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Viscoelastic properties of Ca^{2+}- and Na^{+}-gellan gum aqueous solutions

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Viscoelastic properties of gellan gum aqueous solutions under forces of the order of 10^{-6}–10^{-8} N and displacements of 10^{-3}–10^{-4} m were studied using a magnetic rheometer constructed in our laboratory. The concentration of Ca^{2+} in the gellan gum has a strong effect upon the mechanical behaviors of the solutions: (i) solutions of Specimen 1 (Ca^{2+} 0.5 wt%, $C_p = 1.15\%$) showed negative thixotropy; (ii) abrupt decrease in viscosity was observed in the narrow temperature range (±1°C) for the solution of Specimen 2 (Ca^{2+} 0.1 wt%, $C_p = 1$–3 wt%) and Specimen 3 (Ca^{2+} <0.01%, $C_p = 2$–3%), while rigidity was almost constant in the same temperature range; (iii) the solution of Specimen 3 shows unstable mechanical behavior, and this may be attributed to the inhomogeneity of the order of $\sim 10^{-4}$ m in solution. A small amount of Ca^{2+}, as in the case of Specimen 2, removes this inhomogeneity from gellan gum aqueous solutions. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Gellan gum has a repeating unit as is shown in Fig. 1 (Brownsey *et al.*, 1984), and has found extended applications in the biological and food industries in Japan since 1988. Studies on gellan gum by different laboratories using the same samples were proposed by the Research Group on Polymer Gels affiliated to the Society of Polymers, Japan (The Research Group on Polymer Gels, 1993) following the history of the rheology cultivated by the distribution of polisobutylene from the National Bureau of Standards, and the specimens were kindly offered by the San–Eigen F.F.I. Co. Ltd, Osaka, Japan, and also by the Kelco Co. Ltd, USA, and these were used here as common specimens.

EXPERIMENTAL

The specimens used in this work are:

[Specimen 1]; Untreated, original gellan gum offered by the San–Eigen F.F.I. Ltd, Osaka, Japan (Lot No. 62058A).
[Specimen 2]; Ca^{2+} was reduced from Specimen 1. This was kindly offered by Dr G. Sanderson of The Kelco Co. Ltd.
[Specimen 3]; Ca^{2+} of Specimen 1 was converted to Na^{+} using an ion exchange resin.

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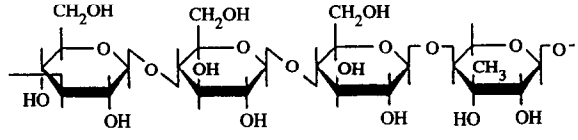

Fig. 1. Repeat unit of a gellan gum molecule.

The molecular weights and the quantitative analytical results (Kubota & Okamoto, 1992; Ogawa & Ogino, 1993) are shown in Table 1. Water used in this experiment was purified by distillation (Autostill Type WG200, the Yamato-Kagaku Co. Ltd, Japan), and the electric conductivity of distilled water was confirmed as less than 0.5×10^{-4} S·m^{-1}. Each solution of gellan gum was prepared by (i) holding for 1 h at 40°C after the specimen was dispersed in water, (ii) stirring for 4 h at 90°C using a magnetic stirrer, and (iii) holding the solution for a definite time at constant temperature (these are our definitions of 'preserving time' and 'preserving temperature').

Several methods for obtaining the viscoelastic values of solutions using a suspended iron ball (Manuel *et al.*, 1984; Hilfiker *et al.*, 1989) or nickel powder (Hiramoto, 1978) have been proposed. The arrangement of our rheometer (Shimazaki, 1992) and the principal method of obtaining the viscoelasticity of solutions (Shimazaki, 1993; Takahashi & Ogino, 1994) are briefly summarized as follows: a ferromagnetic ball is suspended in solution using a

Table 1. Quantitative analytical results and molecular weights

	Specimen 1 (Lot 62053A)	Specimen 2 (Kelco Co. Ltd)	Specimen 3
Na	0.19%	3.03	3.15[a]
K	2.08	0.19	0.004[a]
Ca	0.512	0.11	0.01[b]
Mg	0.146	0.02	0.01[b]
$<M_w>$[d]	2.1×10^{5}[c]	---	
$<M_n>$[e]	0.5×10^{5}[c]	---	

[a] By flame spectrophotometry; [b] by chelatometry; [c] observed at 40°C in TMAC; [d] Kubota & Okamoto (1992); [e] Ogawa & Ogino (1993).

controlled vertical magnetic field. By making use of an image processor, the viscosity, η, and rigidity, G, of the solution were calculated using the relationship $6\pi\eta r = \sin\phi/(\mathbf{m}\omega)$ and $6\pi Gr = \cos\phi/\mathbf{m} + M\omega^2$; here r is the radius of the ball, ϕ the phase angle between sinusoidal external force $F_0 \cdot \exp(i\omega t)$ and the motion of the ball $A_0 \cdot \exp\{(\omega t - \phi)\}$, $\mathbf{m}$ the ratio of A_0 to $F_0(\mathbf{m} = A_0/F_0)$, ω the angular velocity ($= 2\pi/T$: T = period), and M the mass of the ball.

RESULTS AND DISCUSSION

Typical viscoelastic behavior of aqueous solutions of Specimen 1 in stationary oscillation is shown in Fig. 2. If a solution was held for 24 h at 41°C after dissolving (i.e., preserving time = 24 h, and preserving temperature = 44°C), the amplitude of the oscillating ball decreased rapidly after ~10 cycles (Fig. 3). To reconfirm this behavior, solutions were maintained for various preserving times, and it was clearly found that the longer the preserving time, the shorter the starting time of the decay (Shimazaki & Ogino, 1993). At the point when a ball was immobilized, the apparent rigidity, G, should be infinite. This means that under a force of the order of, e.g., 10^{-7} N imposed on the ball of $2r = 5\times10^{-4}$ m, the strain, which is read from the displacement of the picture of a ball on the cathode ray tube, could not be detected. But even at this point, the solution will flow out under its own weight as the cell is inclined; i.e., fluidity still remains. The value of G in this immobilized state was estimated from the plot of G against $1/t$ (Fig. 4) (Shimazaki & Ogino, 1993); here $G = G(A_0/n)$ and $t = t(A_0/n)$ are the rigidity and the time at which the amplitude reaches A_0/n (n = 1,2,3,4...), and the value of $G(0)$ (Pa) $\sim5\times10^{-1}$ was estimated from the extrapolation of $G(A_0/n)$ to $1/t(A_0/n) \rightarrow 0$, here $G(0)$ is the rigidity at $A_0 \rightarrow 0$ after $t \rightarrow \infty$. From the results of Fig. 3, it is clear that the rigidity G of this solution takes only a figure up one place after a ball was immobilized. Thus the solution will not be a 'gel' having a rigid, permanent three-dimensional structure, and this is the issue which has been pointed out in several treatises

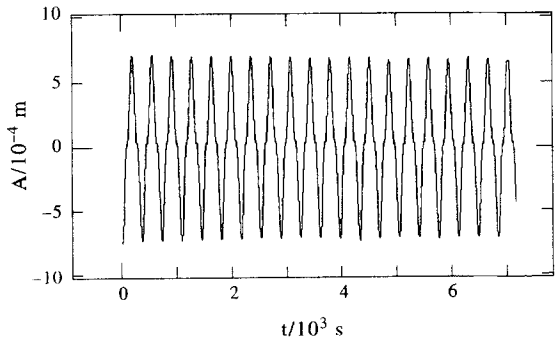

Fig. 2. Typical viscoelastic response for solution of Specimen 1; $C_p/\% = 1.15$, temperature/°C = 41.0, T/s = 360; A_0/m = 7.10×10^{-4}, F_0/N = 2.41×10^{-7}, ϕ/rad = 4.68×10^{-2} η/Pa·s = 1.9×10^{-1}, G/Pa = 7.13×10^{-2}.

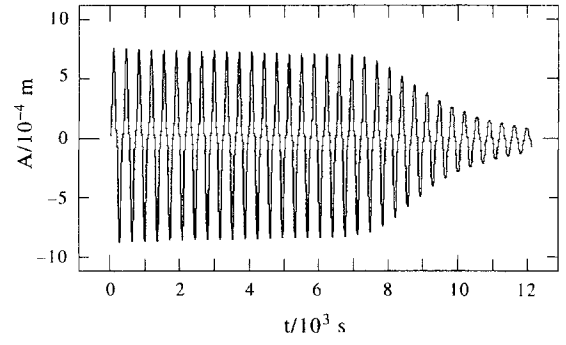

Fig. 3. (Specimen 1). C_p(gellan gum)/wt% = 1.15, temperature/°C = 38, T/s = 360, A_0/m = 7.78×10^{-4}, F_0/N = 2.41×10^{-7}, ϕ/rad = 4.33×10^{-2}. Preserving time/h = 24; Preserving temperature/°C = 41 η/Pa·s = 1.65×10^{-1}, G/Ps = 6.64×10^{-2} (the values are taken from the stationary oscillations before narrowing occurs).

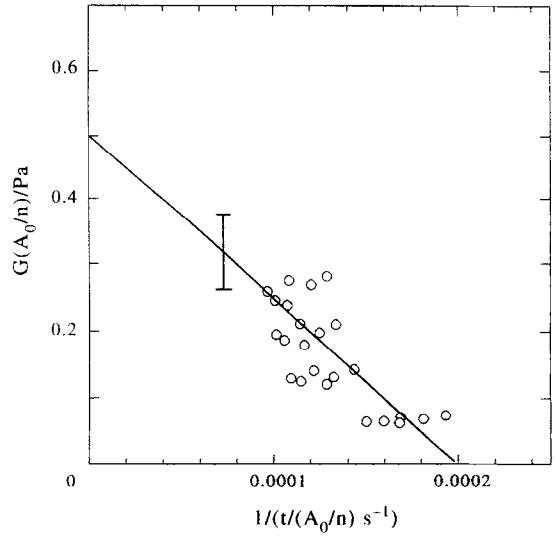

Fig. 4. (Specimen 1). Plot of $G(A_0/n)\sim1/t(A_0/n)$; $G(0)$/Pa $\sim5\times10^{-1}$ was estimated from the extrapolation to $1/t \rightarrow 0$. Preserving time/hrs = 18~96; Preserving temperature/°C = 44, C_p/wt% = 1.15~1.16, t/°C = 38, T/s = 360, F_0/N = 2.41×10^{-7}. (A'_0s have different values for each condition.)

(Paul, 1967a, b; Harrison *et al.*, 1971; Matsuda *et al.*, 1984).

The solution of Specimen 2 (concentration of Ca^{2+} in gellan gum (C_s) = 0.1 wt%) has a striking feature of the temperature dependence of viscosity. For example, in the case of C_p (concentration of gellan gum) = 3.0 wt% and $2r$ (diameter of ball) = 5×10^{-4}, the viscosity of solution changed rapidly from η (Pa·s) = 3.80 to η (Pa·s) = 6.48×10^{-1} in the narrow temperature range of 319.5±0.5 K (Shimazaki & Ogino, 1993). The temperature dependence of viscosity and rigidity in the concentration range from C_p = 3.0 to 1.0 wt% are shown in Fig. 5. Abrupt drops in viscosity were found for each concentration, and the higher the concentration of solutions, the higher the temperature where this fall occurs, while the rigidity was nearly constant in these concentration ranges. These viscoelastic values are listed in Table 2.

The Ca^{2+}-ion in the gellan gum molecule was replaced by the Na^{+}-ion by passing the solution through an ion-exchange resin, and the solution was reduced to a dry powder by 'Freeze Dryer' (The Tokyo Rika-Kikai Co. Ltd, Type FD-5N). This is the Specimen 3, and the content of Ca^{2+} could not be detected by usual chelatometry, because the concentration of Ca^{2+} was lower than that of the limit of the sensitivity of chelatometry (i.e. *C*s 0.01 wt%). Aqueous solutions of Specimen 3 were clear and transparent in contrast to the faint brown solution of Specimen 1, and its mechanical behavior was often unstable. And in some cases, stable oscillations were found after stirring solutions, e.g. for about 120 h at 40°C, and an example of viscoelastic values before and after this treatment is shown in Table 3. The viscoelastic properties described below are obtained from these stable oscillations.

We observed the movement of a ball of 10^{-4} m in diameter (mass 10^{1} mg) under the external force with an amplitude of the order of 10^{-7}–10^{-8} N (10^{-2}–10^{-3} mg weight). If there were heterogeneous structures of the order of 10^{-4} m in solutions, and if the movement of the ball was influenced by this heterogeneity, under this weak external force, apparent unstable oscillations will appear. This heterogeneity in solution as evidenced by the unstable oscillation would disappear after stirring the solution for hours. Small amounts of Ca^{2+}–ion would be effective in making gellan gum aqueous solutions homogeneous over a macroscopic scale ($\sim10^{-4}$m).

The temperature dependence of viscosity and rigidity for the solution of Specimen 3 was also measured under the same conditions as Specimen 2. The abrupt drops in viscosity were also found in the narrow temperature range, while rigidity was nearly constant, as was the case of Specimen 2 and the results are shown in Fig. 6 and Table 2.

Nakamura & Tanaka (1994) reported the viscoelastic properties of aqueous solutions of Specimen 2

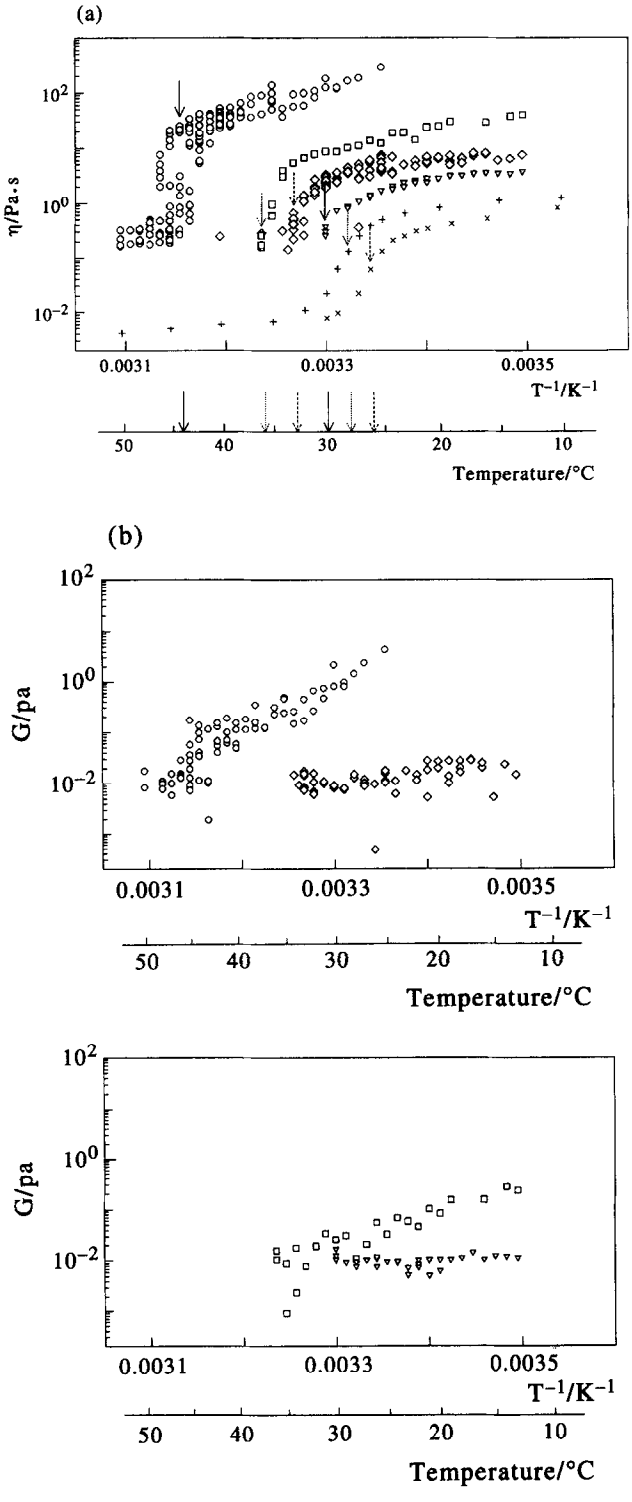

Fig. 5. (Specimen 2). (a): Plot of log $\eta\sim1/T$ (and °C). (b): Plot of $G\sim1/T$. The observed conditions are the same as (a). Diameter of ball/10^{-3} m = 2.5, 1.0, 0.5, 0.39 for C_p = 3.0 wt%, and 0.5 for the other concentrations. Period T/s = 360, $F_0/10^{-7}$ N~0.5 to 2.8. ○: 3.0%; □: 2.0%; ◇: 1.5%; ▽: 1.0%; +: 0.8%; ×: 0.6% (from Nakamura K. (1994)).

(C_p = 0.6–0.8%) using a coaxial rheometer (OD = 12 mm, ID = 10 mm, = 10 mm[1].

The same unit as was used in the original paper.[1] under the angular velocities of (ω/rad·*s*) 10^{0}–10^{1}, and

Table 2. The values of the Eldridge–Ferry plot for Specimens 2 and 3

Specimen 2		Specimen 3	
C_p (wt%)	t_{tr} (°C)[a]	C_p (wt%)	t_{tr} (°C)
3.0	44	3.0	36
2.5	—	2.5	34
2.0	36	2.0	32
1.5	33		
1.0	30		
0.8[b]	28		
0.6	26		

[a] t_{tr} (°C): the temperature at which viscosity drops abruptly; [b] data from Nakamura & Tanaka (1994).

Table 3. Viscoelastic values of Specimen 3 before and after stirring by magnetic stirrer for 120 h at 40°C

	Before[a]	After
C_p (wt%) =	1.66	1.99
Observed at (°C)	33.0 (306 K)	33.0 (306 K)
Period (s)	360	360
A_0 (10^{-3}m)	1.14	0.62
F_0 (10^{-7}N)	1.47	1.30
η (Pa·s)	1.48	2.56
G (10^{-3}Ps)	9.37	0.37

[a] Left for 1 h at 40°C, and stirred for 4 h at 90°C.

also found abrupt changes in η. Their results are also shown in Fig. 5. and Table 2.

The Eldridge–Ferry plot (Eldridge & Ferry, 1954) was examined by using the data of Table 2, and these could be fitted by the same straight line, despite the results from the different measuring methods, as is shown in Fig. 7; i.e. the plot of $\log_e C_p$ vs $1/T_{tr}$ (= temperature at which abrupt change occurs in η) shows a linear relation with the gradient of $\Delta H \simeq 85$ kJ·mol^{-1} (i.e. exothermic) in the concentration range from 0.6 to 2.0 wt% for Specimen 2; here, ΔH is the heat absorbed per mole by the formation of cross-links or junction zones between adjacent polymer chains. The amount of released heat may arise from the formation of weak or physical interactions between several polysaccharide chains as the temperature is lowered below T_{tr}. It is therefore not possible to attribute ΔH to a specific interaction, from this experiment. We may however suggest the following picture: some kind of macroscopic, or local 'structures' are formed as is the case for fresh egg white, in which gel and sol components are dispersed in water. The size of these components is comparable to the order of the ball suspended in the 'solution'. When the concentration of Ca^{2+} was ~0.5 wt%, interactions between sol–gel (or sol–sol or gel–gel) were enhanced by the introduction of Ca^{2+}, and the rigidity would be increased slightly (in the case of Specimen 1). When the concentration of Ca^{2+} is less than 0.1 wt%, the 'structure' in

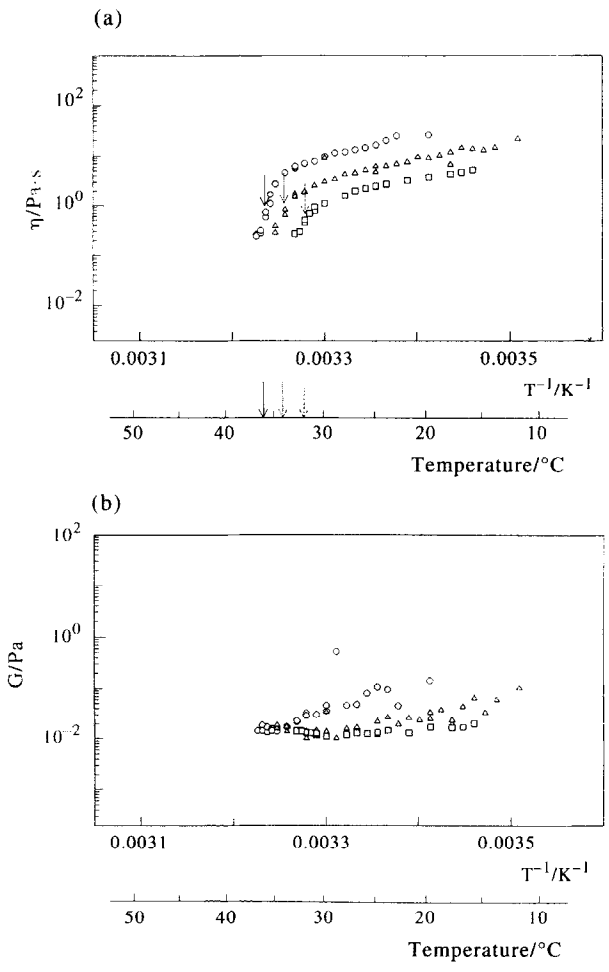

Fig. 6. (Specimen 3). (a) Plot of log η~$1/T$ (and °C). (b) Plot of G~$1/T$. Diameter of ball/10^{-3} m = 0.5, C_p = 3.0~2.0 wt%. Period T/s = 360, $F_0/10^{-7}$ N~0.5–2.8. ○: 3.0%; △: 2.5%; □: 2.0%.

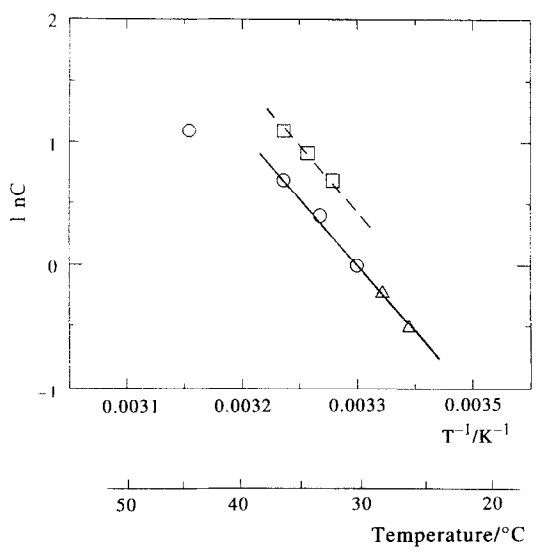

Fig. 7. Eldridge–Ferry plot for Specimen 2 (○) together with the results by Nakamura & Tanaka (1994) (△). The slopes (solid line) were found to be in reasonable agreement; $\Delta H \simeq$ 85kJ · mol^{-1} (−20 kcal · mol^{-1}: exothermic); (the point of 3.0% deviates from this line to the side of small gradient);(- dotted line for Specimen 3 (□)).

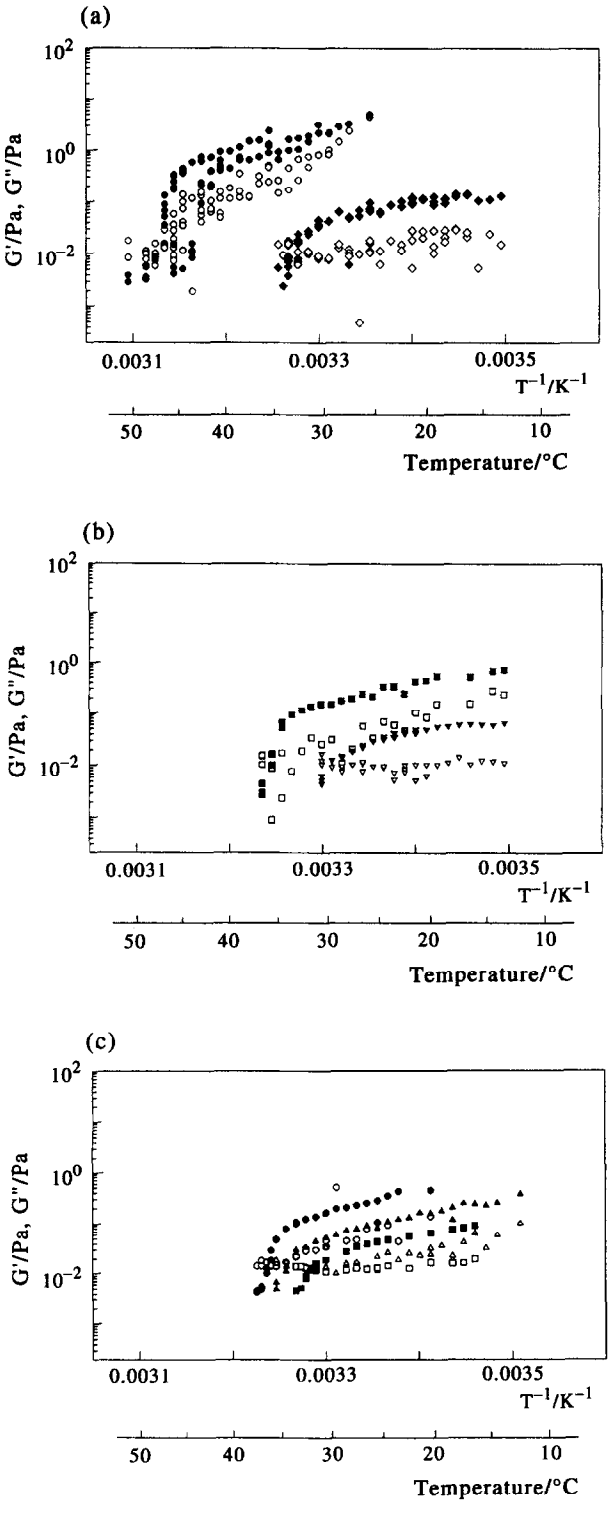

Fig. 8. Plot of G' and G'' against T: (a), (b) for Specimen 2, and (c) for Specimen 3. Keys used here are the same as in Figs 6 and 7 (open symbols for G', solid symbols for G'').

the sol is disrupted as the temperature is increased. This structure disruption results in a decrease in the viscosity of the solution but not the elastic properties if the sol–gel interactions are hardly changed (in the case of Specimen 2).

Reversibility of the change in viscosity or rigidity as the temperature was raised or lowered is now under study.

Clark & Ross-Murphy (1987) classified solutions by the plot of G' and G'' (G^* (complex modulus) $= G' + i \cdot G''$) against ω (angular velocity) as sol state, cross-over region and gel state. We plotted G' and G'' against T, and the results are shown in Fig. 8. The temperatures of the cross-over region in Fig. 8 coincided with the inflexion points of temperatures in Fig. 5.

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