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ARTICLE

Effect of dimethylsulfoxide on the viscoelastic properties and sol-gel transition of cellulose/ionic liquid solutions

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Viscoelastic properties of cellulose solutions with 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and dimthylsulfoxide (DMSO) as solvents were studied by rheological experiments. From the results of rheological behaviors, the non-monotonous decrease of viscosity with DMSO content was observed. When the content of DMSO in [BMIM]Cl/DMSO is lower than 5 wt% in [BMIM]Cl/DMSO, the viscosity and gelation temperature (T_{gel}) decreased with the increase of DMSO. However, the values of viscosity and T_{gel} showed nonlinear change with the further increase of DMSO. It could be understood that DMSO acted as the diluent when the content of DMSO is below 5 wt%. The local micro-aggregation or micro-phase separation of cellulose could be happened when the content of DMSO further increased due to the weak action between cellulose and DMSO.

B Headings should always be subordinate to A headingse.g. Synthetic procedures, Materialsand methods, Crystallography.

C headings should always be subordinate to B headings e.g. General procedure for synthesis of compound X. The main paragraph text follows directly on here.

1. Introduction

In the beginning of this century, ionic liquids (ILs) were found to be able to dissolve cellulose [1]. Since then, a series of ILs which can dissolve cellulose have been reported [2, 3]. The characters of ILs, such as low vapor pressure and strong dissolution ability, are advantages for cellulose processing in engineering [4-6]. However, the viscosity of concentrated cellulose/IL solution is relatively high which makes the common cellulose processing engineering system overload [7]. To reduce the viscosity of cellulose/IL solutions, dimthylsulfoxide (DMSO) was used as the cosolvent in this system [8] (The viscosity of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) is 0.14 Pa.s at 80 °C [9] and the viscosity of DMSO is 0.0002 Pa.s at 20 °C [10]). The solubility of cellulose in IL has been investigated with the addition of cosolvent. Rinaldi [11] found that cellulose dissolved instantaneously in 1,3-dimethyl-2-imidazolidinone (DMI) containing just a small molar fraction of [BMIM]Cl. Xu et al.[12] also reported that cellulose could be dissolved in 1-butyl-3-methylimidazolium acetate ([BMIM]Ac)/DMSO, [BMIM]Ac/ Dimethylformamide (DMF), and [BMIM]Ac/Dimethylacetamide (DMAc) at ambient temperature with high solubility. These investigations show that cosolvents can accelerate the dissolution of cellulose in IL dramatically. Meanwhile, the viscosity of the cellulose/IL solutions was also reduced. Lv et al.[13] studied the rheology of cellulose/1-allyl-3-methylimidazolium chloride ([AMIM]Cl)/DMSO solutions at room temperature. When the concentration of cellulose in both [AMIM]Cl/DMSO and [BMIM]Cl/DMSO is 1.5 wt%, the viscosity of the solutions

decreased with the addition of DMSO from the weight percent of 10 to 50. Wang et al.[14] studied the rheological behavior of cellulose in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl)/DMSO with the content of DMSO from 10 wt% to 50 wt%. It is also found that the viscosity of the solution decreased with the addition of DMSO. However, Hardelin et al.[15] analyzed the viscosity of cellulose/1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) solution with the addition of DMSO, DMF and DMAc with the content of cosolvent from 10 wt% to 90 wt%. The viscosity of cellulose in [EMIM]Ac/DMSO (90/10 w/w) is higher than that in [EMIM]Ac. It seems that the results are not consistent for the different IL systems.

Although most investigations concluded that some cosolvent such as DMSO, DMF and DMAc could accelerate the dissolution of cellulose in IL, Xu et al.[12] reported that the solubility of cellulose in [BMIM]Ac/DMSO increased with the content of DMSO in the low molar range and then decreased with further increase of DMSO.

Compared with the ILs used to dissolve cellulose [7], the viscosity of [BMIM]Cl could be reduced remarkably with the addition of DMSO [13]. In order to discover the effect of small amount of DMSO on the rheological behaviors of cellulose/[BMIM]Cl solutions, the viscoelastic properties and sol-gel transition of cellulose/[BMIM]Cl/DMSO solutions with the content of DMSO in DMSO/[BMIM]Cl from 0 to 12 wt% were studied. The effect of DMSO on the rheological parameters of cellulose solution such as viscosity, dynamic modulus and loss tangent (tanδ) were analyzed. The sol-gel transition of cellulose/[BMIM]Cl/DMSO was discussed with Winter and Chambon's theory. It is interestingly found that the viscosity and sol-gel transition temperature did not follow the monotonous decrease mode in the range from 0 to 12 wt% of DMSO in DMSO/[BMIM]Cl.

2. Experimental Section

2.1. Materials

The cellulose pulp (DP (degree of polymerization) =500) was supplied by Shandong Silver Eagle Chemical Fiber Co. Ltd, China. DMSO (HPLC-grade) was purchased from Shanghai Chemical Reagents Company. [BMIM]Cl was prepared by the equimolar amounts of 1-methylimidazole and 1-chlorobutane at the temperature of 70 °C for 72 h. The prepared [BMIM]Cl was washed by ethyl acetate to remove the residual impurities. Then, the remaining ethyl acetate in the [BMIM]Cl was removed by heating at 80 °C under vacuum. [16].

2.2. Solution preparation

The cellulose was dried under vacuum at 80 °C to constant weight. The 5 wt% cellulose solutions were prepared by stirring at 80 °C. The content of DMSO in [BMIM]Cl/DMSO varied from 0-12 wt %.

2.3. Rheological measurements

The rheology of all solutions was measured on a rotational rheometer (Physica MCR 301, Anton Paar). The 25 mm diameter concentric parallel plate geometry was utilized. The chosen gap was 1 mm for all solutions. Steady shear experiments were examined at a shear-rate range from 0.1-100 s^{-1} at the temperature of 50, 60, 70 and 80 °C. For oscillatory experiments, the linear viscoelastic region was firstly determined by performing a dynamic strain sweep for each solution with a fixed angular frequency of 6.3 rad/s. It was found that all the solutions demonstrated certain linear viscoelastic region of 0.1~80 %. Frequency sweep measurements were tested from the range of 628 rad/s to 0.1 rad/s at the strain of 10%. Temperature sweep measurements were tested from 0~60 °C with the heating rate of 2 °C /min at each fixed frequency (3.14, 6.28 and 12.6 rad/s).

3. Results and Discussion

3.1. Effect of DMSO content on the steady shear rheological behaviors of cellulose/[BMIM]Cl/DMSO solutions

The steady shear profiles of cellulose/[BMIM]Cl/DMSO are shown in Fig.1. The solutions exhibit obvious shear thinning behavior within the DMSO content of 0-12wt %. The onset of shear thinning occurred at similar shear rate and the viscosity of the solution decreased dramatically when DMSO was added in the system. From Fig.1, it is found that the apparent viscosity of the cellulose/[BMIM]Cl/DMSO did not decrease monotonously with the increase of DMSO content.
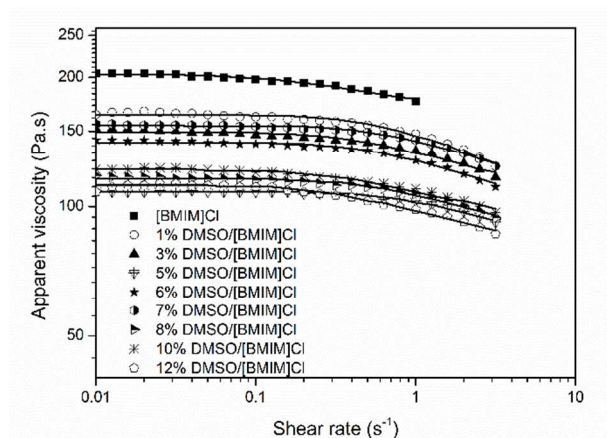
**Fig.1** Steady shear rheological curves of the cellulose/[BMIM]Cl/DMSO solution at 70 °C.

In order to give out a clearer relation between the viscosity and the DMSO content, the apparent viscosities of cellulose/[BMIM]Cl/DMSO and shear rates were fitted with three-parameter Carreau model [17], shown in Eq. (1).

$$\eta(\dot{\gamma}) = \eta_0 (1 + (\tau \cdot \dot{\gamma})^2)^{(p-1)/2} \quad (1)$$

where η_0 is the zero shear-rate viscosity, τ is the relaxation time, and p is the power law exponent.

The variation of shear viscosity of cellulose/[BMIM]Cl/DMSO with the different content of DMSO is shown in Fig.2. The zero shear-rate viscosity (η_0) (shown in Fig.2 (a)) of cellulose/[BMIM]Cl/DMSO decreased with the increase of DMSO within the 5 wt% of DMSO and then showed nonlinear change with the further increase of DMSO. Such phenomenon could be understood from the

interaction between cellulose and ionic liquid, DMSO and ionic liquid, cellulose and DMSO. It was reported that the interaction of cellulose and [BMIM]Cl is in the form of hydrogen bond from Cl⁻ and –OH [18]. DMSO can partially disrupt the ionic association between cation and anion of ionic liquid, enhance its ability of cellulose dissolution and decrease the viscosity of the solution [19, 20]. When the content of DMSO is low, DMSO dramatically decreases the viscosity of ionic liquid by solvation of the cation and anion [19] and act as the diluent in the cellulose solution [20], which does not significantly affect the interaction between ionic liquid and cellulose [20]. However, when the content of DMSO further increases, the micro-aggregations or micro-phase separations in local regions could be imagined due to the possible mico-phase separation of [BMIM]Cl and DMSO [15] or the weak interaction between cellulose and DMSO [22].
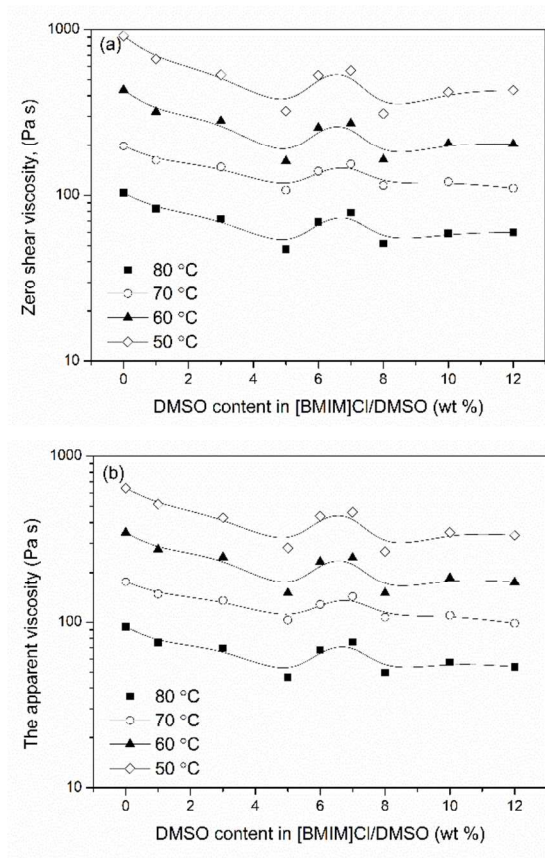

Fig.2 Relation between viscosity and DMSO content of cellulose/[BMIM]Cl/DMSO solutions (a) zero shear-rate viscosity, (b) apparent viscosity of at the shear rate of 1 s⁻¹ (solid lines are provided to guided eye).

The apparent viscosity of the solutions at shear rate of 1 s⁻ which is in the shear thinning region is shown in Fig. 2 (b). The same trend as that of zero shear-rate viscosity was observed, which suggested that micro-morphology of these solutions could not be changed easily under the shear rate in the experimental range.

3.2. Effect of DMSO content on the dynamic oscillation behaviors of cellulose/[BMIM]Cl/DMSO solutions
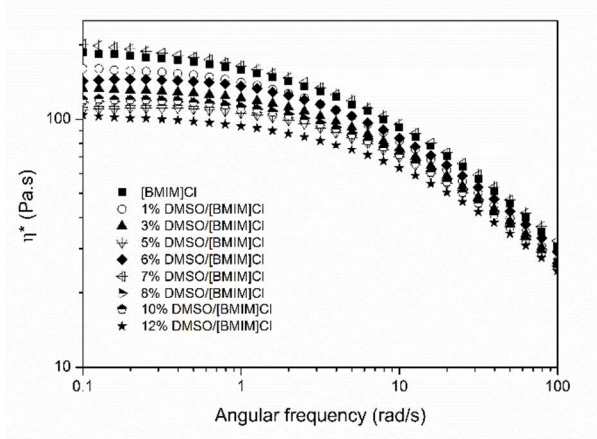

Fig.3 Dynamic oscillation rheological curves of cellulose/[BMIM]Cl/DMSO solution at 70 °C.

The dynamic oscillation rheological curves of the solutions are shown in Fig.3, which show the same trend as that of steady shear profiles. The apparent viscosity and complex viscosity of solutions were compared according to Cox-Merz empirical rule [23] as shown in Fig.4. At high shear rate or frequency, $|\eta^*(\omega)| > \eta(\dot{\gamma})$ of sample [BMIM]Cl and 1 wt% DMSO content. This phenomenon have been found in many polymer/ionic liquid systems [24, 25, 26] which can be interpreted as the disruption of interaction between polymer chains and ionic liquid under shear. However, the $|\eta^*(\omega)| < \eta(\dot{\gamma})$ at all frequency of sample 7 wt% DMSO content, it does not obey the Cox-Merz empirical rule owing to the heterogeneous structure in the solution.
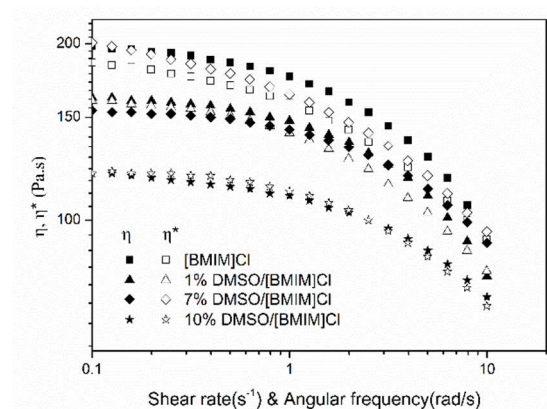

Fig.4 Cox-Merz plots of cellulose/[BMIM]Cl/DMSO solution at 70 °C.

The storage G′ and loss modulus G″ as a function of angular frequency at the temperature 70 °C are shown in Fig. 5. The slopes of G′ at low frequency are 1.45-1.82 except the sample of 7 wt% DMSO. The slopes of G″ are 0.89-0.95. The slopes of G′ and G″ of 7 wt% DMSO content sample are 1.23 and 0.91, respectively. The closer slopes of this sample are related to the super-molecular structure of the solution [24].
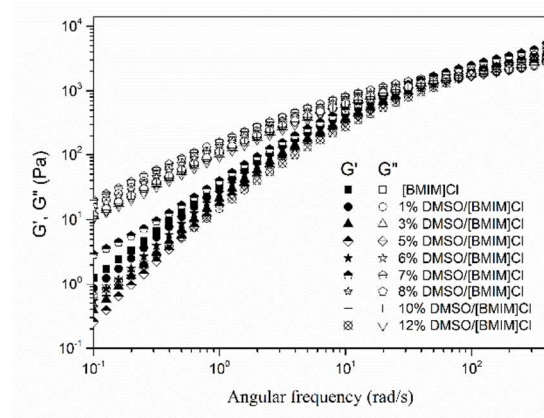
Fig.5 Storage modulus G′ and loss modulus G″ of cellulose/[BMIM]Cl/DMSO solution at the temperature of 70 °C.

The effect of temperature on the dynamic oscillation behaviors of sample 7 wt% DMSO content is shown in Fig. 6. The G′ is smaller than G″ at low temperature, both of them decrease with the increase of temperature, which means that the viscoelastic behavior of the solution is sensitive to temperature [27].
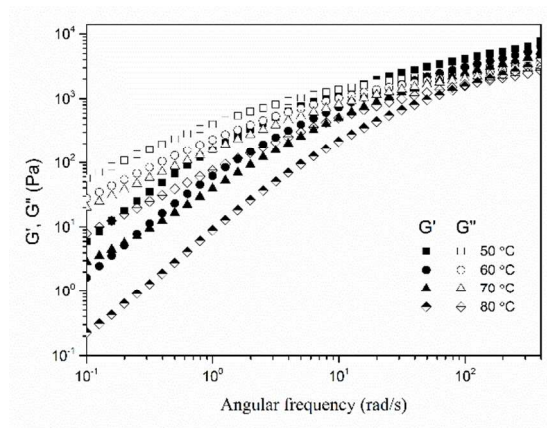
Fig. 6 Storage modulus G′ and loss modulus G″ of cellulose/[BMIM]Cl/DMSO solution of the sample 7 wt% DMSO/[BMIM]Cl at various temperature.

3.3. Effect of DMSO concentration on the sol-gel transition of cellulose/[BMIM]Cl/DMSO solutions

The sol-gel transition of cellulose/[BMIM]Cl at low temperature has been reported [28]. The sol-gel transition process can be discussed with Winter and Chambon's theory as follows [29].

$$G'(\omega) \sim G''(\omega) \sim \omega^n (0<n<1) \qquad (2)$$
$$\tan \delta = G''(\omega)/ G'(\omega) = \tan(n\pi/2) = const \qquad (3)$$

Where n is the scaling exponent or critical relation exponent, which is related to the sol-gel structure.

The gelation temperature (T_{gel}) can be obtained from the intersection plot of multi-frequency tan δ versus temperature as shown in Fig. 7. As shown in Table 1, the sol-gel transition occurred in the mixture solution at the temperature about 10 °C. The T_{gel} shifts to lower temperature with the increase of DMSO within the DMSO content of 5 wt%. The n value is related to the compactness of the gel structure [30]. The n values decreased with the increase of DMSO within the DMSO content of 5 wt%, the gel structure is loosened with the effect of DMSO. The gelation of cellulose/[BMIM]Cl solution can be understood as the micro-phase separation of cellulose-rich phase and [BMIM]Cl rich phase at low temperature [26] or high concentration [28]. Otherwise, the cellulose gel formed when the non-solvent as water was added in the system [31]. The micro-aggregation of cellulose existed in the solution above 5

wt% DMSO content, which would induce the occurrence of micro-phase separation of cellulose at low temperature. Hence, the sol-gel transition of cellulose/[BMIM]Cl/DMSO can be understood as the effective of non-solvent DMSO and super cooled state of the solution.
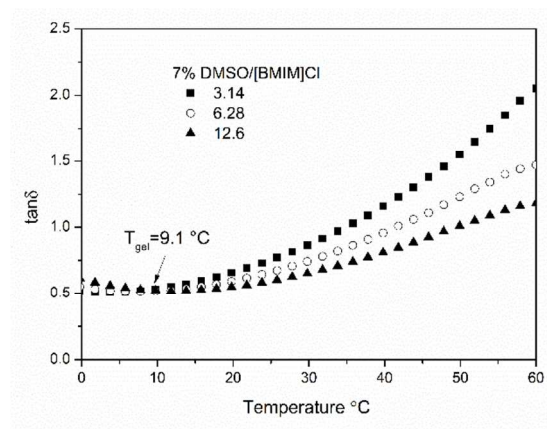
Fig.7 Loss tangent tan δ as a function of temperature for cellulose/[BMIM]Cl/DMSO solution.

Table 1. The viscoelastic parameters of cellulose /[BMIM]Cl/DMSO at gel point.

Solvents being used	T_{gel} (°C)	tan δ	n
[BMIM]Cl	12.0	0.614	0.35
1% DMSO/[BMIM]Cl	10.4	0.532	0.34
3% DMSO/[BMIM]Cl	9.8	0.517	0.30
5% DMSO/[BMIM]Cl	8.5	0.502	0.29
6% DMSO/[BMIM]Cl	11.7	0.497	0.32
7% DMSO/[BMIM]Cl	9.1	0.512	0.28
8% DMSO/[BMIM]Cl	7.7	0.531	0.33
10% DMSO/[BMIM]Cl	4.8	0.520	0.31
12% DMSO/[BMIM]Cl	4.3	0.507	0.32

4. Conclusions

The effect of DMSO on the viscoelastic behavior and sol-gel transition of cellulose /[BMIM]Cl/DMSO solutions was studied by rheology. When the content of DMSO was below 5 wt%, the viscosity, dynamic modulus and T_{gel} of solution decreased with the increase of DMSO. The interaction of cellulose and [BMIM]Cl remained unchangeable, DMSO

acted as diluent in the solution. When the content of DMSO further increased, the viscosity, dynamic modulus and T_{gel} of solution showed nonlinear change, the micro-aggregation or micro-phase separation of cellulose occurred with the effect of DMSO.

Acknowledgments

Conflicts of Interest

The authors declare no conflict of interest.

Notes and references

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