spinning processes of lyocell fibers suggesting that the cellulose solutions in NMMO hydrates are subject to melt fracture, resulting from high elasticity.

REFERENCES

1. Dave, V.; Glasser, W. G. J Appl Polym Sci 1993, 48, 683.
2. Franks, N. E.; Varga, J. K. U.S. Pat. 4,145,532, 1979
3. Franks, N. E.; Varga, J. K. U.S. Pat. 4,196,282, 1980.
4. McCorsely, C. C.; Varga, J. K. U.S. Pat. 4,211,574, 1980.
5. Henry, C. U.S. Pat. 4,290,815, 1981.
6. Varga, J. K. U.S. Pat. 4,324,593, 1982.
7. Berger, W. Chemiefasern/Textilind 1994, 44/96, 747.
8. Wachsmann, U.; Diamantoglou, M. Das Papier 1997, 51, 660.
9. Bang, Y. H.; Lee, K. W.; Cho, K. R.; Wang, Y. S.; Kim, H. D.; Cho, H. H. J Korean Fiber Soc 2000, 37, 673.
10. Davies, S. Textile Horizons 1989, Feb, 62.
11. Cole, D.; Jones, A. Lenzinger Berichte 1990, 69, 73.
12. Kim, S. O.; Shin, W. J.; Cho, H.; Kim, B. C.; Chung, I. J. Polymer 1999, 40, 6443.
13. Kim, D. B.; Lee, W. S.; Jo, S. M.; Lee, Y. M.; Kim, B. C. Polym J 2001, 33, 18.
14. Chanzy, H.; Peguy, A.; Chaunis, S.; Monzie, P. J Polym Sci Polym Phys Ed 1980, 18, 1137.
15. Lee, W. S.; Kim, B. C.; Jo, S. M.; Park, J. S. U.S. Pat. 6,153,003, 2000.
16. Kavanagh, G. M.; Ross-Murry, S. B. Prog Polym Sci 1998, 23, 533.
17. Han, J. H.; Feng, D.; Choi-Feng, C.; Han, C. D. Polymer 1995, 36(1), 155.
18. Kim, D. B.; Lee, W. S.; Jo, S. M.; Lee, Y. M.; Kim, B. C. Polym J 2001, 33, 139.
19. McCorsely, C. C.; Varga, J. K. U.S. Pat. 4,142,913, 1979.
20. Petrovan, S.; Collier, J. R.; Morton, G. H. J. Appl Polym Sci. 2000, 77, 1369.
21. Kim, D. B.; Lee, W. S.; Lee, Y. M.; Kim, B. C. J. Korean Fiber Soc 2000, 37, 681.
22. Han, C. D.; Kim, J. H.; Kim, J. K. Macromolecules 1989, 22(1), 383.
23. Han, C. D. Multiphase Flow in Polymer Processing; Academic Press: New York, 1981; Chap 2.