

Rheology of 1-Butyl-3-Methylimidazolium Chloride Cellulose Solutions. II. Solution Character and Preparation

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ABSTRACT: The focus of this article of a three part series is the effects of preparation and composition on the shear rheology of cellulose in the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). Included are the effects of three different degrees of polymerization, (i.e., average molecular weight), manual versus high shear mixing, a range of cellulose concentrations, and the effects of controlled amounts of lignin and a hemicellulose. The rheology implies that a gel phase develops at higher degrees of polymerization, higher concentration, and at lower

temperatures. The first article focused primarily on shear rheology of cellulose in [Bmim]Cl with a high shear preparation technique, one degree of polymerization, a narrow range of cellulose concentrations, and temperature. The third article focuses on elongational rheology of cellulose in [Bmim]Cl. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1019–1027, 2009

Key words: cellulose dissolution; ionic liquid; shear viscosity; lignin; xylan

INTRODUCTION

Most polymers for manufactured products are considered nonrenewable, because they are derived from petroleum. With the current interest in sustainable consumer products, momentum is growing to find alternative “green” polymer feedstocks.¹ Cellulose is a natural, biodegradable polymer that can be obtained from any number of renewable sources. It is therefore gaining attention as new methods are discovered for processing it into products to replace those from nonrenewable sources.

Cellulose is the main constituent in cotton, the most widely used natural fiber. Cotton fabrics are popular because of their comfort, esthetics, and biodegradability. They do, however, have low wrinkle recovery and poor dimensional stability. Rayon, a regenerated cellulosic fiber found in many apparel and home furnishing items during the 20th century, has the same disadvantages. In addition, the manufacturing process for rayon involves chemicals that are toxic to humans and the environment. A new regenerated cellulosic fiber, lyocell, was developed and produced commercially in the 1980s. Lyocell

fabrics exhibit the aesthetic qualities of rayon and add the comfort of cotton, but they are stronger, more wrinkle resistant, and are manufactured by Lenzing as Tencel[®] using an environmentally benign solvent, *N*-methylmorpholine oxide (NMMO).

Another class of environmentally benign solvents for cellulose is ionic liquids (ILs).² ILs have a negligible vapor pressure (as does NMMO) thus eliminating the emission of volatile organic compounds (VOCs) into the atmosphere.³ In addition ILs can be designed for a specific process, since there are potentially many different anion/cation combinations.⁴ Recent studies have found that cellulose can be dissolved in various ILs⁵ including 1-butyl-3-methylimidazolium chloride ([Bmim]Cl).^{1,6–7} It is speculated that the high chloride ion concentration breaks the extensive hydrogen bonding of cellulose, enabling dissolution even at relatively high concentrations.⁵

To explore applications for these solutions, their rheological behavior must be established under typical polymer processing conditions. The solvent-spun fiber lyocell is produced by the dry-jet wet spinning process,⁸ which should be amenable for IL/cellulose solutions as well. The purpose of this research was to determine the rheological behavior of these solutions to assess their processability. In addition, solutions of cellulose with lignin and xylan added were characterized. These compounds are found in wood, which is highly chemically treated to produce the pure dissolving pulp used for manufacturing

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regenerated cellulosic fibers. If solutions with these additives are similar in rheological behavior to solutions with cellulose only, perhaps a more environmentally benign pulping process could be used.

Ordered liquid formation in cellulose solutions

Our previous Hakke Torque Rheometer Rheocord H90⁹ work at 60 RPM with cellulose NMMO monohydrate indicated that a gel phase occurred at 90°C with a 14 wt % 1720 degree of polymerization (DP) dissolving pulp of cellulose. The torque in this mechanical mixing rose to a maximum of 2.0 Nm after 10 min and then dropped slowly to 1.3 Nm at 2 h. However a 14 wt % 670 DP dissolving pulp of cellulose (as used in the study reported in this article) at 90°C did not form a gel phase and had a steady 0.7 Nm torque over the 2 h period. Furthermore, only a 75% 1720 blend of the two dissolving pulps indicated formation of a gel phase after more than double the stirring time than in the neat 1720 sample.⁹ Our torque rheometer findings are consistent with those of Kosan et al.¹⁰ using a Haake Rheocord 9000 from 10 to 80 RPM. Instead of dissolving pulp they used a 454 DP cellulose from cotton linters. Both the dissolving pulp and the cotton linters are high in cellulose content but the dissolving pulp has been strongly treated chemically. The results by Kosan et al.¹⁰ indicated that in both NMMO monohydrate and [Bmim]Cl the solution process has an initial decrease in torque and viscosity as the suspended fibers dissolve. After dissolution with continued mixing, gel formation occurred with at least fourfold increase in viscosity. With additional mechanical action, the gel is reported to be homogenized and the viscosity decreases by 50% in [Bmim]Cl and 15% in NMMO monohydrate.¹⁰ Kosan et al.¹⁰ reported that the solution of 13.2 wt % cotton linters formed a gel phase at 90°C in NMMO monohydrate peaking at 3.6 Nm after 45 min and dropping to 3.1 Nm after 1 h without further change. They also noted a 13.4 wt % of the cotton linter cellulose formed a gel phase in [Bmim]Cl at 115°C peaking at 4.8 Nm at 80 min and dropping to 3.6 Nm after 100 min without further change.

In addition to gel formation many cellulosic solutions are known to develop liquid crystalline order including cellulose dissolved in the similar solvent NMMO.¹¹ ILs have also been observed to form liquid crystals.¹² Results from a preliminary NMR study in our laboratory with a Bruker 500 MHz unit in collaboration with Dr. Samuel Grant confirmed a gel phase for cellulose in an NMMO/H₂O solution. The 5 wt % 1160 DP dissolving pulp cellulose sample in an NMMO/solvent (17 wt % H₂O) at 50°C had a T_2 value of 31 ms characteristic of a gel as compared to an Alginate gel.¹³ The T_2 of hydrogen

in water is ~ 180 and a liquid crystal would be much lower than the gel. Cellulose/NMMO/H₂O and Cellulose/[Bmim]Cl are very similar.

EXPERIMENTAL

Materials and methods

The IL ([Bmim]Cl) was purchased from Fluka Chemie. Three cellulose dissolving pulps, with degrees of polymerization (DPs) of 670, 1720, and 3900, corresponding to solution average molecular weights of 109,540; 278,640; and 631,800 respectively, were provided by Buckeye Technologies, Memphis, TN. The average molecular weight is the DP times the repeat unit molecular weight, 162. The organosolv lignin and birchwood xylan were purchased from Sigma-Aldrich. The propylgallate was purchased from ACROS Organics.

Solution preparation

Manual preparation

Cellulose/[Bmim]Cl solutions were prepared by heating the [Bmim]Cl, which is a solid at room temperature ($T_m = 41^\circ\text{C}$), to 90°C to obtain the liquid form. The appropriate weight of cellulose dissolving pulp and propylgallate (1 wt % of dried dissolving pulp) were added. Propylgallate increases the thermal stability of the solution.¹⁴ For the modified solutions, lignin and/or xylan were added at this point. The solution was stirred until no visible suspended fibers were present, was clear and formed fine filaments when a spatula was withdrawn (i.e., the viscoelastic properties were evident). If the solution became too cool, and therefore difficult to stir before fine filaments formed, the solution was placed in an oven at 90°C for 5–10 min and then stirred again. The heating and stirring continued until the filaments could be observed. After the filaments became visible, the sample bottles were capped loosely and allowed to cool to room temperature. Once they reached room temperature the sample bottles were capped tightly and stored at room temperature for 1 week prior to testing. The stirring in the manual preparation was by an 8-mm wide spatula in a 3-cm diameter sample bottle. This results in an average shear rate of $\sim 1 \text{ s}^{-1}$ with a stirring rate of 60 RPM. Except for the discussion of manual versus mechanical mixing, all of the samples were manually mixed using this protocol.

Mechanical preparation

Cellulose/[Bmim]Cl solutions were prepared by heating a portion of the IL in a C. W. Brabender Type-6 mixer (C. W. Brabender Instruments) to 90–100°C while stirring at 60 rpm. The cellulose and

TABLE I
Summary of Solutions Prepared

Concentration (wt %)						Carreau parameters and shifting factors for shifting to 90°C										
Total Additives	Cellulose	Lignin	Xylan	DP	Prep Method	80°C				90°C Reference State			100°C			
						η_0	λ	n	a_T	η_0	λ	n	η_0	λ	n	a_T
7	7	0	0	670	Manual	237	1.09	0.64	3.06	80	0.33	0.65	9	0.05	0.82	0.11
10	10	0	0	670	Manual	356	1.53	0.68	2.66	137	0.30	0.70	61	0.16	0.74	0.43
12	12	0	0	670	Manual	1652	3.02	0.59	3.66	464	1.00	0.66	167	0.33	0.70	0.35
15	15	0	0	670	Manual	3283	3.19	0.56	3.62	1009	1.66	0.66	485	1.09	0.71	0.35
3	3	0	0	1720	Manual	393	3.49	0.48	10.63	38	1.20	0.67	14	0.49	0.72	0.36
3	3	0	0	3900	Manual	1404	11.34	0.44	2.82	512	3.42	0.39	208	2.81	0.52	0.30
3	3	0	0	3900	Mech	150	1.16	0.56	1.62	95	0.99	0.56	63	1.05	0.64	0.64
10	10	0	0	670	Mech	558	1.24	0.62	1.81	318	1.77	0.65	260	1.13	0.68	0.80
10	9	1	0	670	Manual	1223	3.47	0.60	2.15	586	2.59	0.64	241	1.42	0.68	0.40
10	9	0	1	670	Manual	695	1.71	0.62	1.81	395	1.30	0.64	259	1.20	0.68	0.64
10	8	2	0	670	Manual	726	2.12	0.61	2.26	331	1.16	0.66	132	1.07	0.75	0.39
10	8	0	2	670	Manual	632	1.47	0.61	1.81	359	0.96	0.63	200	0.58	0.65	0.54
10	8	1	1	670	Manual	456	1.19	0.61	1.94	242	0.72	0.64	130	0.43	0.66	0.52
15	14	1	0	670	Manual	8687	10.42	0.50	1.33	6736	13.64	0.50	4028	9.38	0.42	0.58
15	14	0	1	670	Manual	8294	5.90	0.52	1.71	4987	5.17	0.56	2997	4.64	0.59	0.58

propylgallate (1 wt % of dried dissolving pulp) were then added before the IL was fully liquefied to prevent the IL from leaking out of the mixer. The remaining IL and cellulose were added slowly to minimize the formation of clumps. The solution continued to mix until no visible suspended fibers were present and the solution was clear and formed fine filaments when a spatula was withdrawn. The sample was removed from the mixer, placed in a clean capped container, and stored at room temperature for 1 week prior to testing. The Brabender has trilobal rotors 37.6 mm in diameter and the chamber is 39.2 mm in diameter. Therefore with the 1.6 mm gap and 60 RPM the average shear rate is 74 s^{-1} .

Solution concentrations

Dissolving pulp of 670 DP was used to manually prepare solutions of 3, 7, 10, 12, and 15 wt % of cellulose in [Bmim]Cl. A 3 wt % solution was also prepared with dissolving pulps of 1720 DP and 3900 DP. Solutions containing 1 and 2 wt % lignin and xylan were also prepared with 670 DP cellulose. Additionally, a 10 wt % solution of 670 DP cellulose and a 3 wt % solution of 3900 DP were prepared by the mechanical method described above. A summary of the make-up of the solutions and preparation method is given in Table I. This table and Figures 7 and 8 include shift factors a_T , and Carreau model parameters: zero shear viscosity η_0 , relaxation time λ , and power law index n .

Rheological measurements

Shear rheology of all solutions was measured on the Advanced Rheometric Expansion System (ARES, TA

Instruments). All measurements were taken using parallel plate geometry of 2.5-cm plate diameter and 1.0 mm gap and at temperatures of 80, 90, 100, and 110°C.

The linear viscoelastic domain was first determined by running dynamic strain sweep tests. A strain of 0.1 was found to be within the linear viscoelastic region, and all measurements of complex viscosity and shear moduli were made at that strain. The sample and spatula were heated in an oven for 30 min before placing the solution on the parallel plates for the dynamic frequency tests. A thin layer of standard viscosity silicon oil (20 Pa s at 25°C) was placed on the edges of the specimen sandwiched between the plates to prevent exposure to water vapor in the air. The sample remained between the parallel plates for 5 min before the test was initiated. Data on the angular velocity, complex viscosity, dynamic moduli, $\tan \delta$, and torque were obtained and saved electronically.

Shift factors

The effect of temperature on the shear viscosity of any fluid can be better quantified by shifting the viscosity curves at different temperatures onto a reference temperature viscosity curve to generate master curves and shift factors, from which the activation energy for flow can be calculated. The method of reduced variables^{15,16} was used to develop master curves by plotting the reduced complex viscosity η^* , versus reduced angular velocity ω_r . The shift factors^{15,16} were first defined as in article I of this series¹⁵ so that the reduced variables could be calculated. The experimental data were fitted to the three parameter Carreau model to find zero-shear

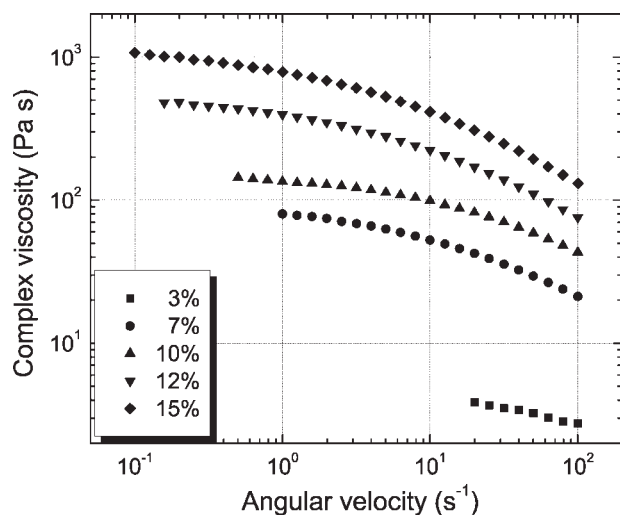


Figure 1 Complex viscosity of DP 670 solutions at 90°C.

viscosities which were used in the calculation of the shift factors. Also, the activation energy for shear flow (ΔE_a) was calculated from the Arrhenius plots of the shift factors.

RESULTS AND DISCUSSIONS

Solution concentration

As shown in Figure 1 there was a progression of both increasing shear viscosity and non-Newtonian character as the concentration of the 670 DP cellulose in [Bmim]Cl increased from 3 to 15 wt %. The 3 wt % solution could only be tested at 80 and 90°C since its viscosity at higher temperatures was lower than the reproducibility limit of the measurements. The curves of the logarithm of the extrapolated zero shear viscosity (using the Carreau model as described in the article I¹⁵) versus temperature as

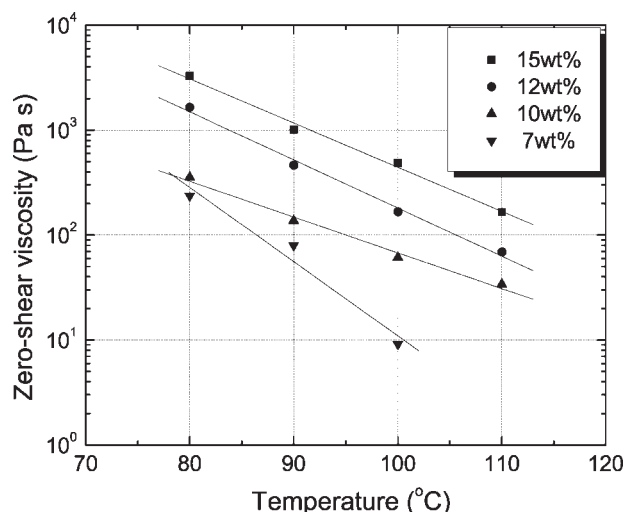


Figure 2 Zero shear viscosity of 670 DP solutions.

TABLE II
Activation Energies for Shear Flow of IL Solutions

Concentration (wt %)	DP	ΔE_a (kcal/mol)	R^2
3 (80 and 90°C)	670	15.56 ^a	1 ^a
7 (80 and 90°C)	670	25.81 ^a	1 ^a
7 (80, 90, and 100°C)	670	43.22	0.9800
10 (80, 90, and 100°C)	670	21.99	0.9970
12 (80, 90, and 100°C)	670	29.09	0.9980
15 (80, 90, and 100°C)	670	26.77	0.9970
3 (80, 90, and 100°C)	1720	44.56	0.9576
3 (80, 90, and 100°C)	3900	25.71	0.9997

^a Note: Only two points were used.

shown in Figure 2 for the 7, 10, 12, and 15 wt % concentrations are consistent except for the 7 wt % at 100°C for these manually mixed samples as discussed below.

The rheology curves for 3 wt % at 80 and 7 wt % at 100°C are similar to the 3 wt % at 90°C (Fig. 1) and comparison of them with the remaining curves suggests that these three solutions are significantly different than higher concentration solutions. These three conditions yielded significantly lower and more Newtonian viscosities. It may well be that these 670 DP cellulose/[Bmim]Cl solutions develop a gel phase at concentrations above 3 wt %, and for 7 wt % at temperatures below 100°C. The activation energy for shear flow in Table II obtained by shifting the data to a reference temperature as reported in the first article¹⁵ would also suggest a difference in behavior. When only the 80 and 90°C data for the 7 wt % solutions are included, the activation energies are comparable with the 10, 12, and 15 wt % values and the 10, 12, and 15 wt % data have excellent coefficients of determination (Table II). This is indicated by the lines in Figure 2. The activation energies for the two 7 wt % and the 10, 12, and 15 wt % data of these manually mixed samples are comparable with the high shear mixed 8, 10, and 12 wt % 670 DP solutions reported in Part I¹⁵ of this three part series of articles. The effect of concentration on the crossover point for the storage and loss moduli is given in Table III. The reciprocal of the crossover point for the storage and loss moduli is the average relaxation time of the polymer solution and related to the average molecular weight.

Degree of polymerization

The three DPs for dissolving pulp used in this study were 670, 1720, and 3900. As noted in Figure 3 for 3 wt % solutions of these samples, the 670 DP solutions at 80°C has more Newtonian and distinctly different behavior than do the 1720 and 3900 DP solutions. At 90°C only the 3900 DP solution does

TABLE III
Crossover Points and Dynamic Moduli

DP	Concentration of cellulose (wt %)	Temperature (°C)	Crossover point		
			Frequency (s ⁻¹)	Relaxation time (s)	G' = G'' (Pa)
670	15	80	5.580	0.1792	3,600
670	15	90	35.28	0.02834	5,200
670	15	100	87.52	0.01143	6,200
670	12	80	NA	NA	NA
670	12	90	50.58	0.01977	3,800
670	12	100	NA	NA	NA
670	10	80	NA	NA	NA
670	10	90	NA	NA	NA
670	10	100	NA	NA	NA
670	7	80	NA	NA	NA
670	7	90	NA	NA	NA
670	7	100	NA	NA	NA
670	3	80	NA	NA	NA
670	3	90	NA	NA	NA
670	3	100	NA	NA	NA
1720	3	80	2.897	0.3452	256.3
1720	3	90	NA	NA	NA
1720	3	100	NA	NA	NA
3900	3	80	0.6058	0.4965	204.4
3900	3	90	2.014	0.4965	234.2
3900	3	100	11.08	0.09025	329.5

not show a tendency toward Newtonian behavior at the lower shear rates measured. This response of the 3900 DP at 90°C and the 3900 and 1720 DP at 80°C is suggestive of a gel phase as were the higher concentrations of the 670 DP samples described in the concentration section of this article. This difference in response was also noted in the crossover points of the storage and shear moduli (Table III). Only at 80°C does the 1720 DP have a crossover point in the accessible range of shear rates, whereas the 3900 DP had distinct crossover points at 80, 90, and 100°C.

The 3900 DP sample at 3 wt % concentration that exhibited consistent behavior at all three temperatures also could be shifted to a master curve with an activation energy given in Table II that is a consistent value with the gel phase in the concentration study. By contrast the activation energy for the 1720 DP sample given in Table II using 80, 90, and 100°C data is similar to that of the apparent isotropic samples in the concentration study. Only the 80 and 90°C data of the 1720 DP samples yield activation energies consistent with gel phase (Table II). This difference in calculated activation energies is depicted by the lines in Figure 2.

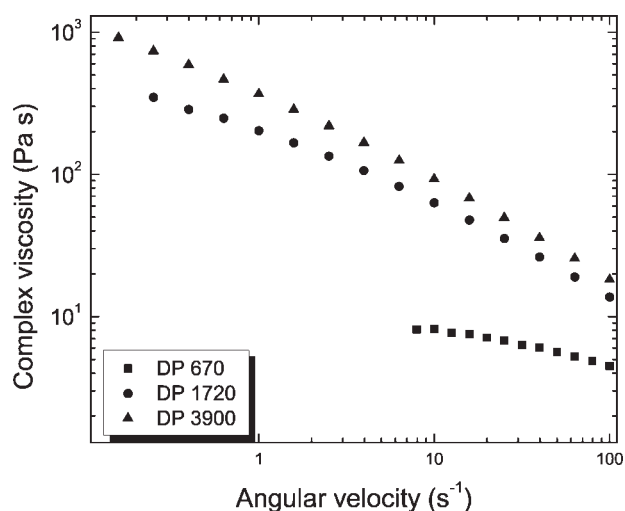


Figure 3 Viscosity of 3 wt % cellulose/IL solutions manually prepared at 80°C.

Preparation method

To investigate the effect of manual versus mechanical mixing in the high shear Brabender mixer the rheology of the 3 wt % 3900 DP and 10 wt % solutions of the 670 DP was measured at 80, 90, and 100°C for both preparation protocols. These combinations of concentration and DP were selected to keep the viscosity in the same range. For the 3 wt % solutions of 3900 DP, the manually mixed samples had higher viscosities than the mechanically mixed samples (Fig. 4), whereas for the 670 DP solutions the reverse was observed (Fig. 5). These results, consistent with those presented above, indicate that the 3900 DP solutions were in an apparent gel phase at all temperatures and concentrations whereas the 670 DP solutions were not at all temperatures. The 3900

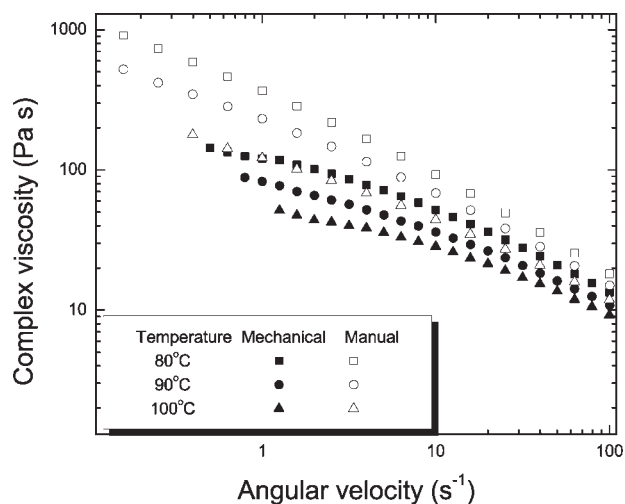


Figure 4 Complex viscosity of 3 wt % 3900 DP cellulose/IL solution manually and mechanically prepared.

DP manually mixed sample probably did not have a sufficient shear history to homogenize the gel phase but the mechanically mixed did. The 670 DP samples that are not as prone to gel formation due to its lower-molecular weight may not have formed a gel when manually mixed (lower viscosity) whereas the mechanically mixed samples probably had a sufficient intense shear history to form a gel. This could contribute to the differences in responses to manual versus mechanical mixing for 3900 DP versus 670 DP solutions.

As shown in Figure 4, the manually mixed 3 wt % 3900 DP complex viscosity versus shear rate is consistently shear rate sensitive over the entire range of $0.1\text{--}100\text{ s}^{-1}$. At 80, 90, and 100°C it is consistent with the behavior of a gel phase that has not been homogenized, whereas the mechanically mixed similar

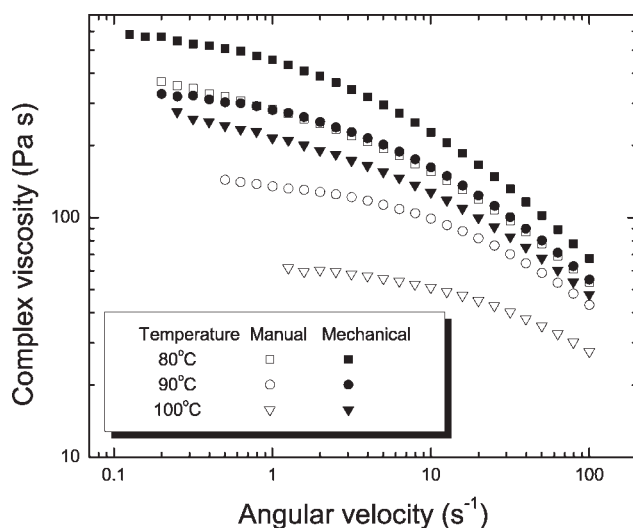


Figure 5 Complex viscosity of 10 wt % 670 DP cellulose/IL solution manually and mechanically prepared.

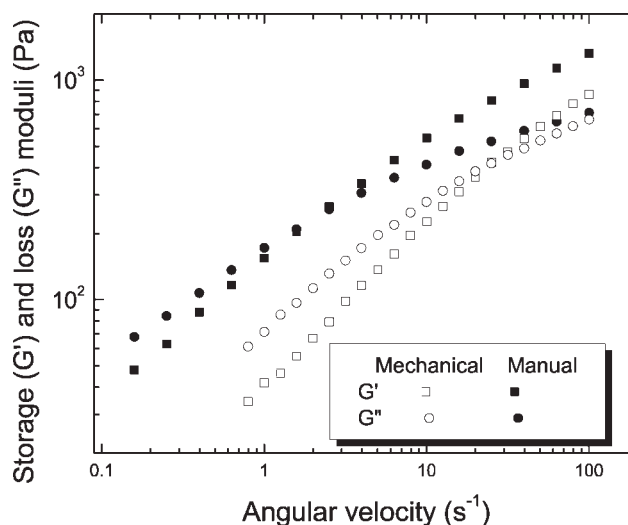


Figure 6 Dynamic moduli for 3 wt % 3900 DP cellulose/IL solution at 90°C mechanically and manually prepared.

sample is less non-Newtonian at lower shear rates perhaps indicative of a gel phase that has been homogenized. The 10 wt % 670 DP manually and mechanically mixed also are less non-Newtonian at lower shear rates. It is possible that the 3 wt % 3900 DP manually mixed sample did not have a sufficient shear history to homogenize the gel that tends to form in this solvent whereas the other samples were either homogenized or a gel phase had not yet formed in the 670 DP manually mixed sample. Carreau model fitting parameters presented in Table I an order of magnitude higher zero shear viscosity at 80°C for manually mixed versus mechanically mixed, and a decreasing difference at 90 and 100°C consistent with the gel phase being homogenized with mechanical mixing but not with manual mixing. Both the 10 wt % 670 DP manually and mechanically mixed samples approached Newtonian behavior at lower shear rates with lower viscosities for the manually mixed samples. This may indicate with the shorter mixing time for these samples that there may not have been sufficient shearing action in the manually mixed samples to form a gel phase whereas there was sufficient shearing action to form and homogenize the gel phase in the mechanically mixed samples. As discussed in the solution section of this article, there is a drop in viscosity upon first dissolution prior to gel formation, followed by an increase with gel formation, and another drop but not to the initial low level after homogenization of the gel.

It should also be noted that the mixing time to form a solution without dispersed fibers in the high shear mixer for the 670 DP samples was only a half hour whereas for the 3900 DP samples 2 h of intensive mixing were required. Apparently, the higher DP solutions are more sensitive to high shear mixing

TABLE IV
Activation Energies for Flow of Different Mixing Methods

Concentration of IL solution (wt %)	DP	Method of preparation	Activation energy for shear flow (kcal/mol)	Coefficient of determination for Arrhenius plot
3	3900	Manual	25.71	0.9997
3	3900	Mechanical	12.17	0.9999
10	670	Manual	21.99	0.9943
10	670	Mechanical	10.53	0.9410

probably because they tend to form a gel phase even at low concentrations.

Further confirmation of the effect of intensity of mixing on solution behavior is shown in the dynamic moduli (Fig. 6). Over the range of frequencies tested, the moduli are consistently lower for the mechanically mixed. The crossover point for the 3900 DP mechanically mixed samples occurred at a higher angular velocity than the manually mixed samples. The moduli nearly doubled at the crossover point for high shear mechanically mixed versus manually mixed solutions (Fig. 6), even though the moduli of mechanically mixed solutions at any frequency are lower than for manually mixed 3900 DP solutions.

The calculated activation energies for the manually mixed solutions were similar to those for other solutions displaying gel phase behavior, while the activation energies for the mechanically prepared solutions were lower (Table IV). The manually mixed 670 DP solutions activation energies were also similar to the mechanically mixed 8, 10, and 12 wt % 670 DP solutions reported in the first article of this series.¹⁵ The observations for the 3 wt % 3900 DP solutions probably indicate homogenization of the gel when high shear and potentially resultant temperature increases are imposed.

It may be that the differences in mechanical versus manual mixing for the 10 wt % 670 DP solutions are indicative of formation of more homogeneous solu-

tions with mechanical mixing compared to manual. Although the 10 wt % 670 DP solutions apparently form a gel phase in both mechanical and manual mixing, the non-Newtonian higher viscosities are not as striking for 10 wt % 670 DP as they are for 12 and 15 wt %. The mechanically mixed 10 wt % 670 DP solutions may be more homogeneous than the manual solutions.

The 3 wt % 3900 DP solution comparisons are probably dominated by whether or not the gel phase has been homogenized. In contrast, the 10 wt % 670 DP solution comparisons may be dominated by the easier dissolution and homogenization for shorter times as the concentration is increased. The difference in crossover points at 80°C is less for the 10 wt % 670 DP solutions than for the 3 wt % 3900 DP solutions, and the moduli at 80°C for the 670 DP solutions are essentially the same for mechanical and manual mixing (Table V).

Cellulose, lignin, and xylan

Previous work by this research group has studied the rheology of cellulosic solutions from untreated and treated sources¹⁷ that have not been as strongly purified as the dissolving pulp used in this study. A related study on solutions from hemp compared with technical grade beech in a similar solvent, NMMO, noted that the residual accompanying substances especially hemicellulose acted as a plasticizer

TABLE V
Crossover Points for Different Preparation Methods and DPs

Concentration of cellulose (wt %)	Preparation method	Degree of polymerization	Crossover point		Temperature (°C)
			Frequency (s ⁻¹)	$G' = G''$ (Pa)	
3	Manual	3900	0.6058	204.4	80
3	Manual	3900	2.014	234.2	90
3	Manual	3900	11.08	329.5	100
3	Mechanical	3900	12.67	413.5	80
3	Mechanical	3900	25.24	423.7	90
3	Mechanical	3900	46.33	466.2	100
10	Manual	670	66.38	2786	80
10	Manual	670	NA	NA	90
10	Manual	670	NA	NA	100
10	Mechanical	670	27.49	2751	80
10	Mechanical	670	52.00	2900	90
10	Mechanical	670	84.84	3128	100

TABLE VI
Change in Crossover Points Coordinates at Different Concentrations and Temperatures

Total additives	Concentration (wt %)			Crossover point		Temperature (°C)
	Cellulose	Xylan	Lignin	Frequency (s ⁻¹)	G' = G''(Pa)	
10	8	0	2	19.21	2328.4	80
10	8	0	2	48.60	2544	90
10	8	0	2	NA	NA	100
10	8	2	0	22.83	2500	80
10	8	2	0	42.05	2526	90
10	8	2	0	78.34	2570	100
10	8	1	1	28.70	2277	80
10	8	1	1	57.32	2336	90
10	8	1	1	NA	NA	100
10	9	0	1	10.50	2056	80
10	9	0	1	28.24	2350	90
10	9	0	1	74.15	2392	100
10	9	1	0	21.63	2590	80
10	9	1	0	41.50	2584	90
10	9	1	0	70.74	2653	100
10	10	0	0	66.38	2786	80
10	10	0	0	NA	NA	90
10	10	0	0	NA	NA	100
15	14	0	1	1.299	3011	80
15	14	0	1	3.693	3300	90
15	14	0	1	9.645	3310	100
15	14	1	0	2.74	4401	80
15	14	1	0	5.41	4485	90
15	14	1	0	10.27	4469	100

and also dissolved in the solvent.¹⁸ To further determine the effects of lignin and hemicelluloses that are present in the other sources, model compounds were formed by adding either organosolv lignin and/or xylan to the dissolving pulp. Organosolv lignin is the least severely treated form of lignin that was available and xylan is the typical linear hemicellulose found in hardwoods.¹⁹ For the comparisons using 670 DP the total concentration of the solutions was kept constant for each series; that is for a 10 wt % solution comparison, 10 wt % cellulose solutions were compared with 9 wt % cellulose with 1 wt % of either lignin or xylan present. The 10 wt % comparisons also included solutions of 8 wt % cellulose

with either 2 wt % lignin, or 2 wt % xylan, or with 1 wt % lignin and 1 wt % xylan.

As shown in Figure 7 the complex viscosity of 8 wt % cellulose with 2 wt % lignin tends toward a Newtonian response at low shear rates as is typical of the 670 DP cellulose solutions alone. Similar responses were noted with 1 or 2 wt % of either lignin or xylan. Manually mixed cellulose solutions with lignin and xylan (Figs. 7 and 8) exhibit higher viscosities than the 10 wt % manually cellulose

TABLE VII
Activation Energy for Shear Flow for Solutions With Additives

Total additives	Concentration (wt %)			ΔE_a (kcal/mol)	R ²
	Cellulose	Xylan	Lignin		
10	8	0	2	23.00	0.9966
10	8	1	1	17.149	0.99995
10	8	2	0	15.781	0.99969
10	9	0	1	21.93	0.9954
10	9	1	0	13.659	0.99799
10	10	0	0	21.99	0.9943
15	14	0	1	10.75	0.9622
15	14	1	0	14.04	0.99988
15	15	0	0	26.77	0.9969

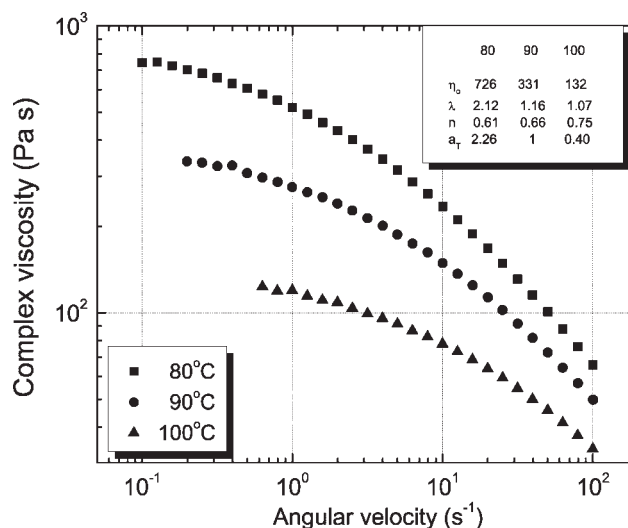


Figure 7 Complex viscosity of 8 wt % 670 DP cellulose/2 wt % lignin/IL solution.

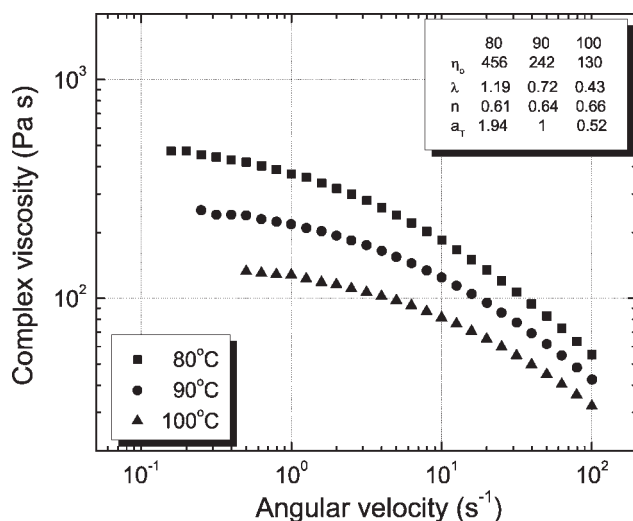


Figure 8 Complex viscosity of 8 wt % 670 DP cellulose/1 wt % lignin/1 wt % xylan IL solution.

solutions shown in Figures 1–5. The effect of adding lignin on the increase of complex viscosity is higher than that of adding xylan and this may be explained by the fact that organosolv lignin is a nonlinear polymer and xylan is a linear hemicellulose with a lower DP, as compared with cellulose. The crossover points for these solutions at 80, 90, and 100°C are given in Table VI and show, as expected, that at 100°C and 90°C some of the samples do not have crossover points in the range of shear rates. Also, of the samples for which the activation energy in Table VII is not in the 20–30 kcal/mol range (8 wt % cellulose with 1 wt % lignin and 1 wt % xylan), consistent with the data for apparent gel phase in previous sections of this article and the first article in this series, do not have crossover point for one temperature.

CONCLUSIONS

The shear rheological behavior of cellulosic solutions in [Bmim]Cl was dependent upon concentration, temperature, preparation method, and amount of lignin and xylan present. The shear viscosity increased with concentration and decreased with temperature and could be shifted to master curves. The solutions develop a gel phase as a function of DP, temperature, and concentration as indicated by rheological behavior including crossover points and shift factors. The 670 DP solutions exhibited behavior associated with a gel state at concentrations above 3 wt %. At 7 wt % the 670 DP solutions appeared to be more ordered below 100°C. The 10 and 15 wt % 670 DP solutions appeared at all tem-

peratures to be more ordered, while the 3 wt % 1720 DP was more ordered at 80°C and the 3 wt % 3900 DP more ordered at 80 and 90°C than at higher temperatures. This may affect the response to preparation methods since 3 wt % 3900 DP solutions that were manually mixed had higher viscosities than the mechanically mixed and the inverse was true for 670 DP solutions. As a result the protocol and particularly the intensity of shearing in preparation of the solution are important and do affect the rheology.

Replacing cellulose in solutions with lignin and/or xylan and keeping the total solute concentration constant increased the viscosity of the solutions. The effect of lignin on the increase in complex viscosity is higher than that of xylan, probably due to the shorter and more linear structure of this hemicellulose.

Cellulosic solutions in the ionic liquid [Bmim]Cl may be used for spinning regenerated cellulose fibers, solution blown for nonwovens production and spinning for carbon fiber precursors. Adding lignin to the solution is expected to increase the carbon fiber yield due to the higher carbon content of lignin, as compared with cellulose.

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