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The rheological properties of weak gels of poly(vinyl alcohol) and sodium borate

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The aim of this work was to establish whether the lifetime of the junction zones in the poly(vinyl alcohol)/borate gels depended on the chemical composition or concentration of the constituents. It was found that the maximum in the distribution of lifetimes was about 0.3 s and independent of the polymer, borate concentrations and of the degree of hydrolysis of the polymer. The gels changed their non-linear rheological behaviour with age, being strain softening when freshly prepared but strain hardening after a few days. This change in behaviour was attributed to a redistribution of borate ions with time. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The behaviour of polymeric gels under shear is strongly affected by the nature of the links between the polymer chains and in particular their lifetime. Where these links are permanent, flow does not occur over any reasonable time scale and where they are of limited time scale, the rheology depends on the time scale of the observation. Weak polymeric gels having temporary crosslinks are well known and examples include polysaccharides with borate ions[1], polyacrylamide with chromate ions[2] and poly(vinyl alcohol) with borate ions[3].

Considerable effort has been spent on the poly(vinyl alcohol) borate system in establishing the nature of the borate/polymer link. N.m.r. studies[4] of both the polymer chain and the ^{11}B spectra of the borate ions have indicated that the $B(OH)_4^-$ binds to alternate OH groups on the polymer, especially when these are in the *meso* configuration. The nature of the junction is not absolutely clear, as there are proposals for the borate ion to link to both chains directly[3,5], while others have suggested that one of the links is via the sodium ion[6,7]. The formation of the crosslink[3,7,8] is exothermic, between 1–2 kJ mol^{-1}, so that gel formation is opposed by increasing temperature[9].

It is well established that a minimum concentration of polymer is needed to allow the gel to form and this concentration corresponds[3] closely to C^*, the overlap concentration. Below this, most of the borate ion/polymer interaction is intrachain, whereas gel formation requires interchain links.

The rheological behaviour of gels is largely determined by the number of links in the gel and their lifetime. The relaxation times[10–14] of viscoelastic materials may be obtained from the frequency dependence of the moduli, G', G''. Mathematical models[13] have indicated possible mechanisms for strain hardening/softening for gels and the present work was initiated to establish any influence of polymer chemistry or composition on these properties. In particular the aim of the work was to establish the influence of crosslink density and polymer characteristics (such as chain length and degree of hydrolysis) on the behaviour of the gel.

EXPERIMENTAL

All rheological measurements were carried out on a strain-controlled Rheometrics RDS-II rheometer fitted with force rebalance transducers of maximum torques of 0.01 and 0.2 Nm. In all cases a 25 mm diameter cone-plate geometry was used. A temperature of 20°C was chosen unless otherwise stated. To prevent water evaporation, sufficient humidity was maintained above the sample.

The poly(vinyl alcohol) (PVOH), was obtained from Nippon Gohsei, Osaka, Japan. The gel samples, shown in *Table 1*, were prepared by dissolving sodium borate and PVOH separately and then mixing by shaking. Gel samples C2 and C4 were heated to 80°C and then allowed to cool, prior to measurement, to determine whether any of the properties depended on preparation method. Bacterial contamination was noticed in some of the samples after a few weeks, and sodium azide (1 mg l^{-1}) was added to sample D to prevent this. Over the time scale of the measurements, no bacterial contamination was noticed.

The manufacturer's data for GM14 are: 86–89% hydrolysed; 20–24 cps viscosity for a 4% solution; GL05:

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Table 1 Poly(vinyl alcohol) properties)

Sample No.	PVOH type	Conc. PVOH (wt%)	Conc. sodium borate (wt%)
A1	GM14	2.25	0.5
A2	GM14	2.25	1.0
B1	GM14	6.6	1.0
B2	GM14	6.6	0.6
B3	GM14	3.3	1.0
B4	GM14	2.0	1.0
B5	KH17	6.6	1.0
B6	GL05	6.6	1.0
C1	GM14	2.2	0.94 (cold prep)
C2	GM14	2.2	0.94 (hot prep)
C3	GM14	2.2	3.74 (cold prep)
C4	GM14	2.2	3.74 (hot prep)
D	GM14	3.3	1.0

86–89% hydrolysed and 4.8–5.8 cps viscosity for a 4% solution; KH17: 78–81% hydrolysed and 32–38 cps viscosity for a 4% solution.

Relaxation spectrum

For any viscoelastic material, the rheology may be modelled by the well-known series of Maxwell spring and dashpot elements, where the ith element has a relaxation strength g_i and characteristic relaxation time of λ_i. The set of (g_i, λ_i) gives the relaxation spectrum of the material. The stress $\tau(t)$ at time t, is given by

$$\tau(t) = -\int_{-\infty}^{t} g/\lambda[\mathrm{e}^{-(t-t')/\lambda}]\gamma(t,t')\,\mathrm{d}t' \qquad (1)$$

where the strain $\gamma(t,t'') = \int_t^{t'} g(t'')\,\mathrm{d}t'$. Non-linear[14] effects may be taken into account, but in this work only the linear part of the moduli data was used. If the (g_i, λ_i) can be determined, the response of the fluid to rheometric deformation can be predicted in the linear region. Several methods have been put forward for establishing the spectrum[15–17] and the numerical method here was to use eleven time constants, logarithmically spaced between about 10^{-3} s and 10^{3} s to fit the G' and G'' data[14].

RESULTS

Linear viscoelastic behaviour

The storage and loss moduli were measured as a function of frequency for all samples, typical results being shown for two PVOH/borate systems in *Figure 1a, b* at different strains. It was found that these materials behaved linearly to strains in excess of 30%, though as discussed later, the strain at which nonlinearity started depended on frequency. The curves of G' and G'' as a function of frequency remained the same at strains below 30%.

The viscoelastic behaviour in *Figure 1* was modelled (as described above) assuming a Maxwell fluid with a distribution of relaxation times. In *Figure 2* the relaxation spectra are shown for a range of PVOH/borate systems with a variety of compositions (see *Table 1*). The general shapes of the relaxation spectra do not depend on polymer molecular mass, concentration or borate ion concentration. The main relaxation times are around 0.1 s, with shorter times from the Rouse modes starting at times faster than 10^{-2} s. These modes were not visible in all data as the 0.01 Nm transducer has a poorer resolution in the high frequency region than the 0.2 Nm transducer. The absolute values of the moduli in the relaxation spectra increase with the number of cross-links present and therefore increase with the polymer and borate ion concentrations.

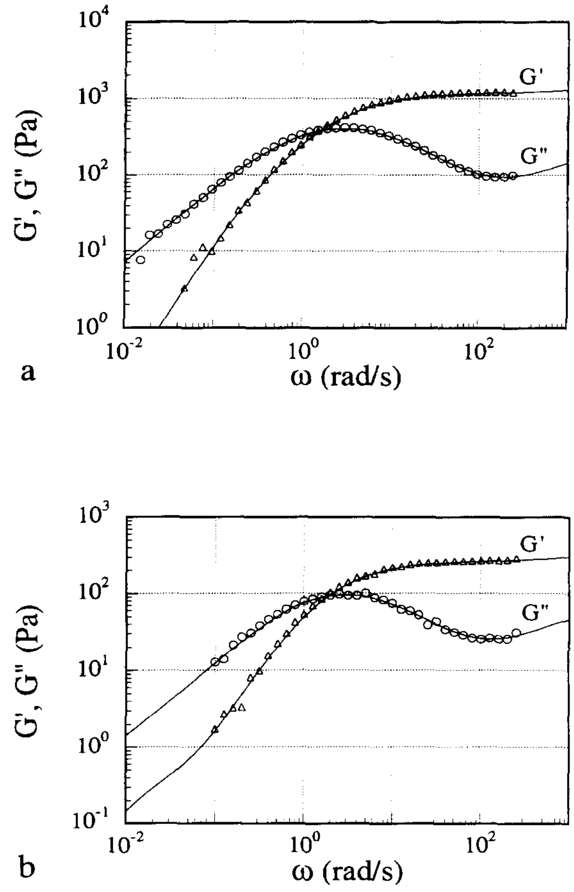

Figure 1 Frequency sweeps; lines drawn are best fit using calculated spectrum of 11 relaxation times. (a) Sample B3; $T = 20°\text{C}$; $\gamma = 10\%$. (b) Sample C1; $T = 20°\text{C}$; $\gamma = 20\%$

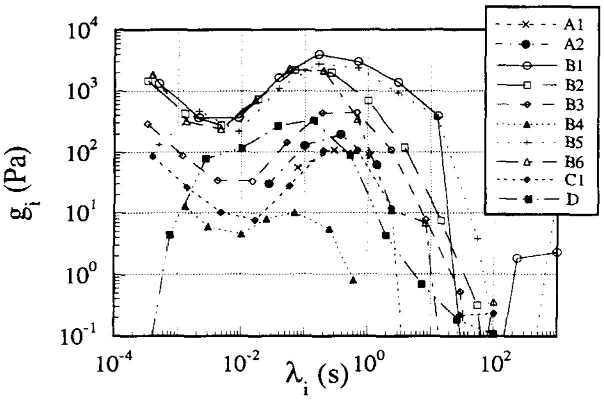

Figure 2 Spectra of relaxation times for samples A1, 2; B1, 2, 3, 5, 6; C1 and D; $T = 20°\text{C}$

The moduli (G', G'') for sample B3 were measured at temperatures between 10 and 60°C (*Figure 3*). The decrease in the moduli is a result of the weaker binding of the borate ion to the PVOH chain as would be expected by the exothermic nature[9] of the binding.

The moduli (G', G'') in the linear region for sample D (*Figure 4*) were measured at 0, 7 and 17 days after

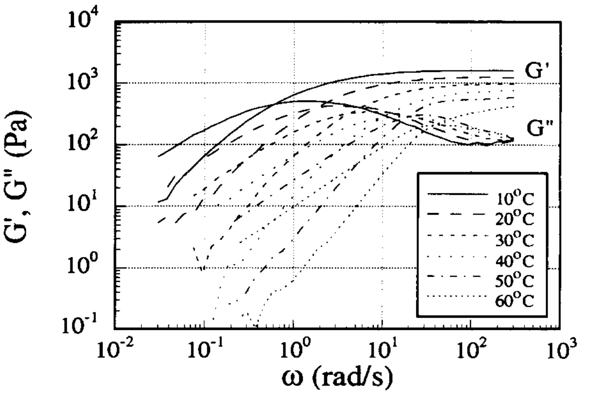

Figure 3 Frequency sweep, G', G'', for sample B3 at six temperatures, 10–60°C at strains of 10, 10, 20, 50, 200 and 300% respectively

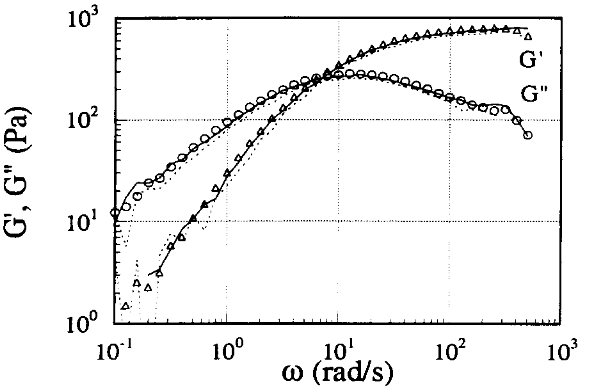

Figure 4 Frequency sweep G', G'' for sample D: immediately after preparation, ○, △; 7 (dotted line) and 17 (full line) days later; $T = 20°C$; $\gamma = 10\%$

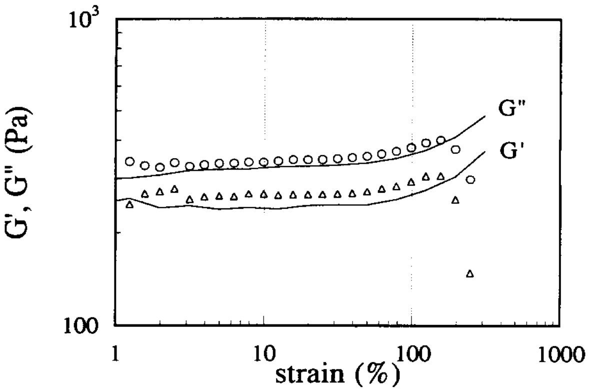

Figure 5 Dynamic strain sweep, G' (△), G'' (○) for samples B3; $T = 20°C$; $\omega = 1\ \mathrm{rad\,s^{-1}}$ immediately (data points) and 14 days (lines) after preparation

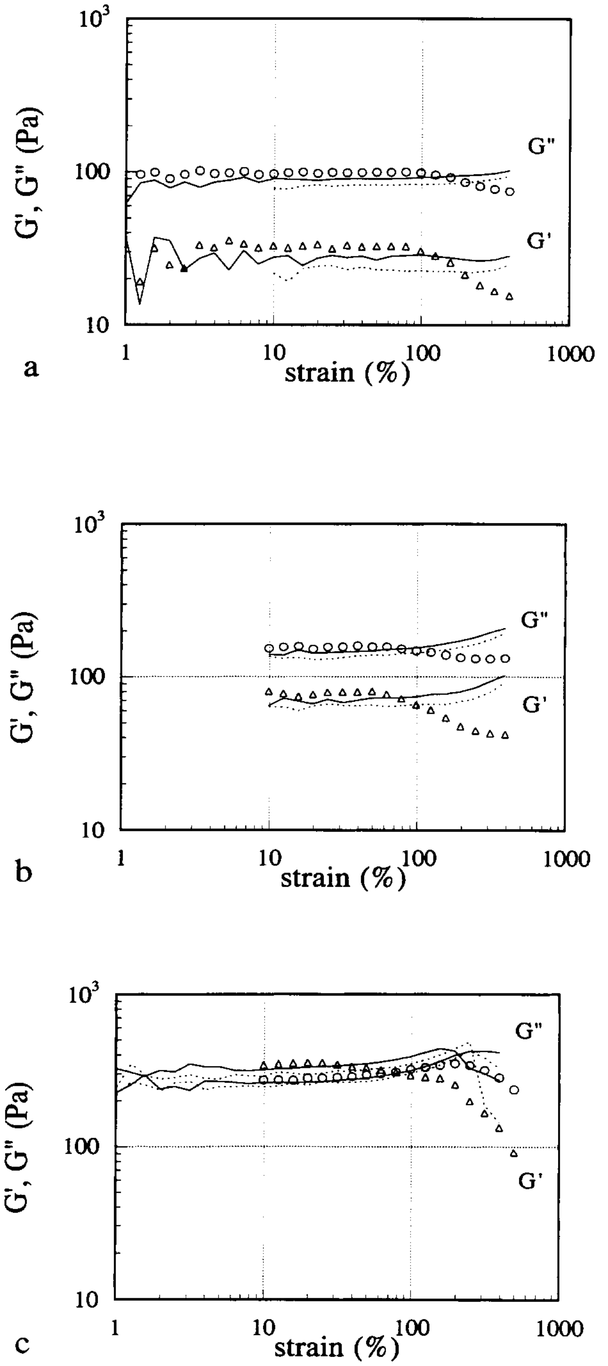

Figure 6 Dynamic strain sweeps, for sample D, $T = 20°C$ at various frequencies. For each frequency, measurements were taken at three times: immediately after preparation (data points) 7 days after preparation (lines); 17 days after preparation (dotted lines). (a) $\omega = 1\ \mathrm{rad\,s^{-1}}$; (b) $\omega = 2\ \mathrm{rad\,s^{-1}}$; (c) $\omega = 10\ \mathrm{rad\,s^{-1}}$

preparation, showing no significant change with age and having a cross-over at about $7\ \mathrm{rad\,s^{-1}}$.

Non-linear behaviour

The non-linear behaviour was measured by performing dynamic strain sweeps on a sample at a number of frequencies as shown in *Figures 5* and *6a–c*. It was found that immediately after preparation, the gels were strain softening, through after about a week, they had become strain hardening prior to softening and remained so after a further 10 days.

The stress relaxation experiments were carried out by subjecting the samples to nearly instantaneous strain and measuring the relaxation of the stress. The results, shown in *Figures 7a, b* for a range of strains between 50 and 500%, demonstrate that the fresh sample is strain softening: the modulus decreases with increasing strain. At times faster than 0.1 s the moduli have (Rouse) contributions from chain motions and are not determined by the cross-links of the gel network alone; in addition for stress relaxation experiments it requires 0.1 s to cease application of strain so that data at shorter times than this are unreliable. *Figure 7b* shows that the material

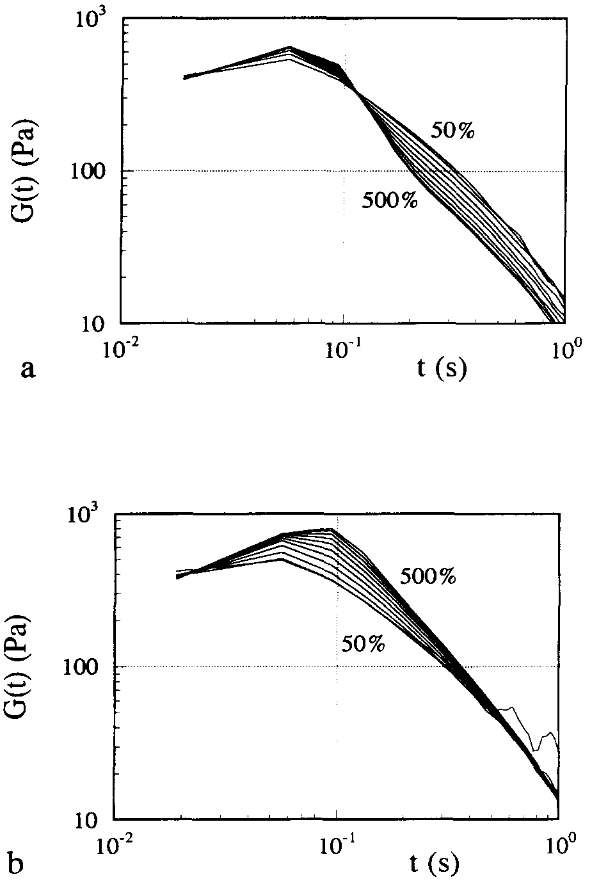

Figure 7 Stress relaxation experiments: $G(t)$ for sample D at strains of 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500%: (a) immediately after preparation; (b) 7 days after preparation

has become strain hardening at an age of 7 days, in agreement with *Figures 5* and *6*.

The strain sweep measurements on a fresh sample, *Figures 8a, b* show strain softening for all frequencies. The linear region which is difficult to define precisely, extends to higher strains for lower frequencies, as also shown in *Figure 6*.

DISCUSSION

The main points to understand are that the relaxation times are independent of chemical composition, the different behaviour of the gels with age and the occurrence of strain hardening.

The relaxation times for the gel samples (*Figure 2*) have a maximum at about 0.3 s, and the distribution of times do not show any systematic variation with gel composition. This indicates that the relaxation process is essentially determined by the lifetime of the borate/polymer link rather than polymer chain entanglement or cross link density[8, 19]. The magnitude of the relaxation moduli do depend on the number of crosslinks and in this system, where the crosslinking borate is in equilibrium with the polymer chains the number of crosslinks depends on both the borate and polymer concentrations. Hence the moduli increase with polymer and borate ion concentrations.

In the linear region the moduli of sample D showed no change over a period of 17 days (*Figure 4*). This is probably because in the linear region they are determined by the total number of cross links, not their distribution.

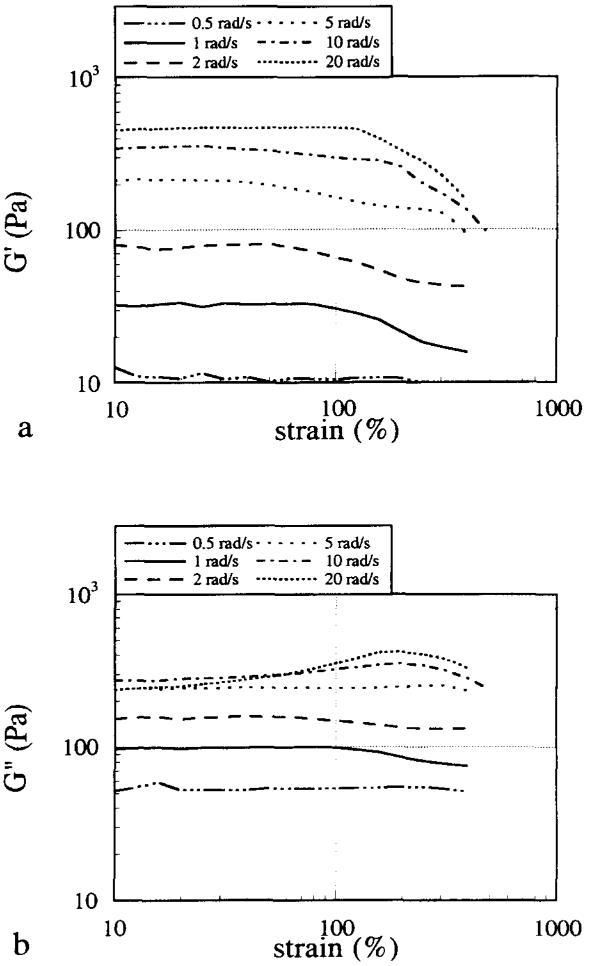

Figure 8 Dynamic strain sweeps at frequencies 0.5, 1, 2, 5, 10 and 20 rad s^{-1} for sample D immediately after preparation

However, in the non-linear region, the moduli do change with age of the gel. *Figures 5* and *6* show that several samples are strain softening at short times after preparation but have become strain hardening after 10 or 17 days. An earlier report[25] has attributed ageing to hydrolysis of the polymer, based on ^{11}B n.m.r., pH and viscosity data. Their measured viscosity decreased by a factor of about 100 over 21 days, a decrease not observed in this study. Thus we believe hydrolysis is not important in our systems. Chemical ageing of crosslinks may be ruled out as the linear spectrum does not change with age. For the same reason bacterial contamination is not significant. The change from strain softening to strain hardening is possibly a result of changes in the architecture of the gel, i.e. the distribution of the borate ion throughout the gel. On mixing the borate solution with the polymer, gelation occurs almost instantaneously and in the initial seconds is visually inhomogeneous and 'lumpy'. This may be because the borate ion is unevenly distributed throughout solution, being concentrated in some regions and more dilute in others. With time the borate ion will redistribute uniformly, though this will be slow as most of the borate is complexed[20] by the polymer at the basic pH in this system. This leads to strain hardening when the complex is uniformly distributed throughout solution. In freshly made gels where the complex is not uniformly distributed, large strains will cause most deformation in the lightly crosslinked regions, leading to strain softening, found for entangled polymer chains.

If the relaxation spectra are mainly determined by the lifetime of the borate/polymer crosslink, the borate distribution throughout the gel will not influence the spectra obtained as seen in *Figure 2*.

Non-linear behaviour (shear thickening and strain hardening) in both polymer[21] and colloid[22] systems has been reviewed recently. Shear thickening of gel systems has been modelled[13,23,24] by comparing the relative rates of association and dissociation of polymer chains during deformation. Several mechanisms for such nonlinear behaviour of a polymer in deformation have been proposed: the finding that in flow more crosslinks are created than lost[12] or a deformation-induced shift from intra- to interchain complexes both lead to shear thickening. Strain hardening may be treated in a similar way.

With a transient network such as exists in this system, the strain experienced by each chain will depend on the rate of deformation. *Figure 8* shows that the point at which the non-linear behaviour begins depends inversely on the frequency of oscillation. This is because at constant strain, the velocity gradient across the gel increases with increasing frequency. For a fixed strain at low frequencies, where the junctions have time to dissociate, viscous motion (as in simply entangled chains), can relax the stress, giving linear behaviour with strain; at high frequencies, when the junctions have insufficient time to dissociate, the measured moduli will depend on strain giving strain hardening or strain softening.

CONCLUSIONS

The rheological properties of gels of poly(vinyl alcohol) and sodium borate have been measured using oscillatory and stress relaxation techniques. The relaxation spectrum for the gels (at slower times than the Rouse modes), determined by the lifetime of the borate/polymer junction has been determined from the oscillatory data. It was found to be about 0.3 s and independent of the chemical composition of the gel. The moduli (G', G'') of the gel were independent of the age of the sample, though they did depend on the age of the gel in the nonlinear region. This was attributed to a change in the architecture of the gel, i.e. to a more uniform distribution of borate ions as the age of the gel increases.

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