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Rheological behaviors of cellulose in 1-ethyl-3-methylimidazolium chloride/dimethylsulfoxide

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ABSTRACT

Dynamic rheological behaviors of α-cellulose 1-ethyl-3-methylimidazolium chloride ([Emim]Cl)/dimethylsulfoxide (DMSO) solutions were investigated in a large range of cellulose concentrations (0.1–10 wt%) at 25 °C. The overlap concentration c^* and the entanglement concentration c_e for cellulose in [Emim]Cl/DMSO were determined to be 0.5 wt% and 2.0 wt% respectively, and the exponents of the specific viscosity η_{sp} versus cellulose concentration c were determined as 1.1, 2.1 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. Under the same cellulose concentration, the complex viscosity η^*, the reptation time τ_{rep} and the relaxation time of a segment between entanglements τ_e all decreased with increasing DMSO content in the solvent, while the number of entanglements of cellulose chains and the molar mass of an entanglement strand M_e both remained unchanged.

1. Introduction

Cellulose, as the most abundant natural polymer worldwide, can be used as a practically inexhaustible resource for the production of environmentally friendly, biodegradable, and biocompatible products (Hans, 1993). Generally, cellulose should be dissolved in some solvent in order to process this natural polymer into desired product. However, due to the numerous inter- and intramolecular hydrogen bonds in cellulose, only a limited number of solvent systems have been used to dissolve cellulose over the past decades (Wang, Gurau, & Rogers, 2012). For example, N-methylmorpholine-N-oxidemonohydrate (NMMO), ammonium fluorides/dimethylsulfoxide (DMSO), LiCl/N, N-dimethylacetamide (DMAc), LiCl/1,3-dimethyl-2-imidazolidinone (DMI), some molten salt hydrates, NaOH-water-urea (or thiourea) solutions and some aqueous solutions of metal complexes were reported to have acceptable dissolving capacity for cellulose (Cao et al., 2009; Heinze & Liebert, 2001). Unfortunately, these solvent systems possess several undesired properties such as toxicity, high cost, difficulty in solvent recovery, or instability in their practical applications (Zhu et al., 2008). Therefore, a continuous search for green and easy-to-handle direct solvents is still necessary for cellulose processing and derivatization.

In 2002, Swatloski et al. reported that the alkylimidazolium-based ionic liquids (ILs) were non-derivatizing and green solvents for cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002), and that their negligible vapor pressure, high polarity, and chemical as well as thermal stability made them be suitable candidates for processing and derivatization of cellulose under homogeneous conditions (Wasserscheid & Welton, 2007). Currently, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) are the most widely studied ILs in literature as cellulose dissolving media (Heinze, Schwikal, & Barthel, 2005; Swatloski et al., 2002; Zhang, Wu, Zhang, & He, 2005), and cellulose of high molecular weight at rather high concentrations around 10–20 wt% can be dissolved in the above mentioned ILs. Therefore, various cellulose products such as fibers, films and composites can be prepared from cellulose/IL solutions (Kosan, Michels, & Meister, 2008; Turner, Spear, Holbrey, & Rogers, 2004; Xu et al., 2008; Zhang et al., 2007). However, there are also some limitations accompanied by the advantages of ILs as solvents for cellulose, such as the slow rate of dissolution, the high viscosity of the solutions obtained, and not to mention the high costs of ILs (Pinkert, Marsh, Pang, & Staiger, 2009). Therefore, advances

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toward the improved process for the dissolution of cellulose are still necessary. Fortunately, the drawbacks of ILs can be minimized by adding co-solvents to cellulose/IL solutions (Fort, Swatloski, Moyna, Rogers, & Moyna, 2006; Fort et al., 2007). Some organic co-solvents, such as N,N-Dimethylformamide (DMF), DMSO and DMI, have been applied frequently for processing and derivatization of cellulose without apparent negative effect on the dissolving capability of ILs for cellulose within a certain concentration range of these co-solvents (Gericke, Liebert, & Heinze, 2009; Gericke, Liebert, El Seoud, & Heinze, 2011; Rinaldi, 2011).

As is well-known, rheological properties have an important influence on many processing operations involving the rapid change of product shape such as fiber spinning, film blowing and non-woven webs melt-blowing processing. Recently, the rheological properties of cellulose dissolved in [Amim]Cl, [Bmim]Cl and [Emim]Ac have been investigated carefully with the solution concentrations from dilute to concentrated regime (Chen et al., 2011; Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Kuang, Zhao, Niu, Zhang, & Wang, 2008; Lu, Cheng, Song, & Liang, 2012; Lu, Song, Cheng, Ji, & Wang, 2013; Sammons, Collier, Rials, & Petrovan, 2008a; Sammons, Collier, Rials, & Petrovan, 2008b; Song, Zhang, Niu, & Wang, 2010). Furthermore, an extensive study of the influences of co-solvent DMSO on ILs and cellulose/ILs solutions was performed at a variety of DMSO and cellulose concentrations (Lv et al., 2012), which suggested that the viscosities of the cellulose/ILs solutions decreased with the addition of DMSO due to the decrease of monomer friction coefficient in cellulose solutions caused by adding DMSO. Lv et al. (2012) also found that the IL/DMSO mixtures were more like θ solvents for cellulose at 25 °C, and the thermodynamic properties of IL/DMSO mixtures were similar with that of ILs for cellulose. Besides, Härdelin, Perzon, Hagström, Walkenström, and Gatenholm (2013) have proved that the empirical Cox–Merz rule can be applied to cellulose/[Emim]Ac/DMSO solutions. However, to the best of our knowledge, there are few reports about the dynamic rheology of cellulose directly dissolved in [Emim]Cl/DMSO mixed solvent.

The goal of this work was to perform a comprehensive investigation on the flow behavior and linear viscoelasticity of cellulose dissolved in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl)/DMSO solvents at 25 °C. In view of this, the cellulose was directly dissolved in [Emim]Cl/DMSO solvent, and cellulose solutions with concentration ranging from dilute regime to semidilute entangled regime were prepared. The scaling prediction and tube theory were used to discuss the influences of cellulose concentration and DMSO content in [Emim]/DMSO solvent on the viscosity and viscoelasticity of cellulose solutions. Moreover, some fundamental parameters of the entanglement network structure, such as the number of the entanglements and the molar mass of an entanglement strand, were calculated.

2. Experimental

2.1. Materials

[Emim]Cl (purity ≧98%) was purchased from Lanzhou Institute of Chemical Physics, and the water content was determined as about 0.5% by the Karl Fischer titration. The α-cellulose (C8002) and the DMSO (D4540) were purchased from Sigma Aldrich. According to literature (Chen et al., 2011), the degree of polymerization (DP) of α-cellulose was 850 and the molecular weight (M) was 1.20×10^5 g/mol for this sample. The polydispersity of molecular weight for this cellulose was unknown due to the technical difficulty in determining it. The water content of DMSO was about 0.1%.

2.2. Sample preparation

The cellulose powder was vacuum-dried at 60 °C for 24 h to remove moisture. The DMSO was first added into the heated [Emim]Cl in a dry glass vessel and then the mixture was stirred at 80 °C for at least 1 h to obtain the solvents with DMSO content varying from 10 wt% to 50 wt%. Afterwards, [Emim]Cl/DMSO and cellulose with different cellulose concentrations were mixed in an internal mixer and the mixture was stirred at 80 °C and 30 RPM rotors speed for at least 2 h to ensure complete dissolution. Thus, cellulose solutions with concentrations from 0.1 wt% to 10 wt% were obtained. To remove air bubbles in the solutions, a high-vacuum pump was used to reduce the pressure of the barrel. Clear cellulose solutions were obtained, and then they were sealed and stored in the desiccators at room temperature to prevent moisture absorption.

2.3. Measurements

For cellulose/[Emim]Cl/DMSO solution with different cellulose concentrations, the dynamic rheological experiments were carried out on an AR-2000 stress-controlled rheometer (TA Instruments, USA) using three measurements: concentric cylinder, cone-plate (40 mm diameter, 2° cone angle) geometry and parallel plates (20 mm diameter). 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'') were measured as a function of angular frequency (ω), which ranged from 0.1 to 500 rad/s, at various temperatures ranging from 0 to 100 °C. 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 smeared around the edges of the measuring cell, and this method was proved effective for stable-in-time measurements.

3. Results and discussion

3.1. Flow curves

Fig. 1 shows the flow curves of some cellulose/[Emim]Cl/DMSO solutions at 25 °C, from which different rheological behaviors depending on the cellulose concentration (c) and DMSO content (c_{DMSO}) can be observed. TTS principle was used to build the master plots and the horizontal shift a_T was calculated by the WLF equation (Ferry, 1980):

$$\log\ a_T = \frac{-c_1(T - T_r)}{c_2 + (T - T_r)} \quad (1)$$

where c_1 and c_2 denote experimental constants, T_r is a reference temperature (here, T_r = 298 K).

The dependence of a_T on the temperature for cellulose in [Emim]Cl/DMSO (70/30 w/w) is shown in Fig. 2.

The complex viscosity of [Emim]Cl/DMSO mixtures decreases with increasing DMSO content, which is similar with some other ionic liquid/organic solvent mixtures (Lv et al., 2012; Seddon, Stark, & Torres, 2000). Due to the decrease of solvent viscosity, the viscosities of cellulose/[Emim]Cl/DMSO solutions also present a decreasing trend, and some examples are given in Fig. 1. In addition, remarkable shear-thinning is observed for the 6 wt% cellulose solution, and the critical shear rate corresponding to the transition from Newtonian to shear-thinning behavior shifts toward higher values with the increase of c_{DMSO} in the solvent.

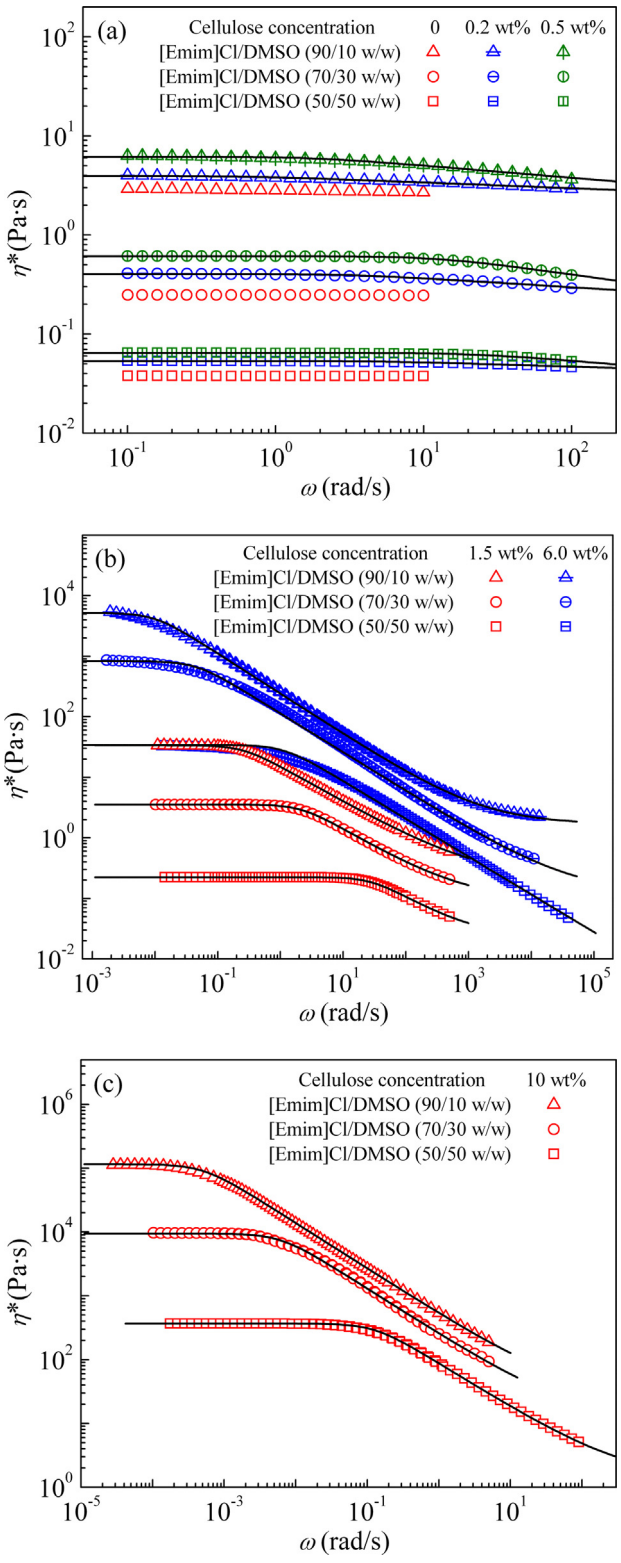

Fig. 1. Dependence of the complex viscosity on the frequency for cellulose/[Emim]Cl/DMSO solutions with different DMSO contents at 25 °C: (a) $c = 0$ to 0.5 wt%, (b) $c = 1.5$ and 6 wt%, (c) $c = 10$ wt%. *Solid lines* are the fitting results according to the Carreau model.

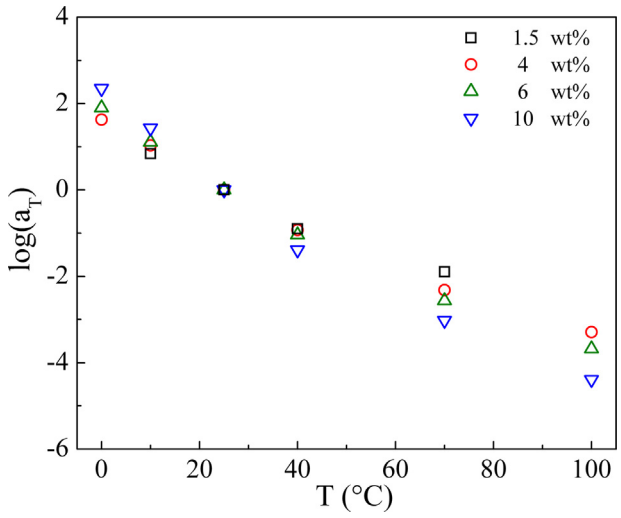

Fig. 2. Relationship between $\log(a_T)$ and the temperature (T) for cellulose dissolved in [Emim]Cl/DMSO (70/30, w/w).

For the low cellulose concentration, a Newtonian plateau is observed at low shear rates, while a slight shear-thinning appears at high shear rates. Meanwhile, the shape of flow curves changes with the cellulose concentration increasing, which indicates a transition from a Newtonian to a non-Newtonian behavior. To simulate the flow behavior of these solutions, the Carreau model (Bird, Curtiss, Armstrong, & Hassager, 1987) was chosen for its simplicity and its ability of describing both monotonic and non-monotonic flow curves.

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

where η^* is the complex viscosity at any given frequency ω, η_0 is the asymptotic values of viscosity at zero-shear rate, η_∞ is the infinite-shear rate viscosity, τ is the relaxation time and n is the exponent of the power law.

3.2. Viscosity-concentration dependence

In order to eliminate the effect of solvent viscosity on the cellulose/[Emim]Cl/DMSO solutions, the specific viscosity $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$ (where η_s is the solvent viscosity) values were calculated at each cellulose concentration c, and the results were shown in Fig. 3 in the form of double logarithmic plot.

The behavior of η_{sp} as a function of c for cellulose/[Emim]Cl/DMSO solutions is analyzed by power law fitting to the data. For all cellulose solutions, there are two abrupt changes in the c dependence of η_{sp}. The first slope change corresponds to the overlap concentration c^* ($c^* = 0.5$ wt%) that delimitates two different states of the polymer solution: dilute and semidilute unentangled solutions, while the second corresponds to the entanglement concentration c_e ($c_e = 2.0$ wt%) at which the microstructure transforms from a semidilute unentangled solution to a semidilute entangled network. Similar values were reported for cellulose/[Bmim]Cl solutions (DP = 220, $c^* = 0.5$ wt%, $c_e = 2$ wt%) solutions (Chen et al., 2011), cellulose/[Amim]Cl solutions (DP = 850, $c^* = 0.5$ wt%, $c_e = 1.5$ wt%) (Kuang et al., 2008) and cellulose/[Amim]Cl/DMSO solutions (DP = 650, $c^* = 0.4$ wt%, $c_e = 1.3$ wt%) (Lv et al., 2012).

Notably, the typical characteristics of the η_{sp} curves can be divided into three segments according to cellulose concentration. Below c^*, the cellulose chains exist as isolated coils that are far apart, and the linear fitting to the plot of η_{sp} as a function of c

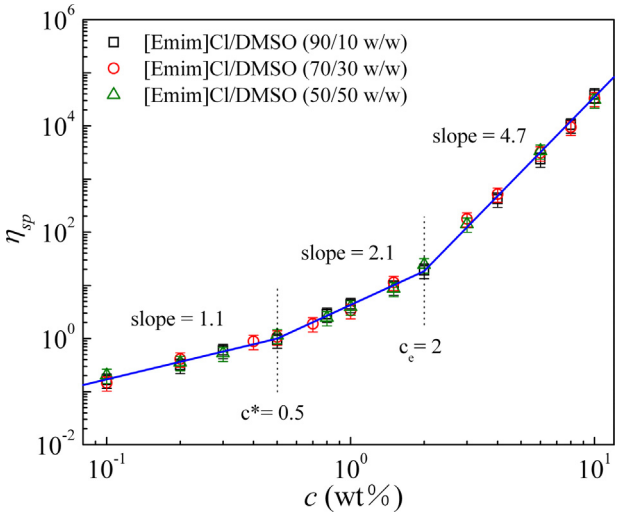

Fig. 3. Cellulose concentration dependence of specific viscosity (η_{sp}) for cellulose/[Emim]Cl/DMSO solutions with different DMSO contents at 25 °C.

yields $\eta_{sp} \sim c^{1.1}$; when $c^* < c < c_e$, the cellulose chains interpenetrate with each other, and the fitting yields $\eta_{sp} \sim c^{2.1}$; when $c > c_e$, the cellulose chains topologically constrain each other to result in entanglement in solution, and the fitting yields $\eta_{sp} \sim c^{4.7}$. It can be found that the plots of the specific viscosity against the cellulose concentration are closely superimposed, and irrespective of DMSO content c_{DMSO}, which means that the conformations of the α-cellulose molecules in those [Emim]Cl/DMSO solvents with different c_{DMSO} are almost identical in terms of rheological properties. Recent work of Colby and co-workers indicated that the slopes of dilute, semidilute unentangled and semidilute entangled regimes should be 1, 2 and 14/3 respectively for neutral polymer in a θ solvent, and 1, 1.3 and 3.9 respectively for neutral polymer in a good solvent (Colby, 2010; Krause, Bellomo, & Colby, 2001; Rubinstein & Colby, 2003). According to these scaling predictions, it is reasonable to regard the [Emim]Cl/DMSO solvent as θ solvent for cellulose at 25 °C, because the exponent is apt to fluctuate slightly depending on the interaction between polymer molecules and the chain character (Colby, 2010; Rubinstein & Colby, 2003). In such a case, the cellulose chains in [Emim]Cl/DMSO solvent adopt a conformation of random walk with zero excluded volume at all solution concentrations. Similar conclusions were also reported for α-cellulose/[Bmim]Cl solutions (Chen et al., 2011) and α-cellulose/[Emim]Ac solutions (Gericke, Schlufter, et al., 2009).

As it is well-known, the overlap concentration equals the concentration inside the pervaded volume of the coil at θ temperature, which can be calculated from chain dimensions (Colby & Rubinstein, 1990; Rubinstein & Colby, 2003) as follows:

$$c^* \approx \frac{Nb^3}{R^3} = \frac{1}{\sqrt{N}} \quad (3)$$

where R is root-mean-square of end-to-end distance, N is the number of Kuhn monomers and b is the Kuhn monomer length. Based on the above discussion, the overlap concentration c^* of cellulose/[Emim]Cl/DMSO solutions is determined as 0.5 wt%, and the values of N of cellulose in these solvents is calculated to be 40,000. An identical value of $N = 40{,}000$ was reported for cellulose ($M = 1.20 \times 10^5$) dissolved in [Emim]Ac (Lu et al., 2013), and a lower value of $N = 25{,}500$ was reported for tunicate cellulose (TC, $M = 4.13 \times 10^6$) dissolved in 8 wt% LiCl/1,3-Dimethyl-2-imidazolidinone (DMI) (Tamai, Tatsumi, & Matsumoto, 2004).

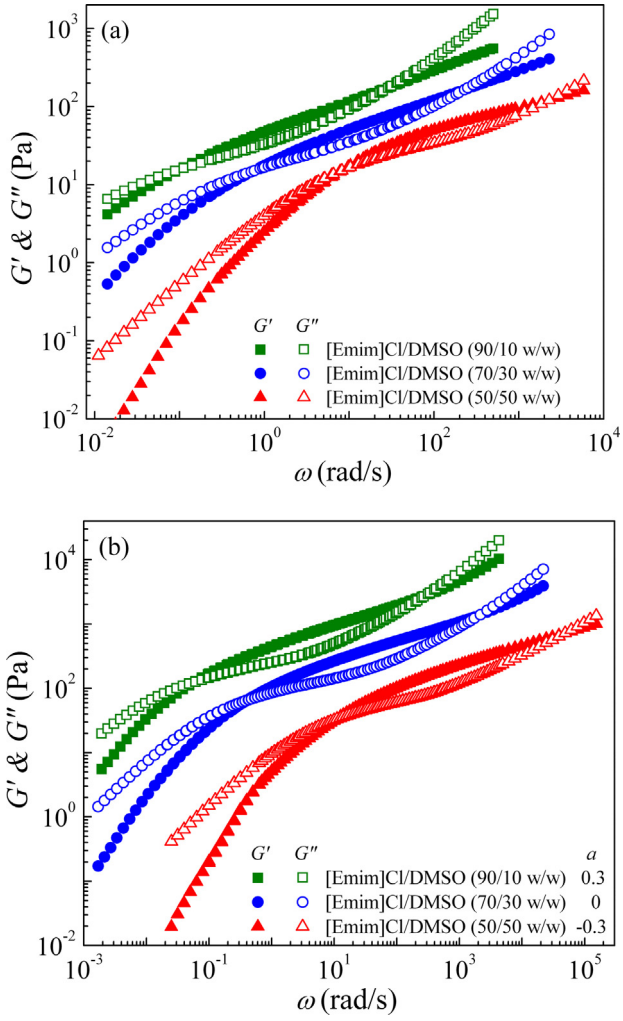

Fig. 4. Dependence of storage modulus and loss modulus on angular frequency for cellulose/[Emim]Cl/DMSO solutions with different DMSO contents at 25 °C: (a) $c = 4$ wt%, (b) $c = 6$ wt%. The data are shifted along the vertical axis by 10^a to avoid overlapping.

3.3. Linear viscoelastic properties

The dependence of storage modulus G' and loss modulus G'' on the angular frequency for 4 wt% and 6 wt% cellulose/[Emim]Cl/DMSO solutions with different DMSO contents is shown in Fig. 4. The time–temperature superposition (TTS) principle was used to construct the master curves of solutions at 25 °C, and the data were shifted along the vertical axis by 10^a in order to avoid overlapping. For 6 wt% cellulose solutions, the master curves have the rheological response for over 8 orders in frequency, and the corresponding data extend from the glassy modulus at high frequencies to the terminal response at low frequencies, thereby almost perfectly characterizing the linear viscoelastic response of these solutions. At very low frequencies, the relationships of $G' \sim \omega^{1.69}$ and $G'' \sim \omega^{0.93}$ for 4 wt% cellulose solutions and $G' \sim \omega^{1.79}$ and $G'' \sim \omega^{0.94}$ for 6 wt% cellulose solutions can be observed, respectively. The deviation from the theory predicted by Maxwell approach describing viscoelastic response of a fluid, $G' \sim \omega^2$ and $G'' \sim \omega$, is probably related to the polydispersity of cellulose.

The G' and G'' values decrease with the increase of DMSO content of the solvent in Fig. 4, and there are two crossover points in each oscillatory share curve, which show the typical behaviors of entangled polymer solutions. The first crossover point at low

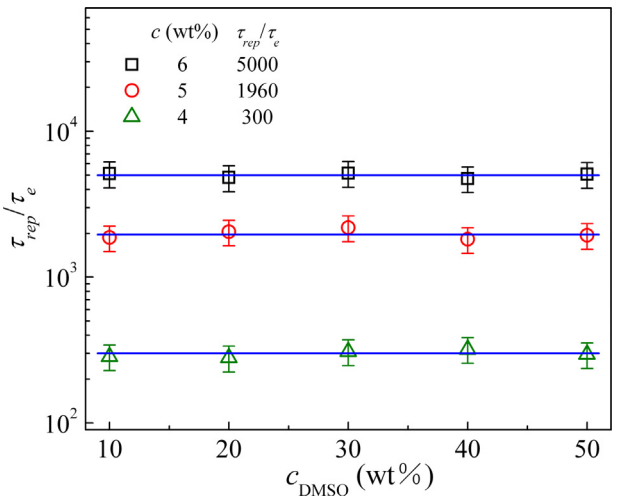

Fig. 5. Effects of DMSO content in [Emim]Cl/DMSO on τ_{rep}/τ_e of cellulose/[Emim]Cl/DMSO solutions at 25 °C.

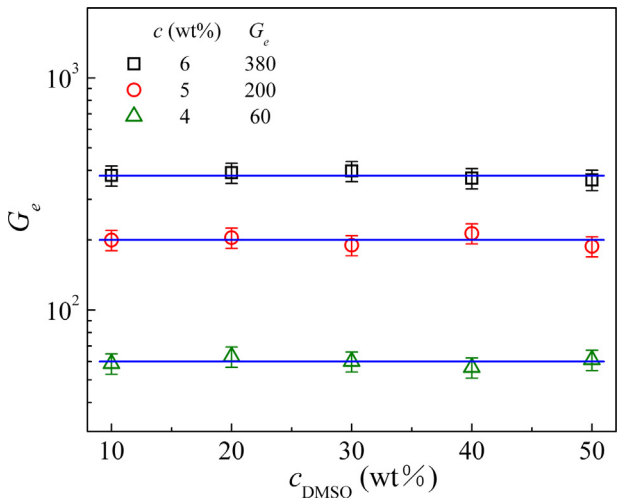

Fig. 6. Effects of DMSO content in [Emim]Cl/DMSO on plateau modulus (G_e) of cellulose/[Emim]Cl/DMSO solutions at 25 °C.

frequencies corresponds to the reptation time (τ_{rep}), while the second corresponds to the relaxation time of a segment between entanglements (τ_e) (Rubinstein & Colby, 2003). With the increase of DMSO content, the frequencies of the two crossover points, ω_{rep} and ω_e, both increase, indicating τ_{rep} and τ_e decrease with increasing DMSO content. As a low viscosity component in solvent, the increase of DMSO content can reduce the monomer friction coefficient of the solvent (Lv et al., 2012), which results in the decrease of frictional resistance of cellulose chains. Therefore, the cellulose chain needs less time to move through a distance of the order of its own size, and so does the entanglement strand of the chain.

It is noted that G' shows a plateau-like behavior between ω_{rep} and ω_e due to the formation of an entangled network formed by self-associated cellulose chains. Based on the tube theory proposed by De Gennes (1979) and Doi and Edwards (1986), the topological interactions between cellulose molecules are important in entangled cellulose solutions at θ temperature, and the cellulose motion can be described by the reptation model with the chain relaxation time given by the reptation time:

$$\tau_{rep} \approx \tau_e \left(\frac{N}{N_e}\right)^3 \quad (4)$$

where N is the number of Kuhn monomers and N_e is the number of Kuhn monomers in an entanglement strand. Obviously, the ratio of τ_{rep} to τ_e is the cube of the number of the entanglements along the chain (Rubinstein & Colby, 2003).

The τ_{rep}/τ_e are plotted as a function of the DMSO content (c_{DMSO}) in the solvent for cellulose/[Emim]Cl/DMSO solutions at 25 °C in Fig. 5. It can be found that τ_{rep}/τ_e dependence of c_{DMSO} can be approximately represented by a straight line for each cellulose solution, and the slopes of the straight lines are all estimated as 0, which indicates the τ_{rep}/τ_e is independent of c_{DMSO}. However, the τ_{rep}/τ_e presents an increasing trend with the increase of cellulose concentration. Based on the discussion in Section 3.2, a cellulose chain in cellulose/[Emim]Cl/DMSO solutions has N = 40,000 Kuhn monomers. Therefore, for the 4 wt% cellulose solutions, an entanglement strand of cellulose contains N_e = 6000 Kuhn monomers, and the whole chain has N/N_e = 6 entanglements. If making the same calculation for other cellulose solutions, comparable values of N_e = 3200, N/N_e = 12 at 5 wt% and N_e = 2340, N/N_e = 17 at 6 wt% can be obtained respectively.

Fig. 6 shows the plateau modulus G_e for 4 wt% and 6 wt% cellulose/[Emim]Cl/DMSO solutions. Due to the high polydispersity of cellulose sample, a modification of the MIN method is used to estimate G_e (Liu, He, Ruymbeke, Keunings, & Bailly, 2006; Lomellini, 1992):

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

where δ is the phase angle. It can be seen from Fig. 6 that the G_e value increases with increasing cellulose concentration and shows significant independence of the DMSO content in the solvent, which is similar to the τ_{rep}/τ_e value.

According to the reptation model (De Gennes, 1979; Doi & Edwards, 1986), G_e and τ_{rep}/τ_e are fundamental parameters of the entanglement network, which relate to the molar mass of an entanglement strand (M_e). The M_e can be estimated as 18,000, 9600 and 6000 for the 4 wt%, 5 wt% and 6 wt% cellulose solutions respectively according to $M_e = M/N \cdot N_e$, suggesting the enhancement of entanglement network of the solutions with increasing cellulose concentration. Thus, the decrease of M_e can be attributed to the increase of cellulose concentration, while the ability for cellulose chains to form entanglement in [Emim]Cl/DMSO solvent remains unchanged with varying c_{DMSO}. In θ solvents, the entanglements between polymer chains are controlled by binary intermolecular contacts, and the number density of binary intermolecular contacts is proportional to the square of polymer concentration (Rubinstein & Colby, 2003). Therefore, under the same cellulose concentration, no significant change of the entanglement network of cellulose solutions occurs with varying c_{DMSO} of the solvent. To clearly understand the detailed mechanisms of such behaviors in these cellulose solutions, further investigation should be carried out by virtue of some more effective characterization techniques.

4. Conclusions

Cellulose was dissolved in the [Emim]Cl/DMSO solvent with DMSO content ranging from 10 to 50 wt%, and the rheological behaviors of cellulose/[Emim]Cl/DMSO solutions in a large cellulose concentration (0.1–10 wt%) were investigated through the dynamic oscillatory measurements at 25 °C. At very low cellulose concentration, the cellulose solution behaved as Newtonian fluids, while with the increase of cellulose concentration, the complex viscosity increased significantly and the critical shear rate corresponding to the transition from Newtonian to shear-thinning behavior shifted to lower values. At the same time, the number of entanglements of cellulose chains N/N_e increased, while the molar mass of an entanglement strand M_e decreased. For cellulose solutions, the overlap concentration and the entanglement

concentration were determined to be 0.5 wt% and 2.0 wt% respectively, and the solutions could be classified into three regimes as dilute, semidilute unentangled and semidilute entangled regimes with slopes of 1.1, 2.1 and 4.7 respectively, which indicated these [Emim]Cl/DMSO solvents were more like θ solvents for cellulose at 25 °C.

Under the same cellulose concentration, the complex viscosity of the solutions decreased with the decrease of [Emim]Cl/DMSO viscosity caused by increasing DMSO content. With the increase of c_{DMSO} in the solvent, the reptation time and the relaxation time of a segment between entanglements both decreased, while the plateau modulus G_e and τ_{rep}/τ_e values remained unchanged, which indicated no significant change of the entanglement network structure (N/N_e and M_e) occurred with varying c_{DMSO} in the solvent.

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