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Flow behavior and linear viscoelasticity of cellulose 1-allyl-3-methylimidazolium formate solutions

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ABSTRACT

The rheological properties of α-cellulose 1-allyl-3-methylimidazolium formate solutions were investigated using shear viscosity and dynamic rheological measurements in a large range of concentrations (0.1–10 wt%) at 25 °C. In steady shear measurement, the overlap concentration (c^*) and the entanglement concentration (c_e) were determined to be 0.5 and 2.0 wt% respectively, and the exponents of the specific viscosity (η_{sp}) versus the concentration (c) were determined as 1.0, 2.0 and 4.7 for dilute, semidilute unentangled and entangled regimes respectively, which were in accordance with the scaling prediction for neutral polymer in θ solvent. The slopes of the relaxation time (τ) against the concentration for semidilute unentangled and entangled regimes were observed as 1.0 and 2.5 respectively. In dilute and semidilute unentangled regimes, failure of the Cox-Merz rule with steady shear viscosity larger than complex viscosity was observed; while the deviation from the Cox-Merz rule disappeared in semidilute entangled regime.

1. Introduction

Cellulose, an almost inexhaustible source of raw materials on the earth, is known to have many attractive properties such as biocompatibility, biodegradability, thermal and chemical stability (Hans, 1993). However, processing and derivatization of cellulose are difficult in general considering this natural polymer is neither meltable nor soluble in conventional solvents due to the numerous intermolecular and intramolecular hydrogen bonds in cellulose chains (Wang, Gurau, & Rogers, 2012). Over the past decades, only a limited number of solvent systems have been used to dissolve cellulose, but these solvents have some limitations including high cost, volatility, toxicity and instability in processing (Zhu et al., 2008). At present, most of them are limited in a laboratory scale, and only the viscose process and lyocell process have been industrialized for manufacturing regenerated cellulose fibers and films. However, both of them have some disadvantages associated with their application, such as complicated technology, generation of poisonous gas and difficulty in solvent recovery during cellulose processing. Therefore, as a key issue for overcoming the disadvantages of traditional processing methods, the development of new technology to dissolve cellulose is getting increasingly important.

In 2002, Swatloski et al. reported that the room temperature ionic liquids (IL) were non-derivatizing and green solvents for cellulose, which disclosed another environmentally benign solvent for cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002). Since then, the development of ILs has attracted considerable commercial interest because of their superior dissolving capacity, environmentally friendly properties, easy recycling, and good recoverability (Pinkert, Marsh, & Pang, 2010). To date, there has been a dramatic surge of interest from both scientific and industrial communities on the application of ILs in cellulose process, including the dissolution of cellulose in some new ILs (Heinze, Schwikal, & Barthel, 2005; Kosan, Michels, & Meister, 2008; Zhang, Wu, Zhang, & He, 2005), the preparation of some new functional cellulose materials by using ILs (Bentivoglio et al., 2006; Laus et al., 2005), and the development of cellulose composite materials from ILs (Rahatekar et al., 2009; Sun et al., 2008). Compared with traditional process, ILs provided a relatively simple and environmentally friendly way to produce cellulose regenerated fibers without chemical modification or derivation, but with fewer processing steps. Moreover, ILs were almost entirely recovered (>99.5%) after being used in the process and can be reused many times (Hermanutz, Gahr, Uerdingen, Meister, & Kosan, 2008). Nowadays, ILs, which may replace the traditional cellulose solvents, have been providing a new and

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versatile platform for the wide utilization of cellulose resources and preparation of novel cellulose-based materials with special properties.

It is well-known that rheological properties have an important influence on many processing operations involving the rapid change of product shape such as fiber spinning, film blowing and nonwoven melt processing. Therefore, comprehension of the rheological characterization of cellulose in ILs plays a significant role in successful production of regenerated cellulose fiber, film, nonwoven and a lot of other products. Recently, some rheological properties of cellulose have been reported in several imidazolium-based ILs, which have been used for preparing cellulose fibers (Kosan et al., 2008). Sammons et al. (Sammons, Collier, Rials, & Petrovan, 2008a; Sammons, Collier, Rials, & Petrovan, 2008b) measured the elongational properties of concentrated cellulose/1-butyl-3-methylimidazolium chloride ([Bmim]Cl) solutions, performed dynamic shear and modulus experiments for the solutions and used Carreau and Cross models to fit the experimental data. Chen et al. (2011) carried out a complete and comprehensive study of linear viscoelasticity and steady shear viscosity of cellulose/[Bmim]Cl solutions from 0.1 to 10 wt%, they found that the solutions were stable super-cooled liquids at 25 °C and [Bmim]Cl was in the θ regime for cellulose near room temperature. Furthermore, the rheological properties of cellulose/1-allyl-3-methylimidazolium chloride ([Amim]Cl) solution were investigated in detail from dilute to concentrated regime (Kuang, Zhao, Niu, Zhang, & Wang, 2008; Lu, Cheng, Song, & Liang, 2012; Song, Zhang, Niu, & Wang, 2010), and an extensive study of the steady state shear rheological properties of cellulose/1-ethyl-3-methylimidazolium acetate ([Emim]Ac) solutions was also performed at a variety of concentrations and temperatures, in which the first attempt to determine Mark-Kuhn-Houwink constants was made (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009). Besides those, Sescousse, Le, Ries, and Budtova (2010) made a comparison of the viscosity properties of cellulose dissolved in two different ILs, [Bmim]Cl and [Emim]Ac, and they reported that both solvents were of the same thermodynamic quality by analyzing a large range of polymer concentrations.

It has long been recognized that most currently used ILs are solid at room temperature, and the liquid ones usually have a high viscosity that limits their use as a solvent due to the low heat and mass transfer rate in their processing efficiency (Lv et al., 2012). Consequently, halogen-free ILs with low viscosity that can dissolve cellulose are strongly desirable. Recently, Fukaya, Sugimoto, and Ohno (2006) found a series of 1, 3-dialkylimidazolium formate ILs exhibiting superior solubility for cellulose, especially 1-allyl-3-methylimidazolium formate ([Amim]COOH) which had a significantly lower viscosity than previously reported halogenated imidazolium ILs. Compared with [Amim]Cl, [Amim]COOH could dissolve cellulose at lower temperatures and obtain cellulose/[Amim]COOH solutions with larger concentrations (Cao et al., 2009). However, so far, there are few reports about the rheological properties of these newly developed solutions. In this paper, cellulose/[Amim]COOH solutions with concentrations ranging from dilute regime to semidilute entangled regime were prepared, and the rheological behaviors of the solutions were investigated using a rheometer. The main purpose of this paper was to characterize the influences of cellulose concentration on the flow behavior and linear viscoelasticity of the cellulose/[Amim]COOH solutions. The concentration dependences of specific viscosity and plateau modulus were studied and contrasted with the results of scaling prediction. Moreover, some unique rheological properties including intrinsic viscosity, overlap concentration and entanglement concentration were also investigated in detail.

2. Experiments

2.1. Materials

The IL of [Amim]COOH was synthesized according to the procedure described in the literature (Fukaya et al., 2006). The water content measured with the Karl Fischer titration was about 0.2%. The density of [Amim]COOH at 25 °C was determined to be 1.05 g/mL by a pycnometer. The α-cellulose (C8002) was purchased from Sigma Aldrich. According to literature (Chen et al., 2011), the degree of polymerization (DP) is 850 and the molecular weight M is 1.2×10^5 g/mol for this sample.

2.2. Sample preparation

The cellulose powder was vacuum-dried at 60 °C for 24 h to remove any moisture before use. [Amim]COOH and cellulose were mixed in an internal mixer and the mixture was stirred at 60 °C for at least 2 h to ensure complete dissolution. Cellulose solutions with concentrations from 0.1 to 10 wt% were obtained, and a high-vacuum pump was used to reduce the pressure of the barrel to remove air bubbles in the solutions. Clear cellulose solutions were obtained, and then they were sealed and stored in the desiccators at room temperature to prevent moisture absorption.

2.3. Rheological measurements

Steady and dynamic rheological experiments were carried out on an AR-2000 stress-controlled rheometer (TA Instruments, U.S.A.) using three measurements: concentric cylinder, parallel-plate (40 mm diameter, 2° cone angle) geometry and parallel plates (20 mm diameter) for cellulose solution with different concentrations. Steady shear experiments were carried out with the shear rate ($\dot{\gamma}$) from 0.01 to 1000 s^{-1} at various temperatures. In the oscillatory shear experiments, the values of the strain amplitude were checked to ensure that all measurements were set as 5%, which was in the linear viscoelastic regime. The dynamic viscoelastic functions such as the shear storage modulus (G') and loss modulus (G'') as a function of angular frequency were measured. The sweep of the angular frequency (ω) was from 0.01 to 500 rad/s. Each test was repeated twice in order to reduce the testing error, and all the data were reduced to a reference temperature at 25 °C by means of the time-temperature superposition (TTS) principle (Ferry, 1980). To prevent absorption of moisture, a thin film of low-viscosity silicon oil was placed around the edges of the measuring cell, and this method was proved efficient for stable-in-time measurements.

3. Results and discussion

3.1. Flow curves of cellulose solutions

Fig. 1 presents the flow curves in terms of shear stress (σ)-shear rate ($\dot{\gamma}$) relationships for 0.1–10 wt% cellulose/[Amim]COOH solutions at 25 °C. The flow curves give straight lines at low polymer concentrations (0.1–0.5 wt%), suggesting Newtonian behavior of the cellulose solution in this concentration regime. The Ostwald-de-Waele equation as $\sigma = k\dot{\gamma}^m$ is used to test the deviation extent of the cellulose solution from the Newtonian liquids (Macosko, 1994), where k is the consistency index and m is the flow behavior index. The value of m for cellulose solutions ranging from 0.1 to 0.5 wt% was approximated to 1 (m = 0.95–0.99), indicating a dilute and Newtonian cellulose solution (Lue & Zhang, 2009). However, with further increase of concentration (>0.5 wt%), a shear-thinning behavior is observed at high shear rates and this shear-thinning tendency becomes more pronounced, indicating the deviation from

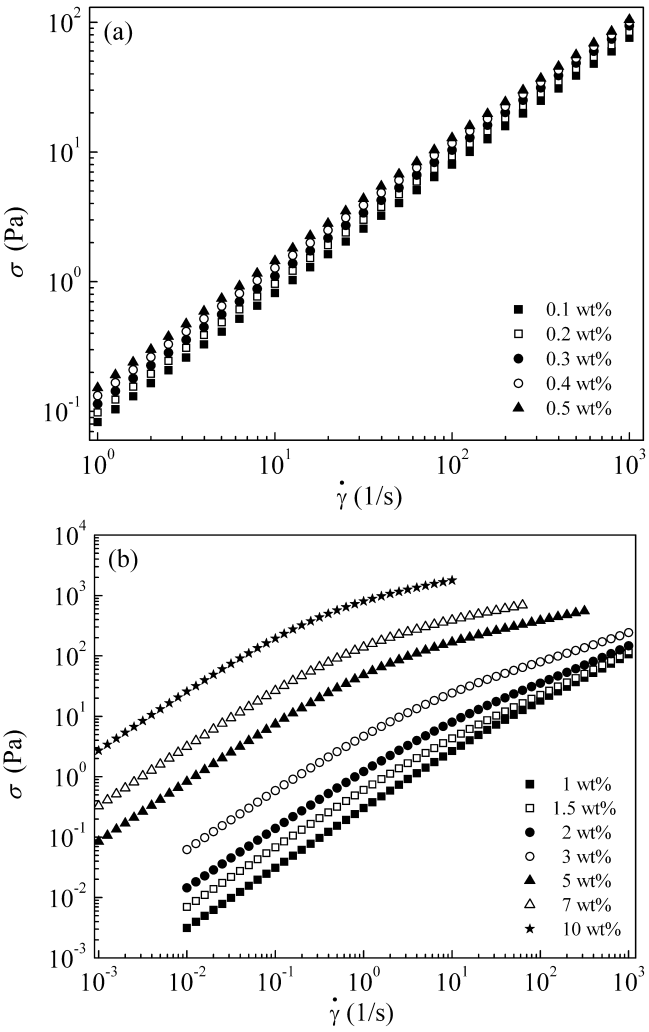

Fig. 1. Dependence of the shear stress on the shear rate for cellulose/[Amim]COOH solution at 25 °C: (a) 0.1 to 0.5 wt%, (b) 1 to 10 wt%.

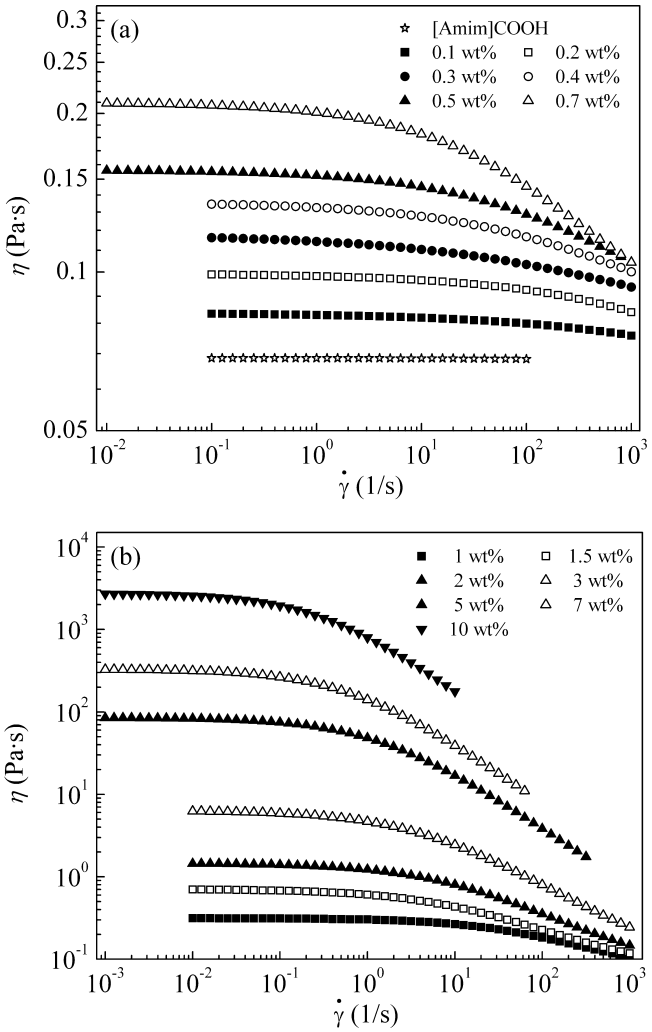

Fig. 2. Dependence of the apparent viscosity on the shear rate for cellulose/[Amim]COOH solution at 25 °C: (a) 0.1 to 0.7 wt%, (b) 1 to 10 wt%.

the Newtonian liquid. Thereby, the Ostwald-de-Waele equation fitting is not always suitable for the cellulose solutions.

Similar shear behavior can be seen in Fig. 2, which shows the dependence of the apparent viscosity (η) on the steady shear of α-cellulose in the concentration range from 0.1 to 10 wt% in [Amim]COOH at 25 °C. At very low concentrations, the apparent viscosity of the solutions keeps constant extending nearly all measurement range of shear rates, while slight shear-thinning behavior is observed at high shear rates. Along with the concentration increase, the apparent viscosity also increases prominently. Moreover, the critical shear rate corresponding to the transition from Newtonian to shear-thinning behavior moves to lower values with the increase of the concentration, which is similar to some other cellulose solutions (Blachot, Brunet, & Navard, 1998; Chen et al., 2011; Lue & Zhang, 2009) and some entangled polymer solutions (Chauvelon, Doublier, Buleon, Thibault, & Saulnier, 2003; Kapoor et al., 1998). This means the highly entanglement network or aggregate of cellulose molecules has formed in the solution. For the lower shear rate, the Newtonian plateau region, where the viscosity has a constant value, appears and the zero shear viscosity (η_0) can be determined by the model of Carreau (Bird, Curtiss, Armstrong, & Hassager, 1987):

$$\eta = \frac{\eta_0}{[1+(\tau\gamma)^2]^{(1-n)/2}} \quad (1)$$

where τ is the relaxation time and n is the exponent of the power law. Clearly, η_0 increases with the increase of the concentration. The zero shear viscosity of [Amim]COOH is determined to be 68.7 mPa s by the Carreau model. Although the value measured by viscometer was reported as 66.0 mPa s (Fukaya et al., 2006), it is not suitable to use viscometer for ILs because they are so hygroscopic that the measurements with the air contact are not reliable. Therefore, the value of 68.7 mPa s is used for the following analysis.

3.2. Viscosity-concentration dependence

In order to eliminate the effect of solvent viscosity on the cellulose/[Amim]COOH solutions, the specific viscosity $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$ (where η_s is the solvent viscosity) values are calculated at each concentration (c) and shown in the form of double logarithmic plot in Fig. 3. The cellulose solutions of different concentrations can be separated into three regimes: dilute, semidilute unentangled and semidilute entangled regime. At very low concentrations, the cellulose molecules are dispersed separately. However, as concentration increases, the macromolecules of cellulose chains start to overlap each other at the overlap concentration (c^*) which delimitates two different states of the polymer solution: dilute and semidilute unentangled solutions (Turner, Spear, Holbrey, & Rogers, 2004). As shown in Fig. 3, the c^* values is 0.5 wt% for cellulose/[Amim]COOH solution at 25 °C. With further increase of

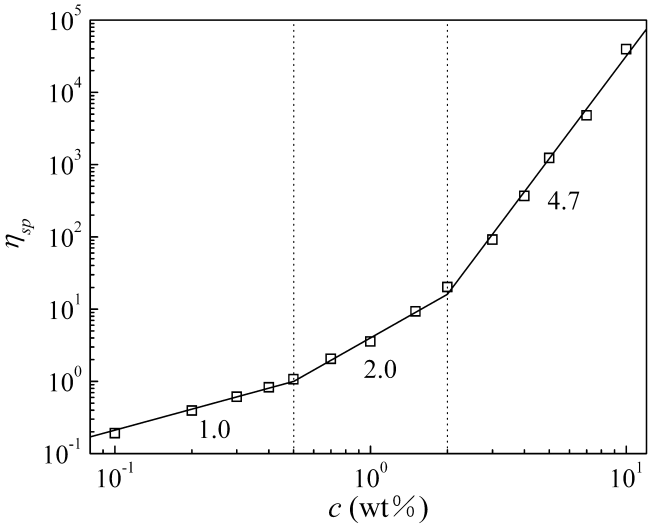

Fig. 3. Concentration dependence of specific viscosity (η_{sp}) for cellulose/[Amim]COOH solution at 25 °C.

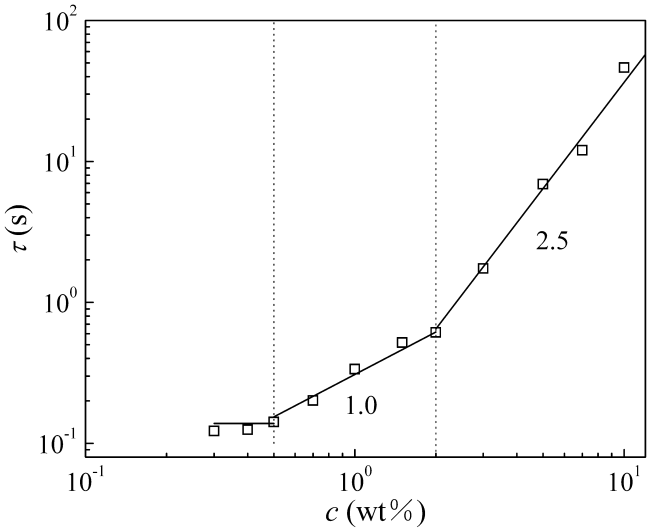

Fig. 4. Concentration dependence of relaxation time (τ) for cellulose/[Amim]COOH solution at 25 °C.

concentration, there is an abrupt change in power law exponent for c dependence of η_{sp} at the entanglement concentration (c_e), where the polymer chains topologically constrain each other and begin to entangle in the solution (Krause, Bellomo, & Colby, 2001). In other words, c_e marks the distinct onset of significant cellulose chain entanglements in [Amim]COOH, and the value of c_e is 2.0 wt%. These results (c^*, c_e and c dependence of η_{sp}) are identical to that of the α-cellulose/[Bmim]Cl solution, as reported in the previous paper (Chen et al., 2011). This means that the conformations of the α-cellulose molecules in those two solvents are almost equal in terms of rheological properties of the solutions. Similar values were reported for cellulose/NaOH/thiourea/H_2O (c^* = 0.1 wt%, c_e = 0.53 wt%) solutions (Lue & Zhang, 2011), cellulose/[Amim]Cl solutions (c^* = 0.5 wt%, c_e = 1.5 wt%) and cellulose/[Amim]Cl/DMSO solutions (c^* = 0.4 wt%, c_e = 1.3 wt%) (Kuang et al., 2008; Lv et al., 2012).

As shown in Fig. 3, the curve of η_{sp}, as a function of cellulose concentration, exhibits abrupt slope changes and can be represented approximately by three straight lines with slopes of 1.0, 2.0 and 4.7 at 25 °C. Recent work of Colby and co-workers indicated that the slopes of dilute, semidilute unentangled and semidilute entangled regime should be 1, 2 and 14/3 for neutral polymer in a θ solvent, and 1, 1.3 and 3.9 for neutral polymer in a good solvent (Colby & Rubinstein, 1990; Colby, 2010; Krause et al., 2001; Rubinstein & Colby, 2003). According to these scaling predictions, cellulose/[Amim]COOH solutions behave more like the neutral polymer in a θ solvent at 25 °C. In such a case, the cellulose chain adopts a conformation that is a random walk of correlation blobs with zero excluded volume at all solution concentrations (Colby, 2010). Similar conclusions were reported for α-cellulose/[Bmim]Cl solution (Chen et al., 2011). However, there were only two regimes, dilute and semidilute regimes, for microcrystalline cellulose (MC) dissolved in [Emim]Ac and [Bmim]Cl (Gericke et al., 2009; Sescousse et al., 2010), and for MC/[Emim]Ac solutions, the slopes of semidilute regime ranged from 4.4 to 2.8 for temperature from 0 to 100 °C correspondingly; while for MC/[Bmim]Cl solutions, the slopes varied from 4.3 to 3.4 for temperature from 70 to 120 °C correspondingly.

The influence of concentration on the relaxation time (τ) for cellulose/[Amim]COOH solution at 25 °C is shown in Fig. 4. It is found that τ increases with increasing cellulose concentration, indicating that the equilibrium time between the entanglement and disentanglement processes with shear rate becomes longer as the polymer concentration increases. The τ dependence of c can be represented approximately by two straight lines in the double logarithmic plot. The concentration at the point where the abrupt change of the slope of the straight line occurs is the entanglement concentration c_e. For semidilute unentangled cellulose solutions, the concentration dependence of the relaxation time exhibits scaling $\tau \sim c$, as expected for semidilute unentangled neutral polymer in a θ solvent. The slope is 2.5 ($\tau \sim c^{2.5}$) for semidilute entangled solution, which is larger than that of the neutral polymer in a θ solvent ($\tau \sim c^{2.3}$) (Colby, 2010). The larger exponent may attribute to the strong interaction and large entanglement between cellulose chains; hence the chain needs more time to diffuse the distance of order of its size (Rubinstein & Colby, 2003).

3.3. Intrinsic viscosity

The intrinsic viscosity [η] is a measure of the hydrodynamic volume occupied by a macromolecule, which is closely related to the size and conformation of the macromolecular chains in a given solvent (Lapasin & Pricl, 1995). The intrinsic viscosity is determined by measuring viscosities of very dilute cellulose solutions and using the Huggins and Kraemer graphical representations (Huggins, 1942; Kraemer, 1938; Gardas, Dagade, Coutinho, & Patil, 2008):

$$\frac{\eta_{sp}}{c} = [\eta] + K_h[\eta]^2 c \tag{2}$$

$$\frac{\ln\ \eta_r}{c} = [\eta] - K_k[\eta]^2 c, \tag{3}$$

where K_h is the Huggins coefficient, K_k is the Kraemer coefficient and $\eta_r = \eta_o/\eta_s$ is the relative viscosity. Concentrations are recalculated in mL/g, taking account of the density of [Amim]COOH at 25 °C. The c dependence of η_{sp}/c and $(\ln \eta_r)/c$ is shown in Fig. 5 for cellulose/[Amim]COOH solution. Both plots of η_{sp}/c and $(\ln \eta_r)/c$ versus c give two straight lines with an identical intercept at $c = 0$, and the intercept corresponds to the intrinsic viscosity [η]. As is shown, the extrapolated intercepts at $c = 0$ of both plots agree within experimental error, and the average of the two values is calculated to be 198 mL/g as the intrinsic viscosity for cellulose/[Amim]COOH solution at 25 °C.

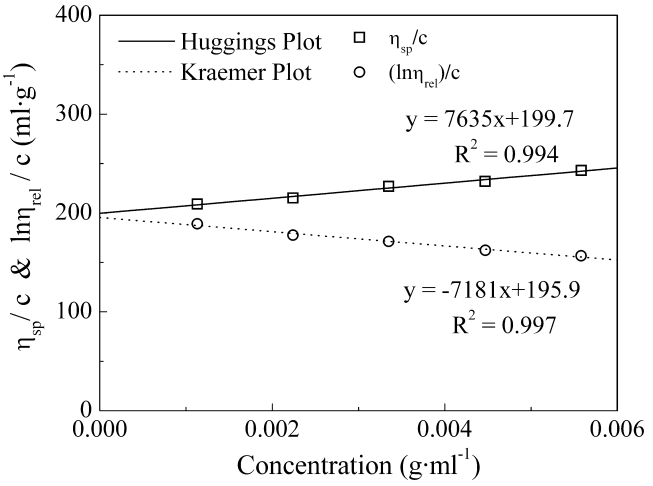

Fig. 5. Intrinsic viscosity: Kraemer and Huggins plots of cellulose/[Amim]COOH solution in dilute regime at 25 °C.

The relationship between intrinsic viscosity, coil size and molar mass is known as the Fox-Flory equation (Flory, 1953):

$$[\eta] = \Phi\frac{R^3}{M} \quad (4)$$

where $\Phi = 2.5 \times 10^{23}$ mol^{-1} is a universal constant for all polymer-solvent system, R is the root-mean-square end-to-end distance, and M is the molecular weight. The coil size of cellulose in [Amim]COOH solution can be estimated as $R = 46$ nm. If making the same estimation for cellulose dissolved in other solvents, comparable values are obtained: for example, R varies from 39 to 56 nm for cotton linters of M from 7.2×10^4 to 12.9×10^4 dissolved in 6 wt% NaOH/4 wt% urea aqueous solution with $[\eta]$ varying from 203 to 332 mL/g at 25 °C (Zhou, Zhang, & Cai, 2004), R equals 352 nm for tunicate cellulose (TC, $M = 4.13 \times 10^6$) dissolved in 8 wt% LiCl/1,3-Dimethyl-2-imidazolidinone (DMI) solution with $[\eta] = 2645$ mL/g, and R equals 217 nm for cotton linter cellulose (CC, $M = 1.7 \times 10^6$) dissolved in 8 wt% LiCl/N,N-dimethylacetamide (DMAc) solution with $[\eta] = 1504$ mL/g at 30 °C (Tamai, Tatsumi, & Matsumoto, 2004). However, the data and comparison have to be taken with care because the determination of M and $[\eta]$ strongly depends on the approach how it is measured and calculated, and more important, the test temperature is also a key factor which can directly affect the $[\eta]$ value. For example the end-to-end distance varies from 18 to 27 nm for microcrystalline cellulose (MC, DP 300) at temperatures from 0 to 100 °C (Gericke et al., 2009), which suggests the intrinsic viscosities decrease with temperature increase. Similar behavior has already been elucidated in detail in the literature (Sescousse et al., 2010). In a word, a convincible comparison can be made only for the same experimental method and measure approach.

3.4. Linear viscoelastic behaviors

The dependence of storage modulus G' and loss modulus G'' on the angular frequency has been investigated for cellulose/[Amim]COOH solutions at various concentration ranging from 0.1 to 10 wt%, and the master curves of the solutions selected from the dilute to entangled region are shown in Fig. 6. In order to avoid overlapping, the data are shifted along the vertical axis by 10^a. For the solutions with cellulose concentration below 2 wt%, G' is always smaller than G'' and no crossover is found within the test frequency range. At low frequencies, the relationships of $G' \sim \omega^2$ and $G'' \sim \omega$ can be observed for the cellulose solutions in dilute regime, which show a typical behavior of non-entangled polymer

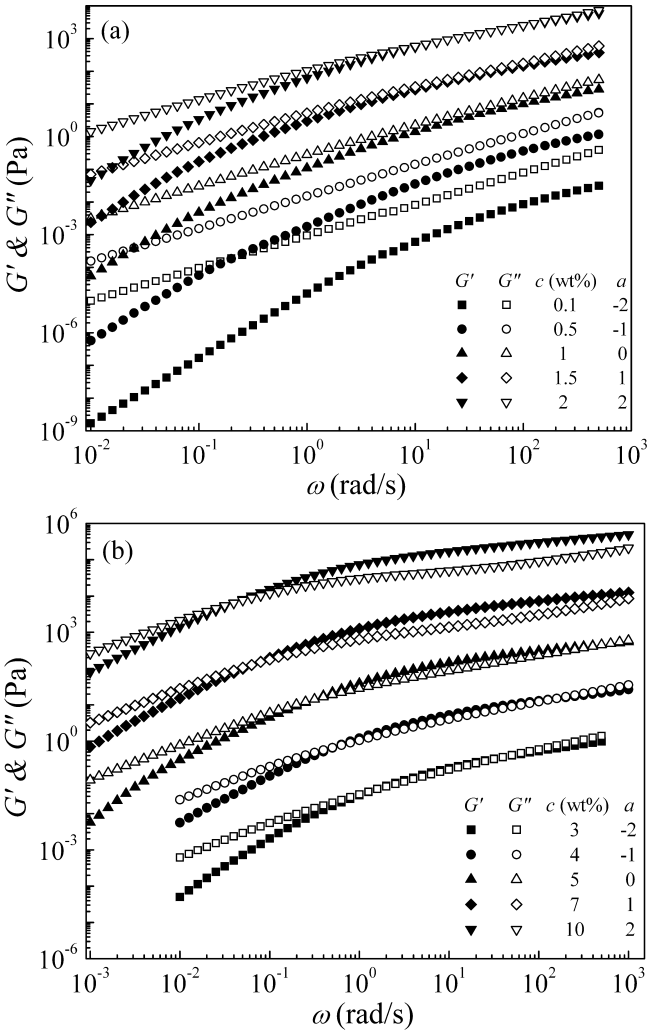

Fig. 6. Dependence of storage modulus and loss modulus on angular frequency for cellulose/[Amim]COOH solutions at different concentrations at 25 °C: (a) 0.1 to 2 wt%, (b) 3 to 10 wt%. The data are shifted along the vertical axis by 10^a to avoid overlapping.

solution (Ferry, 1980). In such a situation, deformation of the cellulose solution takes place so slowly that the majority of the energy is dissipated by viscous flow, leading to the liquid state. At the entanglement concentration ($c_e = 2$ wt%), Rouse-like behavior has been present apparently at high frequency ($10 < \omega < 500$) where both G' and G'' show the same slope of 1/2 (Rouse, 1953), suggesting that the cellulose chain can simply move its monomers by Rouse motion through the [Amim]COOH solvent without dragging any of the solvent molecules with it.

As the cellulose concentration increases from 3 to 5 wt%, sol-like ($G' < G''$) behavior occurs at low frequencies. Compared with G'', the faster increase with frequency of G' leads to the first crossover point and the solution exhibits gel-like ($G' > G''$) behavior in an intermediate frequency range. However, both G' and G'' increase with increasing frequency and show the second crossover, and then G' becomes smaller than G'' again at higher frequencies. The first cross-over corresponds to the reptation disengagement time while the second one is related to the relaxation time of a segment between entanglements (Rubinstein & Colby, 2003). Between the cross-over points, G' shows a plateau-like behavior as a result of the formation of a gel network with the junctions formed by self-associated cellulose chains (Cai & Zhang, 2006). The height of the plateau modules increases and its width expands with the raised

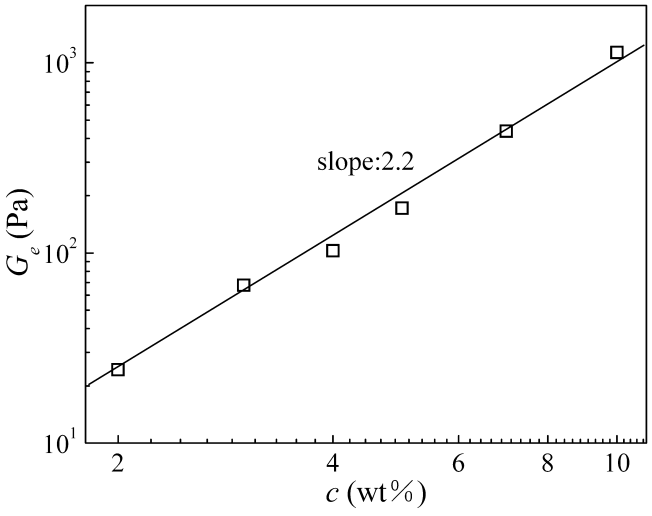

Fig. 7. Concentration dependence of plateau modulus (G_e) for cellulose/[Amim]COOH solution at 25 °C.

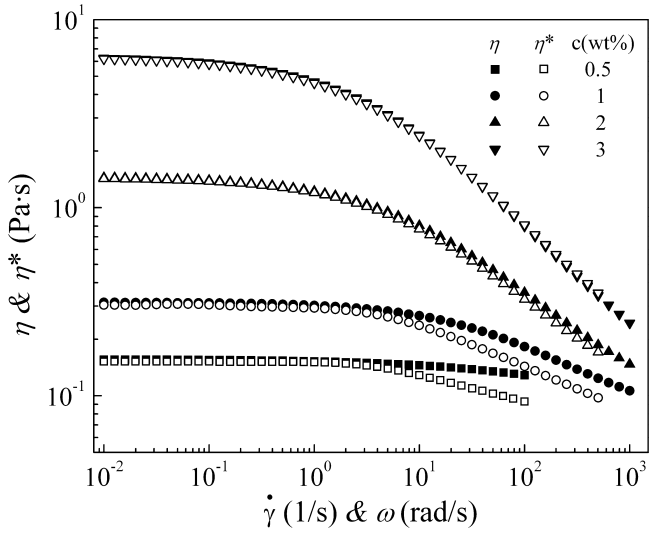

Fig. 8. Cox-Merz plot of cellulose in [Amim]COOH with various concentrations at 25 °C.

cellulose concentration, suggesting the ability of the entanglement networks is enhanced with the increase of polymer concentration. The first crossover evidently moves to lower values and the second crossover slightly increases with increasing cellulose concentration. This can be explained by the observation that molecular chains of cellulose are more close to each other, which reduces their relaxation capacity and results in easy entanglement. For higher concentration (7 and 10 wt%), the second cross-over of cellulose solution is too high to be measured in the measured frequency range.

For entangled polymer solution, the plateau modulus G_e is an important parameter, which can be estimated by several methods (Colby, 2010; Liu, He, Ruymbeke, Keunings, & Bailly, 2006). Due to the high polydispersity of cellulose sample (Chen et al., 2011), a modification of the MIN method has been used to estimate G_e (Lomellini, 1992):

$$G_e = G'(\omega)_{\tan\delta \to \min} \quad (5)$$

where δ is the phase angle. The concentration dependence of G_e of cellulose/[Amim]COOH solutions in the concentration range from 2 to 10 wt% at 25 °C is given in Fig. 7. In this figure, G_e dependence of c can be represented approximately by straight line in the double logarithmic plot. The slope of the straight line is 2.2 for entangled regimes. Based on the theories (De Gennes, 1979), the exponent β in the relationship of $G_e \sim c^{\beta}$ usually lies between 2.25 and 2.5 for flexible macromolecules. The exponent of 2.2 seems slightly lower than the prediction results. However, it is probably reasonable to regard this α-cellulose as flexible polymer because the exponent is apt to fluctuate slightly depending on the solvent quality. It is interesting to compare the concentration dependence of G_e of cellulose/[Amim]COOH solutions with the ones of other solvents. For example, the exponent was 2.14 for TC in LiCl/DMI solution (Tamai et al., 2004); while lower values of 1.9 and 2.1 were reported for dissolving cotton pulp (DCP)/[Amim]Cl/dimethylsulfoxide (DMSO) and DCP/[Bmim]Cl/DMSO solution respectively (Lv et al., 2012). It can be found that, due to different solvent quality, G_e of cellulose/[Amim]COOH solution has stronger concentration dependence than that of other solutions does. According to the predictions (Colby, 2010), the specific viscosity η_{sp} is defined as: $\eta_{sp} \sim G_e\tau$ for semidilute polymer solutions, with τ determined as the reciprocal of the shear rate where shear thinning starts. Thereby, $\eta_{sp} \sim c^{2.2} \cdot c^{2.5} \sim c^{4.7}$ for semidilute entangled cellulose/[Amim]COOH solution can be calculated. It is noted that these scaling exponents are generally in good agreement with values of concentration dependence of specific viscosities from steady shear experiment in Fig. 3. This fact suggests that the concentration dependence for these parameters is self-consistent.

3.5. Relationship between steady and dynamic shear viscosities

The Cox-Merz rule is applied to correlate dynamic and steady shear properties of the solutions, and the magnitude of complex viscosity η^* and apparent shear viscosity η are compared at equal values of shear rate and frequency. The rule provides a sensitive practical test to detect the presence of aggregates in the solutions. Fig. 8 presents the applicability of the Cox-Merz rule for the cellulose/[Amim]COOH solutions. At higher concentrations ($>c_e$), the complex viscosity η^* is equal to the steady shear viscosity η within the whole angular frequency or shear rate ranges. While at lower concentrations ($<c_e$), the values of η^* are lower than those of η at high shear rates, and they coincide only in the Newtonian regime. The deviation from the Cox-Merz rule was also found in other cellulose solutions (Chen et al., 2011; Lue & Zhang, 2009) and other polymer systems such as starch and xanthan (Chamberlain & Rao, 1999; Rochefort & Middleman, 1987). Kuang et al. (2008) reported that, during the steady measurement, high shear rates may disrupt the interaction between cellulose and ionic liquid molecules, and the cellulose molecules tend to entangle with each other, resulting in the high shear viscosity in dilute and semidilute unentangled regimes, and this may have also happened to cellulose/[Amim]COOH solutions. In semidilute entangled regime, cellulose chains fully associate and entangle with each other, resulting in the easy formation of intra- and intermolecular hydrogen bonds. As the concentration further increases, the solution system transform into a more uniform and homogeneous entanglement architecture. The steady shear rate can hardly influence the entanglements architecture due to the strong hydrogen bond intra- and interactions between cellulose chains (Song et al., 2010), and the departure from the Cox-Merz rule disappeared. To clearly understand the detailed mechanisms of such phenomenon presented in this cellulose solution, further investigation by using some more effective characterization techniques, such as light scattering, nuclear magnetic resonance, etc., is still needed.

4. Conclusion

In summary, the rheological behavior of α-cellulose/[Amim]COOH solution was investigated via shear flow and dynamic oscillatory measurements in a large range of concentrations at 25 °C. For all cellulose solutions, a Newtonian plateau was observed at low shear rates while a shear-thinning behavior was observed at high shear rates which fitted the Carreau model. On the basis of the concentration dependences of the specific viscosity, cellulose solutions were separated into dilute, semidilute unentangled and entangled regimes with slopes of 1.0, 2.0 and 4.7 respectively, revealing that cellulose/[Amim]COOH solution was in good agreement with the scaling prediction for neutral polymer in θ solvent. The concentration dependences of relaxation time exhibited scaling $\tau \sim c$ and $\tau \sim c^{2.5}$ for semidilute unentangled and entangled cellulose solutions, and G_e is expected by scaling as $G_e \sim c^{2.2}$ in the entangled regime. The relationship of $\eta_{sp} \sim G_e\tau \sim c^{2.2}.c^{2.5} \sim c^{4.7}$ indicated that the concentration dependences of these parameters were self-consistent for semidilute entangled cellulose/[Amim]COOH solution. The derivation of shear viscosity and complex viscosity from the Cox-Merz rule was observed in dilute and semidilute unentangled regimes; while the Cox-Merz rule was valid in the semidilute entangled regime.

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References

Bentivoglio, G., Röder, T., Fasching, M., Schottenberger, H., & Sixta, H. S. (2006). *"Ionic Liquids as solvents for Cellulose" presentation at the 45th Dornbirn man-made fiber congress* Austria.

Bird, R. B., Curtiss, C. F., Armstrong, R. C., & Hassager, O. (1987). *Dynamics of polymeric liquids, vol 1: Fluid mechanics* (2nd edn). New York: Wiley.

Blachot, J. F., Brunet, N., & Navard, P. (1998). Rheological behavior of cellulose/monohydrate of N-methylmorpholine-N-oxide solutions part 1: Liquid state. *Rheologica Acta*, *37*, 107–114.

Cai, J., & Zhang, L. N. (2006). Unique gelation behavior of cellulose in NaOH/urea aqueous solution. *Biomacromolecules*, *7*, 183–189.

Cao, Y., Wu, J., Zhang, J., Li, H. Q., Zhang, Y., & He, J. S. (2009). Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization. *Chemical Engineering Journal*, *147*, 13–21.

Chamberlain, E., & Rao, M. A. (1999). Rheological properties of acid converted waxy maize starches in water and 90% DMSO/10% water. *Carbohydrate Polymers*, *40*, 251–260.

Chauvelon, G., Doublier, J. L., Buleon, A., Thibault, J. F., & Saulnier, L. (2003). Rheological properties of sulfoacetate derivatives of cellulose. *Carbohydrate Research*, *338*, 751–759.

Chen, X., Zhang, Y. M., Wang, H. P., Wang, S. W., Liang, S. W., & Colby, R. H. (2011). Solution rheology of cellulose in 1-butyl-3-methyl imidazolium chloride. *Journal of Rheology*, *55*, 485–494.

Colby, R. H. (2010). Structure and linear viscoelasticity of flexible polymer solutions: Comparison of polyelectrolyte and neutral polymer solutions. *Rheologica Acta*, *49*, 425–442.

Colby, R. H., & Rubinstein, M. (1990). Two-parameter scaling for polymers in θ solvents. *Macromolecules*, *23*, 2753–2757.

De Gennes, P. G. (1979). *Scaling concepts in polymer physics*. Ithaca: Cornell University Press.

Ferry, J. D. (1980). *Viscoelastic properties of polymers* (3rd edn). New York: Wiley.

Flory, P. J. (1953). *Principles of polymer chemistry*. Ithaca, New York: Cornell University Press.

Fukaya, Y., Sugimoto, A., & Ohno, H. (2006). Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1, 3-dialkylimidazolium formates. *Biomacromolecules*, *7*, 3295–3297.

Gardas, R. L., Dagade, D. H., Coutinho, J. P., & Patil, K. J. (2008). Thermodynamic studies of ionic interactions in aqueous solutions of imidazolium-based ionic liquids [Emim][Br] and [Bmim][Cl]. *The Journal of Physical Chemistry B*, *112*, 3380–3389.

Gericke, M., Schlufter, K., Liebert, T., Heinze, T., & Budtova, T. (2009). Rheological properties of cellulose/ionic liquid solutions: From dilute to concentrated states. *Biomacromolecules*, *10*, 1188–1194.

Hans, A. K. (1993). *Cellulose: Structure, accessibility and reactivity*. London: Taylor & Francis.

Heinze, T., Schwikal, K., & Barthel, S. (2005). Ionic liquids as reaction medium in cellulose functionalization. *Macromolecular Bioscience*, *5*, 520–525.

Hermanutz, F., Gahr, F., Uerdingen, E., Meister, F., & Kosan, B. (2008). New developments in dissolving and processing of cellulose in ionic liquids. *Macromolecular Symposia*, *262*, 23–27.

Huggins, M. L. (1942). The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration. *Journal of The American Chemical Society*, *64*, 2716–2718.

Kapoor, V. P., Taravel, F. R., Joseleau, J. P., Milas, M., Chanzy, H., & Rinaudo, M. (1998). Cassia spectabilis DC seed galactomannan: Structural, crystallographical and rheological studies. *Carbohydrate Research*, *306*, 231–241.

Kosan, B., Michels, C., & Meister, F. (2008). Dissolution and forming of cellulose with ionic liquids. *Cellulose*, *15*, 59–66.

Kraemer, E. O. (1938). Molecular weights of celluloses and cellulose derivatives. *Industrial & Engineering Chemistry Research*, *30*, 1200–1203.

Krause, W. E., Bellomo, E. G., & Colby, R. H. (2001). Rheology of sodium hyaluronate under physiological conditions. *Biomacromolecules*, *2*, 65–69.

Kuang, Q. L., Zhao, J. C., Niu, Y. H., Zhang, J., & Wang, Z. G. (2008). Celluloses in an ionic liquid: The rheological properties of the solutions spanning the dilute and semidilute regimes. *The Journal of Physical Chemistry B*, *112*, 10234–10240.

Lapasin, R., & Pricl, S. (1995). *Rheology of industrial polysaccharides: Theory and applications*. Glasgow: Blackie Academic and Professional.

Laus, G., Bentivoglio, G., Schottenberger, H., Kahlenberg, V., Kopacka, H., Röder, T., et al. (2005). Ionic liquids: Current developments, potential and drawbacks for industrial applications. *Lenzinger Berichte*, *84*, 71–85.

Liu, C. Y., He, J. S., Ruymbeke, E. V., Keunings, R., & Bailly, C. (2006). Evaluation of different methods for the determination of the plateau modulus and the entanglement molecular weight. *Polymer*, *47*, 4461–4479.

Lomellini, P. (1992). Effect of chain length on the network modulus and entanglement. *Polymer*, *33*, 1255–1260.

Lu, F., Cheng, B. W., Song, J., & Liang, Y. (2012). Rheological characterization of concentrated cellulose solutions in 1-allyl-3-methylimidazolium chloride. *Journal of Applied Polymer Science*, *124*, 3419–3425.

Lue, A., & Zhang, L. N. (2009). Rheological behaviors in the regimes from dilute to concentrated in cellulose solutions dissolved at low temperature. *Macromolecular Bioscience*, *9*, 488–496.

Lv, Y., Wu, J., Zhang, J., Niu, Y., Liu, C., He, J., et al. (2012). Rheological properties of cellulose/ionic liquid/dimethylsulfoxide (DMSO) solutions. *Polymer*, *53*, 2524–2531.

Macosko, C. (1994). *Rheology, principles, measurements and applications*. New York: VCH.

Pinkert, A., Marsh, K. N., & Pang, S. H. (2010). Reflections on the solubility of cellulose. *Industrial & Engineering Chemistry Research*, *49*, 11121–11130.

Rahatekar, S. S., Rasheed, A., Jain, R., Zammarano, M., Koziol, K. K., Windle, A. H., et al. (2009). Solution spinning of cellulose carbon nanotube composites using room temperature ionic liquids. *Polymer*, *50*, 4577–4583.

Rochefort, W. E., & Middleman, S. (1987). Rheology of xanthan gum: Salt, temperature, and strain effects in oscillatory and steady shear experiments. *Journal of Rheology*, *31*, 337–369.

Rouse, P. E. (1953). A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *Journal of Chemical Physics*, *21*, 1272–1280.

Rubinstein, M., & Colby, R. H. (2003). *Polymer physics*. New York: Oxford University Press.

Sammons, R. J., Collier, J. R., Rials, T. G., & Petrovan, S. J. (2008a). Rheology of 1-butyl-3-methylimidazolium chloride cellulose solutions. I. Shear rheology. *Journal of Applied Polymer Science*, *110*, 1175–1181.

Sammons, R. J., Collier, J. R., Rials, T. G., & Petrovan, S. J. (2008b). Rheology of 1-butyl-3-methylimidazolium chloride cellulose solutions. III. Elongational rheology. *Journal of Applied Polymer Science*, *110*, 3203–3208.

Sescousse, R., Le, K. A., Ries, M. E., & Budtova, T. (2010). Viscosity of cellulose-imidazolium-based ionic liquid solutions. *The Journal of Physical Chemistry B*, *114*, 7222–7228.

Song, H. Z., Zhang, J., Niu, Y. H., & Wang, Z. G. (2010). Phase transition and rheological behaviors of concentrated cellulose/ionic liquid solutions. *Journal of Physical Chemistry B*, *114*, 6006–6013.

Sun, N., Swatloski, R. P., Maxim, M. L., Rahman, M., Harland, A. G., Haque, A., et al. (2008). Magnetite-embedded cellulose fibers prepared from ionic liquid. *Journal of Materials Chemistry*, *18*, 283–290.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of The American Chemical Society*, *124*, 4974–4975.

Tamai, N., Tatsumi, D., & Matsumoto, T. (2004). Rheological properties and molecular structure of tunicate cellulose in LiCl/1,3-dimethyl-2-imidazolidinone. *Biomacromolecules*, *5*, 422–432.

Turner, M. B., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2004). Production of bioactive cellulose films reconstituted from ionic liquids. *Biomacromolecules*, *5*, 1379–1384.

Wang, H., Gurau, G., & Rogers, R. D. (2012). Ionic liquid processing of cellulose. *Chemical Society Reviews*, *41*, 1519–1537.

Zhang, H., Wu, J., Zhang, J., & He, J. (2005). 1-allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose. *Macromolecules*, *38*, 8272–8277.

Zhou, J., Zhang, L. N., & Cai, J. (2004). Behavior of cellulose in NaOH/Urea aqueous solution characterized by light scattering and viscometry. *Journal of Physical Chemistry B*, *42*, 347–353.

Zhu, S. D., Wu, Y. X., Chen, Q. M., Yu, Z. N., Wang, C. W., Jin, S. W., et al. (2008). Dissolution of cellulose with ionic liquids and its application: A mini-review. *Green Chemistry*, *8*, 325–327.