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Gelation of konjac glucomannan crosslinked by organic borate

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Abstract

A series of thermoreversible konjac glucomannan gels crosslinked by organic borate were prepared. The gel network was formed through the crosslinking reaction between borate ions dissociated from organic borate and the *cis*-diol hydroxyl groups on the mannose units of polysaccharide chains. The rheological properties of the complex gels were studied by dynamic viscoelastic measurement. The gelation kinetics of the gels were studied and the critical gelation points of the gels were exactly determined by the Winter–Chambon criterion. The effects of temperature and composite ratio on the shear storage modulus (G'), the loss modulus (G''), and the sol-gel transition points were investigated. The critical gel-sol temperatures of the complex gels were successfully elucidated by Winter–Chambon criterion. The effect of crosslinking density on the critical gelation temperature and the elasticity of the gels were discussed.

Keywords: Konjac glucomannan; Organic borate; Gelation; Rheological properties

1. Introduction

Konjac glucomannan (KGM) has favorable water-preserving, gelling, thickening, film-forming, and biodegradable properties. KGM is a non-ionic polysaccharide found in tubers of the *Amorphophallus konjac*, which mainly grows in Asia, such as China and Japan. Considerable effort has been devoted to the study of KGM in China, Japan, and Europe for its wide application. KGM is a high molecular weight water-soluble polysaccharide consisting of β-1,4-linked glucose and mannose units, and the glucose/mannose ratio has been reported to be around 1:1.6 (Kato & Matsuda, 1969). There are some branches linked to the main chain of KGM, occurring approximately one in 11 residues, linked at the C-3 positions of mannose and typically 11–16 residues in length (Katsuraya et al., 2003). KGM possesses 5–10% acetyl-substituted residues which are proved to make a contribution to the water solubility to KGM (Dea & Morrison, 1975).

Gels, are as an intermediate state between liquid and solid states, the liquid-like properties originate from the fact that the major constituent (>80%) is water or other solvents, and the solid-like behaviors characterized by a finite modulus are due to the network formed (Nishinari, Zhang, & Ikeda, 2000). Gels are very interesting materials, as they are used widely many industries including the oil industry where they are employed as fracturing fluids (Chatterji & Borchardt, 1981; Grisel & Muller, 1998). Of necessity, fracturing fluids are prepared on the surface and pumped through tubing in the wellbore to the hydrocarbon-bearing subterranean formation. While high viscosity is a desirable characteristic of a fluid within the formation in order to efficiently transfer fracturing pressures to the rock as well as to reduce fluid leak-off, large amounts of power are needed to pump such high viscosity fluids through the well tubing to the subterranean formation or the earth's surface (Goel, Shan, Yuan, & O'Rear, 2001). In order to save power, several methods were adopted to reduce the friction pressure such as delaying the crosslinking of the polymers. This allows the pumping of a low viscosity fluid to the subterranean formation before crosslinking, and the high viscosity would be

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achieved under the surface to accomplish the fracturing mission. Some galactomannan gums such as guar and hydroxypropyl guar may be used with crosslinking agents as fracturing fluids.

Complex gels prepared from polymer and ions have been studied for several decades. Poly(vinyl alcohol) (PVA) is one of the most typical polymers that can be crosslinked by various ions such as borate ions because of the abundant *cis*-diol groups on the PVA chains, and a great deal of research about the PVA–borate complex have been reported (Koike, Nemoto, Inoue, & Osaki, 1995; Ochiai, Fujino, Tadokoro, & Murakami, 1982; Schultz & Myers, 1969; Shibayama, Yoshizawa, Kurokawa, Fujiwara, & Nomura, 1988). A large number of other metallic elements can be used as crosslinking agents, such as chromium, (Allain & Salome, 1987) titanium, (Ahad, 1974) zirconium, antimony (Pezron, Ricard, & Leibler, 1990). Some water-soluble polysaccharides which have *cis*-diol units can also form complex gels in the presence of crosslinking agents. Rheological studies of guar galactomannan/borate complex gels (Tayal, Pai, & Khan, 1999) and schizophyllan/borate complex gels (Grisel & Muller, 1998) have been investigated. The crosslinking reaction of borate with polysaccharide was between the *cis*-diol units in the polysaccharide molecular chains and the free borate ions, resulting in a so-called monodiol and didiol complexation. ^{11}B NMR spectroscopic studies (Pezron, Leibler, & Lafuma, 1989; Pezron, Leibler, Ricard, Lafuma, & Audebert, 1989) on dilute complexation mixtures of borate ion with PVA, guar, or model polyol compounds have been utilized to give further insight into the complexation mechanism by obtaining the values of complexation equilibrium constants and the complexation enthalpy for various measuring conditions.

In our previous work, the rheology of KGM/borate gels was studied and the crosslinking reaction between the KGM chains and the borate ions occured immediately when mixing glucomannan solutions with borate, so the sol-gel transition points can not be observed (Gao, Nishinari, & Guo, 2007). In this work, the rheology of KGM/organic borate gels was investigated. We focused on understanding the gelation kinetics and the rheological properties of the KGM/organic borate system using dynamic viscosity measurements. The sol-gel transition points of the complex gels with different composite ratios were elucidated based on the results from rheological measurements. The effect of KGM concentration, organic borate concentration, and temperature on the sol-gel transition time and the rheological properties were investigated. The mechanism of delayed crosslinking of KGM/organic borate complex systems was discussed.

2. Experimental

2.1. Materials

The KGM sample was purchased from Hubei Meili Hi-tech Industrial Co., Ltd., China. The organic borate was purchased from Daqing Hualongxiang Fine Chemical Plant Ltd., China. The density was 1.24 g/cm^3. The cadmium oxide (CdO) was an analytical reagent and purchased from Shanghai Tingxin Chemical Industrial Regent Ltd., China.

2.2. Viscosity measurements

About 29 wt% of aqueous solution of ethylenediamine was saturated with cadmium oxide (CdO) in an ice-water bath under vigorous stirring and kept below 5 °C for 2 days, and then the supernatant was filtered the supernatant through a G4 glass filter and refrigerated until using. The cadmium content in cadoxen was ca. 1.5 wt%. The KGM sample solutions were prepared by mixing KGM powder with required amount of cadoxen and stirred to make it dissolved. The intrinsic viscosity measurements of the solutions were carried out by using an Ubbelohde-type viscometer (Ningbo Tianheng Instrument Co. Ltd., China) at 25 ± 0.05 °C.

Extrapolation to infinite dilution was made using both Huggins and Kraemer plots from which the intrinsic viscosity $[\eta]$ of KGM was calculated ($[\eta] = 592$ cm^3/g). The flow time of the cadoxen solvent was 195 s. The viscosity-average molecular weights (M_v) of the KGM samples were calculated according to the Mark–Houwink equation (Kohyama, Iida, & Nishinari, 1993) $[\eta] = (3.55 \times 10^{-2}) M_v^{0.69}$, and M_v was calculated to be about 1.32×10^6.

2.3. Preparation of KGM solutions

Powders of KGM samples were dispersed in distilled water by magnetic stirring at room temperature for 1 h and then maintained at 80 °C for 1 h, then cooled to room temperature and stored for 1 day. A series of KGM solutions with different concentrations were prepared.

By using a microsyringe, the required value of organic borate solution was added into 4 g of KGM solution, and then these two solutions were thoroughly mixed by manually stirring using a teflon muddler for about 10 s to obtain KGM/organic borate complex. In this study, the KGM concentrations (C_k) were adjusted to be 4.0, 6.0, 9.0, 12.0, 15.0 g/L, respectively. The concentrations of organic borate (C_{ob}) were adjusted to be 0.6, 0.9, 1.2, 1.6, 2.0 wt%, respectively. Once the KGM/organic borate complex was prepared, it was immediately used to do the following tests.

2.4. Rheological measurements

Dynamic viscosity measurements were carried out using a rheometer (TA instruments Rheology Division, AR 2000, Great Britain) with a parallel plate geometry (40 mm in diameter and 1.5 mm in gap). The strain in all measurements of the present work was set as 1%, which is predetermined to be within a linear viscoelastic regime for the samples. The KGM/organic borate complex solution was poured onto the plate of the instrument, which had been kept at each measurement temperature. The gelation kinetics was studied at constant temperature of 25 °C by using a time sweep at various frequencies. To prevent dehydration during rheological measurements, a thin layer of low viscosity mineral oil was added on the top of the exposed surface of the measured solution. The dynamic temperature sweep measurements were conducted from 95 °C to 25 °C at a cooling rate of 1.5 °C/min, and the measuring frequency and strain are 1 rad/s and 0.5%, respectively.

3. Results and discussion

3.1. Sol-gel transition points

The sol-gel transition is an important physical phenomenon for hydrocolloids with many applications in foods, cosmetics products, petroleum exploitation, and so on (Nishinari & Takahashi, 2003). Viscoelastic properties of concentrated or semidilute polymer solutions are well described by two parameters: the dynamic storage modulus (G'), which represents the elasticity of the network, and the loss modulus (G''), which accounts for the local friction of the polymer chain (Doi, 1980; Ferry, 1980, chap. 4, p. 80).

Fig. 1 showed the time dependence of storage modulus (G') and loss modulus (G'') for the KGM solution (9.0 g/L) in the presence of organic borate (0.6 wt%) at different frequencies and at 25 °C. G' and G'' increased with time and achieved a steadily increased plateau after a period of sharp increase. Initially, the intersection of G' and G'' ($G' = G''$) was observed at the frequency lower than 10.0 rad/s. However, the time of intersection at different frequencies was not the same and shifted to shorter times with the increase of frequency, indicating that the time of intersection is a function of frequency (Huang, Takahashi, Kobayashi, Kawase, & Nishinari, 2002). After the intersection time, G' increased sharply and that dominated the gel response over most time of the sweep, showing that the gel was more elastic in evidence. At the same time, G'' was almost independent of time.

Chambon and Winter (1985) proposed a criterion by which the sol-gel transition can be judged from mechanical spectra for chemical gels, where the critical gelation point corresponding to the is defined as the point at which

$$G'(\omega) \sim G''(\omega) \sim \omega^n, \quad 0 < n < 1 \tag{1}$$

and

$$\tan\delta = G''/G' = \tan(n\pi/2) \tag{2}$$

both hold, where n is the relaxation exponent. A system with n approaching 1 is defined as a purely viscous gel, whereas n approaching to 0 indicates a purely elastic gel (Koike, Takada, & Nemoto, 1998). This criterion has been applied to describe gelation well especially for chemical gelation (Chambon & Winter, 1985; Hellio-Serughetti & Djabourov, 2006; Winter & Mours, 1997). It has also been proved that this criterion can be applied to some synthetic or natural physical gels including poly(vinyl chloride), Te Nijenhuis and Winter (1989) xanthan, Rodd, Dunstan, Ross-Murphy, and Boger (2001) and carrageenan Hossain, Nemoto, and Nishinari (1997).

Fig. 2 showed the time dependence of loss tangent, tan δ, of the KGM aqueous solution ($C_k = 9.0$ g/L) at different frequencies and at 25 °C. The C_{ob} in the solution was 0.6 wt%. The sol-gel transition of the aqueous solution was monitored by the change of tan δ with time. The critical gelation time (t_{cr}) was determined to be 495 s, and n was calculated to be 0.31. From the frequency dependence of the aqueous dispersion at various times at 25 °C as shown in Fig. 3, both G' and G'' became proportional to ω^n at $t_{cr} = 495$ s, where $n = 0.31$ for the two moduli. These results agreed with the formulas (1) and (2) simultaneously.

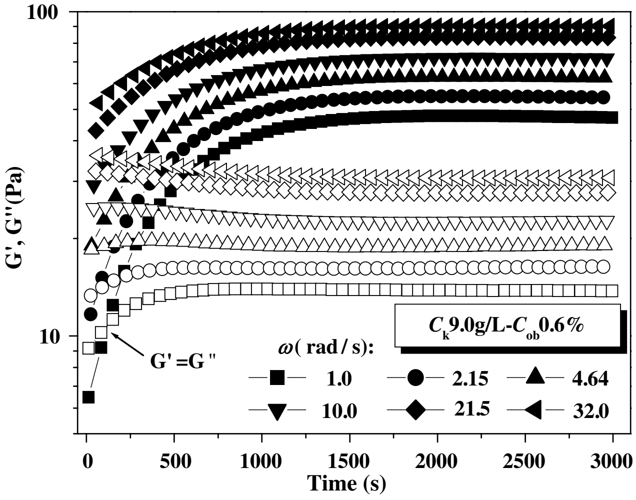

Fig. 1. Time dependence of G' (solid symbols) and G'' (open symbols) of KGM aqueous solution (the concentration of KGM, C_k, was 9.0 g/L) at different frequencies and at 25 °C. The concentration of organic borate (C_{ob}) in the solution was 0.6 wt%.

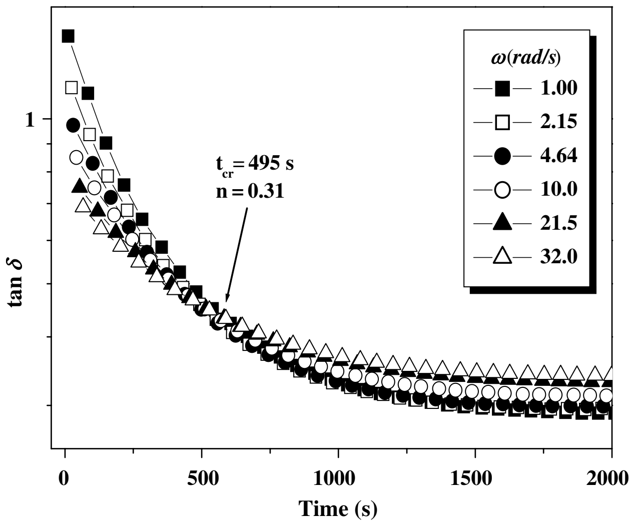

Fig. 2. Time dependence of loss tangent of KGM aqueous (C_k = 9.0 g/L) solution at different frequencies and at 25 °C. The C_{ob} was 0.6 wt%.

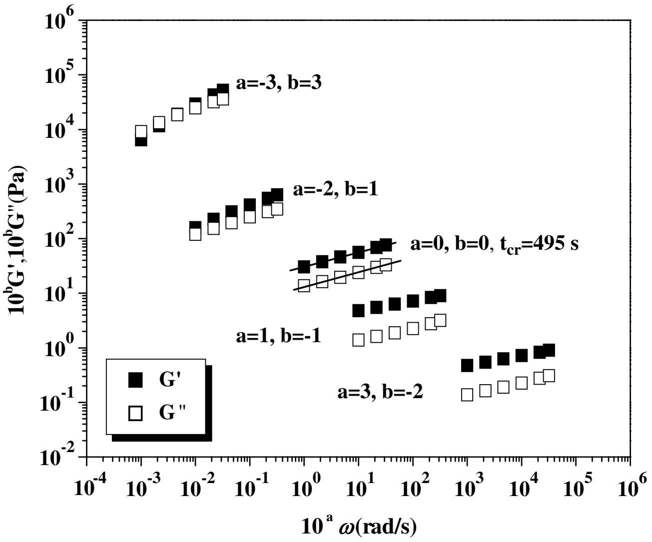

Fig. 3. Frequency dependence of G' and G'' of 9.0 g/L KGM aqueous solution at various time at 25 °C. The data are shifted along horizontal and vertical axes by 10^a and 10^b, respectively, to avoid overlapping. The C_{ob} was 0.6 wt%.

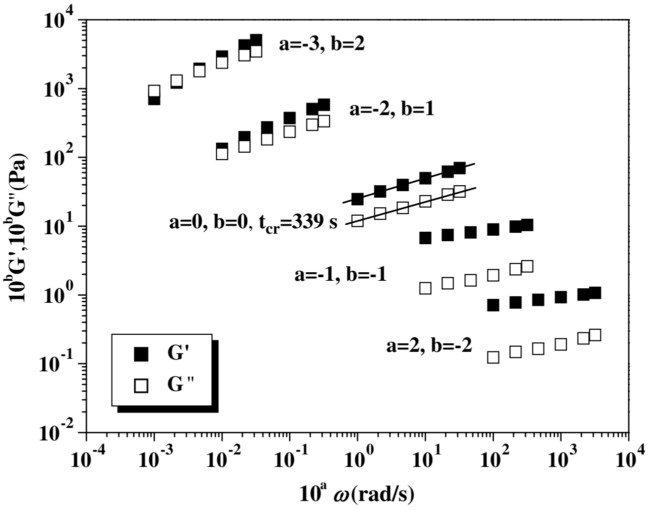

Fig. 5. Frequency dependence of G' and $G''$of 9.0 g/L KGM aqueous solution at various time at 25 °C. The data are shifted along horizontal and vertical axes by 10^a and 10^b, respectively, to avoid overlapping. The C_{ob} was 0.9 wt%.

From Fig. 3 one can observe that G'' was larger than G' at low frequency indicating a liquid-like behavior, and both G' and G'' increased with the increase of frequency. With the increase of time, G' was larger than G'', and the complex showed a solid-like behavior. As shown in Fig. 4 by the time dependence of loss tangent at different frequencies for the KGM/organic borate complex system ($C_k = 9.0$ g/L, $C_{ob} = 0.9$ wt%), the t_{cr} was determined to be 339 s, and the corresponding n was calculated to be 0.32. From the frequency dependence of G' and G'' at various times, as shown in Fig. 5, the curves of G' vs ω and G'' vs ω became parallel to each other at the time of 339 s. The Winter–Chambon method was found to be effective to determine the critical gelation time in the whole concentration range of KGM and organic borate used in this study (some data not shown).

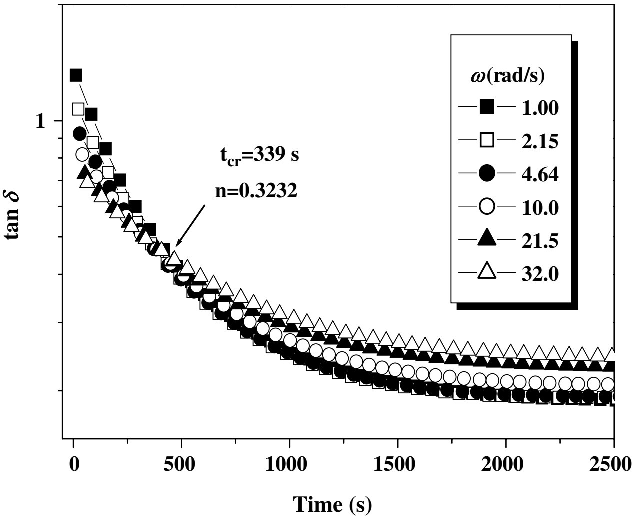

Fig. 4. Time dependence of loss tangent of KGM aqueous (C_k = 9.0 g/L) solution at different frequencies and at 25 °C. The C_{ob} was 0.9 wt%.

Previous studies showed that galactomannan and glucomannan can form gels in the presence of borate (Gao et al., 2007; Tayal et al., 1999). However, the crosslinking reaction between galactomannan chains and borate ions occurs immediately when mixing galactomannan solutions with borate, because the free borate ions in the solution are excessive. As a result, the sol-gel transition point can not be observed. In the KGM/organic borate system, the most borate ions were chelated by the coordination agent through coordinate linkage. Once the subsistent free borate ions were crosslinked with *cis*-diol hydroxyl groups of KGM, the coordinate linkage between the chelated borate ions and the coordination agent was gradually destroyed. As a result, the coordinate balance was interrupted. There is a competition relationship between *cis*-diol hydroxyl groups and coordination agent. While more and more free borate ions were released, the crosslinking points among KGM chains appeared and finally the gel formed. Therefore, the sol-gel transition of KGM solutions in the presence of organic borate can be observed, attributing to the formation process of sufficient crosslinking points. The delayed crosslinking function of crosslinker to hydrocolloid was very important in the application as fracturing fluids (Goel et al., 2001; Dawson, 1992). The organic coordination agent which was called delay additive served to mask the presence of at least a portion of the borate ions at first, thereby providing a reserve of borate ions for crosslinking the fluids as time went on (Dawson, 1992). Some other polysaccharide complex gels also exhibited delayed crosslinking such as schizophyllan/borate complex which was ascribed to be the high rigidity of polymer chains in water (Fang, Takahashi, & Nishinari, 2004; Grisel & Muller, 1998).

3.2. Effect of concentration of KGM and organic borate on sol-gel transition

Fig. 6 showed the value of t_{cr} as a function of C_k while C_{ob} was fixed to 0.6, 0.9, 1.2, 1.6 wt%, respectively. Apparently, the value of t_{cr} of the complex gel decreased with the increase of C_k while C_{ob} was fixed. When C_k ranged from 4.0 g/L to 9.0 g/L, there was a sharp decline of t_{cr}, and the decrease of t_{cr} became slower while C_k was above 9.0 g/L. One can also see that t_{cr} decreased with an increase in C_{ob} at the same value of C_k.

Values of the relaxation exponent n were calculated from the tan δ value according to Eq. (2). The effects of organic borate and KGM concentration on n were also shown in Fig. 7. At the same C_{ob}, the increase in C_k resulted in a continuous decrease in the relaxation exponent n, indicating that the gel became more and more elastic when the concentration of KGM was gradually increased (Gao & Nishinari, 2004a). The value for n of chemically crosslinked gel may be affected by the presence of entanglements (Muthukumar, 1985).

Generally, as the concentration of KGM increased, there were more *cis*-diol sites susceptible to form intermolecular complexes through the free borate ions, so gel formation was favored. Additionally, with the increase of KGM concentration, the self-association of the chains occurred, which could also create chains aggregation even leading to network structures (Gao & Nishinari, 2004b). When increasing concentration of organic borate at a fixed concentration of KGM, more free borate ions were released in the mixture solution. In a word, with the increase of either C_k or C_{ob}, the probability of the cross-linking reaction between KGM and organic borate increased, resulting in faster gelation kinetics and the shorter sol-gel transition time, as shown in Fig. 6.

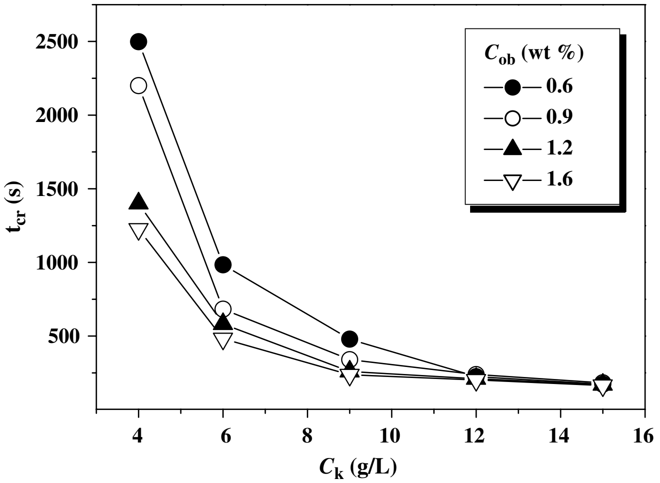

Fig. 6. Sol-gel time (t_{cr}) as a function of C_k while C_{ob} was fixed to 0.6, 0.9, 1.2, 1.6 wt%, respectively.

3.3. Effect of temperature on sol-gel transition

The effects of temperature on the sol-gel transition time (t_{cr}) were illustrated in Fig. 8. The values of C_k and C_{ob} were fixed to 9.0 g/L and 0.6 wt%, respectively. With increasing temperatures from 20 °C to 45 °C, value of t_{cr} decreased from 642 s to 82 s, indicating that the gelation was promoted by raising the temperature as observed previously (Yoshimura & Nishinari, 1999). Increasing temperature promoted the aggregation of molecular chains of KGM and the subsequent formation of junction zones, resulting in a faster gelation rate. As shown in Fig. 8, it was impossible to track the sol-gel transition point above 45 °C because the gelation process was too fast. The effects of temperature on the gelation process may be reflected in the Arrhenius plot of ln ($1/t_{cr}$) vs $1/T$ (Maekaji, 1974) as shown in Fig. 9. The apparent activation energy (E_a) was obtained from the slope of the linear least-squares fitting to the experimental results of ln ($1/t_{cr}$) vs $1/T$. E_a was cal-

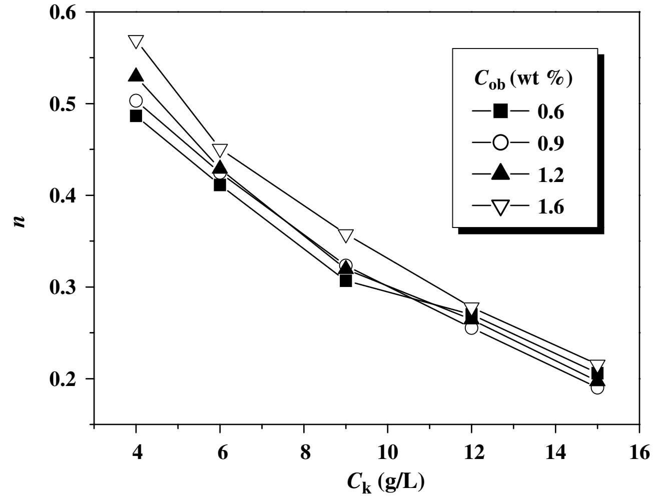

Fig. 7. The value of n as a function of C_k while C_{ob} was fixed to 0.6, 0.9, 1.2, 1.6 wt%, respectively.

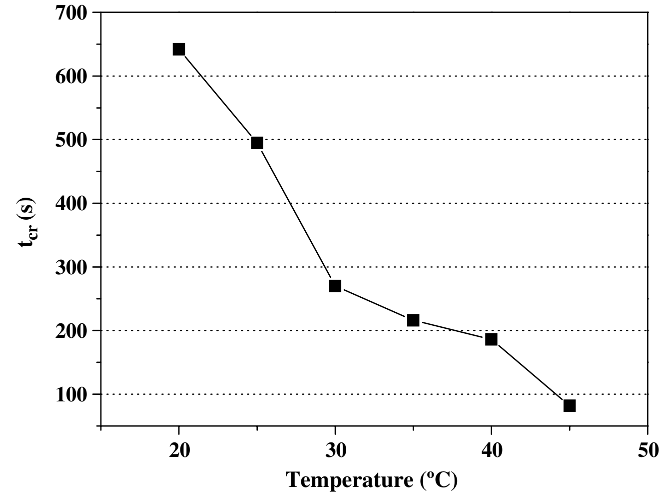

Fig. 8. The values of t_{cr} as a function of the temperature while C_k and C_{ob} were fixed to 9.0 g/L and 0.6 wt%.

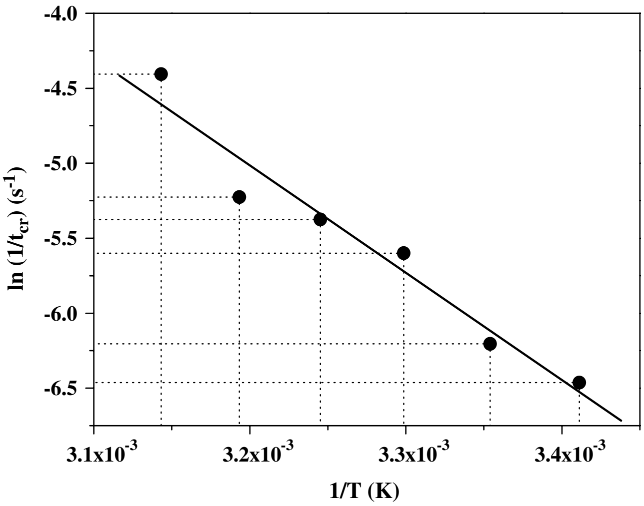

Fig. 9. Arrhenius representations for the effect of the temperature on the gelation rate ($1/t_{cr}$, s^{-1}) of 9.0 g/L KGM solution in the presence of organic borate whose concentration was fixed to 0.6 wt%.

culated to be 59.48 KJ/mol. The activation energy was usually related to the formation and rupture of linkages in "junction zones" during the gelation processes in which several kinds of intermolecular intersections were involved (Huang et al., 2002).

3.4. Determination of gel-sol temperature

For thermoreversible polymer gels used as fracturing fluids, the critical gel-sol temperature (T_{gel}) is an important factor that should be taken into consideration. Above T_{gel}, the complexation between the polymer and the crosslinker is gradually disrupted. It has been reported that the T_{gel} could be determined by a tilting-a-test-tube method for poly (vinyl alcohol)/cong red gel (Shibayama, Ikkai, Moriwaki, & Nomura, 1994) and by a micro-differential scanning calorimeter method for methyl cellulose gel (Li, 2002). In the present study, the validity of determination of T_{gel} by Winter–Chambon method was verified. Fig. 10 showed the temperature dependence of G' and G'' for KGM/organic borate gel ($C_k = 9.0$ g/L, $C_{ob} = 0.6$ wt%) at different frequencies. With increasing temperature, both G' and G'' decreased, and G' decreased faster than G''. It indicated that, with increasing the temperature, the elasticity of the gel decreased and the fluidity of the gel increased. The intersection point of G' and G'' can be observed in Fig. 10, but it strongly depends on the frequency.

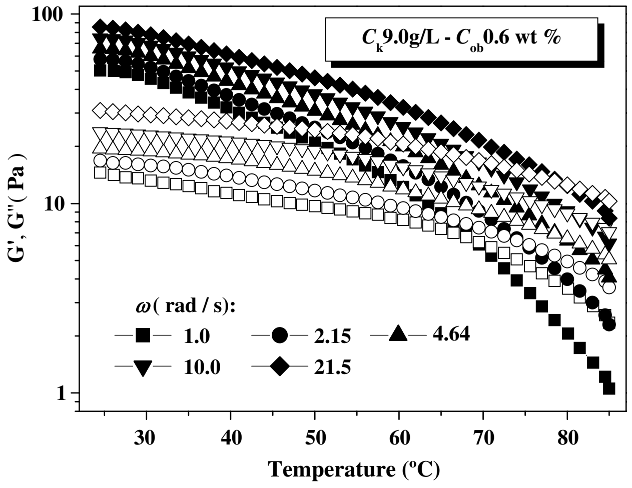

Fig. 10. Temperature dependence of G' (solid symbols) and G'' (open symbols) of KGM/organic borate gel ($C_k = 9.0$ g/L, $C_{ob} = 0.6$ wt%) at different frequencies.

Fig. 11 showed the temperature dependence of loss tangent (tan δ) for KGM/organic borate gel ($C_k = 9.0$ g/L, $C_{ob} = 0.6$ wt%) at different frequencies. Like the determination of the time of t_{cr} for KGM/organic borate gels, the Winter–Chambon method is still effective in determining the T_{gel}. One can observe an intersection point ($T_{gel} = 58.4$ °C) from tan $\delta \sim$ temperature curves at various frequencies, and the curve of $G' \sim$ temperature and $G'' \sim$ temperature was parallel to each other (data not shown). Fig. 12 showed the T_{gel} as a function of C_{ob} while C_k were 6.0 g/L, 9.0 g/L, and 12.0 g/L, respectively. While increasing C_{ob} at the same C_k, T_{gel} increased gradually. It indicated that values of T_{gel} strongly depend on the crosslinking density of the gels. The higher crosslinking density the complex gel had, the higher T_{gel} can be observed. It is reasonable that the higher temperature is needed to disrupt the intermolecular crosslinking linkages of the complex gel with higher crosslinking density.

3.5. Concentration dependence of the rheological properties

Fig. 13 showed the time dependence of G' for KGM solution ($C_k = 9.0$ g/L, $C_{ob} = 0.6$, 0.9, 1.2, 1.6, 2.0 wt%, respectively.) at the frequency of 1 rad/s and at 25 °C. The G' increased sharply at the first stage, corresponding to the gelation process. After all the crosslinks were formed and the gelation process was completed, one can see a pla-

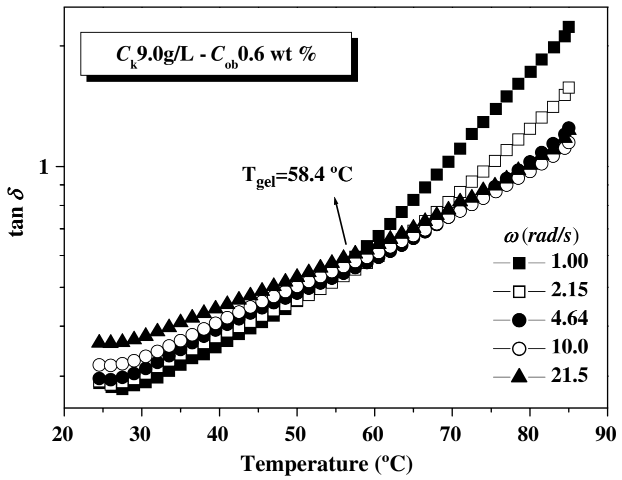

Fig. 11. Temperature dependence of the loss tangent, tan δ of 9.0 g/L KGM aqueous solution at different frequencies. The C_{ob} was 0.6 wt%.

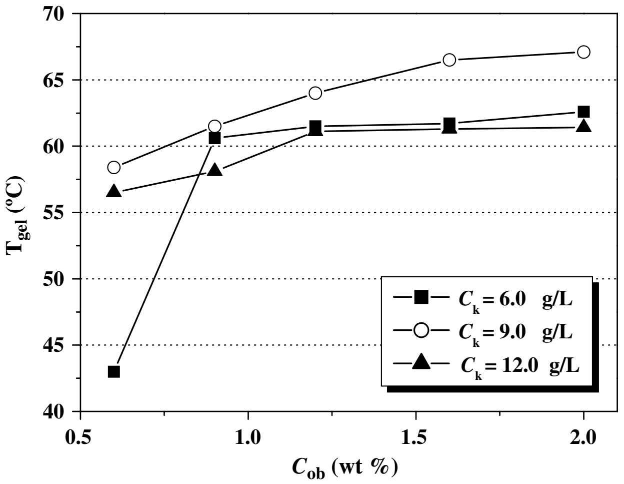

Fig. 12. The values of T_{gel} as a function of the C_{ob} while the concentrations of KGM were 6.0 g/L, 9.0 g/L, and 12.0 g/L, respectively. The C_{ob} were 0.6, 0.9, 1.2, 1.6 and 2.0 wt%, respectively.

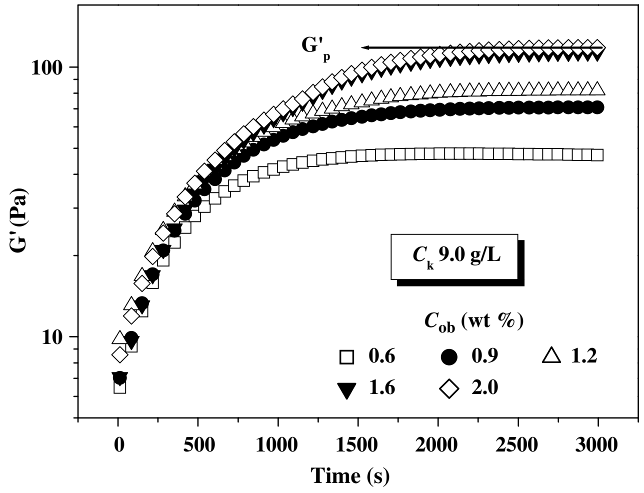

Fig. 13. Time dependence of G' for KGM solution ($C_k = 9.0$ g/L) at the frequency of 1 rad/s and at 25 °C. The C_{ob} in the solution were 0.6, 0.9, 1.2, 1.6, 2.0 wt%, respectively.

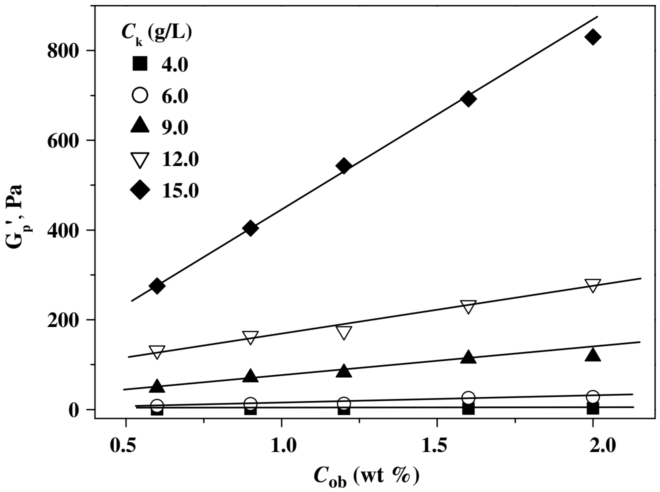

Fig. 14. Plots of G'_p as a function of C_{ob} for the KGM/organic borate complex with various C_k.

teau value of $G'(G'_p)$ independent of time. G'_p as has also been observed for other biopolymer gels which have obvious gelation processes (Fang et al., 2004; Gao & Nishinari, 2004b).

The G'_p of the complex gels with various C_k and C_{ob} were checked, and the result was illustrated in Fig. 14. For all the complex gels with different C_k, the value of G'_p linearly increased with increasing C_{ob}. At the same C_{ob}, G'_p increased with increasing C_k. It indicated that increasing either C_k or C_{ob} resulted in the increasing of elasticity of the gel, attributing to the increasing of crosslinking density. The slope of $G'_p \sim C_{ob}$ curve reflects the influence of KGM concentration on the alteration of elasticity for the complex gels. As shown in Fig. 14, the higher C_k the gel has, the bigger slope the curve of $G'_p \sim C_{ob}$ exhibits. This should be related to the enhancement in degree of chain entanglement with increasing the KGM concentration (Gao & Nishinari, 2004b; Nishinari, 2000). In other words, the higher entanglement of molecular chains of KGM make a contribution to the elasticity of the complex gel besides the effect of increasing the concentration of organic borate.

4. Conclusions

A series of complex gels were prepared through the crosslinking reaction between the *cis*-diol groups on mannose units of KGM molecular chains and free borate ions dissociated from the organic borate aqueous solution. The obvious gelation processes of the gels can be observed by the time dependence of rheological properties. The gelation kinetics of the gels can be characterized by the critical gelation time t_{cr}, which can be exactly determined by using Winter–Chambon criterion based on the results of rheological measurements. The value of t_{cr} was shortened by increasing the concentration of KGM or organic borate and increasing the temperature of rheological measurements. It was found that the critical gel-sol temperature (T_{gel}) of the gels can also be elucidated by Winter–Chambon criterion based on the results of temperature dependence of rheological properties. The value of T_{gel} was obviously increased by increasing the concentration of KGM or organic borate, due to the increase of crosslinking density of the gel. The increase of crosslinking density by increasing the concentration of KGM or organic borate resulted in the enhancement of elasticity of the gel characterized by the plateau value of storage modulus.

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