

Rheology of 1-Butyl-3-Methylimidazolium Chloride Cellulose Solutions. III. Elongational Rheology

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ABSTRACT: The elongational rheology of solutions of cellulose in the ionic liquid solvent 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was measured at 80, 90, and 100°C; 8, 10, and 12 wt% cellulose; Hencky strains 5, 6, 7; and strain rates from 1 to 100 s⁻¹. Master curves were generated by shifting the elongational viscosity curves with respect to temperature and Hencky strain. Also, general master curves were generated by simultaneously shifting with respect to both temperatures and Hencky strain. From the Arrhenius plots of the temperature shift factors, the activation energy for elongational flow was deter-

mined. The elongational rheology of these solutions was elongational strain rate thinning similar to that of their shear behavior and polymer melts and they were also strain hardening. Both effects and the viscosity increased with cellulose concentration. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3203–3208, 2008

Key words: cellulose; ionic liquids; 1-butyl-3-methylimidazolium chloride; elongational viscosity; activation energy

INTRODUCTION

Both shear and elongational rheology are fundamental properties for polymer melts and solutions processing. Extensional deformations play a significant role in many processing operations which involve a rapid change of shape such as fiber spinning, film blowing, blow molding, nonwoven melt processing, and polymeric solutions spraying.¹

Cellulose is the most abundant natural, renewable, polymer and is used in the production of many materials both by processing it as a fibrous raw material or by dissolution in appropriate solvents. Environmental issues have stimulated considerable research in recent years towards finding new environmentally friendly or “green” solvents, such as ionic liquids (IL). Many reports have been published thus far regarding cellulose dissolution in IL, solutions characterization and processing.^{2–11} However, literature is scarce on rheological characterization of IL cellulose solutions, with nothing published on elongational rheology.^{12,13}

In previous articles,^{14,15} the shear rheology of cellulose solutions in [Bmim]Cl was presented and this work reports the elongational rheology determined by studying cellulose solutions of different concentrations at different temperatures and Hencky strains. The solvent [Bmim]Cl was chosen because, as literature shows, it is an ionic liquid that can be used to dissolve and process cellulose solutions. Understanding the rheological characterization of the IL cellulose solutions is the first step towards using it in the production of fibers, nonwoven and a lot of other products.

EXPERIMENTAL

Materials

The cellulose used in this study was a dissolving pulp with a degree of polymerization of 670 (Buckeye Technologies, Memphis, TN) and the IL used was [Bmim]Cl (Fisher), the thermal properties are listed in Table I.¹⁶ Three cellulose/IL solutions of 8, 10, and 12% cellulose by weight were studied at temperatures of 80, 90, and 100°C.

Instruments and experimental technique

Dissolution of cellulose in the ionic liquid solvent was carried out in a Brabender internal mixer. Elongational rheology measurements were done using

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TABLE I
Thermal Properties of 1-Butyl-3-Methylimidazolium Chloride ([Bmim]Cl)

Melting point temperature (°C)	41
Glass transition temperature (°C)	-69
Start temperature of thermal decomposition (°C)	150
Heat capacity @ 25°C (J mol ⁻¹ K ⁻¹)	322.7
Heat capacity @ 50°C (J mol ⁻¹ K ⁻¹)	333.7

the Advanced Capillary Extrusion Rheometer 2000 (ACER 2000, formerly Rheometric Scientific, Piscataway, NJ) and hyperbolic dies of three Hencky strains of 5, 6, and 7.

The sheets of the dissolving pulp were ground to a fine powder and dried in an oven to constant weight. The ionic liquid [Bmim]Cl was melted first in the Brabender mixing chamber and then cellulose powder and propyl gallate (1 wt% on cellulose) were added under continuous mixing at 90°C and 60 RPM. Dissolution was performed until a clear viscous solution was obtained. The time of dissolution varied for different concentration solutions, ranging from one half to 2 h. After dissolution, the samples were removed from the mixing chamber and stored in glass jars at room temperature for future testing.

The elongational viscosity (η_e) was measured over an elongational strain rate range of 1 to 100 s⁻¹. All experiments were conducted at three temperatures of 80, 90, and 100°C as well as with the three hyperbolic dies. The zero-shear viscosity, used in the calculation of the Hencky strain shift factors, was determined by using the ORIGIN[®] graphing software (OriginLab, Corp.) to fit complex viscosity data to Carreau or Cross models as reported in the first article in this series.¹⁴

RESULTS AND DISCUSSION

Measurement of the elongational viscosity by the hyperbolically converging flow technique

A few fundamental aspects and the basic equations for the calculation of the elongational viscosity are given in the following with more detail in reference 1. Hyperbolic convergent dies were designed for the melt or solution to generate a constant elongational strain rate along the channel.^{1,17-19} This can be accomplished by the description of the flow channel surface area with the equation $r^2 = A/(z + B)$, where z is the axial flow direction, r is the radius of the flow channel as a function of z , and A and B are geometry defined constants. B is neglected for these dies because it is orders of magnitude lower than the total value of z . The Hencky strain is defined as the natural logarithm of the ratio of the die entrance area to the exit area for a constant-volume process and represents an area contraction of approximately

150, 400, and 1100 for Hencky strains of 5, 6, and 7. The higher the Hencky strain the higher is the elongational deformation for a particular die. The elongational viscosity is calculated with the following equation¹:

$$\eta_e = \frac{\Delta P}{\dot{\epsilon} \varepsilon_H} \quad (1)$$

where η_e is the elongational viscosity, ε_H is the Hencky strain, ΔP is the pressure difference between the entrance and exit cross sections, and $\dot{\epsilon}$ is the elongational strain rate, given by eq. (2)¹:

$$\dot{\epsilon} = \frac{v_0}{L} (\exp \varepsilon_H - 1) \quad (2)$$

where L is the centerline length of the die and v_0 is the entrance velocity.

Temperature shifting of the elongational viscosity

In the first article of this three-part series,¹⁴ the shear viscosity and temperature shifting based on the reduced-variable method²⁰ were presented. Both Cross and Carreau models²¹ were used to estimate the zero-shear-rate viscosities at different temperatures. The same temperature shift factors can be used to shift both shear and elongational viscosities.²² This can also be supported by the findings of Münstedt,²³ who calculated the activation energies for both shear and elongational flow from the zero shear-rate viscosity and the elongational viscosity at very low strain rates, respectively. He found that the values were identical.

Hencky strain shifting of the elongational viscosity

The dependence of the elongational viscosity on the Hencky strain is a result of orientation developing in the polymeric fluid as it is being attenuated. Two methods have been developed to calculate the Hencky strain shift factors and thus the reduced elongational viscosity and reduced elongational strain rate.²⁴ Method 1 is based on an orientation ratio being equal to the relaxation times ratio. The shift factor, reduced elongational viscosity, and reduced elongational strain rate are defined by

$$(a_H)_1 = \frac{[\text{TR} - 3]_{\varepsilon_{H_0}}}{[\text{TR} - 3]_0 \varepsilon_H} \quad (3)$$

$$[\eta_e(\dot{\epsilon}, \varepsilon_H)]_{r_1} = \frac{\eta_e(\dot{\epsilon}, \varepsilon_H)}{[(a_H)_1]^2} \quad (4)$$

$$(\dot{\epsilon}_r)_1 = (a_H)_1 \dot{\epsilon} \quad (5)$$

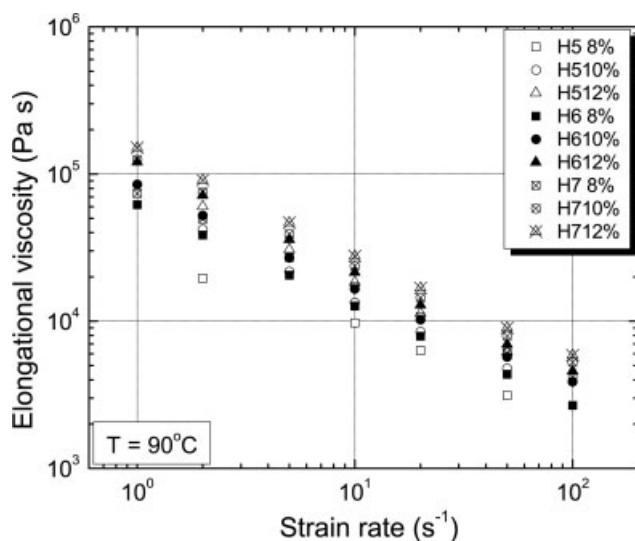


Figure 1 Effect of Hencky strain and cellulose concentration on longitudinal viscosity.

where $(a_H)_1$ is the Hencky strain shift factor defined by Method 1; η_e and η_s are the elongational viscosity and shear viscosity, respectively; η_e/η_s is the Trouton ratio (TR); and subscript r indicates reduced variables. Subscript 0 indicates the values of the variables (shear strain rate, $\dot{\epsilon}$, ϵ_H , and $[TR - 3]$) at the reference state. Method 2 is based on an orientational viscosity ratio. The shift factor, reduced elongational viscosity, and reduced elongational strain rate are defined by

$$(a_H)_2 = \frac{\eta_e(\dot{\epsilon}_0, \epsilon_H) - 3\eta_{s0}}{\eta_e(\dot{\epsilon}_0, \epsilon_{H0}) - 3\eta_{s0}} \quad (6)$$

$$[\eta_e(\dot{\epsilon}, \epsilon_H)]_{r_2} = \eta_e(\dot{\epsilon}, \epsilon_H) \left[\frac{\epsilon_{H0}}{(a_H)_2 \epsilon_H} \right] \quad (7)$$

$$(\dot{\epsilon}_r)_2 = (a_H)_2 \dot{\epsilon} \quad (8)$$

where $(a_H)_2$ is the Hencky strain shift factor defined by Method 2 and η_{s0} is the zero-shear-rate viscosity.

The relative effects of Hencky strain and concentration on elongational viscosity of the ionic liquid solution is shown in Figure 1. A 2% increase in concentration has about the same effect on elongational viscosity as the change of Hencky strain of one unit. The solutions are strain hardening and strain rate thinning, at all concentrations and for all Hencky strains. Hencky strain hardening can be explained by the increase in the orientation of cellulose linear chains at higher strains, a fact proved by both theoretical and experimental results on the rheology of some polyethylene melts and cellulose solutions.^{18,25-27}

Figure 2 illustrates the effect of temperature on the elongational viscosity, whereas concentration

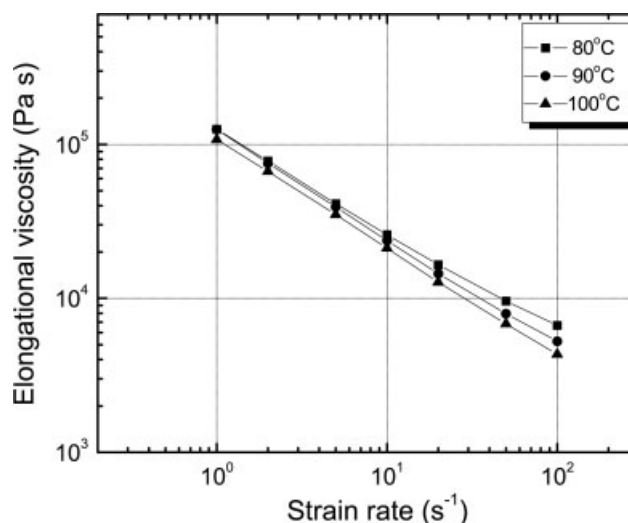


Figure 2 Elongational viscosity of a 10% solution tested in a H7 die.

and the Hencky strain were held constant. Again, this figure indicates a strain rate thinning effect and a decrease of elongational viscosity with the increase in temperature. The higher the strain rate the more pronounced the temperature effect becomes. Using the Carreau model fitting parameters from the shear rheology results in article I of this series of articles,¹⁴ the temperature shifted data is represented in Figure 3. Figure 4 represent the same data as in Figure 3 but instead of the application of the Carreau model fitting parameters, the Cross model fitting parameters from article I¹⁴ were used. As indicated by the coefficient of determination values (R^2 values) both Carreau and Cross models give good temperature shiftings of the elongational viscosity curves.

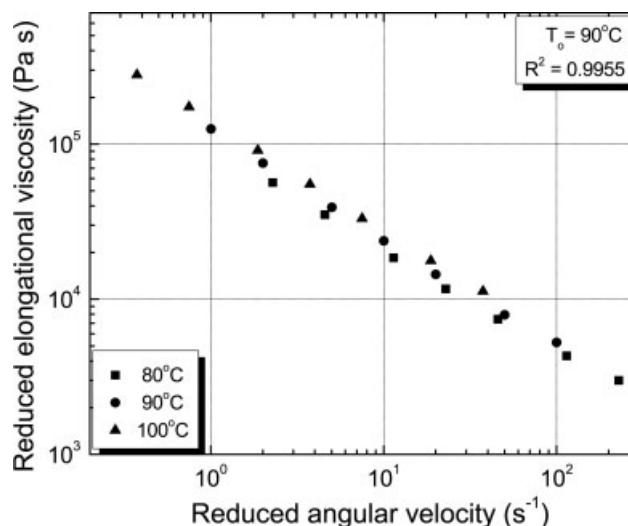


Figure 3 Temperature-shifted elongational viscosity curves for 10% solution using a H7 die and Carreau model fitting parameters.

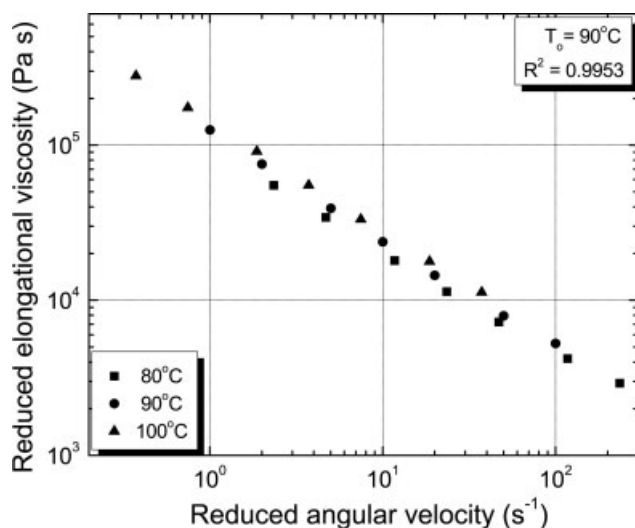


Figure 4 Temperature-shifted elongational viscosity curves for 10% solution using a H7 die and Cross model fitting parameters.

Figure 5 illustrates the temperature-shifted elongational viscosity curves for a 10% solution using the Carreau model fitting parameters. As indicated in the figure, the elongational viscosity increased as the Hencky strain was increased. The same result was observed for the 8 and 12% solutions as shown in Figure 6. Figure 6 illustrates the temperature-shifted elongational viscosity curves for all the solution concentrations using the Carreau model fitting parameters and a Hencky strain of 7. This figure indicates that the elongational viscosity increased as the solution concentration was increased.

As observed in the figures, decreasing the amount of cellulose in the 8% solution would reduce the viscosity of the solution. The R^2 values range from 0.9946 for the 8% solution using a H5 die to 0.9983 for the 12% solution also using a H5 die. These values indicate that the temperature shift for each solution for each die is accurate. The 8, 10, and 12% are not as different in elongation as in shear and the pattern is not as indicative of degradation as in shear. This set of facts could suggest two phases at the higher percentages because a phase separation would influence shear much more than elongational flow. In shear a lower viscosity phase tend to go to the external surface thereby lubricating and reducing the drag at the wall. This is a result of a lack of, or greatly reduced vorticity in elongational flow compared with shear flow.

Finally, as seen from Figures 1 and 2, the effects of temperature and concentration on the elongational viscosity seem rather low and this was also noticed to be valid for lyocell solutions.^{25,28} We use this narrow range of temperature (80–100°C) in our studies on cellulose solutions in NMMO monohy-

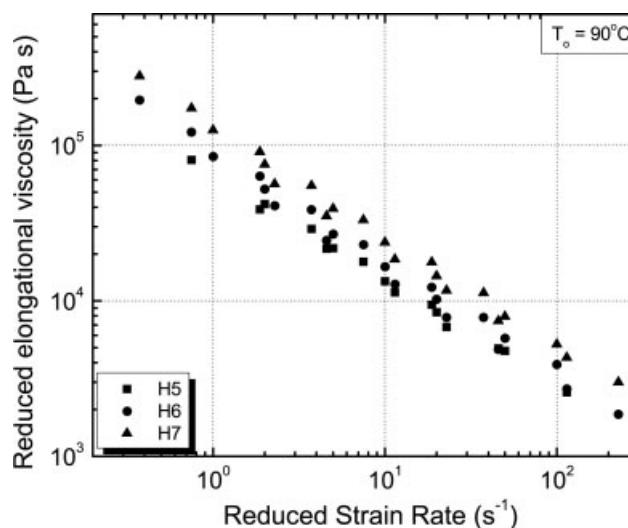


Figure 5 Temperature-shifted elongational viscosity curves for a 10% solution for all Hencky strains.

drate or ionic liquids to limit the thermal degradation.

Simultaneous temperature and Hencky strain shifting of the elongational viscosity

According to the temperature shifting shown previously, a single temperature master curve can be generated from the elongational viscosity curves taken at different temperatures. A single strain master curve can be generated as well from the elongational viscosity curves taken at different Hencky strains. Therefore, by combining these two shifting operations, that is, shifting with respect to temperature and shifting with respect to the Hencky strain, and by using the appropriate shift factors, a generalized

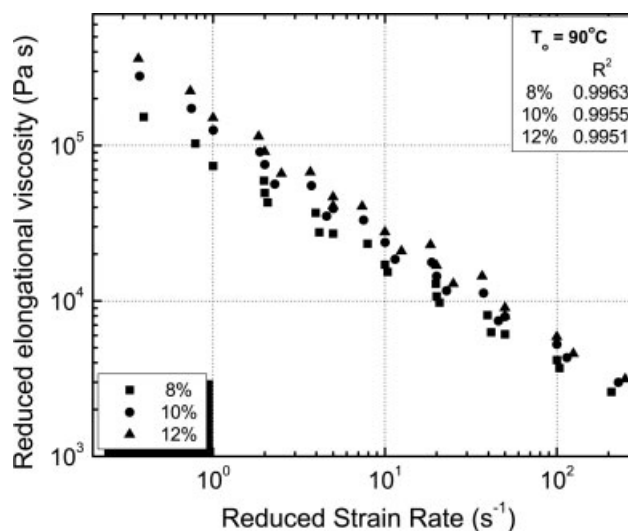


Figure 6 Temperature-shifted elongational viscosity curves using an H7 die for all solution concentrations.

master curve was obtained. This also extended the elongational strain rate range of the experimental geometry. This master curve would facilitate matching the material to the processing conditions. The reduced variables are defined by²⁴

$$\left[(\eta_e)_{r_{TH}} \right]_1 = \frac{\eta_e T_0}{(a_T) T [(a_H)_1]^2} \quad (9)$$

and

$$(\dot{\epsilon}_{r_{TH}})_1 = (a_T)(a_H)_1 \dot{\epsilon} \quad (10)$$

for Method 1 and by

$$\left[(\eta_e)_{r_{TH}} \right]_2 = \frac{\eta_e T_0}{(a_T) T} \frac{\epsilon_{H_0}}{(a_H)_2 \epsilon_H} \quad (11)$$

and

$$(\dot{\epsilon}_{r_{TH}})_2 = (a_T)(a_H)_2 \dot{\epsilon} \quad (12)$$

for Method 2.

In the above equation, T is the temperature, T_0 is the reference temperature, a_T the temperature shifting factor, and subscript $_{TH}$ indicates a reduced variable obtained by using simultaneous temperature and Hencky strain shifting factors.

Figure 7 illustrates the comparison of the master curves of the elongational viscosity shifted to the reference temperature of 90°C and a Hencky strain of 6 for Methods 1 and 2. As indicated, Method 1 had a higher R^2 value. Other reports published by this group show that Method 2 gives slightly better

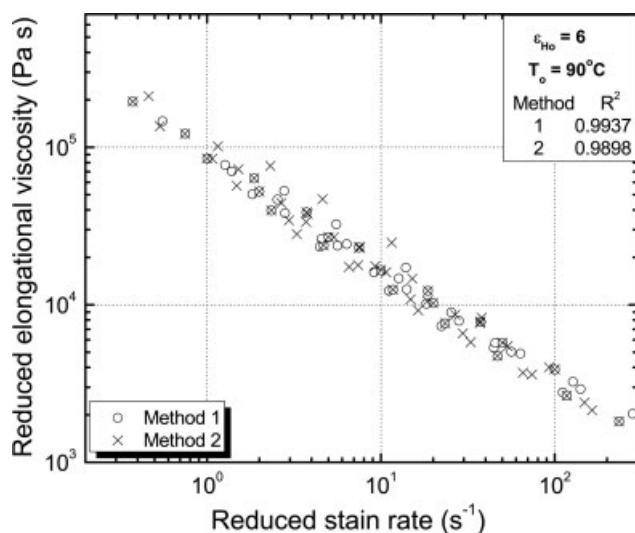


Figure 7 Hencky strain and temperature-shifted elongational viscosity curves for a 10% solution using Methods 1 and 2.

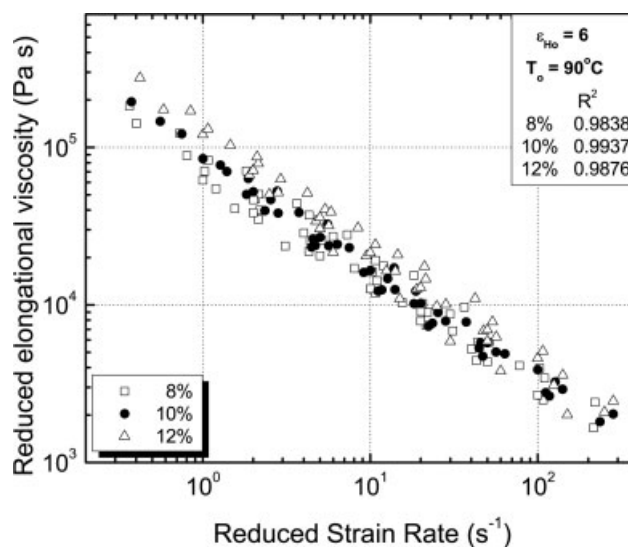


Figure 8 Reduced elongational viscosity for all solutions using Method 1.

results for polyethylenes of different molecular characteristics and nylon resins.^{24,27,29}

Figure 8 illustrates the master curves for all the elongational viscosity data collected. Using Method 1, the curves for all the solution concentrations are shown shifted to the 90°C reference temperature and the Hencky strain of 6. As expected, the 12% solution had a higher elongational viscosity than the 8% solutions. The R^2 values indicate that the temperature shifted and the Hencky strain rate shifted data for 10% solution were more accurate than the 8 and 12% solutions. However, because all of the R^2 values were greater than 0.98, it can be concluded that all the data are in an acceptable accuracy range.

CONCLUSIONS

The elongational viscosity was measured at temperatures of 80, 90, and 100°C for cellulose solutions of 8, 10, and 12 wt% dissolved in 1-butyl-3-methylimidazolium chloride using Hencky strains of 5, 6, and 7. The results show that as the solution concentration increased, the elongational viscosity of the solution increased. The results confirm the intuitive conclusion that the less cellulose dissolving pulp added to the [Bmim]Cl, the more liquid it will remain thus the lower viscosity. Also observed in the results was that an increase in temperature is accompanied by a decrease in the viscosity of the solutions. These results confirm that the elongational rheology of cellulose solutions in [Bmim]Cl behaves as the shear viscosity of most viscous solutions with respect to an increase in temperature. The effect of the Hencky strain rate variation indicated that higher Hencky strain increased the elongational viscosity. The larger exit diameter of the die with the

same inlet diameter, thus the lower Hencky strain rate, would correspond to a lower orientational force to overcome thereby allowing the solution to flow more freely and reducing the elongational viscosity. Two Hencky strain shifting methods were used to ensure the most accurate results possible. Both methods had high R^2 values that allow each to be acceptable on an individual basis. However, Method 1 had slightly higher R^2 values; with the exception of the 12% solution where Method 2 was higher. This indicates that the orientational viscosity ratio of Method 2 had more of an effect on the results than the relaxation time ratio of Method 1 for the 12% solution only and the opposite is true for the 8 and 10% solutions.

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