

PREPARATION AND RHEOLOGICAL PROPERTIES OF CELLULOSE/CHITOSAN HOMOGENEOUS SOLUTION IN IONIC LIQUID

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Cellulose/chitosan homogeneous solutions were prepared in 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) ionic liquid. Steady and oscillatory dynamic rheological properties were studied with a Haake Mars-III rotational rheometer. Rheological results show that cellulose/chitosan [EMIM]Ac solutions are a pseudoplastic liquid, and the viscosity of the solution decreases with increasing of chitosan content. The zero shear rate viscous activation energy of solution is about 52.10 to 62.50KJ/mol, calculated from the Cross and Arrhenius equation. The structural viscosity index of the solution is similar to that of cellulose/N-methylmorpholine-N-oxide solution, which indicates a potential spinnability. The dynamic rheological responses reveal that the Cox-Merz rule holds well with the solutions, and the crossover point of loss modulus and storage modulus shifts to a higher frequency range with increasing temperature.

Keywords: Rheological property; Ionic liquid; [EMIM]Ac; Cellulose/chitosan homogeneous solution

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INTRODUCTION

As the most abundant polysaccharide, cellulose is an extremely important raw material in the pulp, paper, membrane, and textile industries (Swatloski et al. 2002; Hoenich 2006; Cao et al. 2009). Chitosan, a copolymer of glucosamine and N-acetylglucosamine units linked by 1,4-glucosidic bonds, is obtained by N-deacetylation of chitin, which is the next most abundant natural polymer after the lignocellulosic group. Chitosan is a biocompatible polymer that is reported to exhibit a great variety of useful biological properties such as antibacterial, antifungal, and anticholesteremic activities (Pillai et al. 2009; Rinaudo 2006; Sashiwa 2004). In recent years, with the rapid development of material and biomedical sciences, as well as the rise of environmental protection consciousness, there have been many indications of scientific and industrial interest in developing cellulose/chitosan composite materials (Du and Hsieh 2009; Shih et al. 2009; Hasegawa et al. 1994). However, owing to the strong inter- and intramolecular hydrogen bonding between macromolecule chains, there are limited organic solvents that can be used to dissolve both cellulose and chitosan.

The N-methylmorpholine-N-oxide (NMMO) process of cellulose regeneration has been commercialized for nearly twenty years, but it has not replaced the viscose process to date. The main reason is the severe fibrillation of the fibers manufactured. Moreover, the use of NMMO- a thermally unstable solvent- requires a major investment in safety technology (Hermanutz et al. 2008). Shih et al. (2009) prepared a kind of cellulose/chitosan blend film using NMMO as solvent; however, when the chitosan content in the blend exceeded 5% (w/w), the film became coarse and the tensile strength was reduced. Zhuang et al. (2008) prepared a derivative of chitosan, 2-(2-aminoethoxy) ethyl chitosan (AECS), and thus improved its solubility in NMMO, and got a blend material of cellulose/chitosan. Li et al. (2002) prepared O-carboxymethylated chitosan for a blended film of cellulose/chitosan from LiCl/N,N-dimethylacetamide (DMAc) solution. All these methods are of limited interest from the perspective of industrial applications due to their complex nature and high cost.

Ionic liquids (ILs), combining good solubility, negligible vapor pressure, and excellent thermal stability, have been extensively researched and applied as green solvents, especially as a good solvents for cellulose (Laus et al. 2005; Swatloski et al. 2002; Kosan et al. 2008) and chitosan (Xie et al. 2006; Wu et al. 2008; Xiao et al. 2011).

Rheological properties are very important for processing and application of materials in industry. Many studies on the rheology of cellulose in ionic liquid solutions have been published. Collier and co-workers studied the rheology of cellulose in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid solutions, such as shear rheology, and elongational rheology (Sammons et al. 2008; Collier et al. 2009). The rheological properties of cellulose in dilute solutions of 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) were studied by Kuang et al. (2008). Gericke et al. (2009) studied the steady rheology of cellulose in 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) solutions from dilute to concentrated states. However, studies on rheological property of both cellulose and chitosan in ionic liquids are rarely reported. As the preliminary studies to prepare a good green biomass composite materials of cellulose/chitosan, we prepared the cellulose/chitosan homogeneous solutions in the ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac), and the rheological properties of solutions were evaluated in detail to contribute to a better understanding of processing of cellulose/chitosan composite materials.

EXPERIMENTAL

Materials

The cellulose (CE) samples were a kind of bleached softwood dissolving pulp board, which was purchased from Buckeye Florida limited Partnership. The pulp board was dispersed into a fluffy flock-like materials by a pulverizer and then dried at 60°C for 12h in a vacuum oven before usage. The viscosity-average degree of polymerization (DP) was 474, as measured by Ubbelodh viscometer in cuprammonium hydroxide solution.

The chitosan powder (CS) (deacetylation degree > 90%) was obtained from Shanghai Jingchun Industrial Co. Ltd of China and dried at 80°C for 8h in a vacuum oven

before usage. Its viscosity-average molecular weight was 3.91×10^5 g/mol, as measured by Ubbelodh viscometer in acetic acid solution.

N-methylimidazole(AR), chloroethane(AR), and ethanol(AR) were came from Yancheng Cale Chem. Co. Ltd, Shandong Tancheng Yongbin Chem. Co. Ltd and Shanghai Jingchun Industrial Co. Ltd in China respectively, and they were used as received.

Methods

Preparation of [EMIM]Ac ionic liquid

[EMIM]Ac ionic liquid was prepared according to our previous patent (Xu et al. 2009) as shown in Fig.1.

Firstly, N-methylimidazole (1.00 mol) was added into a high-pressure reactor with a reflux condenser and stirrer, and then chloroethane (1.10 mol) was blown in slowly by the aid of nitrogen. The reaction was kept for 48h at 75 to 80°C, and then the residue of unreacted chloroethane were removed by vacuum distillation and finally the intermediate product [EMIM]Cl was obtained.

Secondly, [EMIM]Cl ethanol solution (mass ratio 100:15) was added into potassium acetate ethanol solution (18%w/w) until the mole ratio of [EMIM]Cl to KAc was 1:1.05. After being reacted for 6h at 70°C, the reaction solution was cooled down to -10°C and the precipitation of KCl was removed by filtration and the ethanol was removed by vacuum distillation. The product was dried in vacuum at 80°C for 24h before usage.

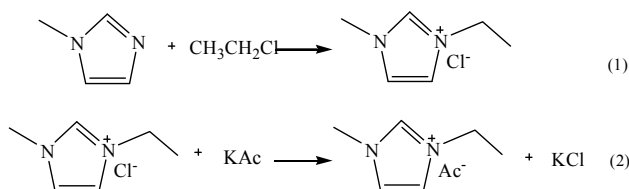


Fig.1. Synthesis of [EMIM]Ac

Preparation of cellulose/chitosan [EMIM]Ac solutions

Cellulose/chitosan [EMIM]Ac ionic liquid solutions were prepared at 90°C under vacuum condition. The ratios of cellulose and chitosan were 8:0, 7:1, 6:2, and 5:3, and the total concentration of solution was 8%(w/w).

Rheological Measurements

Steady-state and dynamic rheological measurements were performed with a HAAKE MARS-III rheometer, equipped with cone-plate geometry. A small geometry (diameter: 35mm, cone angle: 1°, gap: 0.052mm) was used for the experiments at different temperatures. Steady-state measurements were performed with a shear rate ($\dot{\gamma}$) range of 0.1 to 100 s^{-1} . Oscillatory measurements were performed over a frequency range of 0.1 to 100 Hz at the linear viscoelastic regime. The linear viscoelastic regime was found at a frequency of 1Hz according to an oscillation stress sweep. All measurements were performed by embedding with a layer of silicone oil on free surface of solution to avoid water adsorption.

RESULTS AND DISCUSSION

Preparation of Cellulose/Chitosan [EMIM]Ac Solutions

It is reported that [EMIM]Ac can form about 20%(w/w) and 15%(w/w) solutions with cellulose and chitosan respectively (Hermanutz et al. 2008; Duan et al. 2011). From Table 1 we can see that chitosan could be precipitated from [EMIM]Ac after adding cellulose, just as macromolecules are regenerated from ILs by low molecular solvent (Swatloski et al. 2002; Wu et al. 2008). Furthermore, chitosan will be enwrapped by dissolved cellulose in ionic liquid. So, it is difficult to get homogeneous solutions whenever adding CE or CS first in [EMIM]Ac. A homogeneous ionic liquid solution will be obtained when CE and CS is added in [EMIM]Ac at the same time. If the CS is swollen first in ionic liquid for some time and then CE is added, the dissolving time will be shortened.

Table 1. Comparison of four Preparation Procedures of Homogenous Solutions

Procedures	Phenomenon
a: CS was added in CE/[EMIM]Ac solution	CS was enwrapped by CE
b: CE was added in CS/[EMIM]Ac solution	CS was precipitated by CE
c: CE and CS was added in [EMIM]Ac simultaneously	Get homogeneous solutions in 5 hours
d: CS was swollen for 1hour first, then CE was added	Get homogeneous solutions in 3 hours

Steady Rheological Properties of Cellulose/Chitosan [EMIM]Ac Solutions

Steady rheological curves of cellulose/chitosan [EMIM]Ac solutions

The cellulose/chitosan [EMIM]Ac ionic liquid solutions showed typical viscosity-shear rate properties at different cellulose/chitosan ratios (Fig. 2). It can be seen that the CS/CE [EMIM]Ac solution is a pseudoplastic liquid and its viscosity decreases with the increment of chitosan in the solution.

Figure 3 shows the steady rheological curves of different mass fraction of CS/[EMIM]Ac solution at 50°C. It is evident from Figs. 2 and 3 that the shear viscosity of CS/[EMIM]Ac solution was less than CE/[EMIM]Ac at the same concentration. What's more, the CS/[EMIM]Ac solution showed Newton fluid characteristics when the mass concentration of chitosan was less than 3%. That means that the chitosan molecular in the dilute solution had little influence on the steady rheological property of the ionic liquid mixture solution.

The E_{η} values of cellulose/chitosan [EMIM]Ac solutions

Temperature has very important effect on steady rheological properties of solutions. Figure 4 shows the effect of temperature on viscosity of CE/CS [EMIM]Ac solution. It can be seen that the viscosity-shear of solution decreased with increment of temperature, and the rheological properties of the solution approached those of a pseudoplastic liquid.

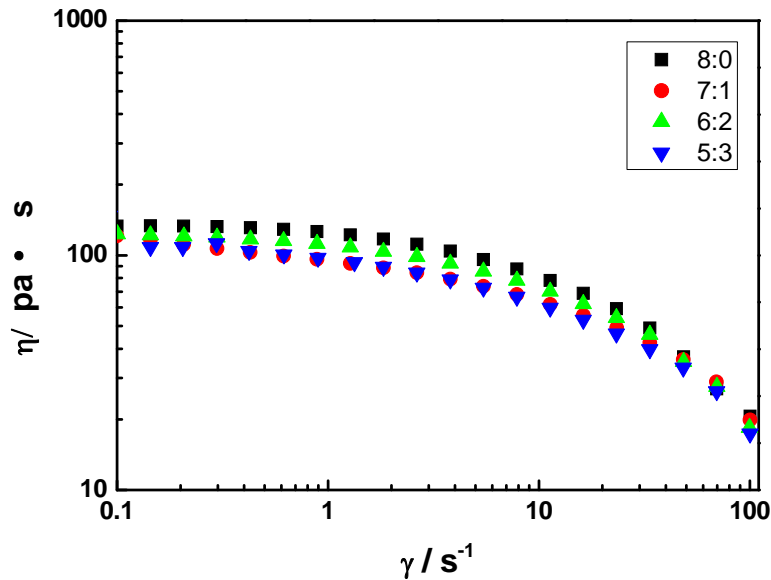


Fig. 2. Steady rheological curves of 8%(w/w) CE/CS [EMIM]Ac solutions with different ratios at 80°C

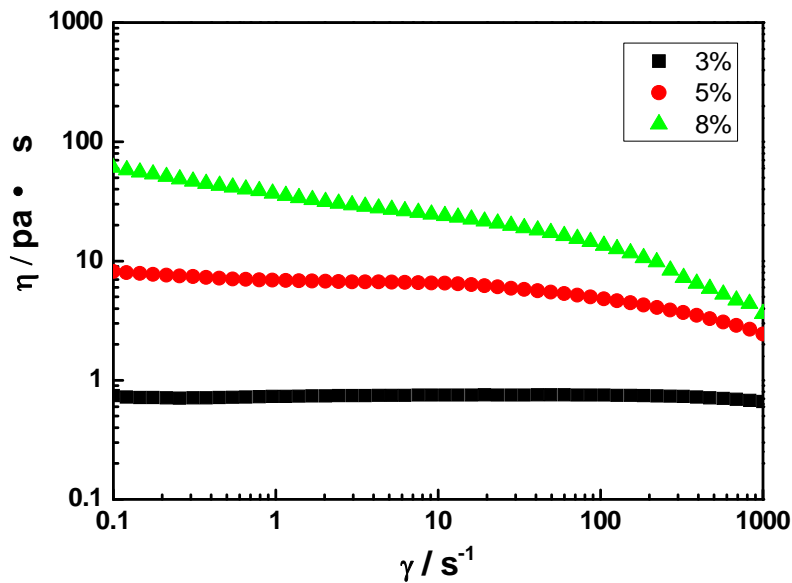


Fig. 3. Steady rheological curves of Chitosan/[EMIM]Ac solutions at 50°C

For a macromolecular material, the influence of temperature on steady rheological property can usually be illustrated by viscous activation energy (E_η), which can be calculated according to Arrhenius equation,

$$\eta_0 = Ae^{E_\eta/RT} \quad (1)$$

where η_0 is zero shear viscosity of the solvent at temperature T , A is a constant, and R is the universal gas constant. Zero shear viscosity is the viscosity at the limit of low shear rate.

The value of η_0 can be acquired from the Cross equation,

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty) / (1 + (\frac{\dot{\gamma}}{\dot{\gamma}_b})^n) \quad (2)$$

where η_∞ is infinite shear viscosity, n is the Cross rate constant, and $\dot{\gamma}_b$ is the critical shear rate, which proves to be a useful indicator of onset shear rate for shear thinning.

For a pseudoplastic liquid, η_∞ is nearly zero, so equation (2) can be written as equation (3):

$$\eta = \eta_0 / (1 + (\frac{\dot{\gamma}}{\dot{\gamma}_b})^n) \quad (3)$$

Then, E_η values of solutions can be calculated from equations (1) and (3).

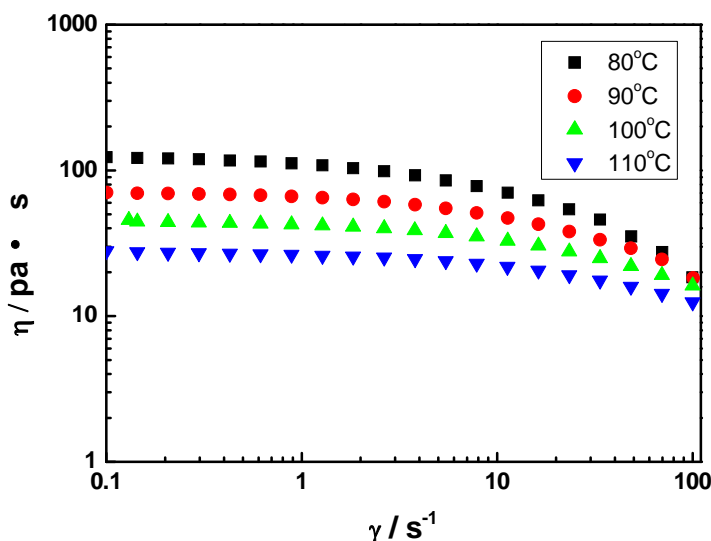


Fig. 4. Viscosity-shear rate curves of 8%(w/w) CE/CS [EMIM]Ac solutions at different temperature(CE/CS = 6:2)

From Table 2 one can see that the E_η values of cellulose/chitosan/[EMIM]Ac solutions ranged from 52.10 to 62.50 KJ/mol with different ratios of cellulose and chitosan, and it was close to the value of 53.97KJ/mol reported by Petrovan et al. (2000) for a lyocell solution of 14% concentration cellulose from a dissolving pulp of DP 855. The E_η values of cellulose/[BMIM]Cl solutions with 8%, 10% and 12%(w/w) were 79.45 to 100.8 KJ/mol, as reported by Sammons et al. (2008). This means that the E_η values of cellulose/chitosan [EMIM]Ac solutions were nearly equal to those of cellulose/NMMO solutions, and were lower than those of cellulose/[BMIM]Cl solutions.

Table 2. E_{η} Values of Cellulose/Chitosan [EMIM]Ac Solutions

Cellulose/Chitosan	E_{η} (KJ/mol)	R^2 values
8:0	56.72	0.9999
7:1	52.10	0.9961
6:2	55.58	0.9996
5:3	62.50	0.9992

Structural viscosity index of cellulose/chitosan [EMIM]Ac solutions

The structural viscosity index ($\Delta\eta$) is a useful experimental parameter for the spinnability of spinning dope. The $\Delta\eta$ value can be calculated from equation (4):

$$\Delta\eta = -(d \lg \eta_a / d \sqrt{\dot{\gamma}}) \times 100 \quad (4)$$

$\Delta\eta$ values of cellulose/chitosan [EMIM]Ac ionic solutions with different CE/CS ratios and temperatures are shown in Table 3.

According to Table 3, the structural viscosity index values of cellulose/chitosan [EMIM]Ac mixture solutions were lower than that of the cellulose [EMIM]Ac solution at the same temperature, which means the fluidity and spinnability of mixture solutions would be better than that of cellulose/[EMIM]Ac solution. This is similar with the results illustrated in Figs.2 and 3, which indicates that the viscosity of cellulose/chitosan [EMIM]Ac solution was lower than that of cellulose [EMIM]Ac solution at the same concentration. Table 3 also shows that the structural viscosity index of solutions decreased with the temperature. The possible reason is that the motions of macromolecules are accelerated as the temperature increases and the fluidity of solutions become better. The degradation of cellulose and chitosan in [EMIM]Ac solution may lead to the decline of viscosity as the temperature rises, but we find that it is negligible when the temperature is under 100°C and the time is less than an hour as reported by Chen et al (2009). This problem will be discussed in detail in our next article.

Table 3. Structural Viscosity Index of Cellulose/Chitosan [EMIM]Ac Solutions

Temperature (°C)	$\Delta\eta$ values			
	CE/CS=8:0	CE/CS=7:1	CE/CS=6:2	CE/CS=5:3
80	8.623	7.775	8.335	8.067
90	6.907	5.881	5.985	5.737
100	4.803	4.574	4.671	4.403

Dynamic Rheological Properties of Cellulose/Chitosan [EMIM]Ac Solutions*Shear viscosity and dynamic viscosity curves of CE/CS [EMIM]Ac solutions*

In order to achieve a better understanding of the rheological properties of cellulose/chitosan [EMIM]Ac solutions, oscillation experiments were carried out.

Figure 5 shows the shear viscosity and dynamic viscosity (η') curves of cellulose/chitosan [EMIM]Ac solutions with different ratios at 90°C, and Fig. 6 shows the shear viscosity and dynamic viscosity of cellulose/chitosan [EMIM]Ac solutions with the ratio of 6:2 at different temperature. It is clear from Figs. 5 and 6 that dynamic viscosity from oscillatory shear at low frequency agreed well with steady shear viscosity in the low

shear rate range, which means that the rheology of cellulose/chitosan/[EMIM]Ac solution is well satisfied with Cox-Merz rule. However, Chen et al. (2009) reported that the rheology of concentrated cellulose/[BMIM]Cl solution didn't fit well with the Cox-Merz rule. The reason may be that the viscosity of [BMIM]Cl used by Chen et al. was much higher than [EMIM]Ac. The melting point of [BMIM]Cl is about 76°C, while [EMIM]Ac is a liquid at room temperature. The results of the comparison indicate that the viscosity of cellulose/[BMIM]Cl solution is higher than cellulose/[EMIM]Ac solution at the same condition and is far higher than those of chitosan/[EMIM]Ac. Furthermore, the concentration of cellulose/[BMIM]Cl solution used by Chen et al. was higher than that of cellulose/chitosan/[EMIM]Ac.

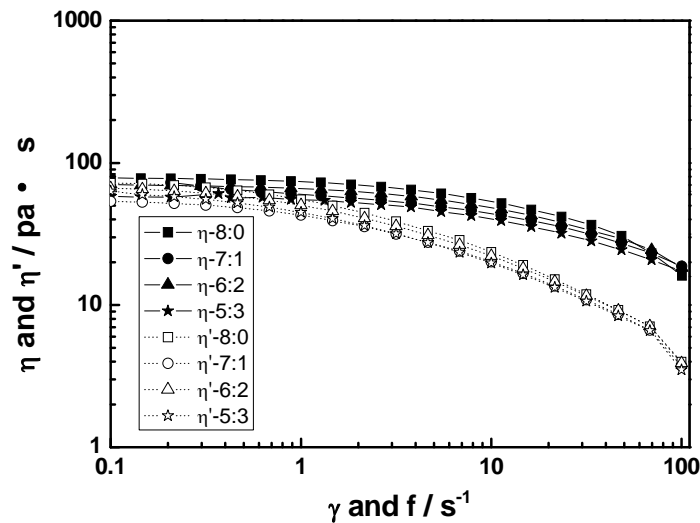


Fig. 5. Shear viscosity and dynamic viscosity curves of CE/CS [EMIM]Ac solutions with different ratios at 90°C

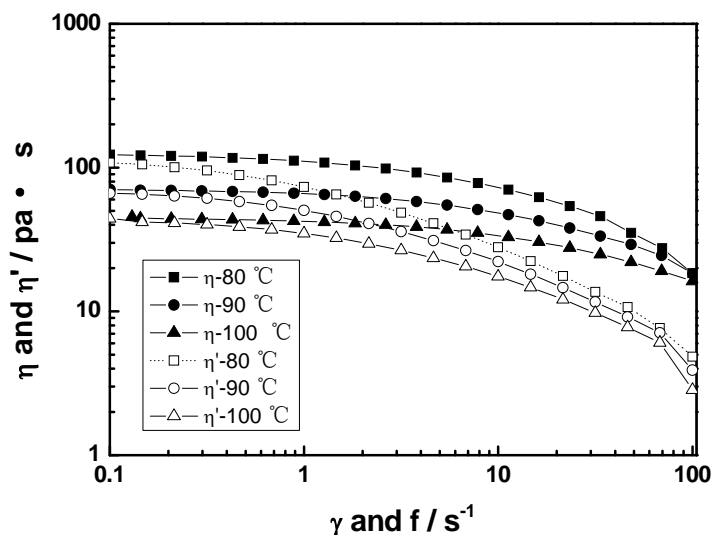


Fig. 6. Shear viscosity and dynamic viscosity curves of CE/CS [EMIM]Ac solutions with the ratio of 6:2 at different temperatures

Storage modulus and loss modulus of CE/CS [EMIM]Ac solutions

The storage modulus (G') and loss modulus (G'') are usually determined as functions of frequency at constant amplitude in the linear viscoelastic range.

Figure 7 shows the changes of G' and G'' as functions of frequency for the 8%(w/w) concentration of cellulose/chitosan [EMIM]Ac solutions with different ratios at 90°C. As can be seen from Fig. 7, there was little difference for both G' and G'' with different ratios of cellulose/chitosan, and the G' and G'' values of cellulose/[EMIM]Ac solutions were slightly higher than those of cellulose/chitosan [EMIM]Ac mixture solutions at the same frequency.

It is clear from Fig. 7 that the G' and G'' values were both increasing with frequency, and the loss modulus G'' was much higher than the storage modulus G' at low frequencies. Deformation takes place so slowly that the majority of energy is dissipated by viscous flow. As the frequency increases, the entanglements of macromolecule chains take place more easily, and so the storage modulus increases more quickly than does the loss modulus until two curves are crossing and then the storage modulus outweighs the loss modulus.

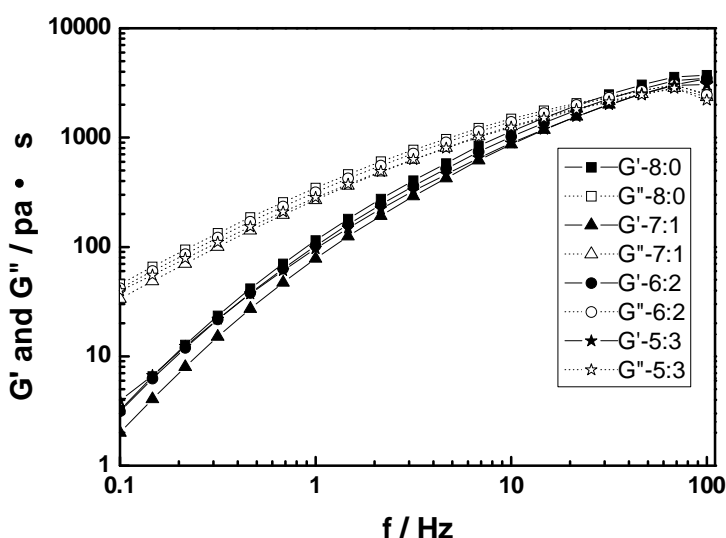
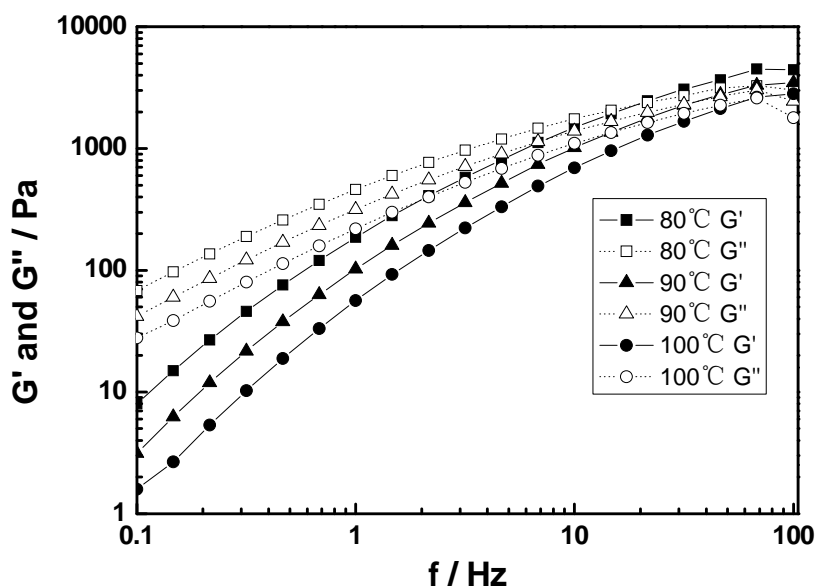


Fig. 7. Changes of storage and loss modulus as function of frequency for CE/CS [EMIM]Ac solutions with different ratios at 90°C

Figure 8 shows the changes of storage modulus and loss modulus as a function of frequency for cellulose/chitosan [EMIM]Ac solutions at different temperatures with the ratio of cellulose/chitosan as 6:2. Both G' and G'' shifted to lower values with the increment of temperature. The reason may be that there are more entanglements and aggregates among macromolecular chains in the solution at low temperature. In addition, the crossing point between G' and G'' was shifted to a higher frequency range with the increment of temperature as summarized in Table 4. This phenomenon agrees well with the rheological property of cellulose in ionic liquid solutions (Chen et al. 2009).

Table 4. Modulus Values and Frequency at the Crossover Point of G' and G'' curves

Temperature (°C)	Frequency (Hz)	Modulus (pa)
80	19.27	2289
90	36.10	2423
100	63.81	2534

**Fig. 8.** Changes of storage and loss modulus as function of frequency for CE/CS [EMIM]Ac solutions with the ratio of 6:2 at different temperatures

CONCLUSIONS

1. Cellulose/chitosan [EMIM]Ac homogeneous ionic liquid solutions were prepared successfully. Steady shear rheological results showed that the solutions were pseudoplastic liquids, and the viscosity of the solution decreased with increasing proportion of chitosan.
2. The zero shear rate activation energy of cellulose/chitosan [EMIM]Ac ionic liquid solutions is about 52.10 to 62.50KJ/mol, as calculated from the Cross and Arrhenius equation.
3. Dynamic rheological experiments showed that the rheology of cellulose/chitosan [EMIM]Ac solution agreed well with the Cox-Merz rule, and the crossover point of G' and G'' shifted to a higher frequency range with increasing temperature.
4. The structural viscosity index of cellulose/chitosan [EMIM]Ac solutions is similar to that of cellulose/NMMO solutions, which indicates its potential as a spinnable liquid.

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