

# Rheological Characterization of Concentrated Cellulose Solutions in 1-Allyl-3-Methylimidazolium Chloride

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**ABSTRACT:** The rheological properties of high concentrated wood pulp cellulose 1-allyl-3-methylimidazolium Chloride ([Amim]Cl) solutions were investigated by using steady shear and dynamic viscoelastic measurement in a large range of concentrations (10–25 wt %). The measurement reveals that cellulose may slightly degrade at 110°C in [Amim]Cl and the Cox–Merz rule is valid for 10 wt % cellulose solution. All of the cellulose solutions showed a shear thinning behavior over the shear rate at temperature from 80 to 120°C. The zero shear viscosity ( $\eta_0$ ) was obtained by using the simplified Cross model to fit experimental data. The  $\eta_0$  values were used for detailed viscosity-concentration and activation energy analysis. The

exponent in the viscosity-concentration power law was found to be 3.63 at 80°C, which is comparable with cellulose dissolved in other solvents, and to be 5.14 at 120°C. The activation energy of the cellulose solution dropped from 70.41 to 30.54 kJ/mol with an increase of concentration from 10 to 25 wt %. The effects of temperature and concentration on the storage modulus ( $G'$ ), the loss modulus ( $G''$ ) and the first normal stress difference ( $N_1$ ) were also analyzed in this study. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3419–3425, 2012

**Key words:** cellulose; 1-allyl-3-methylimidazolium chloride; rheology; viscosity; activation energy

## INTRODUCTION

Cellulose is a renewable, biodegradable, biocompatible polymer, and the most abundant one of all natural substances. However, due to their stiff molecules and close chain packing via numerous intermolecular and the hydrogen bonds between cellulose chains, cellulose is difficult to dissolve in water and common organic solvents.<sup>1</sup> These properties have limited its use in many other products like fibers, films and so on. To date, only a few solvent systems for cellulose have been found, for example *N*-methylmorpholine-*N*-oxidemorphate (NMMO)<sup>2</sup> ammonium fluorides/dimethylsulfoxide,<sup>3</sup> LiCl/*N,N*-dimethylacetamide,<sup>4</sup> some molten salt hydrates (LiClO<sub>4</sub> · 3H<sub>2</sub>O, LiSCN · 2H<sub>2</sub>O)<sup>5</sup> and mixtures of ammonia or ethylenediamine and thiocyanate salts.<sup>6,7</sup> However, these solvent systems possess several undesired properties such as toxicity, cost, difficulty insolvent recovery, or instability in processing.

Swatloski et al.<sup>8</sup> for the first time, reported that the room temperature ionic liquids (IL) are nonderivatizing and green solvents for cellulose, which disclosed another

environmentally benign solvent for cellulose. It is found that cellulose up to 25 wt % can be dissolved in the chloride-containing IL. The IL 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) have been used for homogeneous esterification of cellulose as well as for the formation of films and fibers.<sup>9–12</sup> Nowadays, IL, which may replace the traditional solvents, play more and more important roles in the industrial cellulose processing.

It is well known that the rheological properties play a significant role in many processing operations, which involve a rapid change of shape such as fiber spinning, film blowing, and nonwoven melt processing. So to understand the rheological properties of cellulose/IL solutions as well as the molecular organization of cellulose in these solvents is a crucial prerequisite for the successful process of polymer fiber or film and for chemical derivatization as well. Recently, the literature had reported some viscoelastic properties of cellulose in several imidazolium-based IL in the view of cellulose dissolution and solution spinning.<sup>12</sup> Sammons et al.<sup>13</sup> studied the dynamic and elongational rheological properties of concentrated cellulose/[Bmim]Cl solution. The steady rheology of the cellulose/[Emim]Ac was also studied in a large range of concentration (0–15 wt %).<sup>14</sup> The activation energy values of both the polymer solutions were determined. When [Amim]Cl

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was used for cellulose solvent at polymer concentration below 3 wt %, they all showed a shear thinning behavior at high shear rates; for dilute solutions. There existed another shear thinning region at low shear rates, which could be due to the disruption of the network among the clusters in the dilute solutions.<sup>15</sup>

There are few reports on characterization of rheological properties of concentrated cellulose/[Amim]Cl solution, especially at high concentration. And it is desirable to use this high concentrated cellulose solution to obtain fibers with lower fibrillation and higher flexibility. The objective of this work is to study on the rheological behavior of the concentrated cellulose [Amim]Cl solution. The steady and dynamic rheology of the solutions at different temperature and concentration were investigated in detail.

## EXPERIMENTAL

### Materials

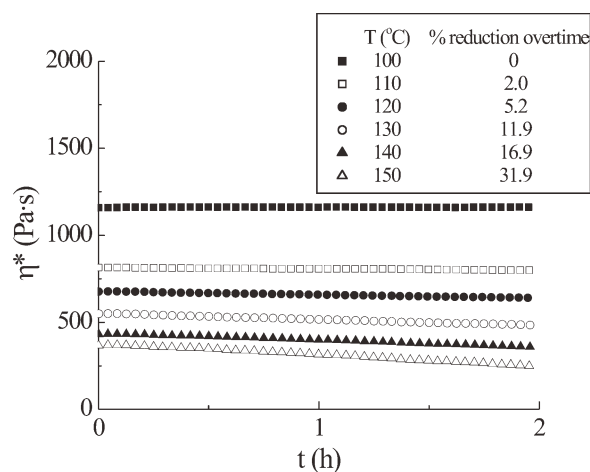
Wood pulp cellulose (WPC) used in this work was provided by Shenyang Chemical Co. (Shenyang, China). The degree of polymerization (DP) was 530, which was determined by GB 5888–86. [Amim]Cl was synthesized according to References 9 and 16. The purity of the IL was above 98% after purification of extraction and rotary evaporation. The water content in the IL measured with the Karl Fischer titration was about 0.5 wt %. The density of [Amim]Cl (1.145 g/cm<sup>3</sup>) was determined with a pycnometer at 25°C and the decomposition temperature is above 250°C.

### Dissolution of cellulose

The sheets of dissolving pulp were ground to a fine powder and were vacuum-dried at 60°C for 24 h to remove any moisture before use. IL and cellulose were first mixed in a mixer, then the mixtures were fed into the Brabender twin-screw extruder (D2040). Screw speed was 10 rpm and the barrel temperature was 110°C. To remove air bubbles in the solutions, a high-vacuum pump was used to reduce the pressure of the barrel. Cellulose concentrations varied from 10 to 25 wt %. Clear cellulose solutions were obtained. They were sealed and stored in a desiccator containing P<sub>2</sub>O<sub>5</sub> at room temperature to protect against moisture absorption. The DP of the regenerated cellulose materials from different concentrations of the solution was around 480 and only small changes of ±3% were observed.

### Rheological measurements

The steady and dynamic rheology experiment was carried out on an AR-1000 stress-controlled rheometer (TA Instruments). Parallel plates (20 mm in diameter)



**Figure 1** Time dependence of the complex viscosity  $\eta^*$  for 10 wt % WPC/[Amim]Cl solution at different temperature at angular frequency of 1 rad/s.

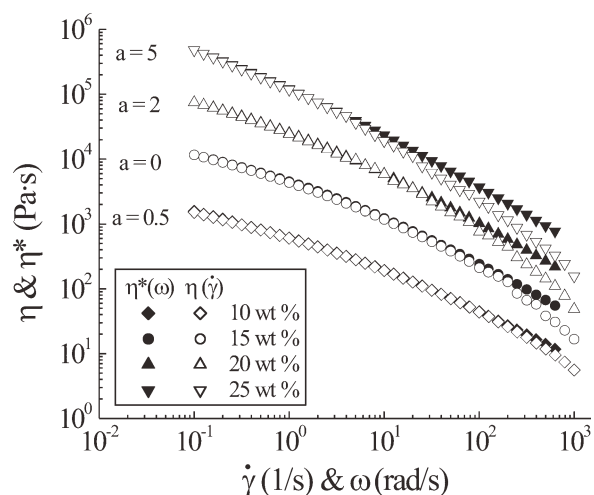
were used. The chosen gap was 1 mm for all the measurements. The values of the strain amplitude were checked to ensure that all measurements were set as 5%, which was in a linear viscoelastic regime. The shear rate ( $\dot{\gamma}$ ) was from 0.1 to 1000 1/s and the sweep of the angular frequency ( $\omega$ ) was from 0.1 to 628.3 rad/s. The dynamic viscoelastic functions such as the shear storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $\eta^*$ )<sup>15</sup> as a function of time, angular frequency and temperature were also measured. It is well known that cellulose/IL solution is, in general, highly hygroscopic.<sup>14</sup> The measuring system used in this study holds a small surface of the solution in contact with the surrounding air and it can cause a uptake of moisture. So to prevent this phenomenon, a thin film of low-viscosity silicon oil was placed around the edges of the measuring cell. It was checked whether this method is efficient for stable-in-time measurements.

## RESULTS AND DISCUSSION

### Degradation of cellulose in ionic liquid

Cellulose in IL may degrade during the measurement process at high temperature. It has been shown that the complex viscosity ( $\eta^*$ ) of cellulose solution decreases as the DP decreases for cellulose.<sup>13</sup> So the change in  $\eta^*$  can be used to determine whether the cellulose degrades. The influence of temperature on  $\eta^*$  of WPC [Amim]Cl solution was investigated by dynamic time sweep experiments at angular frequency of 1 rad/s for 2 h. The result was shown in Figure 1.

When testing at 100°C or below, the complex viscosity of 10 wt % WPC solution remained constant. However, the final viscosity was found to be lower than the initial one at 110°C. The decrease is within



**Figure 2** Cox–Merz plot of WPC/[Amim]Cl solution in different concentration at 100°C. The data are shifted along the vertical axis by  $a$  to avoid overlapping

2.0% in 2 h, while the decrease of final viscosities is up to 31.9% when testing at 150°C. The complex viscosity of WPC solution linearly decreases with increasing time at or above 110°C. As far as cellulose degradation after keeping solution of cotton linters in [Bmim]Cl at 80°C have been reported and cellulose is degraded after being heated at 100°C in [Emim]Ac.<sup>14</sup> It can be concluded that in [Amim]Cl, cellulose may be slightly degraded at 110°C. The degradation may be related to reaction between the IL and carbonyl groups of the cellulose or some oxidation of cellulose chains at high temperature.<sup>17</sup> Therefore, to reduce the experimental errors, the measuring temperature was no higher than 140°C and the sweep of the frequency was from 0.1 to 628.3 rad/s to ensure that the measuring time was no longer than 40 min and the decrease was within the 10% experimental errors.

### Relationship between steady and dynamic shear viscosities

The empirical Cox–Merz rule<sup>18</sup> states that for linear viscoelastic materials the magnitude of the complex viscosity  $\eta^*$  is the same as the steady shear viscosity  $\eta$  at equal values of frequency and shear rate. This rule has been shown to apply successfully for a number of polymer melts and homogeneous solutions,<sup>16,19</sup> but with relative success for aggregating polymers. It needs to be discussed whether this rule is reliable for concentrated cellulose solution. The Cox–Merz plots of the flow and dynamic rheological data of WPC [Amim]Cl solution at various concentrations are shown in Figure 2.

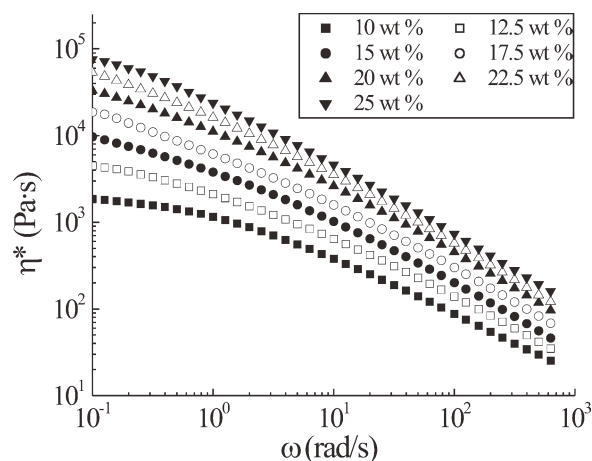
It is observed that the value of  $\eta$  and  $\eta^*$  coincide very well at the concentration of 10 wt %. But with increasing concentration, the  $\eta$  values are relatively

lower than those of  $\eta^*$  at high shear rates and the extent of the deviation also increases. The difference between two values grows wider with the increase of shear rate. This phenomenon is quite different from the semidilute cellulose/[Amim]Cl solutions, which were reported that the value of viscosity are low in dynamic shear but sufficiently high in steady shear at high shear rates. And the departures could be attributed to coexistence of cellulose single chain and large aggregates in the semidilute regime.<sup>15</sup> But in this research, the phenomenon which  $\eta$  is higher than  $\eta^*$  does not appear in the full test range: shear rate or frequency. This is because, at relatively high concentrations, cellulose single chains fully associated with each other to form aggregates, and the solution system transformed into a more uniform and homogeneous entanglement architecture in the concentrated region, and hence the deviations from the Cox–Merz rule were disappeared.<sup>20</sup> However, as the solution concentration increases, the entanglement of cellulose chain is significantly intensified. The polymer chain does not have sufficient space for movement and the flow-ability or fluidity of the solution becomes worse. So, when measured at high shear rate, some of the solution spins out of the plates, resulting in the decrease of  $\eta$  values. In contrast, during the dynamic viscoelastic measurements, this phenomenon will not appear due to the small strain. In view of the above discussion, it can be concluded that the WPC [Amim]Cl solution is satisfied with Cox–Merz rule at 10 wt %. A similar conclusion was reported for some cellulose/NMMO<sup>20</sup> and cellulose/[Bmim]Cl<sup>13</sup> solutions. However, it is not possible to determine whether the rule is suitable for higher concentrations (above 10 wt %) due to the special phenomenon.

### Flow curves of the cellulose solution

The dependence of the complex viscosity on the angular frequency of WPC in the concentration range from 10 to 25 wt % in [Amim]Cl at 100°C is given in Figure 3. Figure 4 presents the effect of temperature on complex viscosity in the 15 wt % cellulose solution. Assuming that the Cox–Merz rule is valid for the concentrated cellulose/IL solution,<sup>13,20</sup> Figures 3 and 4 can represent the changes of shear viscosity with shear rate.

It can be found that the viscosity of the cellulose solution exponentially decreases with the increase in shear rates and exhibited a typical non-Newtonian pseudoplastic behavior. Because of strong hydrogen and van der Waals bonding interactions, cellulose molecules tend to aggregate and tangle with each other even at the dilute concentrations.<sup>21</sup> Therefore, the concentrated WPC solutions display shear thinning at very low shear rates and the Newtonian



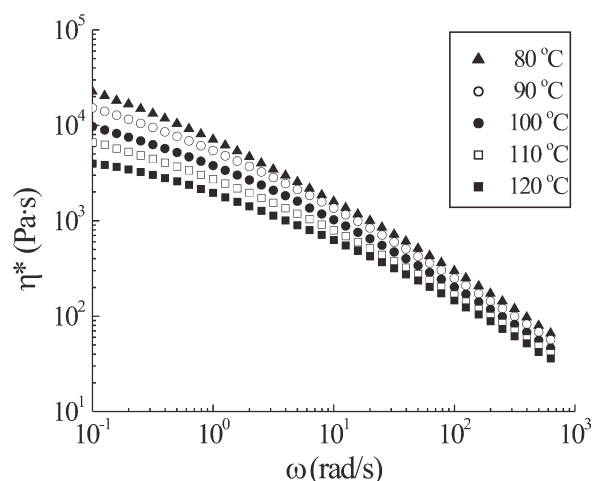
**Figure 3** Dependence of  $\eta^*$  on the  $\omega$  for WPC/[Amim]Cl solution at different concentration at 100°C.

behavior was not observed at all measurement range of shear rates.

The flow curves were fitted using the simplified Cross equation<sup>22</sup>:

$$\eta_{\alpha} = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^{1-n}} \quad (1)$$

where  $\eta_{\alpha}$  is the apparent viscosity,  $\eta_0$  is the zero shear viscosity;  $\lambda$  is time constant,  $n$  is the exponent of the power law and  $\dot{\gamma}$  is the shear rate. The results were presented in Table I. Clearly, the  $\eta_0$  value increases as increase of cellulose concentration ( $c$ ), and at the same time, the exponent value ( $n$ ) become smaller, which means that the non-Newtonian behavior is enhanced. The effects can be explained that the increase of concentration resulted in the increase of molecular chains, leading to the interactions and entanglements of the polymer chains, and restriction of the motion of individual chains. Thus,



**Figure 4** Dependence of  $\eta^*$  on the  $\omega$  for 15 wt % WPC/[Amim]Cl solution at different temperature.

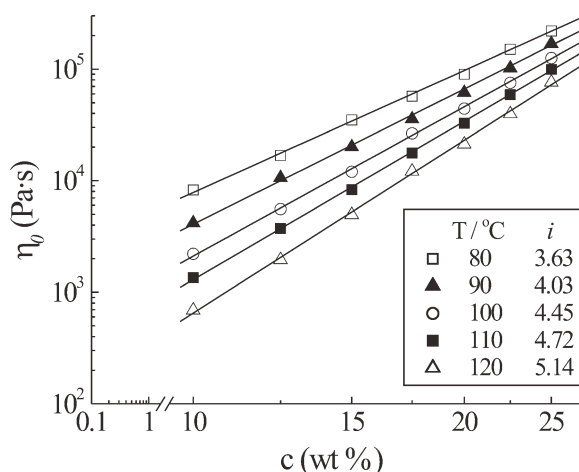
**TABLE 1**  
Values of Cross Parameters for WPC/[Amim]Cl Solutions

Sample $c$ (wt %)	Test Condition $T$ (°C)	$\eta_0$ (Pa·s)	$\lambda$ (s)	$n$
10	100	2209	0.953	0.298
15	100	12000	2.563	0.260
20	100	44330	3.708	0.222
25	100	125700	5.793	0.190
15	80	35060	5.829	0.248
15	120	4938	1.665	0.308

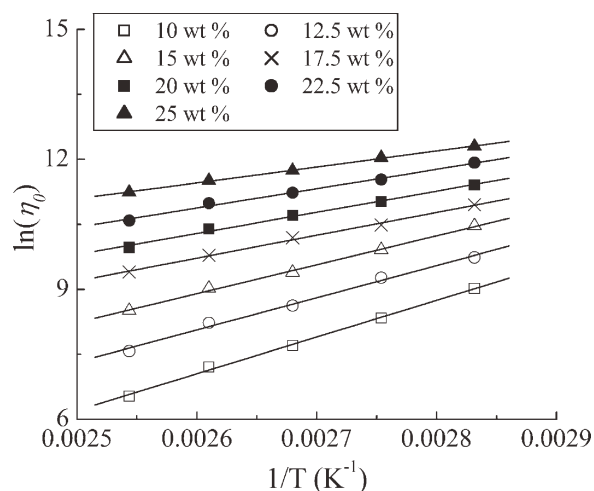
the Newtonian behavior is lost progressively and shear-thinning behavior tendency become more pronounced with increasing polymer concentration. It is evident that  $\eta_0$  values of cellulose/[Amim]Cl solutions decreases with heating, which was typical for classical polymer solutions and for cellulose dissolved in other solvents like NMMO,<sup>20</sup> [Bmim]Cl<sup>13</sup> and [Emim]Ac,<sup>14</sup> and the  $n$  increases from 0.25 to 0.31, which may offer favorable conditions for reduction of the polar intermolecular interactions of hydrogen bonding.

#### Concentration and temperature effect

For the WPC/[Amim]Cl solutions, Figure 5 shows the solution concentration ( $c$ ) dependence of zero shear viscosity at different temperature in the form of double logarithmic plot. For all the cellulose solutions,  $c$  dependence of  $\eta_0$  can be represented approximately by a straight line in the double logarithmic plot. The exponent values ( $i$ ) were calculated for all cellulose/[Amim]Cl solutions and were reported in the Figure 5. The values of  $i$  approximately range from 3.63 at 80°C to 5.14 at 120°C. The power law value is similar to the cellulose/NMMO solution at 75°C ( $i = 4.6$ ). Some lower values which



**Figure 5**  $\eta_0$  as a function of cellulose  $c$  for solutions of WPC in [Amim]Cl at different temperature.



**Figure 6** Arrhenius plot for WPC/[Amim]Cl solutions at concentrations from 10 to 25 wt %.

ranged from  $i = 2.5$  to  $3.0$  were reported for cellulose/[Emim]Ac solution at high temperature ( $60$ – $100^\circ\text{C}$ ). In Figure 5, it can be found that  $i$  value increases with heating. The result is opposite to other IL/ cellulose solutions at relative low concentration. For example, when the measured concentration of [Emim]Ac/cellulose solution ranged from 1 to 10%, The exponent values of viscosity-concentration dependence changed from about 4 at low temperatures ( $0$ – $40^\circ\text{C}$ ) to about 2.5 at high temperatures ( $60$ – $100^\circ\text{C}$ ).<sup>14</sup> This means that the viscosity decreases more slightly with heating at higher solution concentration. The activation energy can give an intuitive way to show this special phenomenon.

The Arrhenius plots of  $\ln(\eta_0)$  versus  $1/T$  at various concentrations are shown in Figure 6. The activation energy ( $\Delta E_\eta$ ) values were calculated by using the Arrhenius equation<sup>23</sup>:

$$\ln(\eta_0) = \frac{\Delta E_\eta}{R} \cdot \frac{1}{T} + \ln A \quad (2)$$

where  $\eta_0$  is the zero shear viscosity,  $\Delta E_\eta$  is the activation energy,  $A$  is a constant characteristic of polymer,  $R$  is the universal gas constant, and  $T$  is the temperature. The results are shown in Table II.

The value of  $\Delta E_\eta$  decreases as the solution concentration increases. It means that the effect of temperature to the viscosity become weaker as the solution concentration increases. The condition is quite different from other cellulose solutions, in which the  $\Delta E_\eta$

**TABLE 2**

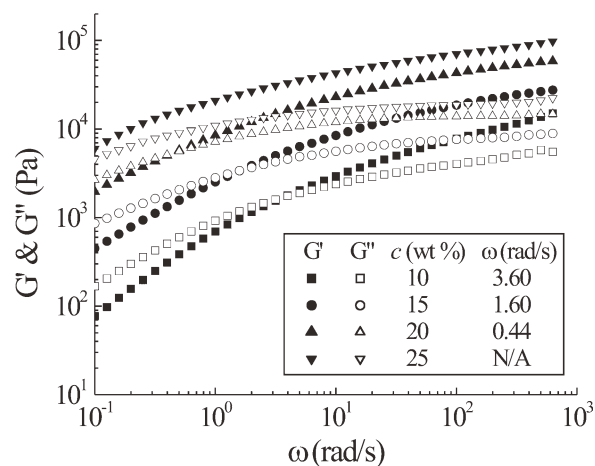
**Activation Energies for the WPC/[Amim]Cl solution**

$c$ (wt %)	10	12.5	15	17.5	20	22.5	25
$\Delta E_\eta$ (kJ/mol)	70.41	61.82	55.48	43.84	40.70	37.17	30.54

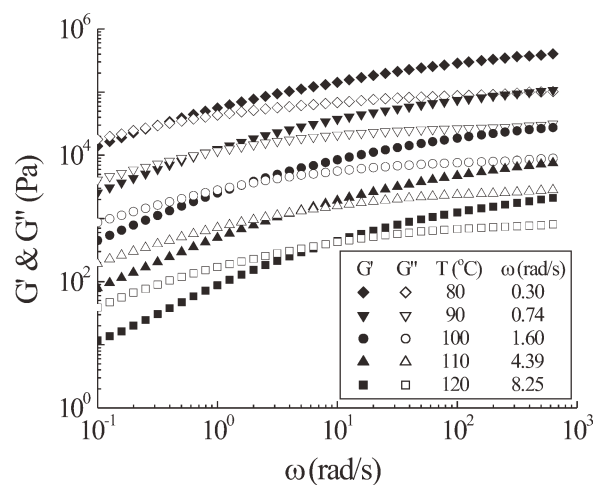
value increases with increasing solution concentration, for example NMMO,<sup>24</sup> [Emim]Ac,<sup>14</sup> and so on. The strong network structure may cause this unusual phenomenon. In the concentrated cellulose solution, the molecular chains are more close to each other, resulting in the easy formation of intrachain and interchain junctions. The junctions cause molecular entanglement and interchain interaction, and finally form the physical network structure. As the number of the junction is relevant to system temperature and solution concentration, the formation and destruction of the network structure will also be dependent upon these two facts. As the solution concentration increases, the number of the junction increases and the network also becomes stronger. It may be difficult to disrupt such structure by heating. Thus, the value of  $\Delta E_\eta$  decreases with increasing solution concentration. To clearly understand the detailed mechanisms of such behavior presented in this cellulose solution, further investigation by using some more effective characterization techniques, such as NMR \*\*\*et al., is still needed.

### Elastic properties

The storage modulus  $G'$  and the loss modulus  $G''$  are usually determined as functions of the frequency at constant amplitude in the linear viscoelastic range. It can be seen from Figures 7 and 8 that dynamic moduli show almost the same trend at all temperatures and concentrations measured. The relations  $G' \sim \omega^2$  and  $G'' \sim \omega$  can not be observed for the cellulose solutions with the concentration of 10–25 wt %, which shows a typical behavior for entangled polymer solutions.<sup>25</sup> At low angular frequency, the WPC solution exhibits sol-like ( $G' < G''$ ) behavior. However, The  $G'$  increases more sharply



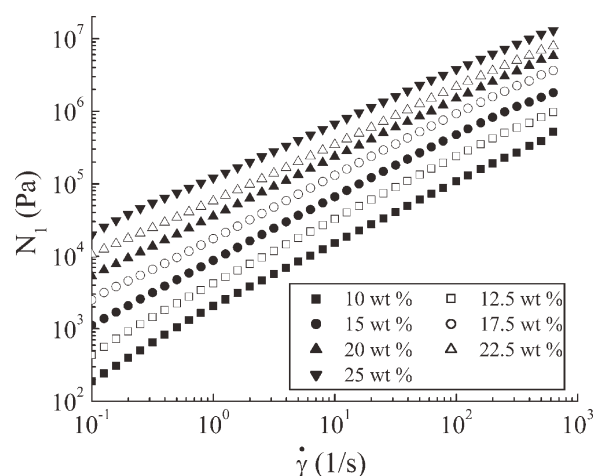
**Figure 7** Dependence of  $G'$  and  $G''$  on for  $\omega$  WPC/[Amim]Cl with different concentrations at  $100^\circ\text{C}$ . (To avoid overlapping, there are only four types of concentrations presented in the figure).



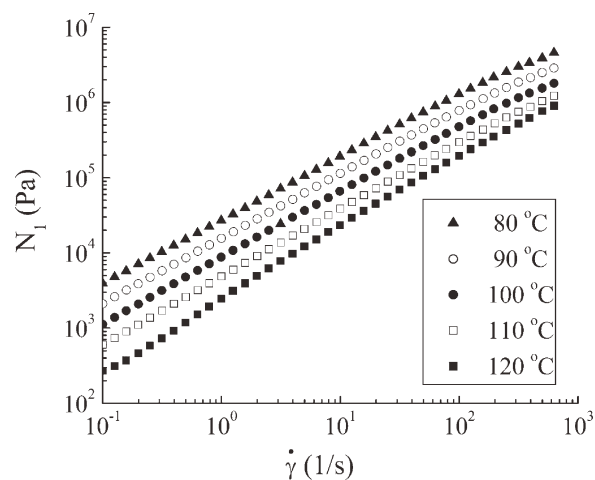
**Figure 8** Dependence of  $G'$  and  $G''$  on  $\omega$  for 15 wt % WPC/[Amim]Cl at different temperature. (The data are shifted along the vertical axis by 10a to avoid overlapping and the value of a is  $-1, 0.5, 0, 0.5, 1.$ )

with frequency than does the  $G''$  and finally the elastic components outweigh the viscous. So the solution exhibits gel-like ( $G' > G''$ ) behavior at high angular frequency.

The two domains of viscoelastic behavior are separated by the so-called crossover point, which is also a measure of the relaxation time (RT) of the solution. In the inset of Figures 7 and 8, the value of  $w$  shows where the crossover point is. It decreases with lowering temperature or increasing concentration. This can be explained by the observation that there exists strong network structure formed by the junctions on the cellulose chain in the concentrated cellulose/IL solution, and this makes the solution more like the elastic solid. Thus, a series of relaxations can be observed in the range of measured frequency. As the concentration increases or the temperature lowers, the number of the junction increases and the



**Figure 9** Dependence of  $N_1$  on  $\gamma$  for WPC/[Amim]Cl solution at different concentration at 100 °C.



**Figure 10** Dependence of  $N_1$  on  $\gamma$  for 15 wt % WPC/[Amim]Cl solution at different temperature.

network becomes much stronger. The elasticity of the solution enhanced and the relaxation capacity decreases. Especially, the RT of 25 wt % cellulose solution is too slow to be measured in the measured frequency. The result indicates that the relaxation of the cellulose chains in the solution becomes slower with lowering temperature or increasing concentration.

The first normal stress difference ( $N_1$ ) obtained is plotted against shear rate for the WPC/[Amim]Cl solution in Figures 9 and 10.  $N_1$  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. The  $N_1$  values increases with lowering solution temperature or increasing cellulose concentration. Owing to chain rigidity, the cellulose molecules are easily oriented, which leads to ordering of molecules like liquid crystalline polymers.<sup>26</sup> The higher cellulose concentration causes the stronger of the rigidity of cellulose molecules and also leads to higher ordering in the solutions due to the increase of intermolecular interaction. When the solution temperature increased, the intra-action and interaction of molecules will be weakened. The molecule chains become disordering, and so, the rigidity decreases. As a result, higher solution concentrations or lower solution temperature give higher  $N_1$  values.

## CONCLUSIONS

The rheological properties of the concentrated WPC/[Amim]Cl solutions were studied by using steady shear and dynamic viscoelastic measurements in a large range of concentrations (10–25 wt %). The 10 wt % cellulose solution is satisfied with Cox–Merz rule by comparison of shear viscosity and complex viscosity. All of the solutions showed a

shear thinning behavior and the Newtonian behavior was not observed over the whole shear rate. The zero shear viscosity was calculated by the simple Cross equation. These viscosity values were used for the analysis of viscosity-concentration and activation energy of WPC/[Amim]Cl solutions. The exponent in the viscosity versus concentration power law value is between 3.63 and 5.14 and increases with temperature increases. The Arrhenius values of the activation energy decrease with cellulose concentration increase and are opposite to the ones for cellulose solution in [Bmim]Cl and [Emim]Cl at relative low concentration (below 10 wt %). The dynamic rheological properties of the cellulose solutions showed a typical behavior for entangled polymer solutions. The first normal stress difference value increases with lowering temperature or increasing concentration.

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