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Dissolution and rheological behavior of deacetylated konjac glucomannan in urea aqueous solution

Shishuai Wang[a,c], Yingfei Zhan[b], Xiaofang Wu[a,c], Ting Ye[a,c], Yan Li[a,c], Ling Wang[a,c], Yijie Chen[a,c], Bin Li[a,c,*]

[a] College of Food Science and Technology, Huazhong Agricultural University, Wuhan 430070, China
[b] School of Resource and Environmental Science, Wuhan University, Wuhan, Hubei 430079, China
[c] Key Laboratory of Environment Correlative Dietology (Huazhong Agricultural University), Ministry of Education, China

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ABSTRACT

Deacetylation adversely affected the solubility of konjac glucomannan (KGM). Herein the dissolution behavior of deacetylated KGM (da-KGM) was studied in 10 wt% urea solution at various temperatures. KGM with different degrees of deacetylation (DD) could be well dissolved at −4 °C. Low temperature was conducive to the dissolution of da-KGM. The result from steady shear showed that the zero-shear viscosity decreased with the increase of DD, with the rheological model being conformed to the Cross equation. Dynamic viscoelastic properties indicated the da-KGM gel formed more easily with increasing concentration, or decreasing temperature and DD. Temperature sweep revealed that gel process could be divided into two stages. The first stage was that both storage modulus (G') and loss modulus (G'') fell until the temperature reached 90 °C. The second stage was that G' and G'' increased abruptly, presenting the transition from sol to gel.

1. Introduction

Konjac Glucomannan (KGM) was a neutral polysaccharide derived from the tuber of *Amorphophallus konjac* and native to Southeast Asia. It was composed of β-(1,4)-linked D-mannose and D-glucose residues in a molar ratio of 1.6:1 (Cescutti, Campa, Delben, & Rizzo, 2002). Acetyl groups attached to the saccharide units were scattered randomly along the molecule, with an occurrence of approximately 1 per 19 sugar residues at C-6 position (Katsuraya et al., 2003). Acetyl groups could control the water-solubility of KGM fractions (Hwang & Kokini, 1991). The acetylated KGM fractions could be thoroughly hydrated to form homogeneous aqueous dispersions in relatively shorter time than native KGM. The hydration time was gradually shortened with an increasing degree of acetylation (Gao & Nishinari, 2004b). Meanwhile, the removal of acetyl groups led to poor water solubility of KGM (Du, Li, Chen, & Li, 2012). It was very difficult to dissolve deacetylated KGM (da-KGM) in aqueous solutions due to considerable inter- and/or intra-molecular hydrogen bonds.

Up to now, da-KGM has been proved to be a good fat analog (Herranz, Tovar, Solo-de-Zaldivar, & Javier Borderias, 2012). Interestingly, deacetylation and freezing could significantly improve the gel strength and even resulted in fibrosis (Li & Sun, 2002). Thus da-KGM, as a material, could have numerous applications in frozen processing, such as fiber modification, dissolution, and regeneration. However, dissolution of da-KGM solutions has been rarely reported. Early in 1973 Maekaji found the peptization of KGM gel was easier to be carried out at lower temperature (Maekaji, 1973). Perols embedded enzyme into konjac gel and made the enzyme released at 4 °C (Perols, Piffaut, Scher, Ramet, & Poncelet, 1997). Recently our group pointed out that da-KGM could be partly dissolved in an ice–water (0 °C) by vigorous stirring (Du et al., 2012). They all showed that the temperature had some effect on the solubility of KGM. But the dissolution mechanism of da-KGM still needed further investigation.

With respect to the dissolution of insoluble cellulose, researchers found urea served as the hydrogen bonds donor and receptor to prevent the approach toward each other of the molecules, leading to a good dispersion of cellulose in the solution (Cai & Zhang, 2006; Jin, Zha, & Gu, 2007). The addition of urea increased the dissolved fraction of cellulose in the solvent by 1.5–2.5 times (Isobe et al., 2013). Cai discovered that the addition of urea dramatically enhances the solubility of cellulose in aqueous alkali (Cai & Zhang, 2005). This solvent could dissolve native

* Corresponding author at: College of Food Science and Technology, Huazhong Agricultural University, Wuhan 430070, China. Tel.: +86 27 87286847; fax: +86 27 87288636.
E-mail address: libinfood@mail.hzau.edu.cn (B. Li).

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cellulose of high degree of polymerization without pretreatment (Cai, Kimura, Wada, Kuga, & Zhang, 2008).

So whether or not urea was conducive to the dissolution of da-KGM? For the first time, we presented KGM samples with different degree of deacetylation (DD) in 10 wt% urea solution at various temperatures to explore the solubility. Meanwhile, the rheological properties of da-KGM solution were also studied as functions of shear rate, angular frequency and temperature. We hope to gain some meaningful information for the purpose of fundamental research and industrial application of da-KGM.

2. Materials and methods

2.1. Materials

The native KGM sample was purchased from Hubei Jian Shi Nong Tai Industry Co., Ltd. (Hubei, China). All chemicals were of analytical grade reagents (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and were used without further purification.

2.2. Da-KGM preparation

KGM with different degree of deacetylation (DD) were prepared according to the previous method (Chen, Li, & Li, 2011). 30.00 g of purified KGM powder with 50 mL of 75% ethanol was mixed in a 250 mL conical flask. The mixed suspension was swelled in a constant thermostat oscillator at 40 °C for 30 min at 150 rpm/min. After that, the suspension with Na_2CO_3 solution was reacted at 40 °C for 24 h. After deacetylation, each sample was washed by 50%, 75%, 95% ethanol for three times respectively to remove excess alkali before dealt with absolute ethanol. The excess of ethanol was evaporated in fuming cupboard followed by vacuum drying for 6 h at 40 °C and the powdered da-KGM was obtained. KGM with different degrees of deacetylation were obtained by changing volume of Na_2CO_3, which were coded as D1, D2, D3, D4, and D5, with the corresponding degree of deacetylation being 22%, 44%, 54%, 76% and 100%, respectively (Tanghe, Genung, & Mench, 1963).

2.3. Solubility test

10 wt% urea aqueous solutions were prepared to a desired temperature. A certain weight of da-KGM was added immediately into it with stirring vigorously for 1 h. The dispersed solution was then centrifuged at 10,000 rpm at 4 °C for 20 min. The remaining undissolved fractions were washed using distilled water, and then dried at 105 °C to a constant weight in a vacuum oven. Thus, the solubility of da-KGM (Sa) in urea aqueous solution was calculated by $Sa = [(W_0 - W_r)/W_0] \times 100\%$, where W_0 was the weight of original da-KGM, and W_r was the weight of the undissolved fractions.

2.4. Characterization

Optical microscope (LEICA Germany) was used to compare the morphological changes and the solubility of da-KGM in 10 wt% urea aqueous solution. The da-KGM solutions were pressed between two glass slides directly after being prepared, and then sealed by paraffin to be observed and photographed.

The dynamic rheology measurement was carried out on a controlled-stress Bohlin AR2000ex rheometer (Bohlin Instruments Ltd., Gloucestershire, UK). The measurements were carried out using parallel-plate geometry (40 mm in diameter and 1 mm gap). A thin film of vaseline oil was gently applied to the edge of each exposed sample in order to prevent moisture loss. Rheological parameters such as storage modulus G' and loss modulus G'' were measured as functions of shear rate, angular frequency and temperature. For each measurement, a fresh da-KGM solution was prepared, and then degassed da-KGM solution was poured into the parallel plate instrument, which had been kept at each measurement temperature without preshearing or oscillating. The values of the strain amplitude were checked to ensure all measurements were set as 10%, which was within a linear viscoelastic regime. Steady shear rate measurements were performed using parallel-plate geometry at 25 °C by varying the shear rate from 0.001 to 100 s^{-1}. Frequency sweep was conducted from 0.1 to 200 rad/s. Temperature was kept within ±0.5 °C over an extended time. The dynamic temperature sweep measurements were conducted from 20 to 100 °C at an angular frequency of 1 rad/s and with the heating rate of 2 °C/min.

3. Results and discussion

3.1. Influence of temperature on dissolution

To clarify the change of solubility, the dependence of *Sa* values on temperature in urea was shown in Fig. 1. At the temperature decreasing from 40 °C to 15 °C, *Sa* value of each sample maintained constant. With the increase of DD, *Sa* fell from about 70% to 50%, indicating that sample D5 was the most difficult to be dissolved. However, as the temperature continued to decrease from 15 °C to −4 °C, *Sa* values of samples increased rapidly until all the samples were able to be dissolved completely. It was worth noting that ice would form in the solvent below −4 °C (freezing point), which was a critical temperature (T_c) of the solution. Although the solvent was a liquid-solid two-phase system below T_c, da-KGM could also be dissolved completely in the solvent system.

The dissolution state of D5 in 10 wt% urea aqueous solution at different temperatures for 1 h was showed in Fig. 2. When the temperature changed from 25 °C to 0 °C, the swelling degree of the da-KGM increased. Transparent da-KGM solution was obtained at −4 °C, indicating the da-KGM was dissolved completely. It could be concluded that −4 °C was the optimum solution temperature.

The relationship between Sa value and temperature could be described by the Arrhenius equation as $\ln Sa = \ln A - Ea/RT$, where *Ea* was the apparent activation energy of dissolution (kJ/mol), *R* was the molar gas constant (0.008314 kJ/molK^{-1}), *T* was the absolute temperature (K), and *A* was a preexponential factor (Su & Puls, 1999). The *Ea* could be obtained from the slope of a plot of $\ln Sa$ vs. $1/T$ using linear least-squares analysis (Fig. 3). Interestingly, the calculated *Ea* value was −21.2 kJ/mol in the range from 10 °C to −4 °C as a result of the dissolution at low temperature.

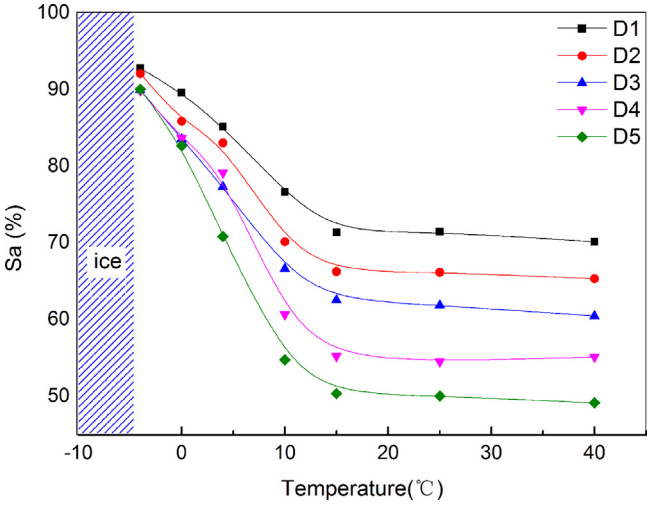

Fig. 1. Dependence of Sa value of da-KGM on temperatures from −10 °C to 40 °C at different DD.

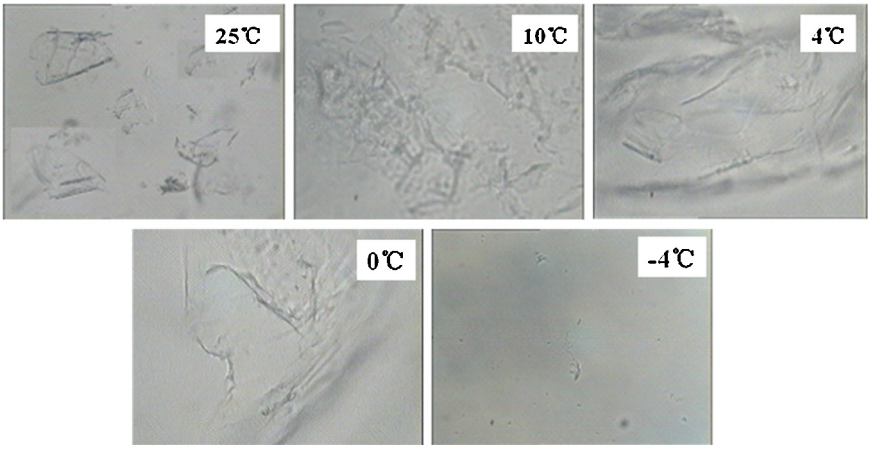

Fig. 2. Optical microscope images of 0.5 wt% D5 dissolved in 10 wt% urea aqueous solution at different temperatures for 1 h.

The negative apparent activation energy in the system suggested that the da-KGM solution state had a lower enthalpy than the solid da-KGM, and the dissolution of da-KGM in aqueous urea solution precooled to low temperature could be described as an entropy-driven process. Usually, the increase of temperature could promote the dissolution of normal polymers, because of the solvation being enhanced by heat movement. However, the solubility of a little polymer increased when the temperature decreased like cellulose and chitin (Qin, Lu, Cai, & Zhang, 2013; Xie, Liu, & Chen, 2007). When solid cellulose was immersed in urea aqueous solution pre-cooled to −12 °C, the hydrogen-bonded network structure between the cellulose macromolecules and small molecules in the solvent was created rapidly to form an inclusion complex, bringing cellulose into the aqueous solution (Cai et al., 2007).

3.2. Steady shear

Fig. 4 showed the steady shear flow curves of 0.5 wt% da-KGM in 10 wt% urea solutions with different DD. The viscosities of all samples fell with the growth of the shear rate. In the da-KGM system, the evolving interactions between da-KGM and urea had an influence on the conformation of da-KGM chains, which played a crucial role in the flow behavior of the system. The solvent could coordinate with the hydroxyl groups of da-KGM in two modes. One was coordination with da-KGM inter-chain and the other was with da-KGM

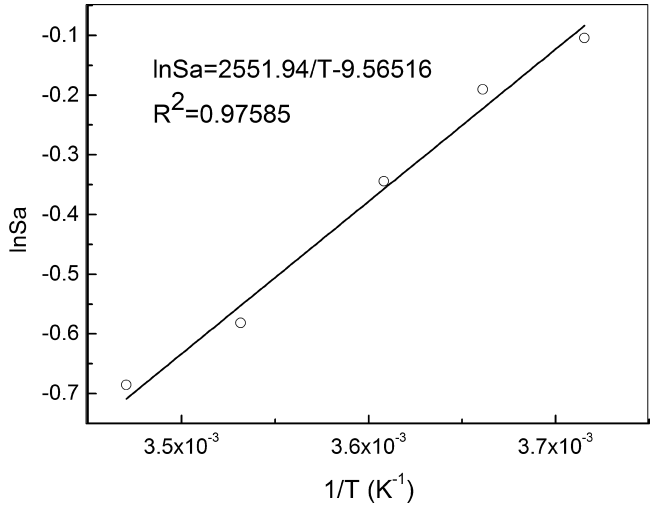

Fig. 3. Arrhenius plots of temperature dependence of *Sa* value for 0.5 wt% D5 in 10 wt% urea aqueous solution in the range from 10 °C to −4 °C.

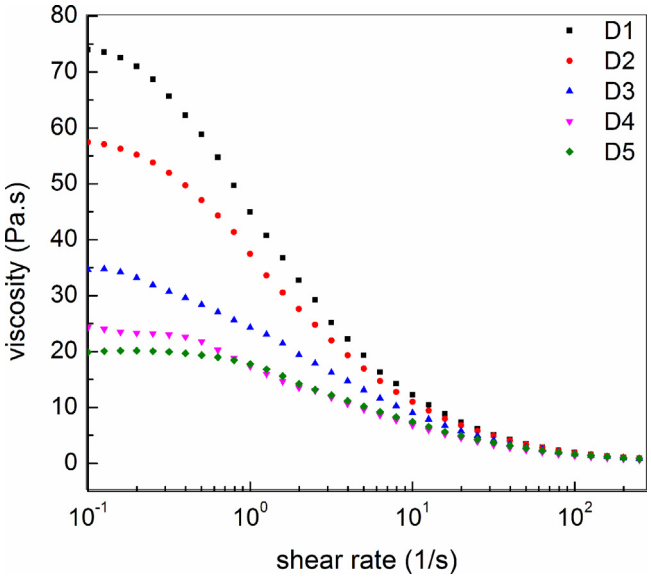

Fig. 4. Steady shear curves of 0.5 wt% da-KGM in 10 wt% urea aqueous solution of different DD.

intra-chain. At low shear rates, long-range interactions between da-KGM and the solvent played a key role in the conformational changes of da-KGM molecules. However, at high shear rates, the timescale of the applied deformation was less than the relaxation time of the chain and the responses from the small fragments of da-KGM chains became prominent.

Here, the Cross equation was the best model to describe the shear-thinning behavior of da-KGM solutions as $\eta = \eta_\infty + \eta_0 - \eta_\infty / 1 + (k\gamma)^m$, where η was the apparent viscosity (Pa s), η_0 and η_∞ were the zero-shear rate and the infinite-shear rate viscosity (Pa s), respectively, k was the time constant (s), γ was the shear rate (s^{-1}), and m was the flow index (dimensionless) (Cross, 1965; Moser, Cornelio, & Nicoletti Telis, 2013). Table 1 showed the

Table 1
Parameters of da-KGM solutions estimated by Cross equation of different DD.

Sample	η_0 (Pa s)	η_∞ (Pa s)	k (s)	m	RMS
D1	84.30	5.511E−8	0.8067	0.8570	5.158
D2	76.13	1.686E−7	0.7771	0.7980	9.461
D3	65.69	6.278E−7	0.7038	0.8217	4.754
D4	36.48	1.777E−7	0.3971	0.8222	4.997
D5	22.11	0.03055	0.2325	0.8112	7.462

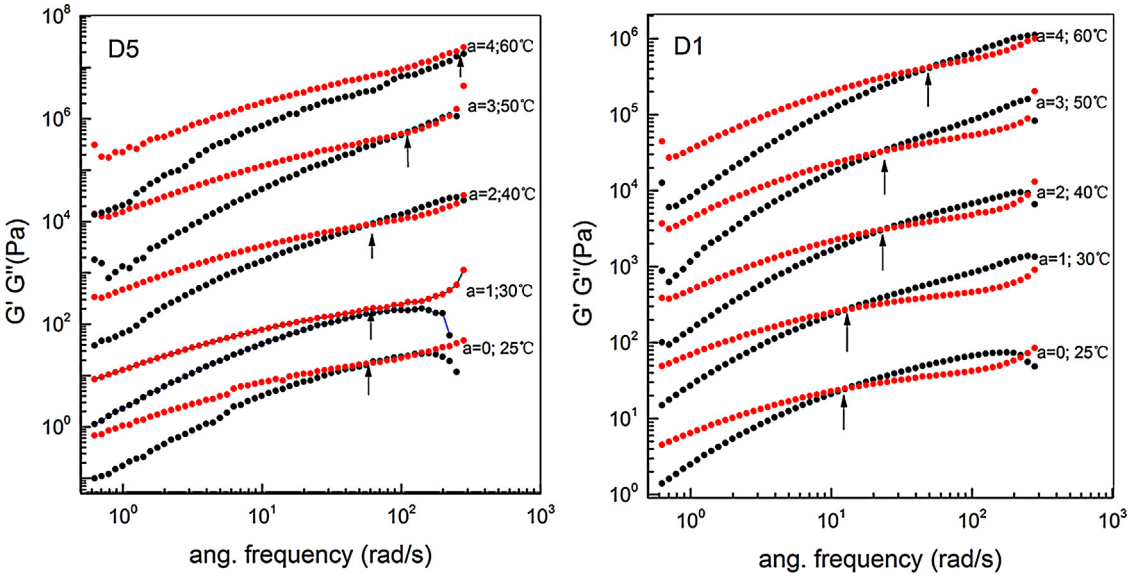

Fig. 5. Storage modulus G' and loss modulus G'' as a function of angular frequency for a 0.5 wt% da-KGM solution at various temperatures. The data were shifted along the vertical axis by 10^a with the given a value to avoid overlapping.

rheological parameters of da-KGM solutions of different DD. The flow index (m) was all over zero and the Cross model fitted the flow curves well. Smaller values of Root Mean Square (RMS) could make better fit (Telis, Lourençon, Gabas, & Telis-Romero, 2006). It could be illustrated that da-KGM solutions exhibited shear-shining behavior. It was in accordance with the results about starch solutions, which owned m values of 0.759 and 0.822 (Shi, Li, Wang, & Adhikari, 2012). Besides, with the increase of DD, the viscosity values at zero-shear rate (η_0) decreased from 84.30 Pa s to 22.11 Pa s, and the time constant (k) changed from 0.8067 s to 0.2325 s. It could be that in the preparation of da-KGM, the alkali led to the degradation of molecular weight. In addition, KGM with greater degree of deacetylation had smaller entanglement force between molecular, and also caused the viscosity at low shear rates to decrease.

3.3. Dynamic viscoelastic properties

Fig. 5 showed storage modulus G' and loss modulus G'' as a function of angular frequency for 0.5 wt% da-KGM solution at various temperatures. G' was associated with the elastic, solid-like behavior of polymers. G'' described the liquid-like response of polymers under the small deformations (Jimenez-Colmenero, Cofrades, Herrero, Solas, & Ruiz-Capillas, 2013). As could be seen that G'' values were larger than G' at lower frequencies, suggesting liquid-like behavior. Both G' and G'' increased with the frequency and showed a crossover, and G'' became smaller than G' at higher frequencies. It indicated the occurrence of the elastic behavior and the formation of the gel network, which involved the aggregation and association of molecular chains. The associated regions were known as junction zones and formed with two or more chains (Rees, 1969).

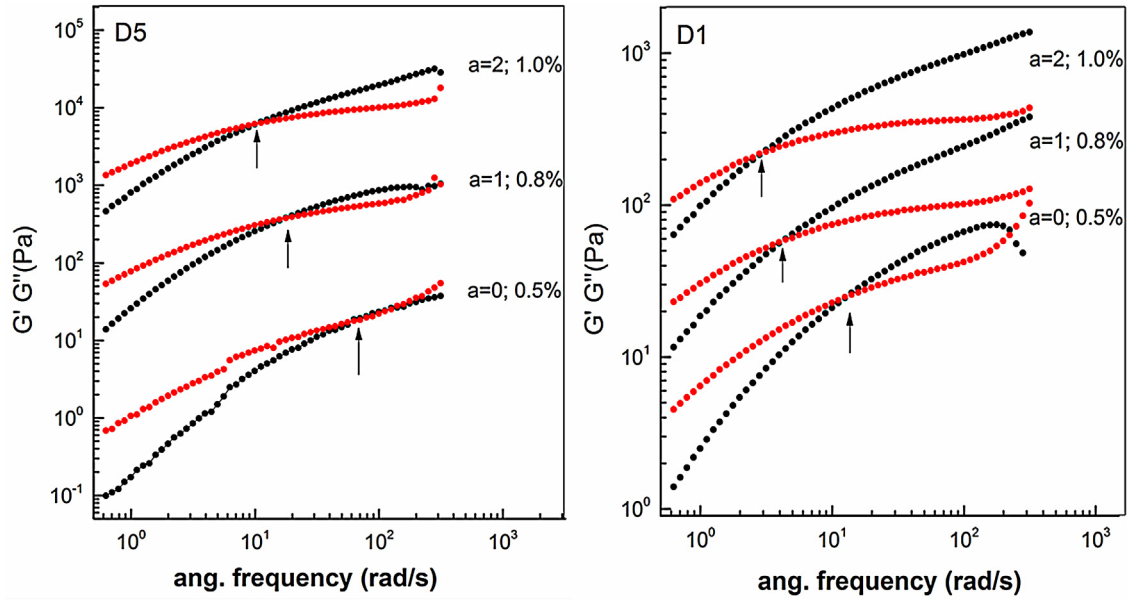

Fig. 6. Storage modulus G' and loss modulus G'' as a function of angular frequency for da-KGM solution at various concentrations at 25 °C. The data were shifted along the vertical axis by 10^a with the given a value to avoid overlapping.

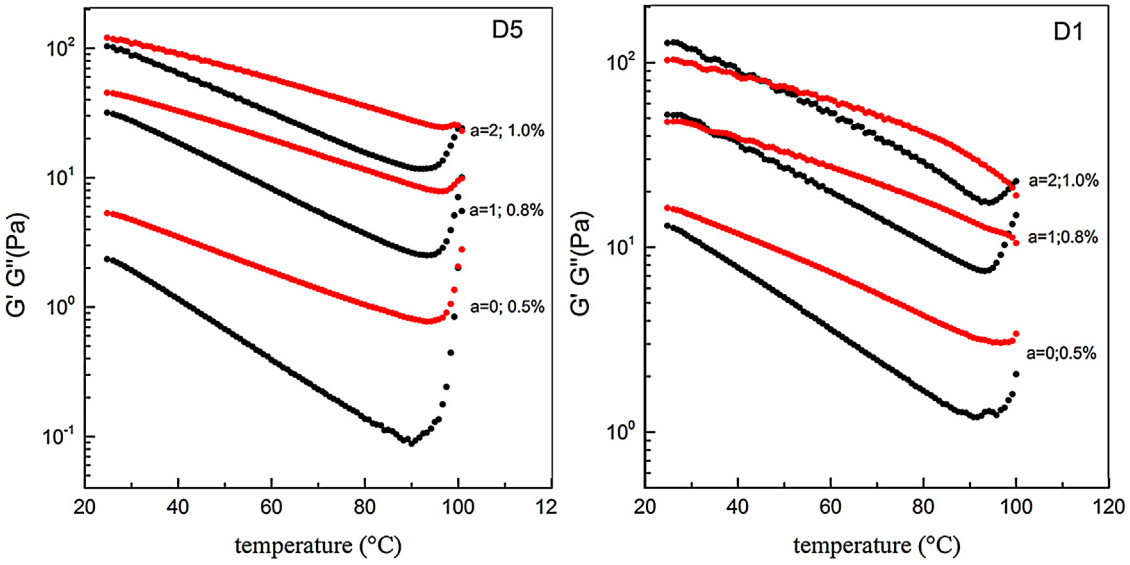

Fig. 7. Storage modulus G' and loss modulus G'' as a function of temperature for da-KGM solution at various concentrations. The data were shifted along the vertical axis by 10^a with the given a value to avoid overlapping.

In addition, with the increase of temperature, the crossover point shifted to a much higher frequency. Because the strength of hydrogen bonds depended on temperature, and the formation of the gel was also related to temperature (Jimenez-Colmenero et al., 2012). Thus, the formation and destruction of the hydrogen bonds were relevant to temperature and other environmental conditions. When the temperature was raised, the hydrogen bond strength between da-KGM and urea became weakened, whereas the intra- and intermolecular hydrogen bonds of da-KGM tended to increase as a result of its strong self-association tendency. It finally induced the formation of gel. A similar phenomenon was observed on the cellulose in NaOH aqueous solution (Guo, Zhou, & Zhang, 2011). Furthermore, at a fixed temperature, D5 had a higher crossover frequency than D1, which suggested the gelation behavior of the KGM dispersions showed strong dependence on the amount of acetyl groups (Huang, Takahashi, Kobayashi, Kawase, & Nishinari, 2002).

The effect of concentration on the rheological properties of the da-KGM system was explored in Fig. 6. It was found that G' was smaller at low frequency, but larger at high frequency than G''. During the long period of oscillation at low frequency, the entanglements of the molecular chains were easy to disentangle, and it behaved as a viscous fluid. But at high frequency, the molecular chains were able to resist the disentanglement because of the short period of oscillation, and it exhibited an elastic solid behavior (Luo, He, & Lin, 2013). At 0.5 wt%, 0.8 wt%, and 1.0 wt%, the crossover frequency of sample D5 occurred at 62.83 rad/s, 17.71 rad/s, and 11.17 rad/s, respectively. But the corresponding values of D1 appeared at 14.07 rad/s, 4.45 rad/s, and 3.15 rad/s. As the concentration of da-KGM rose, the crossover point moved to a much lower frequency. Higher the concentration made faster gelation, which implied the gelation process related closely to an increasing chance for entanglement of macromolecular chains (Cai & Zhang, 2006). During the course, a mass of entanglements formed as reflected in the increasing modulus. We also found at the same concentration, D1 had a lower crossover frequency than D5. The lower crossover frequency represented the stronger effects of entanglement and hydrogen bonding (Gao & Nishinari, 2004a).

3.4. Gelation temperature

G' and G'' as a function of temperature for da-KGM solution at various concentrations were explored in Fig. 7. As could be seen D5 and D1 displayed a similar tendency. With the increasing temperature, G' and G'' reduced gradually, which was due to the destruction of hydrogen bonds between molecular chains (Luo et al., 2013). When the temperature reached about 90 °C, the values increased abruptly, presenting the transition from sol to gel. From D1 at concentrations of 0.8 wt% and 1.0 wt%, G' was higher than G'' at lower temperature, showing the solid behavior. The reason was that at high concentrations the molecules were closer, leading to the formation of temporary network structure. However, D5 at all concentrations did not show a solid behavior at low temperature. Because the greater DD, the more obvious the self-curling of molecular (Du et al., 2012), so it was not easy to be close between intermolecular, and no gel structure was formed at low temperature.

4. Conclusions

Deacetylation adversely affected the solubility of KGM. KGM with greater DD was more difficult to dissolve. However, insoluble da-KGM could be well dissolved in 10 wt% urea solution at −4 °C, with the dissolution behavior following the Arrhenius equation. Temperature had an influence on the dissolution, and low temperature could promote the dissolution of da-KGM. Results from steady shear showed viscosities of da-KGM fell with the growth of the shear rate. Besides, with the increase of DD, the zero-shear viscosity was lower, and the rheological model conformed to the Cross equation. So decreasing the viscosity of da-KGM could provide a wide controlled range of viscosity, because in some occasions high viscosity was undesirable. Dynamic viscelastic measurements revealed a unique gelation of da-KGM solution, which was relative to temperature, concentration and DD. The gelling of da-KGM was formed more easily with increasing concentration as well as falling temperature and DD. The gel process of da-KGM could be divided into two stages. The first stage was that both G' and G'' reduced until the temperature reached about 90 °C. It was because the destruction of hydrogen bonds between molecular chains. The second stage was that G' and G'' increased abruptly, presenting the transition from sol to gel. As the DD increased, the gel temperature slightly elevated.

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