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Gelation behaviors of cellulose solution dissolved in aqueous NaOH/thiourea at low temperature

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Abstract

Cellulose was dissolved rapidly in 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution pre-cooled to −5 °C, as a result of the formation of an inclusion complex (IC) associated with cellulose, NaOH and thiourea, which could bring cellulose to the aqueous system. To clarify the rheological behaviors of the system dissolved at low temperature, this cellulose solution was investigated by dynamic viscoelastic measurement. The shear storage modulus (G') and loss modulus (G'') as a function of the angular frequency (ω), concentration (c), temperature (T) and weight-average molecular weight (M_w) were analyzed and discussed. The results revealed that gels could form in the cellulose solution at either high temperature or low temperature, or for longer time. Interestingly, 4 wt% cellulose solution having cellulose M_w of 12.0×10^4 remained at liquid state for longer time (12 days) at the temperature ranging from 0 to 5 °C. The gels already formed at elevated temperature were irreversible, i.e., after cooling to lower temperature including the temperature of cellulose dissolution (−5 °C), they could not be dissolved to become liquid. The Arrhenius analysis of the temperature dependence of viscosity in the cellulose solution indicated that a high apparent activation energy (E_a) occurred at 0 to −5 °C, suggesting the relatively stable IC structure. However, the viscosity of the cellulose solution increased slowly with an increase in the temperature at 0–40 °C, leading to the negative E_a values. The results suggested that the cellulose solution in NaOH/thiourea system is complex to differ from normal polymer systems.

Keywords: Cellulose gel; Dissolution at low temperature; Rheology

1. Introduction

Hydrogels resulted from polysaccharides have attracted much attention in many areas such as biomaterials, pharmaceutical devices, drug release and controllable sensors [1]. Usually, a synthetic polymer gel is a three-dimensional network formed from flexible chains through either chemical cross-linking or physical entanglement network. The critical change from the liquid state to solid state is known as the sol–gel transition of the polymer solution. Though the gels have been studied for more than 60 years, the gelation has not been satisfactorily described by any theories, because the gels are complex system and each gel has its own complexities [2]. Cellulose is considered as the richest renewable resource, and has high hydrophilicity, so it is a good candidate for hydrogels [3]. The rheological properties of various polymer solutions including cellulose have been studied [4–7]. Most of the gelation in the cellulose solution usually takes place by cooling it below a certain temperature. For example, the cellulose solution in ammonia/ammonium thiocyanate solvent forms thermoreversible gels at temperatures below 30 °C [8]; the physical gelation of the cellulose derivative of 6-hydroxyl groups takes place in a tetrahydrofuran (THF) solution below −3 °C [9]. Moreover, the viscosities of the cellulose solution in *N*-methylmorpholine-*N*-oxide (NMMO) [10,11] and paraformaldehyde/dimethyl sulphoxide (DMSO) [12], respectively, increase with a decrease in temperature, in accordance with the rheological behavior of normal polymer solution. It is noted that thermal gelation also occurs in cellulose/cuprammonium solution because of the partial destruction of the

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complex that leads to the formation of intermolecular hydrogen bonds of cellulose at above 40 °C [13].

In our laboratory, dissolution of cellulose in 1.5 M NaOH/0.65 M thiourea aqueous solution via a freezing/thawing process for 12 h has been investigated [14,15]. However, their route leads to time and energy consuming, and it is unable for its industrialization. Recently, we have developed a new solvent of cellulose, that is cellulose could be rapidly dissolved in 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution pre-cooled to −5 °C within 2 min [16,17]. Moreover the cellulose solution was employed successfully to spin novel multifilament fibers by wet spinning [17,18]. It is worthy noting that the NaOH/thiourea aqueous system performs better solubility of cellulose than the NaOH/urea. In this way, the NaOH/thiourea system supplies us a new path to produce the functional cellulose materials, such as cellulose/chitin beads [19], cellulose/soy protein blends [20] and cellulose/tourmaline nanocrystal composite films [21]. A basic understanding of the sol−gel transition is essential for a successful research and application of the cellulose hydrogels and fibers from the cellulose solution. We are interested in the gelation behaviors of the cellulose solution dissolved at low temperature, which often leads to gelation of the normal polymer solution. Dynamic viscoelastic measurement is a sensitive probe for studying viscoelastic behavior of polymer solutions [8]. In present work, the rheological and gelation behaviors of the system as a function of cellulose concentration, molecular weight, temperature and time were studied by the oscillatory rheology. We hope to gain some meaningful information for the purpose of their fundamental research and industrial application.

2. Experimental

2.1. Materials

Six kinds of cellulose (cotton linter pulp) were supplied by Hubei Chemical Fiber Group Ltd (Hubei, China). The weight-average molecular weights (M_w) of cellulose C-1 was determined in 4.6 wt% LiOH/15.0 wt% urea aqueous solution pre-cooled to −10 °C with laser light scattering to be 12.0×10^4 [22]. The values of the viscosity-average molecular weight (M_η) of the cellulose samples C-1, C-2, C-3, C-4 and C-5 were measured to be 10.9×10^4, 4.3×10^4, 4.8×10^4, 7.8×10^4 and 8.8×10^4 by viscometry in cadoxen and calculated by [23]

$$[\eta] = 3.85 \times 10^{-2} M_w^{0.76} (\mathrm{mL\,g^{-1}}) \tag{1}$$

The cellulose samples were dried for 8 h in a vacuum oven, and then stored in a desiccator until used. Unless otherwise noted, all chemical reagents were purchased in China, with analytical grade.

2.2. Preparation of cellulose solution

A homogeneous cellulose solution in 9.5 wt% NaOH/4.5 wt% thiourea aqueous system was prepared following the method in our previous work [16]. In 86.0 g distilled water, 9.5 g of NaOH and 4.5 g of thiourea were dissolved and then the resultant solution was pre-cooled to −5 °C to prepare a new solvent of cellulose. Desired grams of the cellulose samples were dispersed immediately in the solvent under vigorous stirring at ambient temperature for 5 min to obtain a transparent solution. The cellulose solutions with different concentrations from 4 to 6 wt% for C-1 and from 4 to 9 wt% for C-2 were prepared, respectively. The resultant solutions then were centrifuged at 4000 rpm for 10 min at 5 °C to degas.

^{13}C NMR measurement of the cellulose solution was carried out on a Mercury 600 MHz NMR spectrometer (Varian Inc., USA) at ambient temperature. The cellulose concentration was adjusted to 4%. Sodium salt of 2,2-dimethyl-2-silapentane-5-sulphonic acid (DSS) was used as internal reference to determine the chemical shifts.

2.3. Rheological measurement

Dynamic rheological experiments were performed on a strain-controlled ARES-RFS III rheometer (TA Inc., New Castle, USA) at temperatures from −5 to 60 °C. The cellulose solution degassed was transferred from a glass bottle to the rheometer. The rheometer was equipped with two sensitive force transducers for torque measurements ranging from 0.004 to 1000 g cm. A double-concentric-cylinder geometry was used to measure the dynamic viscoelastic values including the shear storage modulus (G') and loss modulus (G'') as a function of time, temperature or angular frequency. The rheometer was equipped with a cooling/heating bath that was calibrated to maintain the temperature of the sample chamber within ±0.5 °C difference of the set value. The cellulose solution was heated or cooled to desired temperature directly in the rheometer (without shearing or oscillating). Since all measurements were carried out at elevated temperatures, a thin layer of low-viscosity paraffin oil was always added to the periphery surface of the solution in the couette cell to prevent the dehydration and the evaporation of the solvent during the rheological measurements. In the frequency and time sweep measurements, we define the time at which the solution reached the desired temperature as $t = 0$. The sweep of the frequency was done from 0.1 to 200 rad/s. The dynamic viscoelastic measurements of the cellulose solution with the concentration ranging from 4 to 6 wt% were taken at an angular frequency (ω) of 1 rad/s, and low shear strains to ensure the linearity of viscoelasticity.

3. Results and discussion

3.1. Preparation of cellulose solution

Cellulose was rapidly dissolved in 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution pre-cooled to −5 °C within 2 min to form a transparent solution. Fig. 1 shows the results of ^{13}C NMR spectrum of the cellulose solution in 9.5 wt% NaOH/4.5 wt% thiourea/D_2O, its gels formed at both low and high temperatures and regenerated cellulose fiber. In Fig. 1a, sharp

Fig. 1. ^{13}C NMR spectra of 5% cellulose (C-1) in 9.5 wt% NaOH/4.5 wt% thiourea/D_2O aqueous solution (a), CP/MAS ^{13}C NMR spectra of the cellulose gels formed at −20 °C for 24 h (b), and at 60 °C for 24 h (c), respectively, and of regenerated cellulose fibers (without drawn) (d) [17].

signals at 105.1, 80.3, 76.9, 76.7, 75.3 and 62.0 ppm are assigned to the C1, C4, C5 and C3, C2, as well as C6 of cellulose anhydrate glucose unit, respectively. Comparing with the solid state ^{13}C NMR spectrum of the native cellulose I (not shown), peaks for C4 and C6 in the cellulose solution obviously shifted to a higher magnetic field than the cellulose I, indicating that intramolecular hydrogen bonds in cellulose were destroyed. These chemical shifts are similar to those of wood pulp in LiCl/DMI and cellulose in LiCl/DMAc, which are good solvents of cellulose [24–26]. It was confirmed that the 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution is a direct cellulose solvent rather than derivative aqueous solution system. Interestingly, the chemical shifts of cellulose in 9.5 wt% NaOH/4.5 wt% thiourea/D_2O are in the same pattern as those of cellulose in 6 wt% NaOH/5 wt% thiourea aqueous solution, in which the dissolution of cellulose needs undergoing a freeze-thaw cycle [14,15]. This fact has demonstrated that the change of NaOH concentration (as the solvent) and the freeze-thaw cycle process has hardly changed the structure of the cellulose solution, suggesting that the dissolution is a physical behavior. The signal at 181.8 ppm for the cellulose solution represents C=S group of thiourea (not shown). Its position shifts to the higher magnetic field than that of only thiourea in D_2O (at 183.5 ppm, not shown), indicating that a hydrogen-bonding interaction occurs among thiourea, water clusters and NaOH in this system. The low temperature plays an important role in the dissolution of cellulose, that promotes the formation of a stable inclusion complex (IC) hosted by thiourea and NaOH hydrates through hydrogen-bond networks [27]. The IC associated with cellulose, NaOH and thiourea hydrate brings cellulose in the aqueous system, leading to the good dispersion. NaOH hydrates mostly contribute to break the inter and intramolecular hydrogen bonds as a result of the shifting hydrogen bonds between cellulose and NaOH hydrate at low temperature, whereas the thiourea hydrate prevents the cellulose self-association [27]. It is well known that the hydrogen bonds between macromolecules in their solution lead to jelly and/or gel at low temperature. In our cellulose solution, however, the formation of the hydrogen bonds between macromolecules and small molecules at low temperature induces the dissolution, to differ from the polymer solution.

Fig. 1b–d shows CP/MAS ^{13}C NMR spectra of the cellulose gels and regenerated cellulose fibers, respectively. There are no obvious differences in Fig. 1b and c, which represent the spectra of cellulose gels formed at low temperature (−20 °C) and high temperature (60 °C), respectively. Both of them exhibited four main peaks at 105.6, 87.6, 75.0 (77.0, 73.0) ppm, assigned to the C1, C4, C5 (C3, C2), as well as C6 peak lines at 62.4 ppm. The chemical shifts of the gels are assigned to cellulose II, and similar to the regenerated cellulose fibers. The results strongly indicate that the native cellulose could be dissolved in the present solvent system. Moreover, it is confirmed that the cellulose solution did transform into cellulose II in the gels.

3.2. Gelation of cellulose solution

The rheological properties of cellulose in 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution have been investigated to determine whether these solutions were gelling and under what conditions. As mentioned above, our cellulose aqueous solution is a very complex system with various types of interactions going on among cellulose, NaOH hydrate, thiourea hydrate and water. Therefore, we have chosen the crossover of G' and G'' curves as a qualitative indicator of the gel point of cellulose solution, which only shows the transition current under external factors' influences [28,29]. It should be pointed out that the gel point determined by this method is frequency dependent. For consistency of comparison, we chose the frequency of 1 rad/s for all samples studied in the determination of the gel point and gelation time. Fig. 2 shows the angular frequency dependence of the G' and G'' of the cellulose solution with different concentrations. The data are shifted along vertical axes by 10^a with the given a value to avoid overlapping. At 30 °C, 4 wt% cellulose (C-1) solution behaves as a viscous fluid, whereas with an increase of the cellulose concentration, the difference between the G' and G'' becomes small at low frequency. For 6 wt% cellulose solution, the G' becomes flatter than the G'' (less frequency dependent with the scale of $G'(\omega) = \text{constant}$ at $\omega \rightarrow 0$), and is higher than the G''; i.e., the system behaves more like an elastic solid. It is noted that a clear plateau of G' curve for 6 wt% cellulose solution

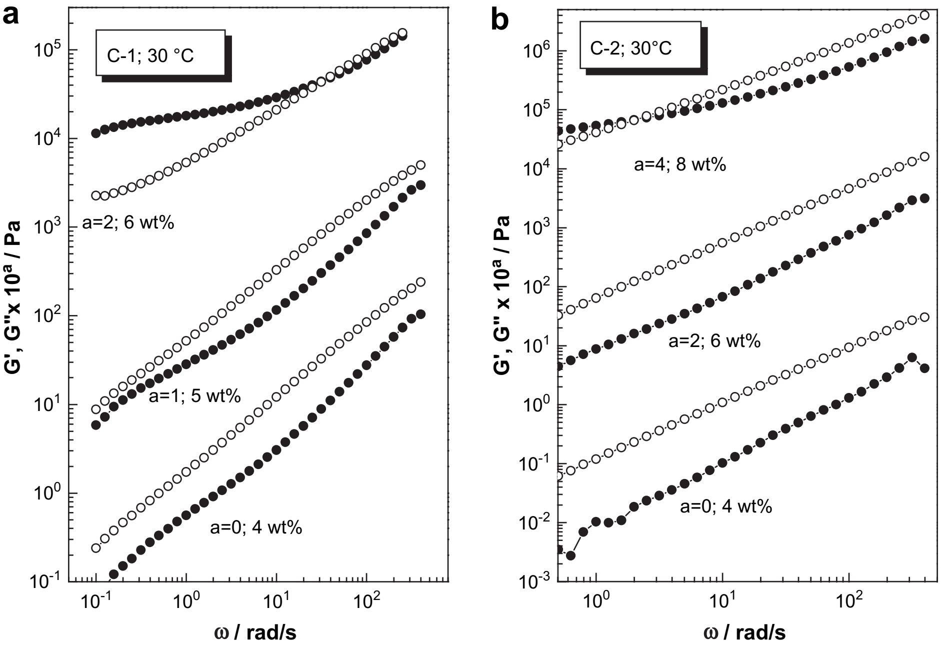

Fig. 2. Angular frequency dependence of storage modulus (G', ●) and loss modulus (G'', ○) for cellulose aqueous solutions with indicated concentrations at 30 °C. The data are shifted along vertical axes by 10^a with the given a value to avoid overlapping.

appears at low frequency range, indicating the existence of a more aggregation. The G' values for the C-1 cellulose solutions at 6 wt% and C-2 at 8 wt% are larger than G'' at lower frequencies, suggesting an elastic behavior. The results indicate that cellulose solution with relatively high concentration is more elastic than that with low concentration at 30 °C. It can be explained that at relatively high concentration, the molecular chains are much close to each other and much easier to aggregate with each other to form a three-dimensional network, which shows much more elasticity.

The dynamic frequency dependence of G' and G'' for the cellulose (C-1) solution at 30, 25 and 20 °C for different incubation times are shown in Fig. 3. To clarify the influences of the incubation time, the angular frequency dependence of G' and G'' curves of the cellulose solution with different times is discussed as follows. The 5 wt% cellulose solution at 30 °C and initial time (0 min) behaves as viscous liquid, and G' is smaller than G'' in the range of measured frequencies as shown in Fig. 3a. With the prolonging time, G' increases more rapidly than the G'', and G' exceeds G'' at low frequency for 12 min, in which the G' curve becomes flatter than that of the G''; thus the system behaves as solid state. After 12 min, the rheological behavior of the cellulose solution considerably differs from that of the initial trace; this suggests that gelation has taken place. With an increase of the incubation time to 90 min, the range where G' exceeds G'' expends to a relatively high frequencies. Finally, G' becomes flatter at a low frequency for 240 min, and is considerably higher than G'' in most of the range of frequencies, indicating the gelation. It is noted that 5 wt% cellulose solutions at 25 °C and 20 °C (Fig. 3b and c) exhibit a relatively slower tendency of the gelation than the case at 30 °C. When the cellulose concentration decreases from 5 wt% to 4 wt%, a longer gelation time appears in Fig. 3d. This indicates that the gelation time increases with a decrease of the cellulose concentration and a drop of the temperature; it suggests that self-aggregation of the cellulose chain in the solution becomes slower. Therefore, the gelation of the cellulose solution is related to the cellulose concentration, the incubation time, and the temperature. Contrary to the normal polymer solution, the elevation of temperature could induce the gelation of the cellulose solution. This can be explained that the IC structure in the cellulose solution has been destroyed partially or completely at elevated temperature, leading to the self-association and entanglement of cellulose molecules.

3.3. Effects of molecular weight and concentration

The G' and G'' curves in Fig. 4 for the cellulose solution having M_η of 4.8×10^4 exhibit typically dominant viscous behavior in the frequency range from 0.01 to 100 rad/s, whereas the one with M_η of 10.9×10^4 displays a much more elastic behavior at low frequency. As the molecular weight increases, the cellulose solution with the same concentration exhibits relatively more elasticity on the whole. This phenomenon can be explained that as the length of the cellulose chain increases, its relaxation capacity decreases, resulting in easy entanglement of the chains. In view of the above results, decreased molecular weight leads to the relatively stable liquid state of the cellulose solution. Anyhow, the molecular weight distribution (MWD) is also an influence here. If the MWD is too wide, the dissolution is not thorough. It indicated that the large molecular weight part were swelling or formed micro-gels in the solution, which leads to the cellulose solution containing cellulose gels and the native cellulose I.

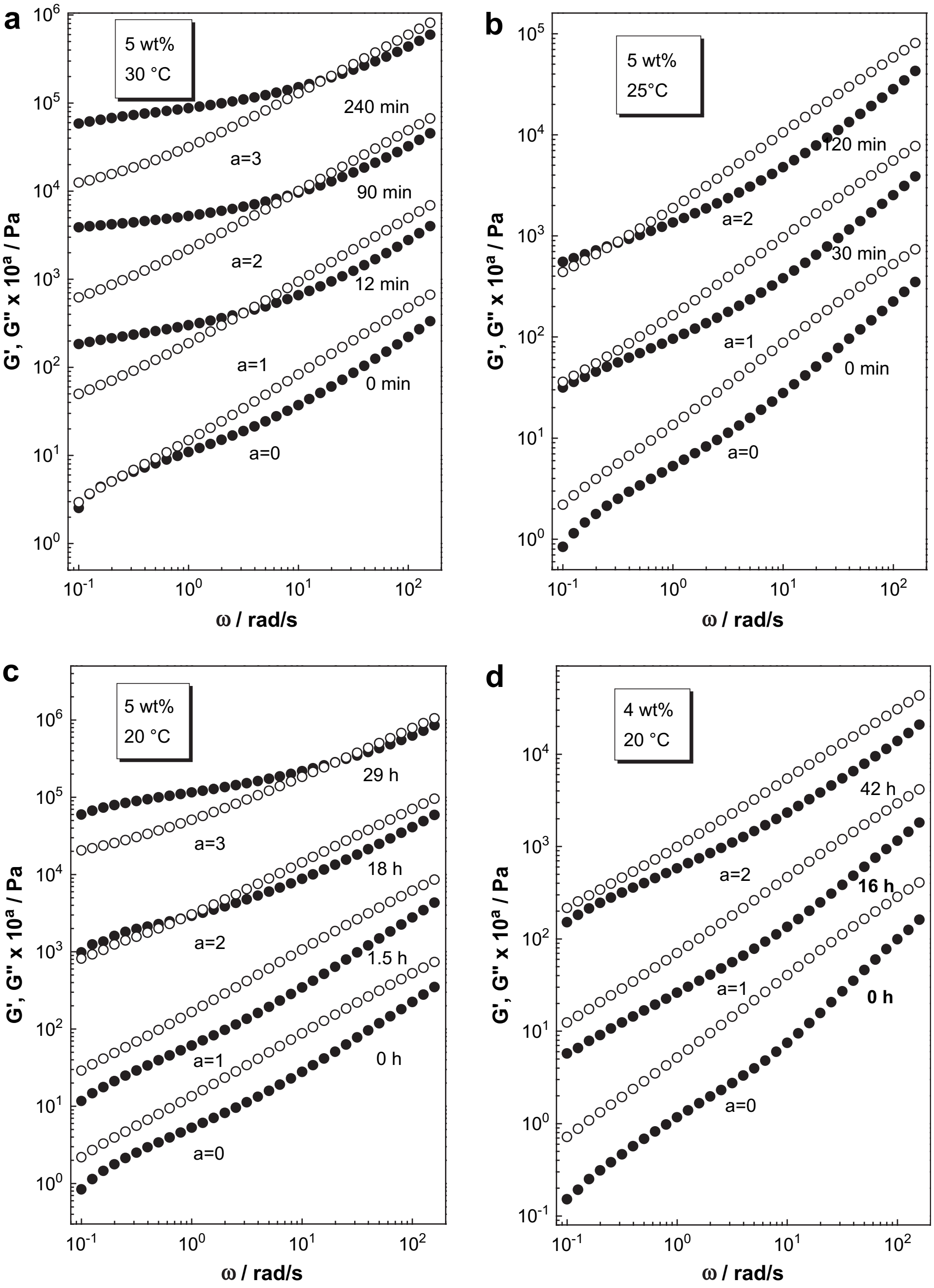

Fig. 3. Angular frequency dependence of storage modulus (G', ●) and loss modulus (G'', ○) of the cellulose (C-1) solution at specific temperature at various time periods. The data are shifted along vertical axes by 10^a with the given a value to avoid overlapping.

Fig. 5 shows the angular frequency dependence of G' and G'' for 5 wt% cellulose solution at different temperatures at initial stage (0 min). In the 5 wt% cellulose (C-1) solution the crossover has appeared at 35 °C. However, the 5 wt% cellulose (C-2) solution having relatively low M_w remains in the flueric features at a relatively high temperature (40 °C). This confirms that the cellulose solution having low M_w is more stable at ambient temperature. Therefore, the sol–gel transition more easily occurred in the cellulose solution with high cellulose M_w than that with low one, in accord with the Fig. 4 results.

Fig. 6 shows the temperature dependence of G' and G'' curves for the C-1 and C-2 cellulose solutions with a heating rate of 2 °C/min. In 4 wt% C-1 cellulose solution, G' curve crosses over G'' at about 35.9 °C, and can be divided into three parts. The first region is the one below 35 °C, where all G' values are lower than those of G'' and the gap between them tends to decrease as the temperature increases. It shows the common viscoelastic behavior of a viscous liquid. It should be noted that G' reaches a lowest value at 30 °C before the crossover point, and then increases gradually. This region is not responsible for the gel state, because G'' value is always higher than G', which is characteristic of liquid behavior. The increase of G' is as a result of the partial formation of cellulose aggregate through its self-association in the solution. Subsequently, both G' and G'' increase gradually, but G'

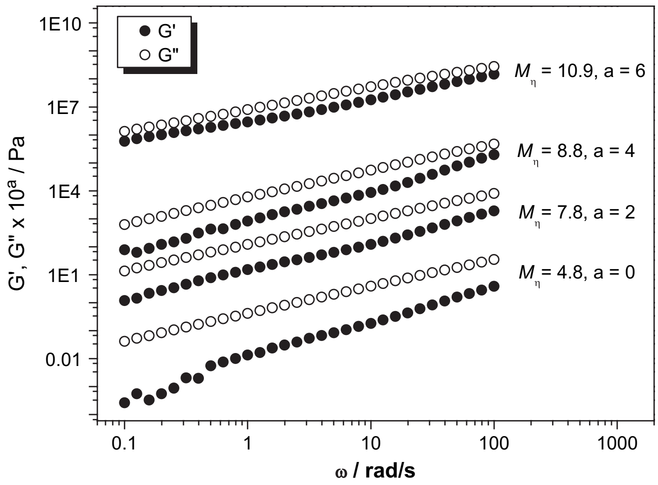

Fig. 4. Storage modulus (G', ●) and loss modulus (G'', ○) of the 4 wt% cellulose solutions having different molecular weights at 20 °C. The data are shifted along the vertical axis by 10^a with the given a value to avoid overlapping.

exhibits a much higher increasing rate than that of G''; this suggests that the elevation of the temperature mainly induces the increase in elasticity of the system. The second region is the one past the cross point, where G' values outgrow those of G'', indicating that an elastic gel network has formed. Interestingly, the G' and G'' increase dramatically with increase of temperature until about 60 °C, and then the increase of G' slows down to eventually reach the onset of a plateau. The G' and G'' curves in 5 and 6 wt% cellulose of the C-1 cellulose solution show a similar pattern. However, the distance between the on-start point of the G' and the cross point of G' and G'' appears to shorten as the concentration increases. Interestingly, the continued heating causes a slight drop of G' and an abrupt increase of G'', reflecting a characteristic of a phase separation. This can be explained that the turbidity and precipitation in the cellulose solution have undermined the gels, leading to the decrease of the elastic modulus and the increase of loss modulus because of the improvement of the fluid. From the analysis of the intersection temperature extracted from G' and G'' curves, the gelation temperature decreases with an increase of the cellulose concentration. Moreover, at the higher concentration varied from 5 to 9 wt%, the gelation temperature of the C-2 cellulose solution having relatively low M_w also decreases. This indicates that the decrease of the molecular weight of cellulose could account for the increase of the critical gelation concentration, and the rise of the gelation temperature. It is worth noting that the sol–gel transition temperature significantly shifts to lower temperatures with an increase of the polymer concentration; this suggests that the aggregation and entanglements of the cellulose chain can be caused not only by heating but also by elevated concentration. The reason for this could be that the elevation of the polymer concentration leads to the collision chance of the cellulose, promoting the formation of the aggregates and cross-linking network structure.

3.4. Effects of temperature and time on gelation

The time dependence of G' and G'' for 5 wt% C-1 cellulose solution under different temperatures (0, 25 and 30 °C) at $\omega = 1$ rad/s are shown in Fig. 7. It is noted that the system is able to maintain the viscous liquid at 0 °C for longer time. Interestingly, the gelation of the cellulose solution took place easily at 30 °C, whereas it did not occur at 0 °C over the used time. This suggests that the rheological behavior of the cellulose solution is very sensitive to the variation of the

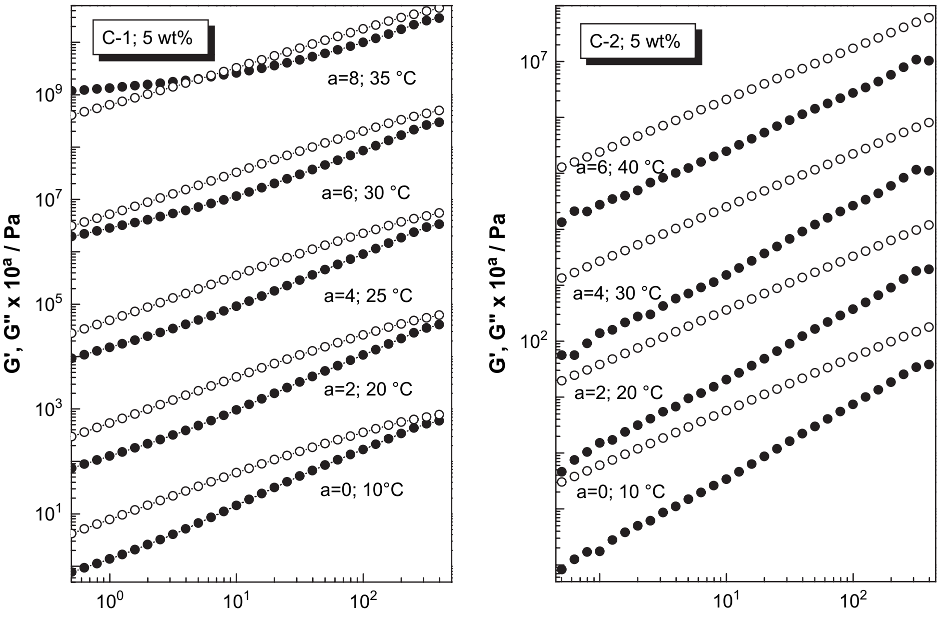

Fig. 5. Angular frequency dependence of storage modulus (G', ●) and loss modulus (G'', ○) of 5 wt% cellulose (C-1) and (C-2) solutions at different temperature. The data are shifted along vertical axes by 10^a with the given a value to avoid overlapping.

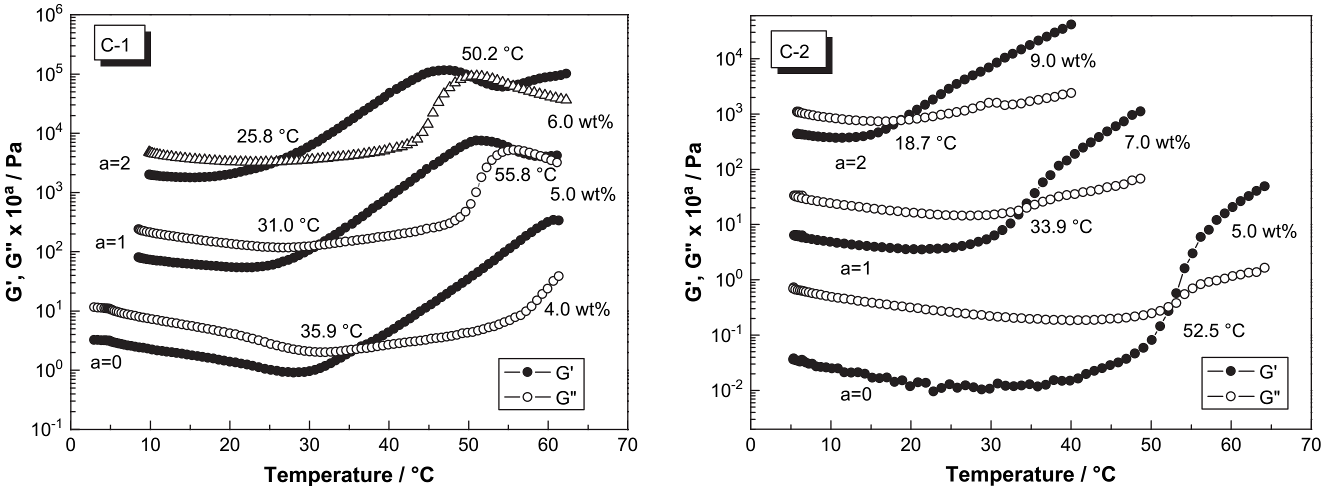

Fig. 6. Temperature dependence of storage modulus (G', ●) and loss modulus (G'', ○) of the cellulose solutions of different concentrations at the elevated temperature with a heating rate of 2 °C/min at a frequency of 1 rad/s. The data are shifted along vertical axes by 10^a with the given a value to avoid overlapping.

temperature. In the cellulose solution system, the IC structure formed through hydrogen-bonding networks remains at 0 °C. With an increase in temperature, the hydrogen-bonding network structure of IC could be destroyed, depending on the relationship between the stability of the hydrogen bonds and temperature. When the IC structure has been destroyed completely, the self-association tendency of cellulose molecules plays a key role in the formation of gels. As temperature increases, the inclusion complex becomes more unstable, and leads to the aggregation of the cellulose chains, exhibiting the gelation.

Fig. 8 shows dependence of the gelation time (t_{gel}) and equilibrium modulus (G_{gel}) of the cellulose solution on temperature. It appears that the t_{gel} value dramatically increases from 0.3 h at −5 °C to the maximum of 290 h at 0 °C, and then reduces greatly to 49 h at 10 °C. With the temperature being raised further, the gelation time slowly reduces. At above 40 °C, the cellulose solutions had been gelled prior to the measurement. The unique dependence of the gelation time on temperature in the cellulose solution further proves that the gelation is very sensitive to the temperature change. It is noted that either a heating or a cooling treatment can induce the gelation processing. However, the cellulose solution can be stored at 0–5 °C for a long time (12 days), and still remains at its stable liquid state. The storage time of the cellulose solution in NaOH/thiourea at 0–5 °C is longer than that in NaOH/urea (7 days) [30], indicating a higher stability of the cellulose solution in NaOH/thiourea than that in NaOH/urea system. In addition, the fact that the G_{gel} values decrease with the increase in temperature implies a relatively high modulus appeared at low temperature. To clarify the unique gelation behavior, we have performed Arrhenius analysis of this system. Fig. 9 shows Arrhenius temperature dependence of the viscosity (η) of 4 wt% cellulose solution. There are three straight lines with different slopes in the temperature range from −5 to 40 °C, as a result of the complex system. Arrhenius plot of the apparent viscosity of 25 wt% cellulose solution in NMMO/H_2O has exhibited two lines with different slopes,

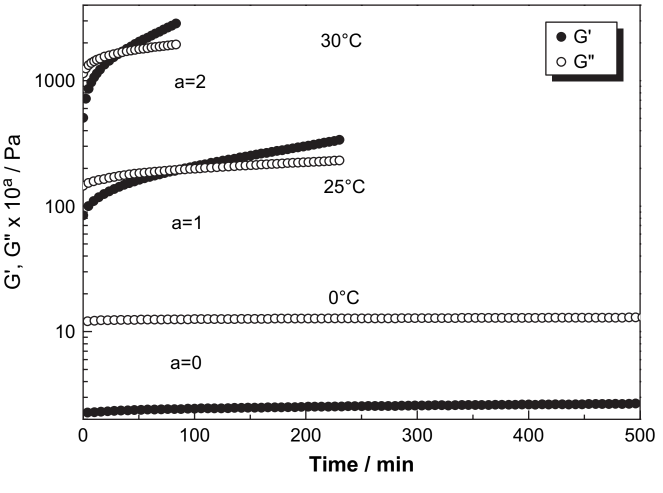

Fig. 7. Time dependence of storage modulus (G', ●) and loss modulus (G'', ○) of 5 wt% C-1 cellulose aqueous solution at different temperature and at a frequency of 1 rad/s. The data are shifted along vertical axes by 10^a with the given a value to avoid overlapping.

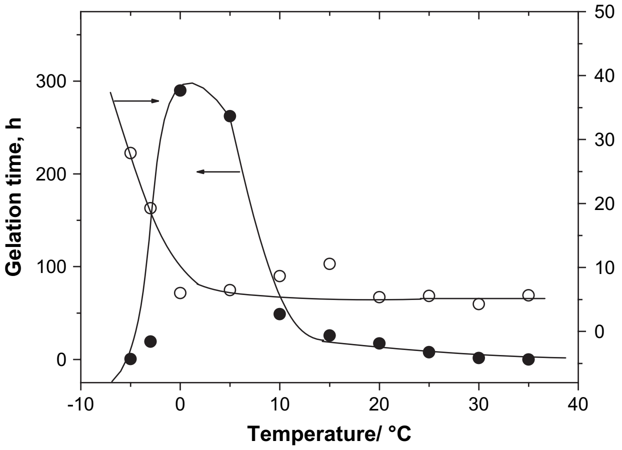

Fig. 8. Gelation time (t_{gel}) ●, and equilibrium modulus (G_{gel}) ○, as a function of temperature for 4 wt% cellulose (C-1) solution.

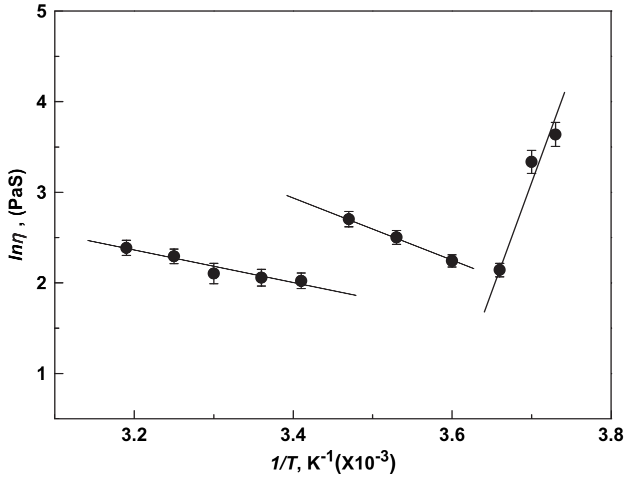

Fig. 9. Arrhenius temperature dependence of the viscosity (η) of 4 wt% cellulose solution (C-1).

indicating that the anisotropic to isotropic phase transition occurred in the temperature range from 95 to 100 °C [10]. It can be believed that the interaction between molecules, chains entanglement and phase separation in our solution have occurred at the low or high temperature. This linearity of the plots means that the temperature dependence of η follows the Arrhenius law, and apparent activation energy (E_a) can be estimated approximately from the slopes in Fig. 9. The activation energy provides valuable information on the sensitivity of the cellulose solution towards change in temperature. The lower the activation energy, the less sensitive is the material towards the temperature [31]. The calculated E_a value is 181.2 kJ/mol in the temperature range from −5 to 0 °C. The dependence of viscosity on temperature below 0 °C is a normal trend for polymer solution. However, the E_a value is higher than those of cellulose solution in NMMO [11] and 9% NaOH aqueous solution [32]. This suggests that the IC structure in the cellulose solution is at higher stable state and the relatively strong interaction between ICs exists at 0 to −5 °C. We have proven that the formation of IC hosted by thiourea and NaOH, in which cellulose chain associated with NaOH hydrates as guest was encaged, leads to good dissolution of cellulose in the aqueous solution. Moreover, the primary ICs could self-assemble to form a stable IC shaped like sphere at low temperature [27]. Thus, the interaction between the stable IC spheres strengthened with a decrease of temperature at 0 to −5 °C, leading to the enhancement of viscosity. However, negative E_a values appear in the temperature range from 0 to 40 °C and there are two lines with different viscosities. The E_a values are −29.6 and −15.7 kJ/mol, respectively, indicating an unusual rheological behavior. Usually, at relatively high temperature, the elevated temperature aids the motion of macromolecules and the expansion of solution space, so that the space among macromolecules becomes exaggerated and the fluid ability of solution increases, which leads to the decrease of viscosity. Simultaneously, as temperature rises, the IC spheres gradually disassociate to become small or unstable single ICs [27]. In this case, the disassociated ICs easily aggregate, and the aggregation increases with the elevation of the temperature, leading to the increase of viscosity. Therefore, the counteracted results form two effects, leading to the negative E_a with lower value at 0–15 °C. When temperature further rises, the IC structure had been broken partially or completely, the self-aggregation and chain entanglement of cellulose occurred as a result of the exposure of its −OH groups, leading to the formation of gel. The viscosity values in this solution at 15–40 °C drop abruptly, indicating an existence of phase separation. The whole results revealed that the cellulose solution is stable and follows the normal polymer solution rules in the temperature range from −5 to 0 °C, whereas, it becomes an unstable and/or inhomogeneous system at elevated temperature.

3.5. Irreversible sol–gel transition by heating and cooling

To clarify the sol–gel behavior of the cellulose solutions, dynamic viscoelastic measurements were carried out using the same rates of heating and cooling in the similar range of temperature by using the same rate of thermal scanning cycles. Fig. 10 shows the G' and G'' curves for 5 wt% cellulose solution under the heating and cooling processes at rates of 2 °C/min with an angular frequency of 1 rad/s. In the heating process from 25 to above 55 °C, the crossover of G' and G'' lies at 32 °C. In the region from 32 to 55 °C, G' curve is always higher than G'', showing a characteristic elastic behavior. To verify the occurrence of thermoirreversible sol–gel transition, the cooling process starting from 55 °C was conducted. The result indicates that the plateau of the G' and G'' curves formed at elevated temperature changes barely with the decrease of the temperature, confirming the thermoirreversible sol–gel transition. Therefore, the cellulose gels formed in this case possess a stable network structure containing a large amount of water. The entanglement networks could not be broken by the cooling treatment. To gain straightforward evidence, the sol–gel transition of the cellulose solution was

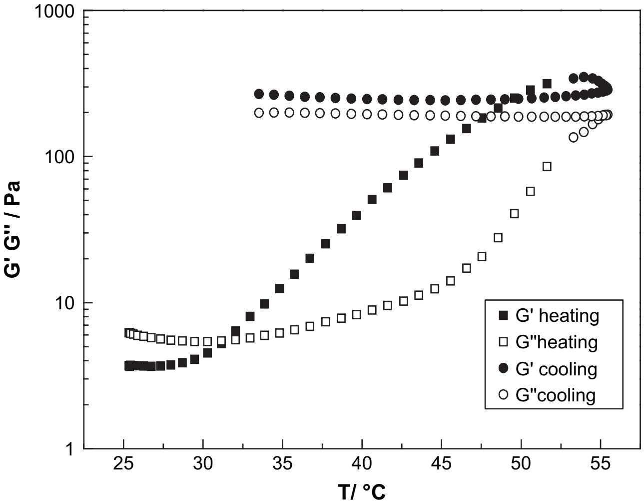

Fig. 10. Storage modulus (G') and loss modulus (G'') as a function of temperature in a heating and a cooling processes for 5 wt% cellulose solution (C-1). The heating and cooling rates were about 2 °C/min.

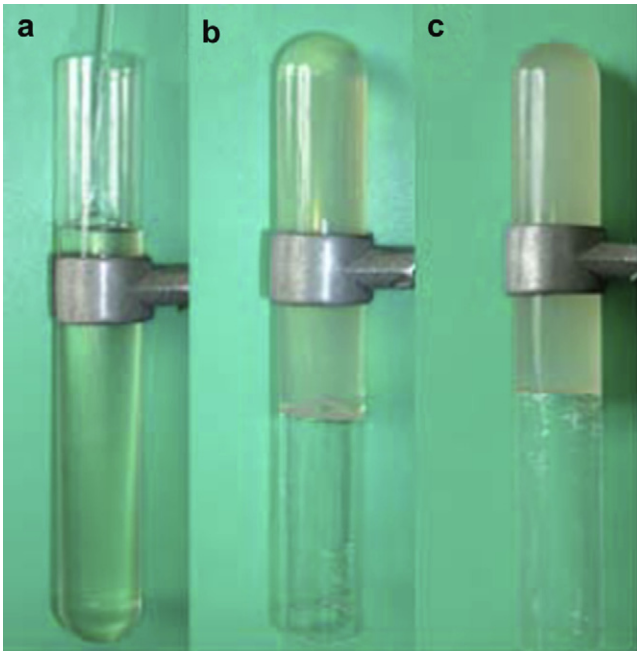

Fig. 11. Photos of 4% cellulose solution (C-1) as liquid at 25 °C within 1 h (a), as gels by heating at 45 °C (b) and as gels after complete freezing at −20 °C (c).

examined by visual observation. The photos of the cellulose solution and gels taken at 45 and −20 °C are provided in Fig. 11. The 4 wt% cellulose (C-1) solution (a) exhibits a transparent liquid at 25 °C within 1 h, whereas it becomes a gel (b) at about 45 °C for 20 min. Further more, the gel remains in its solid state (c) after being cooled down to −5 °C and then further to −20 °C after complete freezing, at which the cellulose should be able to dissolve; but actually they did not. Therefore, the cellulose gel could not turn to transparent solution after being cooled to the lower temperature, including initially dissolving temperature and freezing temperature. The sol−gel transition of the cellulose in 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution is a thermoirreversible process (by heating or cooling treatment). Interestingly, there is no considerable chemical reaction of cellulose during the gelation of cellulose solution at both high and low temperatures as shown in Fig. 1, however, the gel can not be transited again to liquid by cooling treatment like dissolution. This can be explained that when the cellulose gel formed at elevated temperature, the composite of the solvent system could be changed as a result of the reaction between NaOH and thiourea [33]. We have observed that the whole system turned yellow, which was tested to be as a result of the existence of sulfur. Therefore, the resultant solution system could not be transferred to liquid again at −5 °C.

4. Conclusions

Cellulose was rapidly dissolved in 9.5 wt% NaOH/4.5 wt% thiourea aqueous solution pre-cooled to −5 °C with the ability of obtaining a transparent cellulose solution without derivation. The results of dynamic viscoelastic measurements indicated that the sol−gel transition of the cellulose solutions occurred at either elevated concentration, elevated or reduced temperature or after prolonged time. The cellulose solution was proved to be a complex system, so the intersection of G' and G'' curves was used to determine the gel point at certain frequency. The gelation temperature of the cellulose solution having M_w of 12.0×10^4 decreased with an increase of the concentration, but it increased for the cellulose solution with a relatively low M_w. It was indicated the significant effects of the molecular weight and polymer concentration on the cellulose gelation. Interestingly, the gelation time of 4 wt% C-1 cellulose solution was shorter when at below −5 °C or above 30 °C, but it remained at stable liquid state for a long time in the temperature range from 0 to 5 °C. The sol−gel transition of the cellulose solution was very sensitive to the variation of temperature. By heating or cooling, the cellulose solution could transform into gels which were assigned to cellulose II, and the sol−gel transition was an irreversible process as a result of changing of the solvent structure. A high apparent activation energy of the cellulose solution occurred at 0 to −5 °C, suggesting the relatively stable IC structure.

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