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Thermoreversible konjac glucomannan gel crosslinked by borax

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Abstract

Dynamic viscoelastic measurements were carried out for novel konjac glucomannan/borax gels. Gel networks were formed through the crosslinking reaction between borate ions dissociated from borax and the *cis*-diol sites on the polysaccharide chains. At lower oscillation frequencies, the complex gels behave like a liquid, whereas at higher frequency they relax like true gel materials with a predominant elastic relaxation response. An obvious plateau value of storage modulus (G') and a maximum and minimum in loss modulus (G'') were observed on the relaxation spectrum. The characteristic viscoelastic functions were studied as a function of concentrations of konjac glucomannan and borax, strain, and temperature. The storage and loss moduli obey time–temperature superposition by using the empirical shifting factors, which are corresponding to the rheological properties with respect to the longest relaxation time. Relaxation and crosslinking energies for the gels were calculated from the Arrhenius representations of the shift factors. The experimental finding indicates the nature of dynamic crosslinking for the complex gels.

Keywords: Konjac glucomannan; Gel; Rheology; Thermoreversible gels

1. Introduction

Considerable effort has been devoted to the study of polymer–ion complexes over the past several decades due to their wide range of application such as in petroleum or food industry as fracturing fluids (Chatterji & Borchardt, 1981; Tsuchida & Nishide, 1977). A large number of chemical elements including chromium (Allain & Salome, 1987), titanium (Ahad, 1974), zirconium, antimony (Pezron, Ricard, & Leibler, 1990), and boron (Schultz & Myers, 1969) have been used as crosslinking agents. Borate ions have long been known (Choi, Kim, Blackwell, & Lyoo, 2001) to form complexes with *cis*-diol groups (hydroxyl pairs) or with polyhydroxy compounds. Poly (vinyl alcohol) (PVA) is one of the most typical polymers that can be crosslinked by various ions and extensive studies about PVA–borate complex have been reported (Cheng & Rodriguez, 1981; Koike, Nemoto, Inoue, & Osaki, 1995; Lin, Yu, & Cheng, 2000; Ochiai, Shimizu, Tadokoro, & Murakami, 1981; Ochiai, Fujino, Tadokoro, & Murakami, 1982; Schultz & Myers, 1969; Shibayama, Sato, Kimura, Fujiwara, & Nomura, 1988; Shibayama, Yoshizawa, Kurokawa, Fujiwara, & Nomura, 1988; Shibayama et al., 1992). Studies on the structure and properties of aqueous PVA/borate complex have recently been reviewed by Te Nijenhuis (1996).

As for the complex from water-soluble polysaccharide and borate, guar galactomannan/borate system has been firstly studied. Rheological studies (Kesavan & Prud'homme, 1992; Pezron et al., 1990; Tayal, Pai, & Khan, 1999) have investigated the effect of polymer and borate concentration, temperature, solution pH, and molecular weight of guar on characteristic rheological properties obtained from the frequency dependence of relaxation spectra. Recently,

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rheological properties of the schizophyllan/borate system have been reported (Fang, Takahashi, & Nishinari, 2004; Grisel & Muller, 1998).

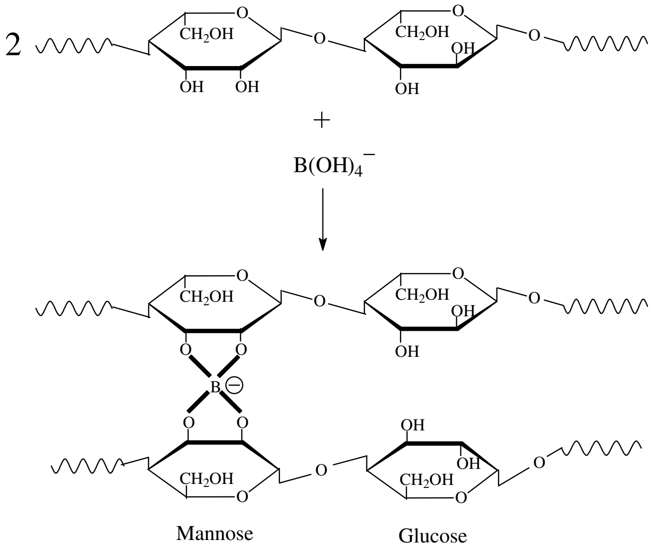
The mechanism of the crosslinking reaction of borate ion with synthetic or natural polyhydroxy polymers is generally believed to be a so-called monodiol and didiol complexation formed between diol units and borate ion:

$$P + B^- \overset{K_1}{\rightleftharpoons} PB^- \tag{1}$$

$$2P + B^- \overset{K_2}{\rightleftharpoons} P_2B^- \tag{2}$$

where P refers to the *cis*-diol unit of the polymer and B^- refers to $B(OH)_4^-$, and PB^- and P_2B^- are the 1:1 (monodiol) and 2:1 (didiol) complex structures, respectively. K_1 and K_2 are the corresponding complexation equilibrium constants. The detailed status of complexation depends on the concentrations of polymer and borate ion, ion strength of solution, and temperature. Extensive ^{11}B NMR spectroscopic studies (Jasinski, Redwine, & Rose, 1996; Pezron, Leibler, Ricard, & Audebert, 1988a; Pezron, Ricard, & Audebert, 1988b; Pezron, Leibler, & Lafuma, 1989a; Pezron, Leibler, Ricard, Lafuma, & Audebert, 1989b) on dilute complexation mixtures of borate ion with PVA, guar, or model polyhydroxy compounds have been utilized to make further insight into the complexation mechanism by obtaining the values of complexation equilibrium constants and the complexation enthalpy at various measuring conditions including ion strength by adding inorganic salts and temperature.

In this study, we firstly report the complexation between konjac glucomannan (KGM) and borax ($Na_2B_4O_7 \cdot 10H_2O$). KGM is a neutral polysaccharide isolated from the tubers of *Amorphophallus konjac* C. Koch. It consists 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 backbone, but the exact branched position is still in debate (Katsuraya et al., 2003). A scheme for the complexation between *cis*-diol groups on the mannose units of KGM and borate ions (typically provided by the dissociation of borax) is shown in Scheme 1. Two *cis*-diol pairs of different KGM molecules can be connected by a borate ion to form an interchain crosslink. The presence of these crosslinks gives rise to gel-like properties. In this paper, we focus on understanding the rheological properties of KGM/borax complex gels using dynamic viscoelastic measurement. By measuring the frequency dependence of relaxation spectra, we correlate the effect of various measuring conditions including KGM concentration, borax concentration, and temperature on the characteristic moduli and relaxation times for the complex gels.



Scheme 1. Schematic representation of the complexation between KGM and borax ions.

2. Materials and experimental

2.1. Materials

The raw KGM sample was a gift from Shimizu Chemical Co. (Hiroshima, Japan) and further purified by mixing with three times weight of 50 wt% and 80 wt% ethanol for 2 h, respectively, and with waterless ethanol for 4 h, and then vacuum-dried at 60 °C for 4 h. The intrinsic viscosity of cadoxen solution of KGM sample was measured to be 557 $cm^3\,g^{-1}$ by using an Ubbelohde type viscometer (Kaburagi Scientific Instruments Co. Ltd., Tokyo, Japan) at 25 ± 0.02 °C. The viscosity-average molecular weights of the KGM were calculated according to the Mark–Houwink equation (Kohyama, Iida, & Nishinari, 1993) $[\eta] = 3.55 \times 10^{-2} \cdot M^{0.69}$ to be 1.2×10^6. Borax was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used as received. Previous studies (Pezron et al., 1988b; Sinton, 1987) show that borax dissociates completely into equal quantities of boric acid and monoborate ion

$$B_4O_7^{2-} + 7H_2O \rightarrow 2B(OH)_3 + 2B(OH)_4^- \tag{3}$$

and an acid–base equilibrium is established between boric acid and monoborate ions (Sinton, 1987)

$$B(OH)_3 + H_2O \overset{K_A}{\rightleftharpoons} B(OH)_4^- + H^+ \quad pk_A = 9.0\text{–}9.2 \tag{4}$$

Therefore, the total concentration of borate ions in a borax solution is twice the initial borax concentration. Under basic conditions (pH > 11), the borax is present only as borate ions and the concentration of borate ions becomes four times the initial borax concentration (Sinton, 1987).

2.2. Preparation of KGM/borax gels

Powders of KGM samples were dispersed in distilled water at room temperature for 1 h and were heated to 80 °C and then maintained at 80 °C for 1 h and cooled to room temperature. The aqueous KGM solutions were equilibrated at room temperature for 2 days.

Required amounts of borax were dissolved in distilled water under stirring at 60 °C to obtain a series of borax solution with different concentrations. By using a microsyringe, 200 μL of borax solution was added into 3.0 g of KGM solution, and then these two solutions were thoroughly mixed by manually stirring using a teflon muddler. In all cases, gel was formed instantly. The resulted gel was centrifuged at 3000 rpm/min for 30 min to remove the visible bubbles before the rheological measurements. In this study, the pH values of all the mixture systems are self-buffered to be around 9.0 by borax.

2.3. Rheological measurements

Dynamic viscoelastic measurements were carried out using a Fluids spectrometer RFS II (Rheometrics Co., Ltd.) with a parallel plate geometry (50 mm in diameter and 1.0 mm in gap). The strain in all frequency dependent measurements of present work was set as 0.5% which is prechecked to be within a linear viscoelastic regime. KGM/borax gel sample preheated to the measuring temperature was transferred onto the sample plate of the instrument which had been kept at each measurement temperature (25 °C, except for the measurements of temperature dependent relaxation spectra). Mineral oil was added on top of the enclosed sample plate to cover the free surface of the sample in order to prevent evaporation. In frequency sweep measurements, shear storage and loss moduli were recorded at 0.01–100 rad/s. In strain sweep measurements, shear storage modulus was recorded at the strain of 0.125–1000% and at the frequency of 1.0 rad/s.

3. Results and discussion

3.1. Dynamic viscoelastic behavior

It is well known that removal of the 5–10% acetyl substituted residues in KGM generated by addition of a moderate alkali results in the chain association and gel formation (Maekaji, 1974, 1978). Even in the absence of alkali, conformation change of KGM chains occurs when pH > 11, and this change is enough for the gel formation of KGM (Kohyama & Nishinari, 1990). According to Eq. (4), the natural pH of a borax solution is close to the pK_A of boric acid. In this study, the pH value of the mixture system is self-buffered to be around 9.0 by borax (Pezron et al., 1990, 1988b; Sinton, 1987). Therefore, no deacetylation reaction occurred during the mixing and measuring process. When mixing borax with KGM solution, the gel was formed instantly. The same phenomenon was observed during the sample preparation of PVA/borax and guar/borax gels (Cheng & Rodriguez, 1981; Pezron et al., 1990; Schultz & Myers, 1969). However, for the formation of schizophyllan gel induced by borate ion complexation, gelation process always lasts for several hours and the critical sol–gel transition point can be observed on the time course of storage modulus (Fang et al., 2004; Grisel & Muller, 1998). This difference in gelation kinetics is ascribed to be the flexibility of polymer chains in water (Pezron et al., 1989b), and one may reasonably expect that interchain borate ion complexation is easier for flexible polymers than for rigid schizophyllan (Yanaki, Kojima, & Norisuye, 1981).

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). Fig. 1 shows the frequency dependence of G' and G'' for the KGM solution ($c_k = 10.0$ g/L) in the absence and presence of borax ($c_b = 11.8$ mM). For the pure KGM solution, G'' dominates the solution response over most of the frequency domain, indicating the principlely viscous nature of KGM solution (Gao & Nishinari, 2004; Zhang et al., 2001). Crosslinking the KGM by borate ion complexation results in an obvious increase in both moduli, with G'' being affected more strongly. For KGM/borax gel, one can see the typical features of the plateau zone characterized by a weak frequency dependence of $G'(\omega)$ and the marked maximum and minimum of $G''(\omega)$. One can also see a region similar to the glass-to-rubber transition region observed for melts and concentrated solutions of polymers. These features of KGM/borax complex gel are very close to those of previously reported concentrated polystyrene solutions (Masuda, Kitagawa, Inoue, & Onogi, 1970; Onogi, Masuda, & Kitagawa, 1970; Osaki, Nishimura, & Kurata, 1985). The same relaxation behavior was observed for PVA/borate (Lin et al., 2000; Schultz & Myers, 1969; Te Nijenhuis, 1996) and guar/borax (Kesavan & Prud'homme, 1992; Pezron et al., 1990; Tayal et al., 1999) complex gels. From Fig. 1, the intersection point of G' and G'' did not correspond to the maximum of G'', suggesting that the viscoelastic behavior cannot be described by only one

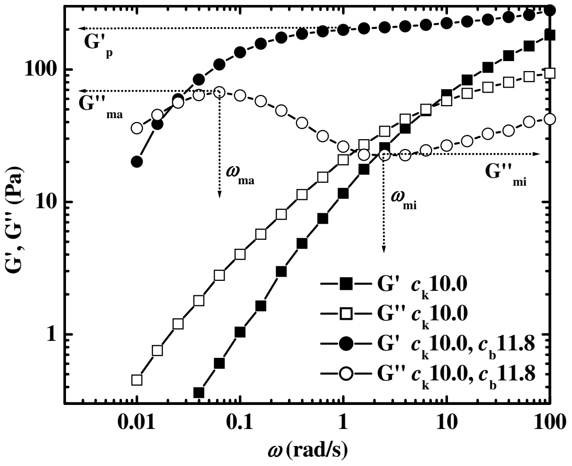


Fig. 1. Frequency dependence of G' and G'' for KGM solution ($c_k = 10.0$ g/L) in the absence and presence of borax ($c_b = 11.8$ mM). The measuring temperature is 25 °C, and the same hereinafter.

relaxation time and by one Maxwell element (Koike et al., 1995).

In this work, we will be particularly interested in the characteristic parameters of the following rheological functions: the plateau value of elastic modulus G'_{p}, the maximum of loss modulus G''_{ma} and its correlated frequency ω_{ma}, and the minimum of loss modulus G''_{mi} and its correlated frequency ω_{mi} (Fig. 1). The rheological behavior of concentrated polymer solutions in the rubbery zone is fundamentally affected by the entanglement couplings between molecular chains (Masuda et al., 1970; Onogi et al., 1970). According to modified Rouse theory (Ferry, Landel, & Williams, 1955) and Chompff–Duiser theory (Chompff & Duiser, 1966; Chompff & Prins, 1968), the relaxation spectrum is predicted to show a maximum of characteristic entanglement slipping mechanism. As a result, the curve of G'' versus ω should have a maximum, and that of G' versus ω should show a very flat plateau. The characteristic frequency corresponding to the G''_{ma} (ω_{ma}, see Fig. 1) gives a good indication of the longest relaxation time τ_r ($\tau_r = 1/\omega_{ma}$) according to reptation model, (de Gennes, 1971; Cates, 1987) which describes τ_r as the time for a given macromolecules to disengage by a snakelike motion from a tube made up of neighboring chains.

3.2. KGM and borax concentrations dependence of rheological parameters

Fig. 2a and b show the frequency dependence of G' (a) and G'' (b) for KGM/borax gels with $c_k = 7.5$ g/L and various c_b (2.36–47.2 mM). The highest value of c_b was chosen as 47.2 mM in this work because of the difficulty in preparing a borax solution with concentration higher than 50 mM (Cheng & Rodriguez, 1981) and the occurrence of serious syneresis when c_b in the complex gel is too high as observed for schizophyllan/borax system (Grisel & Muller, 1998). Polyborate species may exist in moderately alkaline and highly concentrated borax solutions. However, ^{11}B NMR study (Pezron et al., 1988b) have shown that even at high borax concentration, the polyborate concentration is negligible. From Fig. 2, one can see that characteristic viscoelastic parameters were strongly dependent on c_b. For the complex gels containing the lowest c_b (2.36 mM), both the plateau region of G' and maximum in G'' become unconspicuous, in contrast to the very flat plateau regions of G' and sharp peaks of maximum in G'' when $c_b > 5.90$ mM. The difference in G'_{p}, G''_{ma}, and ω_{ma} becomes unobvious when $c_b > 17.7$ mM.

For semidilute polymer solutions, the relaxation moduli at very long times can be fitted with an exponential function $G(t) = G\exp(-t/\tau_r)$ (Ferry, 1980; Osaki et al., 1985). The longest time τ_r has also been considered equal to the reptation time (Cates, 1987; de Gennes, 1971). For KGM/borax gels, however, the reptation of a KGM chain should be hampered by borate ion complexation because any individual KGM chain might be reversibly linked to a neighboring chain through crosslinks. One can see from Eqs. (1)–(4) that the whole chemical equilibria involving dissociation of borax in water, formation of borate ions, and complexation between *cis*-diol sites on KGM chains and borate ions determine the number of crosslinks. The network of KGM/borax gel is formed with temporarily crosslinked chains. Therefore, the longest relaxation time should represent the reciprocal of exchange rate for the formation of intermolecular crosslinks. Although it is difficult to describe the relaxation behavior of KGM/borax gels using a single relaxation time (Figs. 1 and 2), the typical frequency ω_{ma} can still be a good indication of the characteristic relaxation time for the relaxation mechanism. Fig. 3a and b shows the typical master curve of reduced moduli of KGM/borax gels indicated in Fig. 2. The superposition is good especially in the terminal zone. At very high frequency ($\omega/\omega_{ma} > 20$ for G'/G''_{ma} and $\omega/\omega_{ma} > 2$ for G''/G''_{ma}), values of $G'G''_{ma}$ and G''/G''_{ma} cannot be superposed, ascribed to the interference of times relating to local motions of chain segments between two crosslinks with the longest relaxation time for the large scale motion of the polymer chain (Pezron et al., 1990). The successful application of superposition principle denotes that gels with different concentrations of KGM and borax can have the same rheological properties (G'_{p} and G''_{ma}) if the number of interchain complexes is identical. The value of ω_{ma} can be

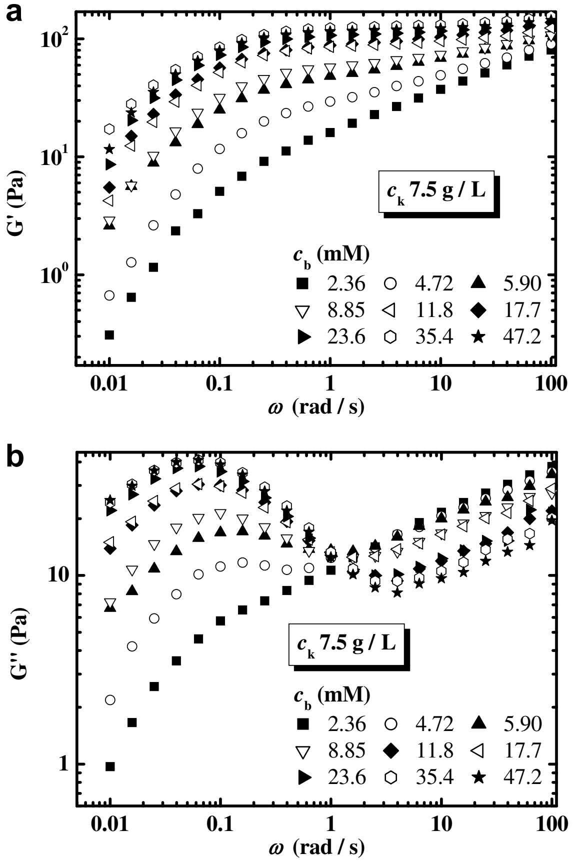


Fig. 2. Frequency dependence of G' (a) and G'' (b) for KGM/borax gels ($c_k = 7.5$ g/L, $c_b = 2.36$–47.2 mM).

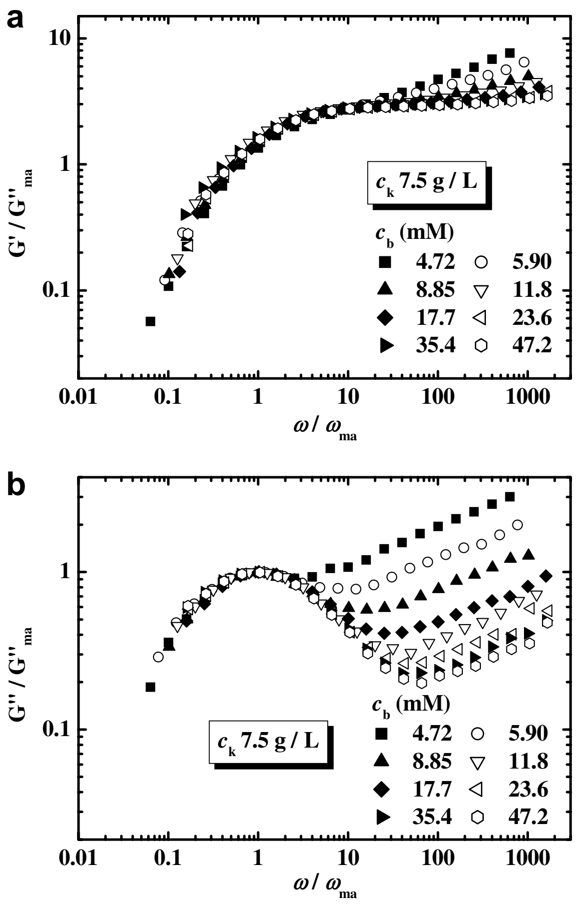


Fig. 3. Master curves of reduction elastic (a) and loss (b) moduli for KGM/borax gels indicated in Fig. 2.

regarded as a characteristic of viscoelastic function for KGM/borax gels.

We check the viscoelastic properties of KGM/borax with various concentrations of KGM ($c_k = 5.0$–15.0 g/L) and borax ($c_b = 2.36$–47.2 mM) (data not shown). It was found that increasing c_b at a fixed c_k resulted in the increase of G'_p and G''_{ma}. For the characteristic frequency, ω_{ma} became increasingly lower with increasing c_b, which is in reverse with the change of ω_{mi}. These observations of c_b dependence of rheological data reveal the gradual change in effective degree of crosslinking and chain entanglement (Cheng & Rodriguez, 1981; Fang et al., 2004). It was also found that when increasing c_k, at the same c_b, G'_p and G''_{ma} increased, ω_{ma} became increasingly lower, and ω_{mi} became increasingly higher. This should be related to the enhancement in degree of chain entanglement with the increase of c_k, as discussed in previous study (Gao & Nishinari, 2004; Nishinari, 2000). Fig. 4 shows G'_p as a function of c_b for the KGM/borax gels with various c_k. For all complex gels with different c_k, G'_p linearly increased with increasing c_b, and then G'_p leveled off or slightly decreased. This observation is similar to that for PVA/borax (Cheng & Rodriguez, 1981; Schultz & Myers, 1969) and guar/borax (Pezron et al., 1990) gels. From Scheme 1, KGM chains become charged when the borate ion complexation occurred. Furthermore, it has been proposed that only a small part of borate ions coming from the dissociation of borax is responsible for the interchain crosslinking (Pezron et al., 1990, 1989a). Therefore, the existence of charged KGM chains and free borate ions resulted in the electrostatic repulsion, which hindered the free KGM chains from further interchain crosslinking (Ochiai et al., 1982; Pezron et al., 1990, 1988a, 1988b, 1989a, 1989b).

Since all the lines with different KGM concentrations have the same intercept and only the slopes varies with KGM concentrations (Fig. 4), G'_p can be formulated as

$$G'_p = K_p \cdot \log(c_b/c_{b,0}) \tag{5}$$

where $c_{b,0}$ is the minimum of borax concentration for a wall-to-wall gel to form ($c_{b,0} = 1.48$ mM, see Fig. 4) and K_p is a function of polymer concentration and is independent of borax concentrations. K_p (the slope of the straight line in Fig. 4) was plotted against c_k, as shown in Fig. 5. The solid line represents the result of linear least-square fit to the data in a double logarithmic representation. Noticeably, K_p at various c_k can be well approximated

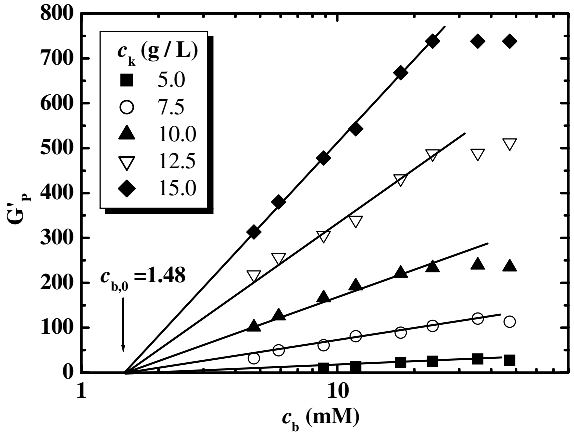


Fig. 4. Plots of G'_p as a function of c_b for the KGM/borax gels with various c_k.

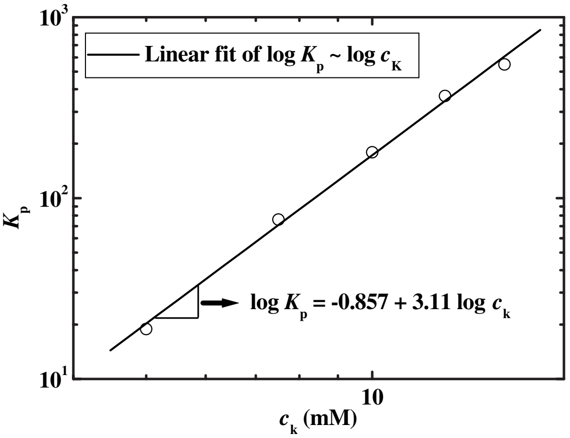


Fig. 5. Plot of K_p from Fig. 4 as a function of c_k.

using linear fitting. The slope of the linearly fitted line was 3.11, and a power dependence of K_p can be formulated as follows according to the result of linear fitting (Fig. 4)

$$K_p = 0.140 \cdot c_k^{3.11} \tag{6}$$

Combining Eqs. (5) and (6) gives

$$G'_p = 0.140 \cdot c_k^{3.11} \cdot \log(c_b/c_{b,0}) \tag{7}$$

where c_k is in g/L and c_b and $c_{b,0}$ are in mM. The exponent 3.11 in the KGM concentration dependence of elastic plateau modulus ($G'_p \propto c_k^{3.11}$) is comparable to that found by Pezron et al. (1990) for the variation of the plateau values of the elastic modulus of guar/borax gels in 1 M NaCl solution with the concentration of guar c_g ($G'_p \propto c_g^{2.6}$) and by Cheng and Rodriguez (1981) for the PVA concentration c_p dependence of the plateau values of the elastic modulus for PVA/borax gels ($G'_p \propto c_p^{4.7}$). Osaki et al. (1985) has correlated the plateau values of the elastic modulus of a semidilute solution of high molecular weight polystyrene in a good solvent with the concentration of polystyrene (c) as $G'_p \propto c^{2.4}$.

Experimental results of G'_p and G''_{ma} listed in Table 1 was plotted versus $c_k^{3.11} \cdot \log(c_b/c_{b,0})$ according to Eq. (7), as shown in Fig. 6. The solid straight line represents the calculated results of G'_p according to Eq. (7), and the dotted straight line represents the results of linear fitting from the data of G''_{ma} obtained from Table 1. Note that results of G'_p and G''_{ma} of the complex gels when $c_b = 47.2$ mM (for $c_k = 5.0$ and 7.5 g/L, respectively) and $c_b = 35.4$ or 47.2 mM (for $c_k = 10.0$, 12.5, and 15.0 g/L, respectively) were not included in Fig. 6, because of the obvious deviation of G'_p from the linearly fitted lines according to Fig. 4. It seems that the rheological data of G'_p when c_b was smaller than 35.4 mM basically obey the relation in Eq. (7) (see Fig. 6), although most experimental data are 5% higher than the calculated data. Results from Table 1 and Fig. 6 also indicated that the ratios G'_p/G''_{ma} for all the gels are constant at about 2.8, which is smaller than the value 3.2 reported by Pezron et al. (1990) for guar/borax gels and the average value 3.56 reported by Raju, Menezes, Marin, and Graessley (1981) for concentrated solutions of various linear polymers.

Table 1
Comparison of the values of critical strain γ_c and yield stress τ_c of KGM/borax gels ($c_k = 10.0$ g/L) with various borax concentrations

c_b (mM)	2.36	4.72	5.90	8.85	11.8	17.7	23.6	35.4	47.2
γ_c (%)	75	75	74	75	75	74	75	74	74
τ_c (Pa)	74	160	255	365	425	435	478	379	277

The measurements were repeated three times, and the average value was considered as τ_c.

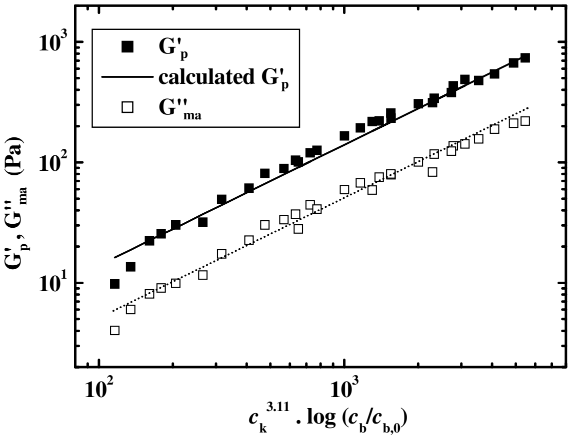


Fig. 6. Master curve relating characteristic moduli (G'_p and G''_{ma}) of KGM/borax gels to KGM and borax concentrations (same samples as in Fig. 3) according to Eq. (7).

3.3. Strain dependence of rheological properties

Fig. 7 shows the strain (γ) dependence of G' for KGM/borax gels with $c_k = 10.0$ g/L and various borax concentrations in the strain range of 0.125–1000%. At $\gamma < 100\%$, the complex gels with all borax concentrations give true gel mechanical spectra: $G' > G''$ and both moduli largely independent of strain (data of G'' not shown). When $\gamma > 100\%$, G' abruptly decreased as strain increased, indicating the breakage of crosslinks within the gel network and a transition from linear to non-linear behavior. According to previous reports (Rueb & Zukoski, 1997), the strain amplitude at which G' just begins to decrease by 5% from its maximum value was determined and taken as a measure of the limiting or critical strain γ_c of the sample. Illustration for determination of γ_c through the strain dependence of reduced modulus G'/G'_0, where G'_0 is the maximum of G' corresponding to the strain independent stage, is shown in the inset of Fig. 7. Interestingly, the values of γ_c for the complex gels (listed in Table 1) were found to be around 75%, basically independent of borax concentrations. The variation in borax concentration did lead to the difference in crosslinking density of the network chains, judged from the dependence of elastic modulus on borax concentration (Fig. 2). However, the experimental finding

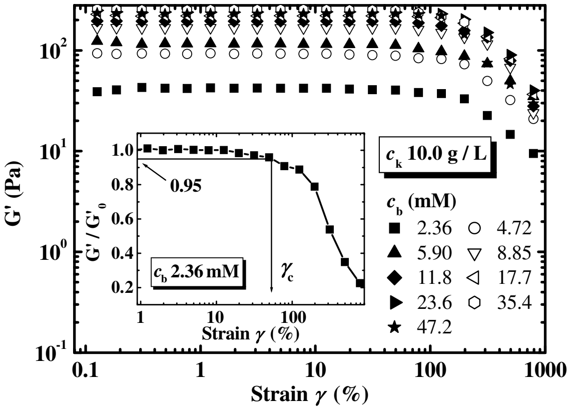


Fig. 7. Strain dependence of G' for KGM/borax gels ($c_k = 10.0$ g/L and $c_b = 2.36$–47.2 mM), measured at 1.0 rad/s and at 25 °C.

of borax concentration independence of critical strain γ_c suggests that the flexibility of KGM chains crosslinked by borate ions were not influenced by the status of chain crosslinking.

Ross-Murphy and Shatwell (1993) suggested that small and intermediate oscillatory shear strain sweep measurements can be used to find out the distinctions between strong and weak gels from food biopolymers. Based on the strain dependence of reduced modulus, they concluded that the complex modulus for strong gels is essentially strain independent (linearly viscoelastic) for strain $\gamma \geqslant 25\%$, whereas for weak gels it becomes strain dependent when $\gamma > 5\%$. It seems that KGM/borax gels should be classified into strong gels in view of the significantly high $\gamma_c = 75\%$. It should be noted that the viscoelastic behavior of KGM/borax gel is strongly dependent on the measuring frequency and typical characteristics of true gel ($G' > G''$ and G' independent of frequency) can be observed only when the frequency $\omega > \omega_{ma}$ (Fig. 1), which is obviously different from the conventional chemical gels with permanent chain crosslinks (Ross-Murphy, 1995).

Fig. 8 shows the strain dependence of elastic stress ($G' \cdot \gamma$) for KGM/borax gels with $c_k = 10.0$ g/L and various borax concentrations in the strain range of 0.125–1000%. Yang, Scriven, and Macosko (1986) suggested a method to pinpoint the critical stress by plotting the product of the elastic modulus and strain amplitude ($G' \cdot \gamma$) as a function of strain (γ). A maximum in such a plot corresponds to the presence of a yield stress τ_c. The values of τ_c determined according to this method are listed in Table 1. With increasing the borax concentration, τ_c firstly increased and then decreased when $c_b > 23.6$ mM. This alteration tendency of τ_c is very similar to that of G'_p as observed in Fig. 4. This suggests that elastic stress of the complex gel strongly depends on the number density of elastically active chains (Pai & Khan, 2002).

Both critical strain γ_c and yield stress τ_c are expected to be dependent on KGM concentration. We observed that the values of γ_c decreased from 90% to 70% with increasing c_k from 3.0 to 12.5 g/L. However, we cannot determine the values of γ_c for all the gels with $c_k = 15.0$ g/L and the values of τ_c for some gels with $c_k > 10.0$ g/L because of the instrumental limitation. For gels with $c_k > 10.0$ g/L, we found that only the values of τ_c for the gels with relatively low c_b (2.36 and 5.90 mM) and with the highest c_b (35.4 and 47.2 mM) can be detected, and those of τ_c for the gels with the intermediate c_b exceeded the instrumental limitation. This observation, however, also supported the experimental finding from Table 2 with respect to the borax concentration dependence of τ_c. The further study on large deformation measurements for KGM/borax gels is expected to check their detailed mechanical properties.

Table 2
The values of G''_{ma} and ω_{ma}, as well as horizontal and vertical shift factors for KGM–borax gels as a function of temperature

Temp (°C)	G''_{ma} (Pa)	ω_{ma} (rad/s)	a_T	b_T
10	92.1090	0.01582	2.2206	0.8878
15	86.8567	0.02220	1.5824	0.9415
20	81.7725	0.03513	1.0000	1.0000
25	78.7508	0.04941	0.7110	1.0384
30	73.2327	0.08335	0.4215	1.1166
35	69.6026	0.1252	0.2806	1.1749
40	66.2095	0.1573	0.2233	1.2351
45	62.9274	0.2485	0.1414	1.2995
50	59.6243	0.3969	0.08851	1.3715
55	55.1152	0.6244	0.05626	1.4836

3.4. Temperature dependence of rheological properties

Fig. 9 shows temperature dependence of G' for KGM/borax gel ($c_k = 10.0$ g/L, $c_b = 35.4$ mM) on heating and cooling (15 °C → 55 °C → 15 °C, 1.0 °C/min). Raising the temperature increased the fluidity of the complex gel, indicating the dependence of crosslink density on temperature.

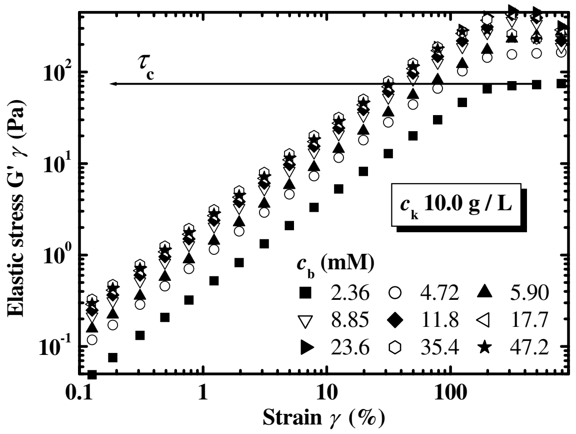


Fig. 8. Strain dependence of elastic stress for KGM/borax gels ($c_k = 10.0$ g/L and $c_b = 2.36$–47.2 mM), measured at 1.0 rad/s and at 25 °C.

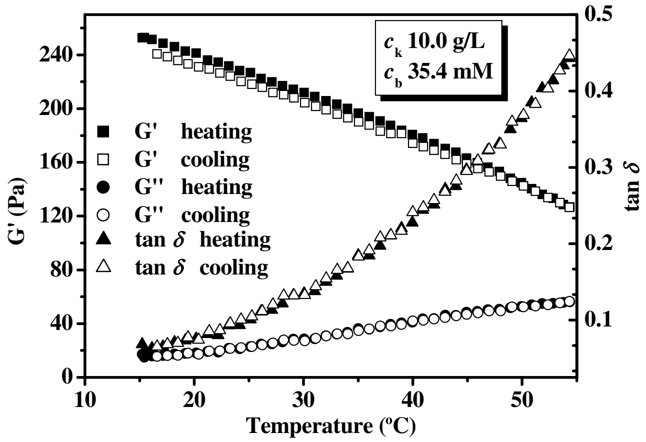


Fig. 9. Temperature dependence of G', G'', and $\tan\delta$ for KGM/borax gel with $c_k = 10.0$ g/L and $c_b = 35.4$ mM. The measuring frequency and strain are, respectively, 1 rad/s and 0.5%. The heating and cooling rate are both 1.0 °C/min.

Previous studies (Jasinski et al., 1996; Pezron et al., 1988b) have shown that complex formation in reactions between polymer and borate ions (Eqs. (1) and (2)) is exothermic and the complexation equilibrium constant decreases with increasing temperature. Therefore, the increase in G' with temperature expected from the entropic nature of rubbery elasticity is negligible compared to the decrease in G' due to the reduction of crosslink density. Results of Fig. 9 also indicated the thermally reversible nature of KGM/borax gels.

Time–temperature superposition increases the accessible frequency window of the linear viscoelastic experiments. It is based on the presupposition that all of the relaxation modes of the polymer system respond with temperature in the same way. By using this principle, a master curve of the relaxation response of polymer system can be obtained using the shift factors

$$b_{\mathrm{T}}G'(\omega,T) = G'(\omega a_{\mathrm{T}}, T_{\mathrm{ref}}) \tag{8}$$

$$b_{\mathrm{T}}G''(\omega,T) = G''(\omega a_{\mathrm{T}}, T_{\mathrm{ref}}) \tag{9}$$

where a_{T} and b_{T} are the horizontal and vertical shift factors and T_{ref} is the reference temperature. Schultz and Mayer first suggested that for PVA/borax gels, the master curve can be obtained only by applying a vertical shift in addition to the Williams–Landel–Ferry horizontal shift conventionally used for polymer solutions (Schultz & Myers, 1969). It should be noted that the master curves for so far reported PVA/borax or guar/borax gels are normally obtained by manually shifting the curves of $G \sim \omega$ at different temperatures in relation to the curve at the chosen reference temperature (Cheng & Rodriguez, 1981; Pezron et al., 1990; Schultz & Myers, 1969) or by utilizing the software RHIOS of the Rheometrics Incorporation (Kesavan & Prud'homme, 1992; Tayal et al., 1999).

Fig. 10 shows the temperature (10–55 °C) dependence of G' (a) and G'' (b) for KGM/borax gel ($c_{\mathrm{k}} = 10.0$ g/L, $c_{\mathrm{b}} = 35.4$ mM). Obviously, G'_{p} and G''_{ma} decreased with increasing temperature. The values of G''_{ma} and the corresponding frequencies ω_{ma} obtained from Fig. 10 are listed in Table 2. Both G''_{ma} and ω_{ma} linearly changed with temperature. This reminds us to determine the horizontal and vertical shift factors for each temperature by

$$a_{\mathrm{T}} = \omega_{\mathrm{ma,ref}}/\omega_{\mathrm{ma}} \tag{10}$$

$$b_{\mathrm{T}} = G''_{\mathrm{ma,ref}}/G''_{\mathrm{ma}} \tag{11}$$

where $\omega_{\mathrm{ma,ref}}$ and $G''_{\mathrm{ma,ref}}$ are the ω_{ma} and G''_{ma} at the reference temperature (chosen as 20 °C). The values of a_{T} and b_{T} are listed in Table 2. The thus obtained master curves

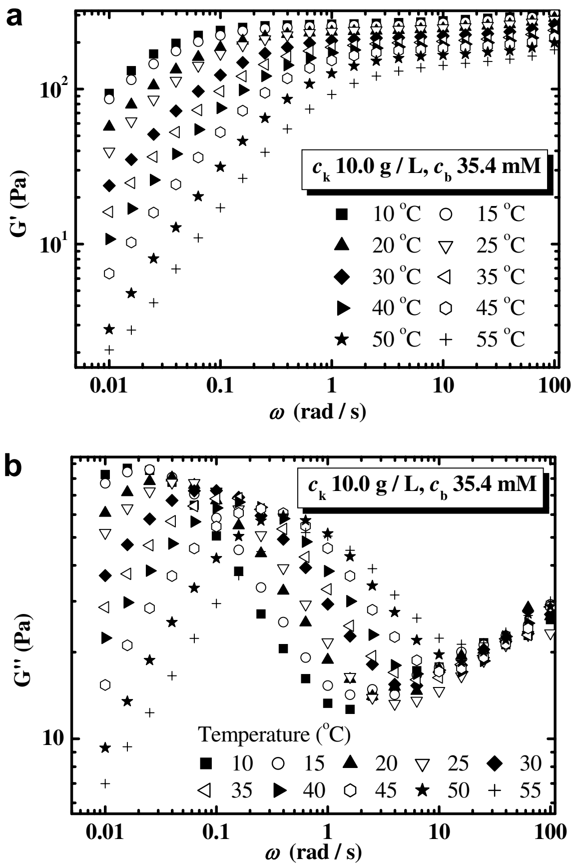


Fig. 10. Temperature dependence of G' (a) and G'' (b) for KGM/borax gel ($c_{\mathrm{k}} = 10.0$, $c_{\mathrm{b}} = 35.4$ mM).

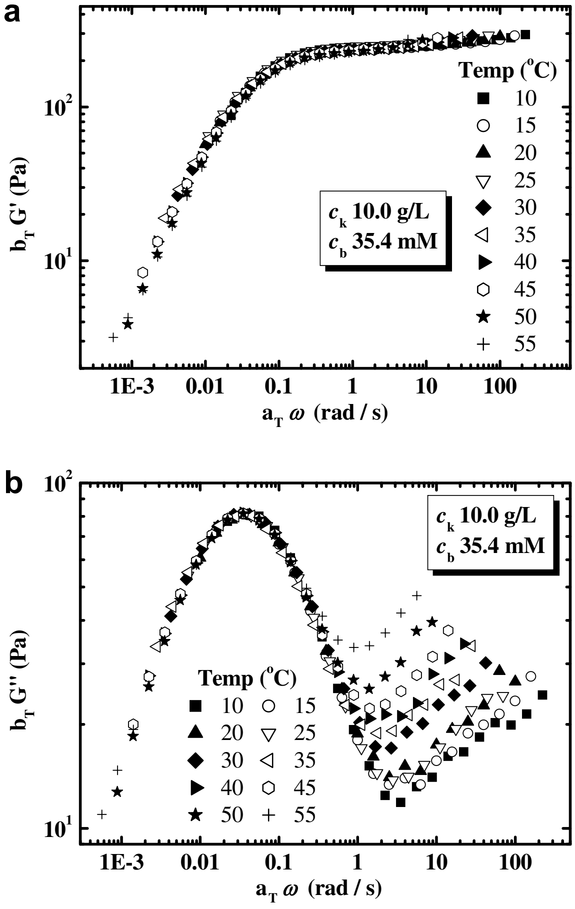


Fig. 11. Master curves of G' (a) and G'' (b) for KGM/borax gel ($c_{\mathrm{k}} = 10.0$ g/L, $c_{\mathrm{b}} = 35.4$ mM) from 10 to 55 °C. The reference temperature is 20 °C.

for $G'$and G'' are shown in Fig. 11a and b, respectively. The data of G' and G'' are well superposed in the entire relaxation zone for G' and in the terminal zone for G''. Actually, the curves of $G'' \sim \omega$ were horizontally shifted with respect to the longest relaxation time by determining the values of a_T using Eq. (10). Since short-time relaxation modes are unaffected by the widely spaced borate crosslinks, the relaxation processes in the transition zone at higher frequency do not superpose, as shown in Fig. 11b. Similar superposition behavior (overlapping at low and moderate frequency and divergence at high frequency) has been reported (Kesavan & Prud'homme, 1992; Pezron et al., 1990; Tayal et al., 1999) for time–temperature, time–pH, and time–polymer molecular weight superposition of guar/borax gels.

The same shift factors determined according to the characteristic G''_{ma} and the corresponding frequency ω_{ma} (Eqs. (10) and (11)) can be successfully used for the shifting of $G' \sim \omega$ curves to obtain good master curve, which is an indication of the validity of the time–temperature superposition. One can see that there are only minor changes in G'_p (Fig. 10a) and G''_{ma} (Fig. 10b and Table 2) for the gels over a wide temperature range, and thus only minor vertical shift factors are needed to obtain the master curves. This indicated that the borate ion crosslinkage does not change the "mesh" size of the gel network (judged from the values of b_T), but it does change the longest time scales for chain interaction (judged from a_T) (Kesavan & Prud'homme, 1992; Tayal et al., 1999).

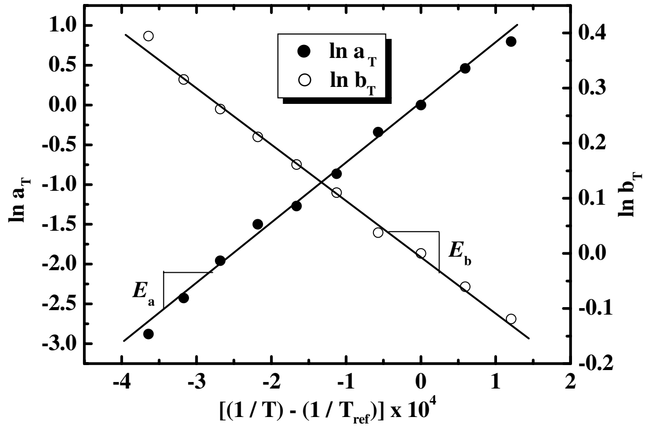


Fig. 12. Plots of a_T and b_T as a function of reciprocal of absolute temperature (Table 3) using Arrhenius representation.

The shift factors of time–temperature superposition for thermoreversible gels can generally be fitted using Arrhenius representation

$$\ln a_T = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \tag{12}$$

$$\ln b_T = \frac{E_b}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \tag{13}$$

where E_a and E_b are the apparent activation energies, which are, respectively, corresponding to the relaxation energy and crosslinking reaction energy (Pezron et al., 1990; Schultz & Myers, 1969). Plots of shift factors as a function of reciprocal of absolute temperature are shown in Fig. 12. Good linear fits are obtained for both a_T and b_T in the temperature range of the present study. The absolute values of E_a and E_b drawn from the slopes of linearly straight lines are listed in Table 3.

Time–temperature superposition by using the shift factors determined from the G''_{ma} and ω_{ma} (corresponding to the longest relaxation time) was found to be effective to the KGM/borax gels with various KGM and borax concentrations. In most cases, good linear fits of a_T and b_T can be obtained (data not shown). Table 3 listed the results of E_a and E_b for some KGM/borax gels, and those for some other complex gels are also listed. It seems that E_a is basically independent of KGM and borax concentrations, while E_b is affected by that. Comparing E_b of the gels with the same c_b (23.6 mM) and different c_k (5.0, 7.5, 10.0 g/L), E_b decreased with increasing c_k. E_b of the gels with the same c_k (10.0) also decreased with c_b (11.8, 23.6, 35.4 mM). This observation seems in line with the conclusion that the efficiency of crosslinking decreases as the concentration of polymer or borax increases (Cheng & Rodriguez, 1981). E_b of the gels ($c_k = 10.0$ g/L) with $c_b = 23.6$ and 35.4 mM are obviously lower than that of the gel ($c_k = 10.0$ g/L) with $c_b = 11.8$ mM. Cheng and Rodriguez (1981) have also found that excess borons change the gel structure and decrease the activation energy required for breaking individual crosslinks. By using ^{11}B NMR, Pezron et al. (1989a) have observed a sharp decrease of complexation constants with increasing borax concentration for different poly (hydroxyl compound)/borax systems. Additional ^{11}B NMR measurements will provide further information about the effect of borax and KGM concentrations on the equilibrium constants of borate complexation reactions.

Table 3
List of the values of E_a and E_b for KGM/borax gels in the present study and guar/borax and PVA/borax gels from previous reports

System	KGM/borax					Guar/borax		PVA/borax	
	c_k5.0 c_b 23.6	c_k 7.5 c_b 23.6	c_k 10.0 c_b 11.8	c_k 10.0 c_b 23.6	c_k 10.0 c_b 35.4	Pezron et al. (1990)	Kesavan and Prud'homme (1992)	Schultz and Myers (1969)	Cheng and Rodriguez (1981)
E_a/kJ mol^{-1}	69.7	64.5	71.3	61.1	62.6	58	81.5	42	
E_b/kJ mol^{-1}	15.8	13.9	12.3	8.5	8.4	14	27.8	21	10.5

4. Conclusions

The crosslinking of KGM in aqueous solution with borate ions coming from the dissociation of borax formed thermoreversible gels. The dynamic viscoelastic behavior of these gels can be characterized by three parameters: the plateau values of elastic modulus G'_{p}, the maximum in loss modulus G''_{ma}, and the frequency ω_{ma} corresponding to G''_{ma}. Superposition principle was successfully applied to obtain the master curves of reduction moduli for the gels with different KGM and borax concentrations by referring to the values of ω_{ma} and G''_{ma}. Effect of KGM and borax concentrations on G'_{p} can be described using an empirical formula. The critical strain for the gel at the same KGM concentration was found to be independent of borax concentration, whereas the yield stress firstly increased with increasing borax concentration and then decreased. Time–temperature superposition principle was successfully applied to the gels and the master curves with six decades in frequency were obtained, where the horizontal and vertical shifting factors were determined in relation to the values of ω_{ma} and G''_{ma} at different temperatures. The values of apparent activation energies corresponding to the relaxation and crosslinking reaction are 61–72 kJ mol^{-1} and 8.4–16 kJ mol^{-1}, dependent on the KGM and borax concentrations. The crosslinks in the gel network is dynamic in nature and affected by concentrations of KGM and borax as well as temperature.

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