

# Rheology of Cellulosic *N*-Methylmorpholine Oxide Monohydrate Solutions of Different Degrees of Polymerization

S. PETROVAN,<sup>1</sup> J. R. COLLIER,<sup>1</sup> I. I. NEGULESCU<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, The University of Tennessee, 419 Dougherty Engineering Building, Knoxville, Tennessee 37996-2200

<sup>2</sup> School of Human Ecology, Louisiana State University, Baton Rouge, Louisiana 70803

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**ABSTRACT:** Preparation and shear and elongational rheology of cellulose solutions of different degrees of polymerization (DP) in *N*-methylmorpholine oxide monohydrate (lyocell) were investigated. The dissolution process takes place in two stages, depending on the content of low and high DP fractions from the dissolving pulp blends. The influence of the DP of cellulosic chains on elongational and shear viscosity is greater at low deformation rates. Low DP solutions behave more like viscous fluids and the increase of the chain length brings about an increase of the elastic component. Orientation induced by the convergence flow is enhanced by the higher DP cellulosic chains. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 396–405, 2001

**Key words:** cellulose solution; *n*-methylmorpholine oxide monohydrate solvent; cellulose dissolution; degree of polymerization; elongational viscosity; shear viscosity; dynamic moduli; Trouton ratio; flow orientation

## INTRODUCTION

Rheological characteristics of polymer melts and polymer solutions are important for both processing and final-product quality. In fiber spinning, due to the elongational character of the flow in the fiber-formation stage, the elongational viscosity plays a fundamental role in the quality of the resultant fibers. Lyocell fibers are a novel alternative—environmentally more friendly—to the older and environmentally challenged viscose procedure. Generically, lyocell fibers are prepared from lyocell solutions, that is, cellulose dissolved in *N*-methyl morpholine oxide (NMMO), in the

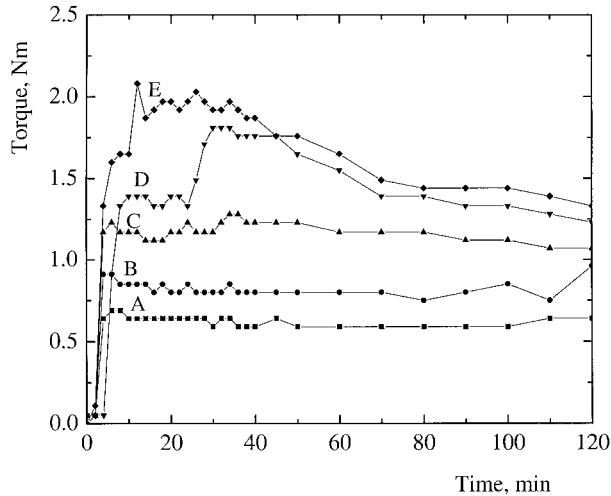
near monohydrate (NMMO · H<sub>2</sub>O) form. Many articles have been published so far, dealing with the preparation and characterization of cellulose and other polysaccharide solutions in NMMO,<sup>1–16</sup> shear rheology,<sup>17–19</sup> spinning conditions and fiber properties,<sup>20–25</sup> and solutions to the fibrillation characteristic of the new type of fiber.<sup>26–28</sup> The only topic that seems to be less taken into account is the influence of the DP of cellulose on the shear and elongational viscosity of lyocell solutions.

This article presents the dynamic shear and elongational rheology of lyocell solutions prepared from blends of dissolving pulps of different degrees of polymerization (DP). Fundamentals on elongational viscosity and entropy of orientation measurement are only briefly presented as these can be found elsewhere.<sup>29</sup>

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Correspondence to: J. R. Collier.

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**Figure 1** Variation of the rotor torque in the course of the lyocell solutions' preparation: (A) cellulose DP 670; (B) cellulose DP 932; (C) cellulose DP 1195; (D) cellulose DP 1457; (E) cellulose DP 1720.

## THEORETICAL CONSIDERATIONS

The equations describing the flow are equations of continuity (mass balance), motion (momentum balance), and energy (energy balance)<sup>30</sup>:

$$\frac{D\rho}{Dt} = -\rho[\nabla \cdot \mathbf{v}] \quad (1)$$

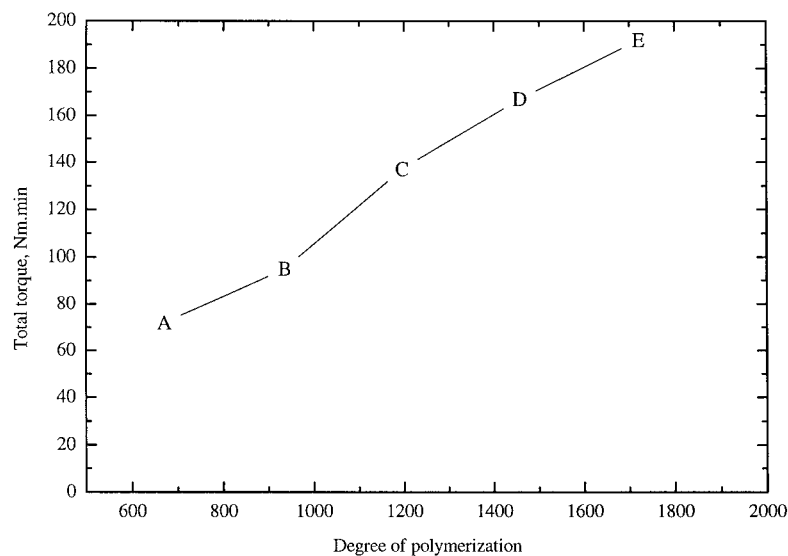
$$\rho \frac{D\mathbf{v}}{Dt} = \nabla P - [\nabla \cdot \boldsymbol{\tau}] + \rho \mathbf{b} \quad (2)$$

$$\rho \frac{D\hat{H}}{Dt} = -[\nabla \cdot \mathbf{q}] - (\boldsymbol{\tau} : \nabla \mathbf{v}) - \frac{DP}{Dt} \quad (3)$$

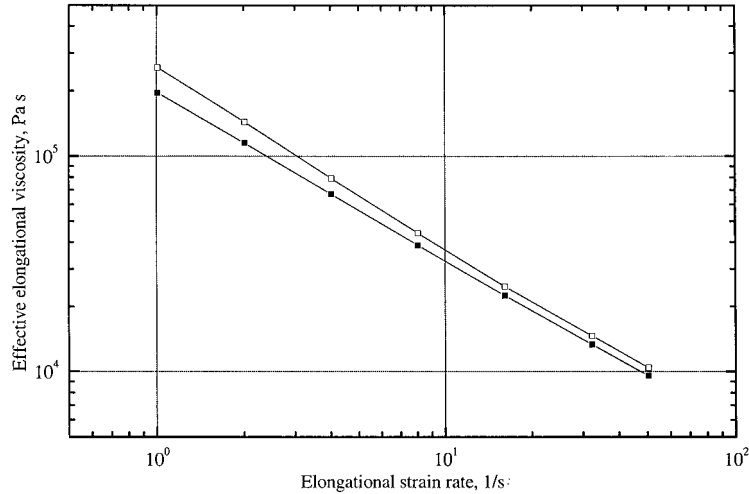
where  $\boldsymbol{\tau}$  is the stress and vectors  $\mathbf{v}$  and  $\mathbf{q}$  denote the velocity and energy flux, respectively. The body force term  $\mathbf{b}$  represents, primarily, the force necessary to orient the material; this term would also include a gravitational component if the latter were significant. The first-order tensor operator  $\nabla$  denotes the gradient. The scalar terms  $P$ ,  $\rho$ , and  $\hat{H}$  are the pressure, density, and enthalpy per unit of mass, respectively.

The semihyperbolic flow channel was designed to apply a constant elongational strain rate. Therefore, the flow is homogeneous and the elongational stress components are also constant. This result, coupled with the insignificance of the shearing gradients, caused the stress-gradient terms in the momentum balance equation to be zero, and the inertial terms were also negligible (the pressure gradients calculated from them were two to three orders of magnitude lower than were the observed ones and the calculated values were independent of the fluid character).<sup>29</sup>

The effective elongational viscosity,  $\eta_{\text{eff}}$ , is defined as



**Figure 2** Total torque for lyocell solutions' preparation: (A) cellulose DP 670; (B) cellulose DP 932; (C) cellulose DP 1195; (D) cellulose DP 1457; (E) cellulose DP 1720.



**Figure 3** Effective elongational viscosity for lyocells from pulps of different cellulose DP: (■) DP 670; (□) DP 1720.

$$\eta_{\text{eff}} = - \frac{\Delta P}{\dot{\epsilon} \epsilon_h} \quad (4)$$

$$\epsilon_h = \ln \frac{A_{\text{en}}}{A_{\text{ex}}} \quad (6)$$

where  $\Delta P$  is the pressure difference and  $\dot{\epsilon}$  is the elongational strain rate.

The elongational strain rate can be calculated using the following equation:

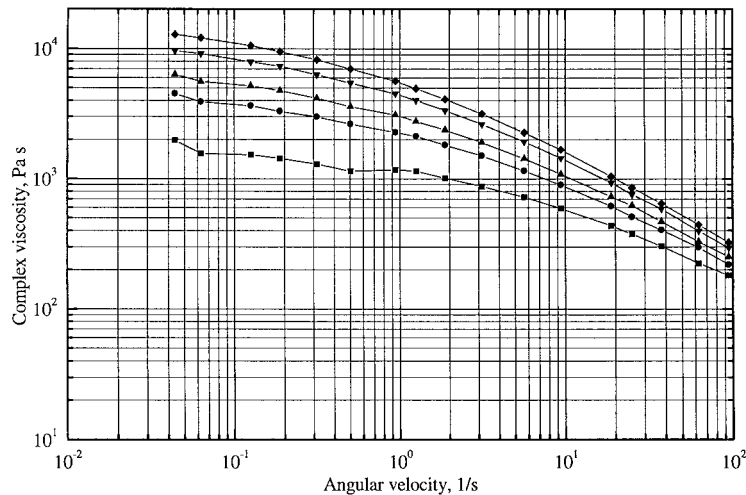
$$\dot{\epsilon} = \frac{v_0}{L} (\exp \epsilon_h - 1) \quad (5)$$

where  $A_{\text{en}}$  is the entrance area;  $A_{\text{ex}}$ , the exit area;  $L$ , the centerline length; and  $v_0$ , the initial velocity at the entrance cross-section area of the flow channel (i.e., of the die).

The enthalpy and the entropy of orientation can be estimated as follows<sup>29</sup>:

where  $\epsilon_h$  is the Hencky strain defined as

$$\Delta H = -\dot{\epsilon} \epsilon_h (\eta_{\text{eff}} - 3\eta_s) \quad (7)$$



**Figure 4** Complex viscosity for lyocells from pulps of different cellulose DP: (■) DP 670; (●) DP 923; (▲) DP 1195; (▼) DP 1457; (◆) DP 1720.

**Table I** Parameters of the Carreau Viscosity Equation [Eq. (9)] for the Lyocell Solutions Prepared from Dissolving Pulps of Different Cellulose DP

Cellulose DP	Carreau Viscosity Equation Parameters			
	$\eta_{\infty}$	$\eta_0$	$\lambda$	$n$
670	1	1762.19	7.442	0.736
932	1	4263.19	7.596	0.642
1195	1	6078.26	7.239	0.605
1457	1	9554.97	7.409	0.573
1720	1	12721.14	7.657	0.548

$$\Delta S = \frac{\Delta H}{T} \quad (8)$$

where  $\eta_s$  is the shear viscosity at the same shear rate as that of the elongational strain rate and  $T$  is the temperature of the solution in K. To obtain eq. (8), the Gibbs free energy is assumed to approach zero for this quasi-equilibrium, steady-state flow process.

## EXPERIMENTAL

### Materials

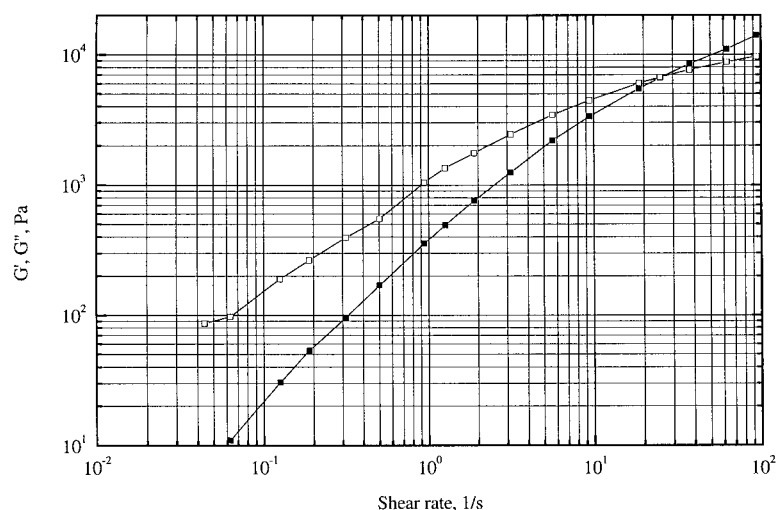
Two dissolving pulp samples (Buckeye Technologies, Inc., Memphis, TN), of DP 670 and 1720,

respectively, were used to prepare blends of an intermediate DP. The DP of the dissolving pulps was measured by the supplier by using the CED viscosity method. The solvent, (NMMO · H<sub>2</sub>O, mp  $\cong$  71°C) was prepared from a 50/50 aqueous solution (NMMO 50%, Aldrich, Milwaukee, WI) by distilling off the water to the corresponding monohydrate composition. Propylgallate (1% versus dried pulp) was added to NMMO 50% to prevent cellulose degradation in the course of the lyocell solution preparation and during rheological characterization. Because we did not measure the DP of the cellulose in the lyocell solutions, all data on DP refer to the DP of the original dissolving pulps.

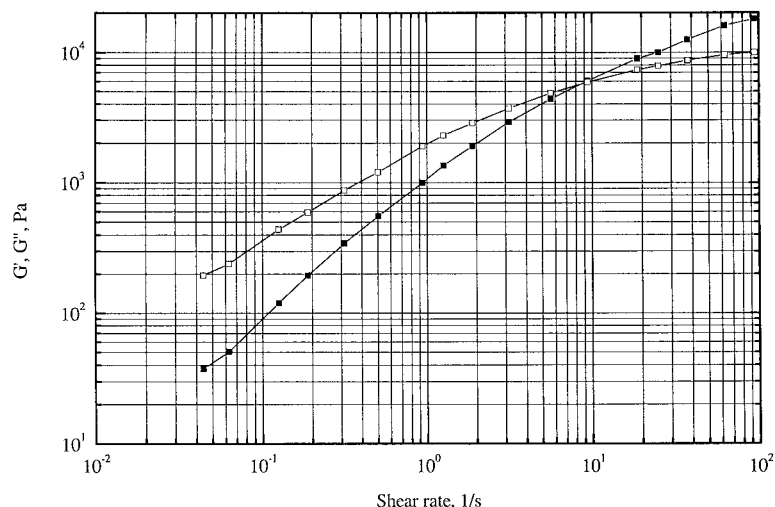
### Equipment and Experimental Technique

Preparation of the lyocell solutions was performed on a Haake Torque Rheometer Rheocord H90, equipped with internal mixer rotors of Z type. The pulp blend and the corresponding amount of NMMO · H<sub>2</sub>O in the solid state were introduced in the mixing chamber and dissolved by mixing at 60 rpm for 2 h at 90°C. The viscous cellulose solution was quickly removed from the mixing chamber, molded as an approximately 3-mm sheet in a polyethylene bag, and stored in a desiccator. The sheets were broken in small pieces (pellets) before use. Cellulose concentration in the lyocell solutions was 14% (by weight).

The elongational viscosity of the cellulose solutions was determined using an ACER 2000 rheometer (Advanced Capillary Extrusion Rheometer,



**Figure 5** Dynamic moduli for lyocell solution, prepared from DP 670 dissolving pulp, at 90°C: (■)  $G'$ ; (□)  $G''$ .

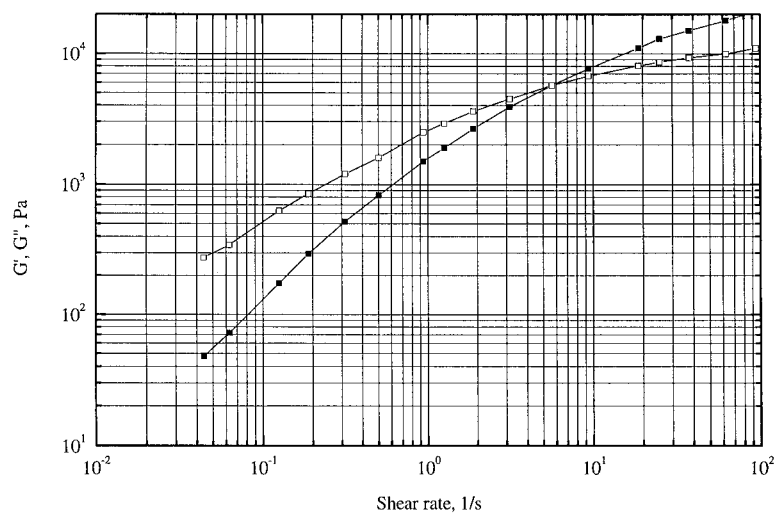


**Figure 6** Dynamic moduli for lyocell solution, prepared from DP 932 dissolving pulp, at 90°C: (■)  $G'$ ; (□)  $G''$ .

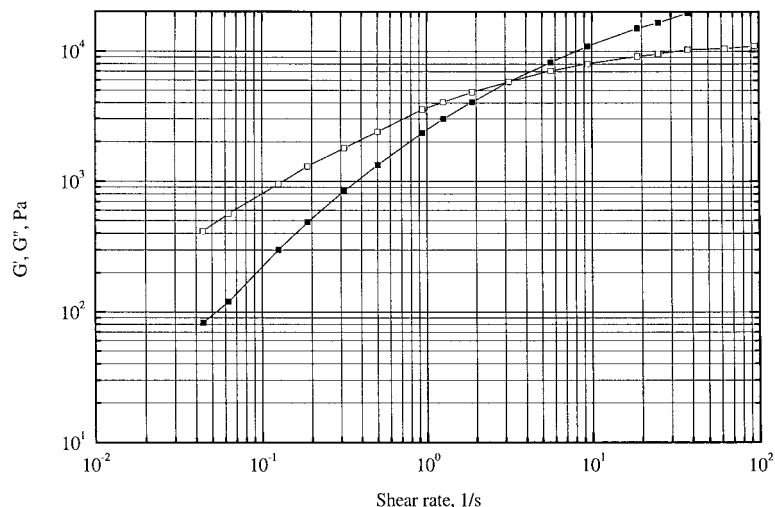
Rheometric Scientific). Two semihyperbolic dies of Hencky strains 6 and 7, respectively, were used to measure the elongational flow properties. Pellets of the solid lyocell sample were charged into the barrel and allowed to melt and attain the prescribed steady-state temperature. Only freshly prepared lyocell solutions were added in one run. The experiments were performed by sweeping the chosen elongational strain rates until a steady state of pressure was accomplished for each particular strain rate. Data on steady-state pressure differences were used to calculate the effective elongational viscosity. One or more vis-

cosity curves were obtained from a single charge of the barrel.

Dynamic rheological measurements were performed on a Bohlin VOR 405 constant-strain instrument using parallel-plate geometry ( $d = 20$  mm at a gap of 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 a viscosity standard silicon oil (29.1 Pa s at 25°C). Data on time, frequency, dynamic viscosity, moduli, torque range of the torsion bar, and strain were recorded, saved, and converted to a text file. For



**Figure 7** Dynamic moduli for lyocell solution, prepared from DP 1195 dissolving pulp, at 90°C: (■)  $G'$ ; (□)  $G''$ .



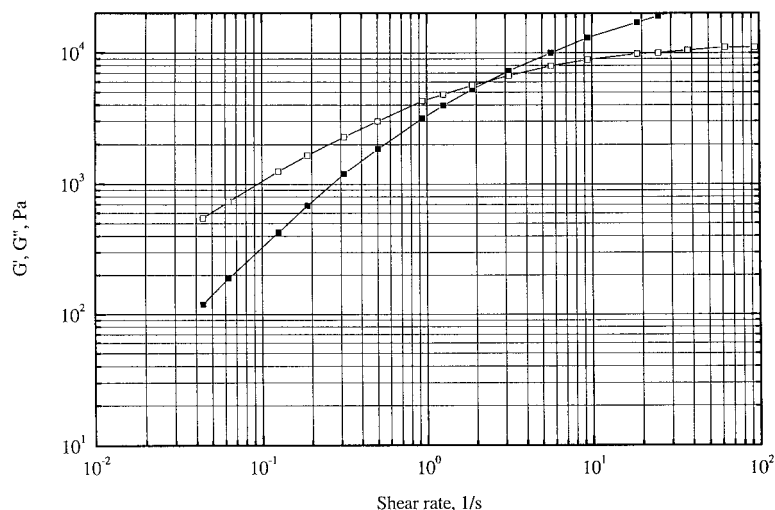
**Figure 8** Dynamic moduli for lyocell solution, prepared from DP 1457 dissolving pulp, at 90°C: (■)  $G'$ ; (□)  $G''$ .

better reproducibility, all experiments were made using only one torsion bar, previously calibrated and recalibrated from time to time with the same standard viscosity oil.

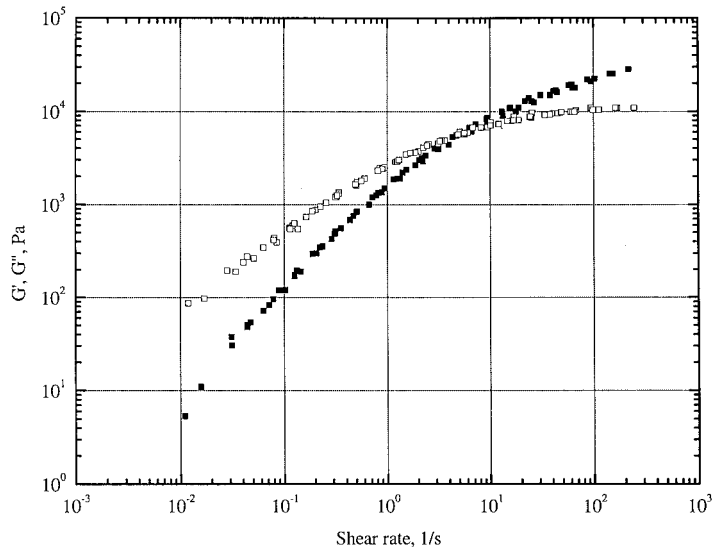
## RESULTS AND DISCUSSION

The energetic aspects of the preparation process of the lyocell solutions from blends of pulps of different DP are presented in Figures 1 and 2. As seen in Figure 1, the dissolution of cellulose aggregates seems to take place in stages, according

to the DP of the cellulosic raw material. As curves C, D, and E show, there are two main stages, defined by the in-step shape of the torque–time curves. The first stage, occurring at a lower torque, may correspond to the dissolution of the lower DP cellulose fraction from the blend, having a lower viscosity, as seen from the viscosity curves. Concurrently, the swelling of the higher DP fraction takes place and, finally, during the dissolution of this fraction, a new increase in viscosity is recorded. The dissolution process can be considered completed when the torque attains a steady-state value. In this state, the instrument



**Figure 9** Dynamic moduli for lyocell solution, prepared from DP 1720 dissolving pulp, at 90°C: (■)  $G'$ ; (□)  $G''$ .



**Figure 10** Dynamic moduli master curves at 90°C: (■)  $G'$ ; (□)  $G''$ .

is working as a rheometer at a constant average shear rate given by the rotational speed of the rotors. The total torque values (i.e., the areas under the curves in Fig. 1) needed to perform the dissolution of the cellulose from pulp blends is presented in Figure 2. As expected, the torque increased with the mean DP of the cellulose blend.

The effective elongational viscosity for the two original pulps is given in Figure 3. A linear relationship between the effective elongational viscosity and the elongational strain rate was recorded and this trend was noticed also for other lyocell solutions.<sup>32</sup> The influence of the DP of cellulosic chains on the effective elongational viscosity of solutions is more obvious at low deformation rates and decreases as the strain rate increases.

Plots of the complex viscosity of lyocell solutions are presented in Figure 4. As in the case of the effective elongational viscosity, the complex viscosity shows a trend of “shear-thinning” behavior. At low angular velocities, approach to a quasi-Newtonian range might be noticed. Also, it is noted that the influence of the DP of the dissolving pulp on the complex viscosity decreased as the strain rate increased, that is, the same trend observed for elongational viscosity, but to a greater extent.

The trend of the complex viscosity curves toward a quasi-Newtonian range suggests trying to fit the experimental data with the Carreau equation<sup>31</sup>:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2}, \quad (9)$$

where  $\eta_0$  is the zero-shear-rate viscosity;  $\eta_\infty$  the infinite shear-rate viscosity;  $\lambda$ , a time constant; and  $n$ , the “power-law exponent” or flowing index. Use of the complex viscosity,  $\eta^*$ , for the determination of the zero shear-rate viscosity for the lyocell solutions is based on our experimental findings<sup>32</sup> that show that the Cox–Merz rule

$$\eta^*(\omega) \equiv \eta(\dot{\gamma}) \quad (10)$$

is valid for such systems.

Parameters of the Carreau equation for our lyocell solutions are given in Table I for the infinite shear viscosity  $\eta_\infty = 1$ . It was noticed that choosing the infinite shear viscosity in the range  $0 \leq \eta_\infty \leq 0.01\eta_0$  does not significantly change the other three parameters from the Carreau equation.

The zero shear-rate viscosity increases with the increase of the DP due to the increase in the length of the polymeric chains. The decrease of the “power-law exponent” with the increase of the DP shows an enhancement of the pseudoplastic character of the lyocell solutions by increasing the polymeric chain length. This is also seen in Figure 4, showing a higher “shear-thinning” effect in the case of lyocell solutions prepared from a higher cellulose DP dissolving pulp.



**Table II** Shift Factors for Dynamic Moduli at Different DP

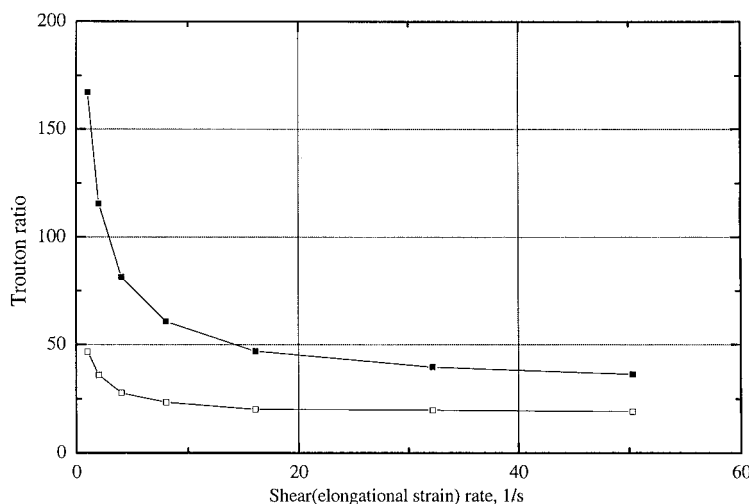
DP of Dissolving Pulp	Shift Factors for	
	$G'$	$G''$
670	0.25	0.27
923	0.705	0.65
1195	1.00	1.00
1457	1.63	1.79
1720	2.3	2.60

Dynamic moduli show almost the same pattern for all blends (Figs. 5–9). At low deformation rates, lyocell solutions behave more like a viscous liquid (loss modulus  $G''$  being larger than the storage modulus  $G'$ ), but at high angular velocities, elastic properties become more evident. The two domains of viscoelastic behavior are separated by the so-called crossover point, which is shifted to lower angular velocities as the mean DP of the cellulose blend is increased. Note, however, that the moduli values at the crossover are essentially constant. This means that the higher the DP, the more elastic the character of the resultant lyocell solution. This finding is important for spinning and drawing processes of lyocell fibers, as well as for the mechanical properties of the spun fibers. Shifting of  $G'$  and  $G''$  curves from Figures 5–9 resulted in the master curves presented in Figure 10. The crossover point for these two master curves has the coordinate  $G' = G'' = 5150$  Pa and an angular velocity of  $4.2 \text{ s}^{-1}$ . The angular veloc-

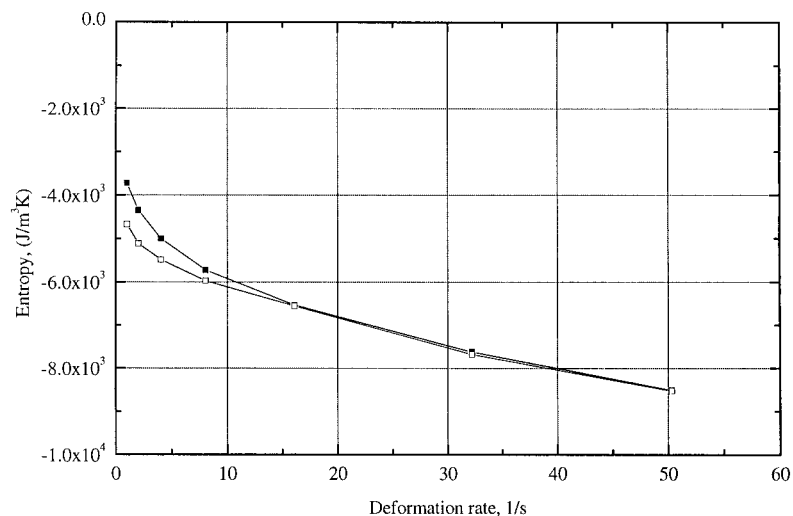
ity at the crossover point is related to the relaxation time of cellulose chains from solution, which, in turn, is related to the molecular weight (or the DP) of cellulose blend (Figs 5–9). For example, the angular velocity at the crossover point decreased from  $25.77$  to  $2.4 \text{ s}^{-1}$  for DP 670 and 1720, respectively, while the relaxation time (i.e., the reciprocal of the angular velocity expressed in radian/s) increased from  $0.0388$  to  $0.417 \text{ s}$ . The shift factors used to form the master curves for the two dynamic moduli are listed in Table II. The cellulose solution made with a pulp blend of cellulose DP 1125 was chosen as the reference solution. The shift factors for the two moduli were slightly different, particularly for higher DP blends.

The Trouton ratio, that is, the ratio between the effective elongational viscosity and the shear viscosity at the elongational strain rate equal to the shear rate, is a measure for the deviation from simple fluid behavior. This characteristic is presented in Figure 11 for Hencky strain 7. The Trouton ratio is higher for a somewhat narrow range of low deformation rates and almost constant for the rest of the tested deformation rates. This is because the complex viscosity has a quasi-Newtonian character at low angular velocities, whereas the effective elongational viscosity is still strain thinning at low strain rates.

The estimated change in the entropy of orientation of cellulosic chains with the DP is presented in Figure 12. Higher values were recorded for solutions made from higher DP dissolving pulp blends, suggesting that the orientation abil-

**Figure 11** Trouton ratio as a function of deformation rate: (■) DP 670; (□) DP 1720.





**Figure 12** Entropy of orientation for a 14% lyocell from dissolving pulps of different cellulose DP: (■) DP 670; (□) DP 1720.

ity of cellulosic chains increased with the DP. At low deformation rates, the orientation was lower, but the effectiveness of the deformation on the orientation was higher. As the deformation rate increased, the orientation also increased.

## CONCLUSIONS

The dissolution process in  $\text{NMMO} \cdot \text{H}_2\text{O}$  of the blends of cellulose made from dissolving pulps of low and high DP of cellulose takes place in two stages, as is revealed by the torque–time curves. This is particularly specific for blends having a slightly different ratio of the two pulps. The elongational viscosity of concentrated solutions of cellulose (14% by weight) in  $\text{NMMO} \cdot \text{H}_2\text{O}$  shows a “strain-thinning” behavior. The influence of the DP of cellulosic chains is greater at low elongational strains and decreases as the deformation rate increases. The shear-thinning behavior is characteristic for the complex viscosity of lyocell solutions. At low angular velocities, approach to a quasi-Newtonian domain was noticed and the influence of the DP decreased as the deformation rate increased. At low deformation rates, the lyocell solutions behave more like viscous fluids but elastic properties develop at high angular velocities. The increase of the DP brings about an enhancement of the elastic component. The Trouton ratio is higher at low deformation rates and is almost constant at medium or high shear or strain rates. The value of this ratio is apparently

characteristic for the molecular weight of cellulose in solution. Lyocell solutions show an apparent higher orientation of cellulosic chains as their length increases (higher DP).

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## REFERENCES

1. Michels, C.; Meister, F. *Papier* 1997, 4, 161–165.
2. Berger, W.; Keck, M.; Philipp, B. *Cell Chem Technol* 1988, 22, 387–397.
3. Woodings, C. R. *Int J Biol Macromol* 1995, 17, 305–309.
4. Purz, H. J.; Graf, H.; Fink, H.-P. *Papier* 1995, 12, 717–728.
5. Chanzy, H.; Chumpitazi, B.; Peguy, A. *Carbohydr Polym* 1982, 2, 35–42.
6. Gagnaire, D.; Mancier, D.; Vincendon, M. *J Polym Sci Polym Chem Ed* 1980, 18, 13–25.
7. Cahanz, H.; Nawrot, S.; Peguy, A.; Smith, P. *J Polym Sci Polym Phys Ed* 1982, 20, 1909–1924.
8. Bocek, A. M.; Petropavlovsky, G. A.; Kallistov, O. V. *Cell Chem Technol* 1990, 24, 727–734.
9. Michels, C. *Papier* 1998, 1, 3–8.
10. Schrempf, C.; Schild, G.; Ruf, H. *Papier* 1995, 12, 748–757.
11. Lenz, J.; Schurz, J. *Cell Chem Technol* 1990, 24, 3–21.

12. Lenz, J.; Schurz, J. *Cell Chem Technol* 1990, 24, 679–692.
13. Katrib, F. A.; Chambat, G.; Joseleau, J. P. *Cell Chem Technol* 1988, 22, 305–314.
14. Lang, H.; Laskowski, I.; Lukanoff, B.; Schleicher, H.; Mertel, H.; Franz, H.; Taeger, E. *Cell Chem Technol* 1986, 20, 289–301.
15. Collier, J. R.; Collier, B. J.; Petrovan, S.; Negulescu, I.; Romanoschi, O. In 54<sup>th</sup> Southwest Regional Meeting of the American Chemical Society, Baton Rouge, LA, Nov. 1–3, 1998.
16. Romanoschi, O.; Collier, J. R.; Collier, B. J.; Petrovan, S.; Negulescu, I. In *Kenaf: Properties, Processing and Product*, developed from a symposium sponsored by the American Chemical Society, Mississippi State University, 1998.
17. Navard, P.; Haudin, J.-M. *Br Polym J* 1980, Dec, 174–176.
18. Navard, P.; Haudin, J.-M. *J Appl Polym Sci* 1986, 32, 5829–5839.
19. Navard, P.; Haudin, J.-M. In *Cellulose: Structure, Modification and Hydrolysis*; Young, R. A.; Rowell, R. M., Eds.; Wiley: New York, 1986; pp 247–261.
20. Chanzy, H.; Paillet, M.; Vuong, R. In *Wood and Cellulosics, Industrial Utilization, Biotechnology, Structure and Properties*; Kennedy, J. F.; Phillips, G. O.; Williams, P., Eds.; Halsted: New York, 1987.
21. Navard, P.; Haudin, J.-M. *Polym Process Eng* 1985, 3, 291–301.
22. Chanzy, H.; Paillet, M.; Hagege, R. *Polymer* 1990, 31, 400–405.
23. Mortimer, S. A.; Peguy, A. A.; Ball, R. C. *Cell Chem Technol* 1996, 30, 251–266.
24. Mortimer, S. A.; Peguy, A. A. *Cell Chem Technol* 1996, 30, 117–132.
25. Mortimer, S. A.; Peguy, A. A. *J Appl Polym Sci* 1996, 60, 1747–1756.
26. Nicolai, M.; Nechwatal, A.; Mieck, K. P. *Text Res J* 1996, 66, 575–580.
27. Mortimer, S. A.; Peguy, A. A. *J Appl Polym Sci* 1996, 60, 305–316.
28. Anonymous, *Technol Text* 1994, 3, 18–23.
29. Collier, J. R.; Romanoschi, O.; Petrovan, S. *J Appl Polym Sci* 1998, 69, 2357–2367.
30. Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; Wiley: New York, 1960.
31. Bird, R. B.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids, Vol. 1, Fluid Mechanics*, 2<sup>nd</sup> ed.; Wiley: New York, 1987.
32. Petrovan, S.; Collier, J. R.; Morton, J. M. *J Appl Polym Sci* 2000, 77, 1369–1377.