Carbohydrate Polymers **12** (1990) 279–293

Rheological Properties of Galactomannan-Based Gels. Part 2 – Ion Cross-Linked Galactomannan Gels

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(Received 23 November 1988; accepted 10 March 1989)

ABSTRACT

The mechanical properties of borate cross-linked galactomannan gels were studied. The gels were prepared by using borate ions as cross-linking agents in alkaline media. The resulting gels were analyzed on an Instron testing machine and their Young's modulus, stress relaxation and creep behavior were measured as a function of borate concentration, ionic strength, pH, and gum type. The stress relaxation behavior allowed cross-linking associated to alkaline media to be differentiated from cross-linking due to borate ions. Alkaline cross-linking was favored by galactomannans with a high galactose content. The possibility of obtaining galactomannan gels cross-linked by antimonate ions was also investigated and the gels compared to those obtained with borate ions. Several stress relaxation mechanisms were thus established and discussed.

INTRODUCTION

In the first part of this study, some rheological properties of guar gum and hydroxypropylguar gum (HPG) in alkaline media have been investigated (Noble *et al.*, 1990). The possibility of obtaining 'strong' gels using high concentrations of these gums has been demonstrated. We will focus here on the rheological properties of gels obtained through the use of high concentrations of galactomannan gums, cross-linked by specific ions. Several ions, which cross-link galactomannans to produce gels have been mentioned in the literature (Chrisp, 1967; Chudzikowski, 1971). The use of titanium ions as a cross-linking agent has recently been investigated by several methods (Zasadzinski *et al.*, 1986; Kramer *et al.*,

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1987, 1988) and the active role of colloidal (titanium dioxide) particles has been demonstrated.

Borate ions are well-known cross-linkers (Deuel *et al.*, 1948). The mechanisms of complexation and reticulation of galactomannan chains by these ions have received great attention (Noble & Taravel, 1987, 1988; Gey *et al.*, 1988; Pezron *et al.*, 1988*a*). Phase diagrams of this system have also been investigated (Pezron *et al.*, 1988*b*). The present work describes some rheological properties of 'strong' gels obtained in the presence of borate ions in alkaline media. The use of antimonate ions as a cross-linker (Ahad, 1974) will also be explored.

EXPERIMENTAL

Information about materials and the preparation of gels and rheological measurements has been given in the first part of this study (Noble *et al.*, 1990).

Materials

In addition to the galactomannan gums previously described, some natural gums obtained from different species have been used in this study. Carob gum has been kindly provided by MRS (Velizy-Villacoublay, France) and cassia and tara gums have been obtained from Diamalt (Munchen, Germany). Their characteristics are given in Table 1.

Rheological measurements

Mechanical testing of gels through uniaxial compression has been performed using three kinds of small deformation experiments. In addition to Young's modulus measurements and stress relaxation tests previously described (Noble *et al.*, 1990), experiments were performed in order to

TABLE 1
Some Characteristics of Galactomannans from Different Vegetal Species

Gum	*Moisture content (%)*	*Protein content (%)*	*Yield on purification (%)*	*Galactose content (%)*	*[η] (ml.g^{-1})*
Carob	7·2	0·8	—	23·0	990
Cassia	6·0	7·1	33	19·9	830
Tara	7·1	3·5	68	31·1	750

quantify the viscosity of the gel samples. In the procedure adopted, the gel sample is submitted to a constant stress for a period of 30–60 min. The stress value is low enough to stay in the linear viscoelastic region throughout the experiment. The variation of the sample deformation is recorded as a function of time and an example is given in Fig. 1. The magnitude of the viscous flow component relative to the total deformation is usually about 8%.

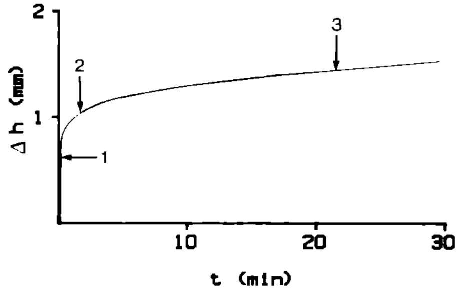

Fig. 1. Creep experiment recording. Details are explained under Experimental.

The first part of the creep curve corresponds to the instantaneous elasticity of the sample. The second part represents the delayed elasticity and lasts between 5 and 20 min, depending on the sample. In the third part, a linear relationship between deformation and time can be observed, corresponding to Newtonian flow behavior. The slope of this line is related to the viscosity η_0 of the gel. As the desired stress cannot be obtained instantaneously with the machine used, the first and second parts of the creep curve have not been reported. Only the viscosities of the gels are presented here.

Using a constant stress σ_T, the creep compliance function is defined at any time t by:

$$D(t)=\frac{\varepsilon(t)}{\sigma_T} \tag{1}$$

where $\varepsilon(t)$ represents the relative strain at t:

$$\varepsilon(t)=\Delta h(t)/h_0$$

where Δh is the deformation of the sample and h_0 its initial height. We will consider that for small deformations, the cross-sectional area of the sample remains constant, and thus:

$$\sigma_T=\frac{F_T}{S}$$

F_T being the constant stress applied to the sample.

Equation (1) then becomes:

$$\Delta h(t) = \frac{F_{\mathrm{T}} h_0}{S} D(t) \tag{2}$$

When a simple shear creep experiment is performed, the creep compliance function $J(t)$, in the Newtonian flow zone, shows a linear variation with a slope of $1/\eta_0$ (see above). When a compression test without any volume change (the Poisson ratio being equal to 0·5) is performed, the relation $J(t) = 3D(t)$ can be used to convert the results of a simple shear experiment to an uniaxial compression test. Equation (2) becomes:

$$\Delta h(t) = \frac{F_{\mathrm{T}} h_0}{3S} J(t)$$

The slope of the linear part of the plot of Δh against t is $F_{\mathrm{T}} h_0 / 3S\eta_0$ and the value of this slope gives a direct access to the viscosity η_0 of the gel.

The results have been shown to be reproducible, within ± 5%.

RESULTS AND DISCUSSION

Whatever the cross-linking ion, the general properties of the gels obtained are identical to those previously described for gels prepared in alkaline medium (Noble *et al.*, 1990).

Gels in the presence of borate ions

Rheological studies of borate cross-linked polymer systems (Schultz & Myers, 1969; Maerker & Sinton, 1986; Kramer *et al.*, 1988; Pezron, 1988) have generally consisted of simple shear dynamic experiments carried out on 'weak' gels. The polymer concentration is usually low (about 5 g liter^{-1} for guar and hydroxypropylguar gels). In the present work, more concentrated gels (polymer concentration ~ 70 g liter^{-1}) have been studied through uniaxial compression. All gels have been prepared using a buffer solution (NaOH, KCl) of pH = 12 and ionic strength $I \sim 0{\cdot}06$ (Bates & Bower, 1956).

The simultaneous presence of borate ions and of an alkaline medium favoring interchain associations (Noble *et al.*, 1990) gives a quite complex situation. One of the goals was to discriminate gelation effects due to borate ions, from gelation due to the alkaline medium.

Borate concentration dependence

Sodium tetraborate (borax) $Na_2B_4O_7$, $10H_2O$ has been used as a source of borate ions. In aqueous solution, this electrolyte dissociates totally into equal quantities of boric acid and borate ions:

$$Na_2B_4O_7 + 7H_2O \rightarrow 2Na^+ + 2B(OH)_4^- + 2B(OH)_3$$

A buffer solution of pH = 9·1 (which is the pK_A of boric acid) is thus formed. In a highly alkaline solution the equilibrium

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^-$$

is totally shifted to the right, and only borate ions are present in the solution. Borate concentration is always low enough to avoid the formation of polyborate species (Momii & Nachtrieb, 1967).

Results are presented relative to borax concentration C_B (in grams per liter) in the alkaline buffer solution. The previously described gums (guar and HPG) have been used at a concentration of 70 g liter^{-1}. The hydration delay, already present in alkaline solutions (Noble *et al.*, 1990), is increased by the presence of borate ions (Chudzikowski, 1971; Gey *et al.*, 1988). A linear variation of the setting time of the gels with borate ion concentration is thus observed. It has been suggested (Gey *et al.*, 1988) that the hydration delay in alkaline borate solution could be a result of monocomplexation by the borate ions on the suspended polymer surface, slowing or even preventing polymer–water interactions. The present result is qualitatively in agreement with this hypothesis.

Young's moduli of gel samples in the presence of borate ions have been measured (Fig. 2). The dispersion of the experimental results leads to large values of the standard deviation for each experimental point, and can be explained by the difficulty in obtaining an homogeneous dispersion when the mixture is prepared: problems of sedimentation and aggregation of polymer granules often occur. For borax concentrations higher than 0·2 g liter^{-1}, both polymers show the same behavior: a linear variation of Young's modulus with borate concentration. This kind of behavior is still operative at lower borate concentrations for the HPG gum, but for guar gum Young's modulus drops off very rapidly at low borate concentrations. Viscosity values obtained from creep experiments on guar gum gels (Fig. 3) confirm this behavior at low borate concentrations.

These results have to be compared with those obtained in alkaline solutions without borate (Noble *et al.*, 1990) and may be explained in the following way:

— For HPG gum, a pH value of 12 is sufficient for the formation of all the junction zones capable of forming in alkaline media. The addi-

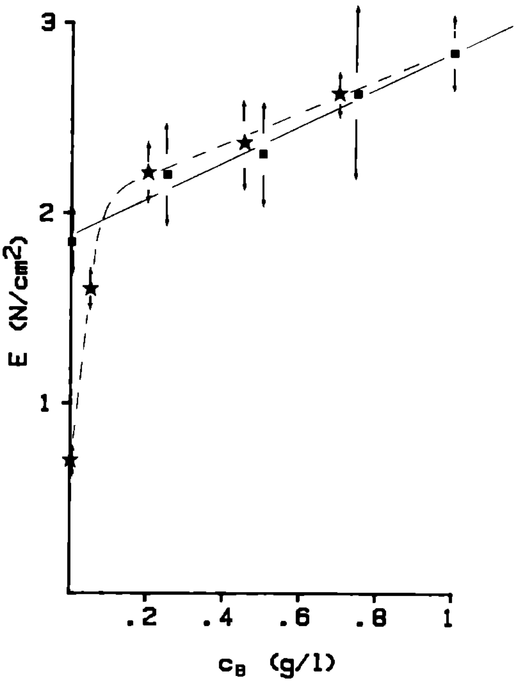

Fig. 2. Young's moduli in the presence of borate ions (buffer, pH 12). ■ HPG (70 g l^{-1}); ★ Guar (70 g l^{-1}).

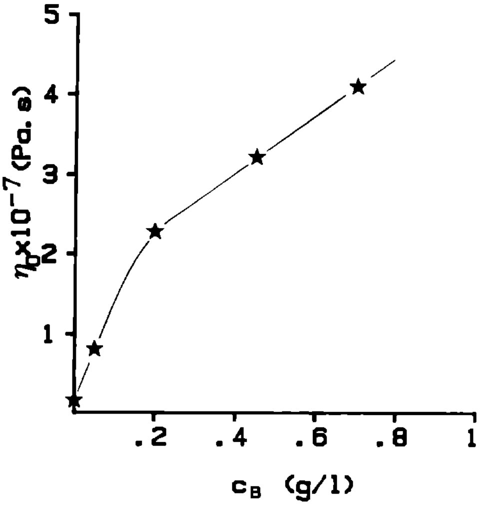

Fig. 3. Viscosity of a 70 g l^{-1} guar sample at pH 12 as a function of borax concentration.

tion of borate ions in the solution creates new interchain cross-links, the number of which is proportional to borate concentration, in accordance with the dicomplexation equilibrium already described (Gey *et al.*, 1988). The variation of the Young's modulus is a macroscopic consequence of this phenomenon.

- For guar gum, the gelation in alkaline medium is not complete at pH = 12. Initially, the borate ions added to the solution reinforce interchain contact zones, and so the Young's modulus (for $C_B = 0{\cdot}2$ g liter^{-1}) quickly rises to the value expected in a very alkaline medium (pH > 13). When more borate ions are added, the evolution is the same as for the HPG gum. The idea of cross-linking ions welding together already weakly associated polymer chains has been suggested in a similar situation (Zasadzinski *et al.*, 1986) for guar with titanate cross-linkers.

Ionic strength dependence

Young's modulus measurements have been performed for gels of HPG gum (70 g liter^{-1}) in the presence of borate ions ($C_B = 0{\cdot}7$ g liter^{-1}) using various solutions. A decrease of the modulus when the ionic strength increases has been detected. This could be due to polyelectrolyte effects, as already noticed for weaker gels (Pezron, 1988).

Use of other natural galactomannan gums

Gels can be obtained using different natural galactomannan gums in the presence of borate ions. The hydration delay is, in general, much smaller than for guar and HPG gums.

A linear variation of the Young's modulus with borax concentration has been observed for each of the gums studied (for $C_B > 0{\cdot}1$ g liter^{-1}), as previously noticed for guar and HPG gums.

Comparison between the stress relaxation curves obtained for these different gums (Fig. 4) gives complementary information. In order to limit the effects that could be due to differences in Young's moduli, gels with similar moduli have been compared. The behavior at long times ($t > 3$ min) of the guar and tara gels is very close to the one obtained for HPG gels in the absence of borate ions. However the curves obtained for carob and cassia gums are quite different; these gels show a greater relaxation, particularly at long times.

A tentative explanation of these results includes the following assumptions:

(1) The relaxation behavior of a gel depends on the nature of the cross-links in the gel network.

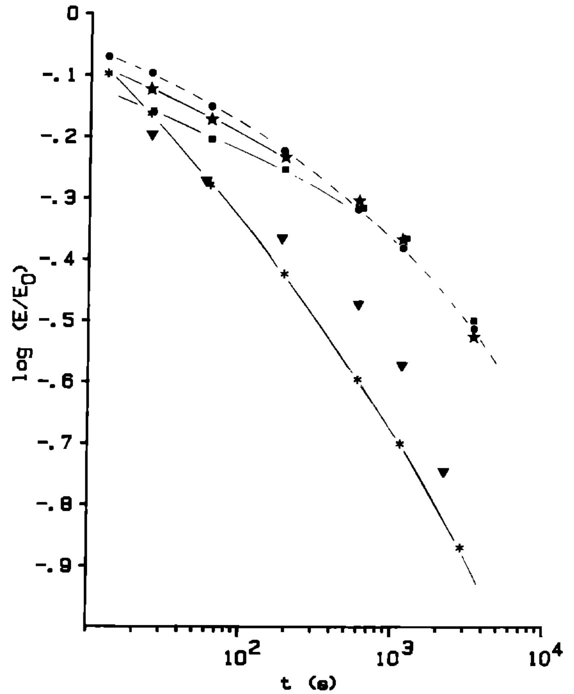

Fig. 4. Stress relaxation curves for gels prepared from gums of different origin (buffer, pH 12 and borax). ★ Guar (70 g l^{-1}) with 0·7 g l^{-1} borax (E_0 = 2·63); ■ Tara (70 g l^{-1}) with 1·0 g l^{-1} borax (E_0 = 3·70); ▼ Cassia (70 g l^{-1}) with 1·5 g l^{-1} borax (E_0 = 3·26); ✱ carob (50 g l^{-1}) with 1·0 g l^{-1} borax (E_0 = 2·54); ● HPG (70 g l^{-1}) without borax (E_0 = 1·92).

(2) Two types of cross-linking are present here:
  — alkaline cross-linking.
  — cross-linking through borate ions.

(3) The relaxation mechanisms associated with borate ions cross-linking are much faster than the relaxation mechanisms associated with alkaline cross-linking.

Relaxation through borate ions is present in all gels and leads at short times ($t < 3$ min) to a deviation when compared to a purely alkaline gel. This deviation quickly vanishes when alkaline cross-linking plays a major role in the gel. Except at short times, guar and tara gels behave as purely alkaline gels. In contrast, carob and cassia gels seem to follow a different behavior, which can be attributed to borate ions. Alkaline cross-linking seems very restricted in the latter gels.

It is concluded that alkaline cross-linking seems favored for galactomannans with a high galactose content (guar, tara) and not for galactomannans with a lower galactose content (carob, cassia).

Gels in the presence of antimonate ions

The possibility of obtaining galactomannan gels cross-linked by antimonate ions [$Sb(OH)_6^-$] has been mentioned in connection with explosive engineering (Ahad, 1974) and petroleum engineering (Hsu & Burnham, 1983). No study of the mechanical properties of these gels has been reported.

The first goal was to determine suitable pH conditions for the setting of these gels.

pH dependence

Potassium hexahydroxoantimonate (V), $KSb(OH)_6$ has been used as a source of antimonate ions. In pure water, its maximum solubility is about 25 g liter^{-1}, and dissolution is slow at room temperature. This electrolyte is used in analytical chemistry as a sodium ion reagent, the sodium salt $NaSb(OH)_6$ being totally insoluble. The presence in solution of sodium ions thus has to be avoided.

Young's modulus measurements have been performed on gels prepared from HPG gum (70 g liter^{-1}) and potassium antimonate [$KSb(OH)_6$] = 1 g liter^{-1}), using buffers of ionic strength 0·02 (without sodium ions) (Fig. 5).

No measurement has been possible for pH < 7: the polymer hydration is so fast that a complete dispersion of the gum is not possible. Cross-linking through antimonate ions reduces as the pH increases. For pH > 12, no gel formation can be observed. This type of cross-linking seems to be inconsistent with alkaline cross-linking, and the presence of antimonate ions seems to hinder any alkaline cross-linking.

For these reasons, the following experiments have been made in pure water in the absence of electrolytes other than $KSb(OH)_6$. The results obtained with two polymers, HPG gum and purified carob gum, will be reported.

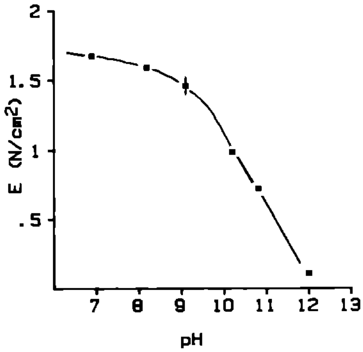

Fig. 5. PH dependence of Young's modulus for gels prepared from HPG in the presence of antimonate ions. See text for further details.

Hydroxypropyl guar gels

Whatever the concentration of antimonate ions, the dispersion of HPG gum gives homogeneous mixtures up to 70 g liter^{-1} of polymer. These mixtures quickly become very viscous. No appreciable hydration delay exists and the setting time of the gel cannot be measured: the mixture does not flow before introduction into the oven. Such gels can also be prepared using a 'cold procedure' without storage in the oven, but their setting is quite slow (several hours) due to kinetic factors.

The dependence of Young's modulus on potassium pyroantimonate concentration is shown in Fig. 6. Viscosity values obtained from creep experiments show a similar dependence. For low pyroantimonate concentrations, the shape of the curves suggest the absence, in this medium, of any cross-linking other than from antimonate. Two rates of variation of the modulus with cross-linker concentration clearly appear, with a tendency towards a linear dependence at high antimonate concentrations ($C_{Sb} > 1$ g liter^{-1}).

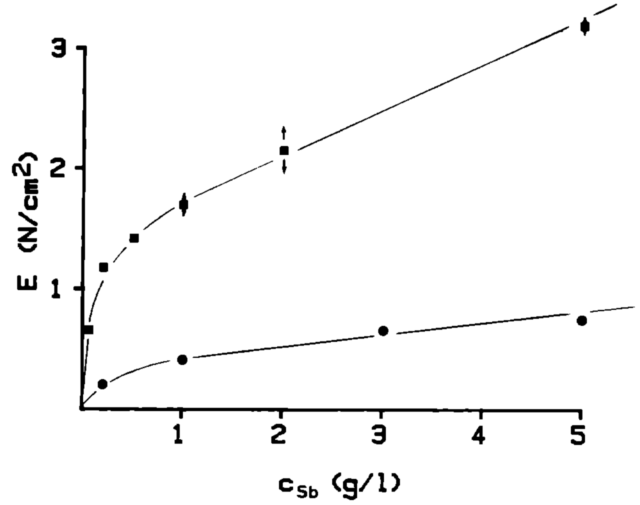

Fig. 6. Young's modulus as a function of antimonate concentration. ● HPG (35 g l^{-1}) in water; ■ HPG (70 g l^{-1}) in water.

These observations can be explained in the following way: in the absence of antimonate ions, the mixture is not a strong gel and no modulus can be measured. When antimonate ions are added, a 'loose' network of linked chains is first created, inside of which numerous free chains are present. There is a rapid increase in Young's modulus with ion concentration as the number of free chains becomes less and less important. Over a certain antimonate concentration (about 1 g liter^{-1} for a polymer concentration of 70 g liter^{-1}), all the chains are presumably connected to the network. A further increase in cross-linker concentration will then only promote an increase in the density of cross-links which corresponds to the linear dependence observed for higher antimonate concentrations. Stress relaxation behavior of some of these gels has also been investigated (Fig. 7). In general, these gels have a limited relaxation on the time scale studied. For instance, for HPG = 70 g liter^{-1} and $KSb(OH)_6$ = 2 g liter^{-1}, the stress after 1 h is still 75% of the initial stress. Antimonate cross-linked gels have a relaxation behavior quite close to the other biopolymer gels (agarose, gelatin), but remain very difficult to break.

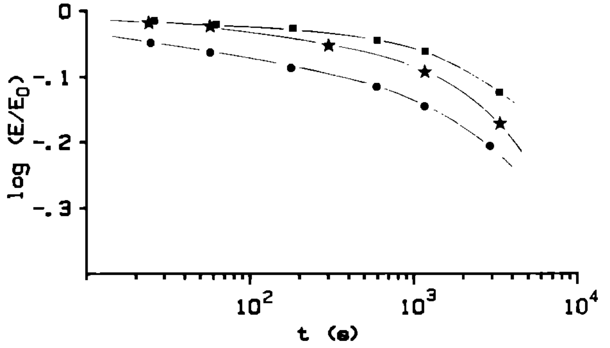

Fig. 7. Antimonate concentration dependence of the stress relaxation for HPG in water. Antimonate concentration $KSb(OH)_6$ is: ■ 2·0 g l^{-1}; ★ 1·0 g l^{-1}; ● 0·2 g l^{-1}.

Carob gum gels

Dispersion of the purified carob gum in an antimonate solution is quite similar to the preceding case, with a fast hydration of the polymer. Homogeneous mixtures can be obtained up to a polymer concentration of 50 g liter^{-1}. Young's modulus measurements give results similar to those of HPG gum, but higher values of the moduli can be reached.

When the potassium antimonate concentration is over 3 g liter^{-1}, a surprising decrease in the Young's modulus is observed. It can be correlated with the turbidity of the gels: up to a concentration of 2 g liter^{-1} transparent gels are obtained, for 3 g liter^{-1} the gels are slightly opaque and for 5 g liter^{-1} opaque and sticky gels are obtained.

Viscosity measurements on the same gels confirm this dependence: a maximum viscosity is obtained for an antimonate concentration between 1 g liter^{-1} and 2 g liter^{-1}.

These observations could be explained by phase separation phenomena similar to the demixing transition observed in the guar–borate system (Pezron *et al.*, 1988*b*)). One could expect that any microscopic phase separation would result in a degradation of the mechanical properties of the gels at a macroscopic level. Recent results obtained for polyacrylamide gels (Baselga *et al.*, 1987) confirm this point of view. Stress relaxation curves recorded for these gels are similar to those obtained for HPG gum in the presence of antimonate ions.

A detailed study of this system, including turbidity measurements, would certainly have both a fundamental and practical interest.

CONCLUSION

During this study of gels obtained in alkaline media and of ion cross-linked gels, several ways of obtaining galactomannan-based gels have been explored. The striking feature of the study is the observation that different cross-linking mechanisms lead to quite different mechanical properties of the gels. A comparison of the stress relaxation curves obtained for different kinds of gels (Fig. 8) is representative of this fact.

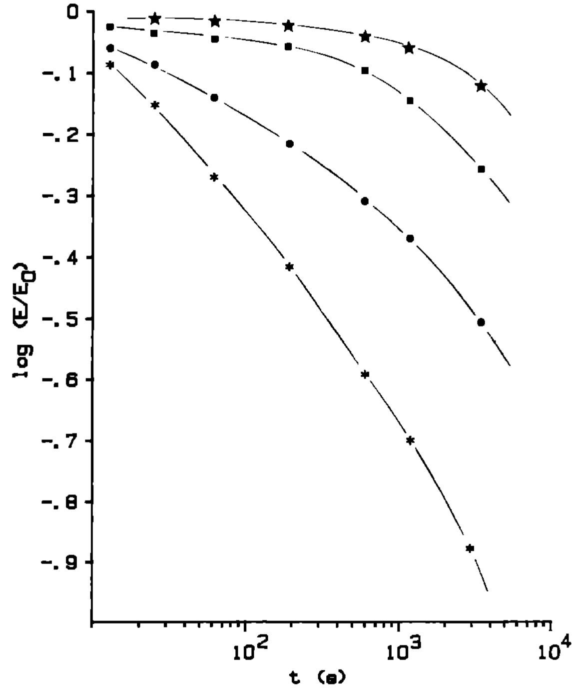

Fig. 8. Stress relaxation curves obtained for different types of gels. ★ HPG (70 g l^{-1}) and KSb(OH)$_6$ (2 g l^{-1}), (E_0 = 2·15 N/cm^2); ■ HPG (70 g l^{-1}) and 0·1 M NaOH, pH 13 (E_0 = 2·24 N/cm^2); ● HPG (70 g l^{-1}) and buffer, pH 12 (E_0 = 1·85 N/cm^2); * Carob (50 g l^{-1}) in buffer, pH 12 and 1 g l^{-1} borax (E_0 = 2·54 N/cm^2).

It was noticed, using several samples of different polymers, that the medium characteristics and consequently the nature of the cross-links, are responsible for the shape of the relaxation curves. The nature of the polymer gum has a limited influence on the stress relaxation properties of the gels.

The great diversity of the relaxation curves, as seen in Fig. 8, corresponds to differences in the mechanical behavior of the gels: antimonate cross-linked gels and gels in very alkaline media have elastomer-like properties and a tendency to keep their own shape. In contrast, borate cross-linked gels tend to adopt the shape they are forced to, and to creep under their own weight.

TABLE 2
Mathematical Analysis of the Relaxation Curves for Different Types of Gels

Medium	*Term 1*		*Term 2*		*Term 3*		*Term 4*
	f_1 %	τ_1 *(s)*	f_2 %	τ_2 *(s)*	f_3 %	τ_3 *(s)*	f_4 %
Pyroantimonate ion	92·4	16900	2·5	1060	2·1	188	3·0
Very alkaline (pH = 13)	84·5	8400	8·3	327	0	—[a]	7·2
Alkaline (pH = 12)	47·0	8480	17·5	482	14·4	112	21·1
Borate ion (pH = 12)	21·4	6320	12·5	688	23·9	168	42·2

[a]—, Signifies no term 3.

A mathematical analysis of the relaxation curves (Table 2) using a three element Maxwell model usually gives three terms with relaxation times greater than 1 min. The first relaxation time is quite different for each of the three cross-linking mechanisms studied. The relative importance of this first component, as measured by the coefficient f_1, strongly depends on the conditions and varies from 92·4% (antimonate cross-linking) to 21·4% (borate cross-linking). On the contrary the coefficient f_4 which represents the relative importance of very short relaxation times, increases from 3% (antimonate cross-linking) to 42·2% (borate cross-linking).

An interpretation of these parameters is always difficult, but the great diversity of the results obtained is certainly a consequence of very different physical states.

The degree of association of polymer molecules is clearly increased in alkaline media, promoting chain–chain interactions via hydrogen-bonding in opposite to chain–solvent interactions. After the addition of borate ions, new interchain cross-links are created, involving the formation of dicomplexes (Noble & Taravel, 1988) and reinforcing the already existing aggregations.

Antimonate cross-linking in a neutral medium is quite different and remains to be investigated under several aspects (structure and properties of the gels).

ACKNOWLEDGEMENTS

The authors wish to thank the 'Société Nationale Elf Aquitaine', Pau, France, for financial support and a fellowship to one of the authors (O.N.). In particular they thank Drs J. P. Bimond, J. P. Messines and Mr Lassus-Dessus for valuable and helpful suggestions.

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