Carbohydrate Polymers **12** (1990) 203–217

Rheological Properties of Galactomannan-Based Gels. Part 1 — Guar and Hydroxypropylguar Gels in Alkaline Media

O. Noble,* T. Turquois & F. R. Taravel

Centre de Recherches sur les Macromolécules Végétales, CNRS, BP 53 X, 38041-Grenoble cedex (France)

(Received 1 October 1988; revised version received 16 February 1989; accepted 10 March 1989)

ABSTRACT

Gels have been prepared from guar and hydroxypropyl guar gums by heating in alkaline media.

The rheological properties of the gels have been examined using an Instron testing machine. Two kinds of small deformation experiments have been performed: Young's modulus measurements and stress relaxation tests.

The influence of various parameters: pH, polysaccharide concentration on the formation of gels, has been investigated. It is shown that gel formation occurs at lower pH for hydroxypropyl guar compared with unmodified guar.

INTRODUCTION

In the present study, some rheological properties of galactomannan-based gels are investigated as a means of obtaining temporary plugging agents for petroleum engineering. Polysaccharide-based gels are commonly used in this type of application (Horner & Walker, 1965; Black & Melton, 1966) because of their unique properties, and among the polysaccharides that provide a three dimensional network, guar gum and its derivatives are the most frequently used.

*Present address: Aqualon France, ZI, 27460 Alizay, France.

Carbohydrate Polymers 0144-8617/90/$03.50 —

Legume-seed galactomannans are polysaccharides which consist of linear chains of (1→4) linked β-D-mannopyranosyl residues, to which are attached (1→6) linked α-D-galactopyranosyl groups as single-unit side-chains. The proportion of α-D-galactopyranose units in the polymer varies from 15% to 49%, depending on the species from which the gum is extracted (Dea & Morrison, 1975). Aqueous solutions of galactomannans are generally considered as viscoelastic fluids, with an 'entanglement' network behaviour, for concentrations up to 3% (Richardson & Ross-Murphy, 1987). No evidence for gel formation in these solutions has been found, except for the formation of weak gel networks on freeze–thaw treatment of *Ceratonia siliqua* (carob gum) solutions (Dea *et al.*, 1986). Nevertheless, two types of galactomannan-based gels have been recognized and used for several years:

— 'mixed' gels are obtained by the use of mixtures of certain galactomannans (carob gum in particular) and other polysaccharides such as agarose, carrageenans and xanthan (Dea & Morrison, 1975). Such gels are widely used in the food industry and their properties have been extensively investigated.
— ion-crosslinked gels are commonly used in various fields. Borate ions have been the most used crosslinker for many years (Deuel *et al.*, 1948). The use of Cu, Ca, Al and Cr salts (Chudzikowski, 1971) and of transition metal salts (Chrisp, 1967) has also been mentioned.

Depending on galactomannan concentration, a wide range of textures from 'weak' gels which do not retain their shape, to 'strong' gels, which behave like elastic solids, can be obtained (Seaman, 1980).

Some rheological properties of ion-crosslinked gels will be examined in the second part of this study. We will focus here on the properties of solutions and gels of guar and its derivatives in alkaline media.

EXPERIMENTAL

Materials

Commercial grades of natural and chemically modified galactomannan gums were kindly provided by Hercules (Bergamo, Italy) and MRS (Velizy-Villacoublay, France). Apart from the polysaccharide itself, these gums contain a certain quantity of moisture and proteins, and a lower content of fibers and ashes (Seaman, 1980). The protein content of the gums was estimated from the nitrogen ratio determined by microanalysis

(after multiplication of the value obtained by 6·25). The results, together with the moisture contents, are presented in Table 1.

Because of the amount of gum necessary for the experiments, commercial grades were used without any purification for gel preparations. However, viscosity measurements and chromatographic determination of the galactose content were performed on purified materials.

Purification was performed using the classical method for galactomannans (Doublier, 1975): the gum is first gently poured (2 g litre^{-1}) into water at 60°C, and left under strong stirring for 1 or 2 h. Insoluble material (including proteins) is removed by centrifugation. The galactomannan polysaccharide is then precipitated by addition of 95° ethanol (2 volumes of ethanol for 1 volume of solution). The precipitate is washed with ethanol, crushed and dried under vacuum. The solid obtained is mechanically ground into a powder. The yield from this purification procedure is given in Table 1 for each gum studied.

The galactose content of the purified polymers was determined by HPLC, as an alternative to the classical alditol-GLC method (Albersheim *et al.*, 1967). After complete hydrolysis of the polymers by sulphuric acid and neutralization, the separation of the peaks corresponding to galactose and mannose on a Biorad HPX 87P column is total. A quantitative determination of the relative proportion of galactose is therefore possible, after a correction due to the response factor of each monomer. Results are given in Table 1.

The degree of substitution (d.s.) of O-(2-hydroxypropyl) modified guar gums is the average number of O-(2-hydroxypropyl) groups present on the polymer per glycosidic unit. It was determined by ^{1}H nuclear magnetic resonance: a value of d.s. = 0·48 ± 0·05 was found for HPG.

Preparation of gels

One of the goals was to prepare homogeneous gels of well defined geometry, in order to study their mechanical properties. Attention was

TABLE 1
Typical Analysis of Guar and Hydroxypropylguar (HPG)

Gum	*Moisture content (%)*	*Protein content (%)*	*Yield on purification (%)*	*Galactose content (%)*	$[\eta]$ *ml g*$^{-1}$
Guar	9·3	6·0	67	38·4	1280
HPG	5·2	1·9	77	46·7	1040

focused on gels containing high concentrations of galactomannan gums (30–80 g litre^{-1}) of commercial grade, the gels obtained were not fully homogeneous on a microscopic scale. In general they were opaque to light. The non-thermoreversibility of these gels, and the difficulties of dispersion of galactomannan gums in pure water led to the following preparation procedure:

(1) Preparation of an alkaline solution with a known pH.
(2) Dispersion of the polymer in this solution, under strong stirring.
(3) Introduction of the mixture into cylindrical cells and storage in an oven at 120°C.
(4) Regular shaking until the gel sets.
(5) Standing of the cells in the oven, for a determined time.
(6) Return to room temperature.
(7) Removal of the gel from the cells and storage in a high humidity atmosphere at room temperature.

The cylindrical cells that were used gave samples of 18·7 mm diameter and variable height ($14 < h_0 < 20$ mm), which did not need to be cut for mechanical testing. The surface of the gel was generally smooth and did not stick to glass or teflon.

Rheological measurements

Viscosities of dilute solutions
Intrinsic viscosities were determined with a FICA automatic Ubbelhode viscometer. Starting solutions (concentration ~0·5 g litre^{-1}) were filtered with 0·45 μm membranes. The exact polysaccharide concentration was determined by the anthrone method (Morris, 1948; Loewus, 1952).

Viscosities of semi-dilute solutions
Viscosities were determined as a function of NaOH concentration, at zero shear rate on a Contraves Low Shear 30, at 25°C.

Mechanical testing
The gels studied were 'strong' gels. Their mechanical properties were examined using uniaxial compression on an Instron 4301 testing machine, without lubrication of the gel surfaces. Two kinds of small deformation experiments were performed: Young's modulus measurements and stress relaxation tests.

— Young's modulus measurements are obtained through a progressive deformation of the gel sample under the action of the upper plate of the

testing machine, which moves at a constant speed. A recording of the force F applied on the sample relative of its deformation Δh shows a well-defined linear part, up to a relative deformation $\Delta h/h_0$ of roughly 10% (h_0 is the initial height of the sample). Young's modulus is thus defined as the stress/strain ratio:

$$E = \frac{\sigma}{\varepsilon} = \frac{F/S}{\Delta h/h_0}$$

S being the cross-sectional area of the cylindrical sample which is supposed to stay constant during the experiment for small deformations. Measurements were performed on a series of around 10 samples prepared under the same conditions in order to obtain an average value and the standard deviation. The Young's modulus obtained is dependent on the speed of the upper plate of the testing machine. A speed of 5 mm min^{-1} was chosen for all measurements (Christianson *et al.*, 1986). Values obtained under these conditions could not be considered as quasi-equilibrium moduli corresponding to the rubber plateau, but as indicative values only allowing a comparison of gels prepared under different conditions. For these reasons, the correction proposed by Christianson *et al.* (1985) for gels compressed without lubrication were not taken into account, as it did not significantly reduce the dispersion of the experimental results.

— Stress relaxation tests were performed for periods of about one hour. The gel sample is initially submitted to a quasi instantaneous Δh deformation, sufficiently small to stay in the domain of stress–strain linearity. This deformation is then kept constant and the time dependence of the stress is recorded.

The relaxation modulus is defined at time t as:

$$E(t) = \frac{\sigma(t)}{\varepsilon} \text{ with } \sigma(t) = \frac{F(t)}{S} \text{ and } \varepsilon = \frac{\Delta h}{h_0}$$

using the definitions and approximation already given. The relaxation modulus is thus at every instant proportional to the measured stress.

Relaxation curves are usually presented in logarithmic scales $\log E(t)$ versus $\log t$ (Ferry, 1980). In order to allow an easy comparison of relaxation curves between gels of different Young's moduli, a reduced representation was adopted:

$$\log \frac{E(t)}{E(t=0)} = f(\log t), \text{ with } \frac{E(t)}{E(t=0)} = \frac{F(t)}{F(t=0)}$$

which simplified the calculations. In reality, the initial deformation is not instantaneous, but results from a compression at constant speed from $t=0$ to $t=t^*$ (Fig. 1).

In the experiments t^* was around 10 s, which was negligible on the time scale of the experiment. So, in the following t^* was considered as the time origin. The expression for the relaxation modulus

$$E(t)=\frac{\sigma(t)}{\varepsilon^*}$$

can be used for $t>10\,t^*$ (Smith, 1979). Before this limit, several approximations have been proposed to evaluate $E(t)$ (Lin & Aklonis, 1980).

To study the long time relaxation behaviour of the gels, the expression

$$E(t)=\frac{\sigma(t)}{\varepsilon}$$

was used. A study of short time relaxation behaviour of the gels would require further experiments. Nevertheless experimental data for $t<100$ s were recorded. In general they were consistent with the rest of the points corroborating the trend of the stress relaxation curve.

The relaxation curves were analyzed using a generalized Maxwell model for liquid behaviour:

$$E(t)=\sum_{i=1}^{n} E_i e^{-t/\tau_i}$$

The parameters of this model were determined following Inokuchi's graphical method (Inokuchi, 1955). A three element model (Fig. 2) was sufficient to describe the relaxation behaviour of the gels for $t>100$ s

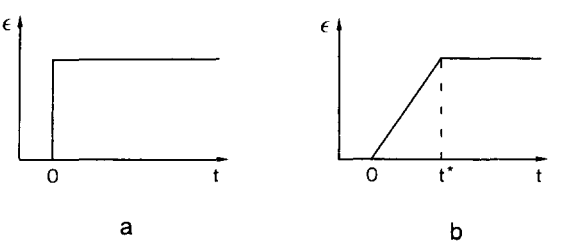

Fig. 1. Schematic strain versus time plots for a theoretical (a) and practical (b) experiment.

(Arakawa, 1961; Comby *et al.*, 1986). According to the preceding discussion, relaxation phenomena for $t < 100$ s have not been analyzed.

In order to compare gels of different Young's moduli, the results were presented in a reduced way: the expression

$$E(t) = \sum_{i=1}^{n} E_i e^{-t/\tau_i}$$

is normalized, giving

$$\frac{E(t)}{E(t=0)} = \sum_{i=1}^{n} f_i e^{-t/\tau_i}$$

with

$$f_i = \frac{E_i}{E(t=0)} \text{ and } \sum_{i=1}^{n} f_i = 1$$

$E(t=0)$ could be obtained from corresponding Young's modulus measurements. In the description adopted, the normalized relaxation modulus could be described for $t > 100$ s by a sum of three terms

$$\frac{E(t)}{E(t=0)} = f_1 e^{-t/\tau_1} + f_2 e^{-t/\tau_2} + f_3 e^{-t/\tau_3}$$

with $\tau_1 > \tau_2 > \tau_3$.

The existence of terms with short relaxation times ($\tau < 1$ min) was taken into account by the supplementary parameter $f_4 = 1 - (f_1 + f_2 + f_3)$. In the results, we will present f_i values as a percentage of $f_1 + f_2 + f_3 + f_4$.

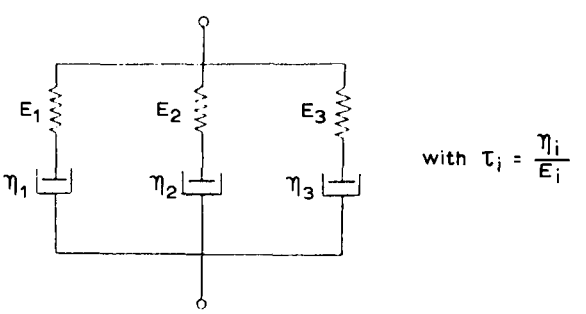

Fig. 2. Mechanical model for stress relaxation.

RESULTS AND DISCUSSION

Viscosity of dilute and semi-dilute solutions

Intrinsic viscosities are determined using a purified sample of guar (from MRS France). Table 2 shows the data obtained as a function of NaOH concentration.

At a NaOH concentration above 0·3 M, the solution is no longer filterable. This, with the measured values for intrinsic viscosities and Huggins constants, clearly demonstrates that alkaline solutions are bad solvents for guar and that an aggregation phenomenon occurs. This also could be linked to the degree of hydration that could be different.

The relative viscosities determined at zero-shear rate for semi-diluted solutions of guar also indicate a decrease in the viscosity following NaOH addition. The phenomenon is even more pronounced when the concentration of the polymer is increased. Of course in order to clarify this point (guar is a neutral polymer) more data are needed. Is the pH effect attributable to ionization of hydroxyl groups at high pH or to change in the molecular conformation? The question is still open.

From these data it seems that the reinforcement of chain–chain associations with a concomitant lowering of chain–solvent interactions in alkaline media, leads to aggregation phenomena in dilute solutions and to gelation in more concentrated systems.

Mechanical properties of high concentrated gels

The preparation of media containing high concentrations of guar gum or derivatives is generally a problem, due to the thickening properties of these gums.

The viscosity of solutions of guar gum increases rapidly when the concentration is increased. In pure water, a maximum concentration of

TABLE 2
Intrinsic Viscosity and Huggins Constant vs. NaOH Concentration for Purified Guar (from MRS France)

C_{NaOH}	0	0·05 M	0·1 M	0·15 M	0·2 M	0·25 M	0·3 M
$[\eta]$ ml g^{-1}	967	876	812	757	693	625	589
k'	0·52	0·55	—	0·74	0·98	—	1·11

gum of about 30 g litre^{-1} can be obtained: the medium does not flow and is so viscous that no more gum can be dispersed.

In alkaline media the gums can be more easily dispersed, as the polymers are not immediately soluble in these solutions at room temperature. The hydration of the polymers occurs progressively when the temperature is increased, leading to an increase in the apparent viscosity. During this stage, the dispersion kept in waterproof cells at 120°C is submitted to regular shaking to avoid sedimentation and keep the medium homogeneous. After a certain time, the dispersion does not flow any more: the gel is considered to have formed and the delay observed before this phenomenon occurs will be called the setting time. This definition is obviously purely subjective as the apparent setting of the gel does not correspond to the establishment of a true equilibrium in the medium: the solubilization of the polymer certainly continues after the setting of the gel. For this reason, the preparations are kept at 120°C for at least 45 min, or for another period of time equal to the setting time. In the procedure adopted, a Teflon piston (with a small hole) prevents air from being trapped in the sample. Also a test tube, filled with the same dispersion, is used together with the cell in order to estimate the setting time of the gels (by turning the tube upside down).

Mechanical testing of the gels after various periods of time at 120°C, have shown that such a delay is sufficient to obtain an equilibrium state of the gel, the polymer being now totally solubilized. Longer standing can lead to a modification of the mechanical properties of the gel, due to polymer degradation.

General properties of the gels

For every gum and all the medium conditions, the gels obtained showed some common properties:

(1) The gels contain a high polymer concentration (30 g litre^{-1} to 80 g litre^{-1}).
(2) These gels can be considered 'stable': i.e. when the gel is removed from the cell at room temperature and stored under a wet atmosphere, it keeps its geometrical shape for at least a few hours. After this period, a progressive packing can sometimes be observed, corresponding to the creep of the gel under its own weight. In other situations, the gel will keep its geometry for weeks.
(3) None of the gels that we have studied is subject to syneresis, even when they are stressed.

(4) These gels are not thermoreversible and no sol–gel transition has been observed up to a temperature of 120°C.
(5) Apart from the creep effect already mentioned, aging in a wet atmosphere has no influence on the rheological properties of the gels. However, in order to avoid any problem resulting from bad storage of the gels, aging has generally been limited to a few hours and was always less than 24 h.
(6) Even when they are submitted to high compression stresses, and thus to high strains, the gels do not rupture: samples are very malleable and can only be broken when very high local shear stresses are applied.

This quite original property for polysaccharide gels is certainly connected with the flexible behaviour of galactomannan chains, compared to other gel forming polymers (agarose, pectin,...). The nature of the crosslinks may also play an important role in providing such physical properties.

After being submitted to a large strain, the capacity of the gels to recover their initial shape is variable and seems to be correlated with the relaxation behaviour of the gel (as discussed in another paper).

pH dependence

The preparation of samples according to the procedure described never gives gels when pure water or a neutral salted solution is used. On the other hand, the use of alkaline solutions and of guar or hydroxypropyl guar gums gives cohesive gels. The nature of the alkaline electrolyte employed does not seem to have a great influence on the mechanical properties.

We have studied the influence of pH on the formation of gels using various buffer solutions of ionic strength close to 0·1, avoiding the use of borate solutions as borate ions are well known crosslinkers for galactomannans (Noble & Taravel, 1987; Gey *et al.*, 1988).

The gums (guar and HPG) have been used at the concentration of 70 g litre^{-1}. The results are given in Table 3 (setting time of the gels) and in Figs 3 (Young's moduli) and 4 (relaxation curves).

The hydration delay in alkaline medium is much more important for the HPG gum than for the natural guar gum (Table 3). This delay is highly pH-dependent: at very high pH, the solubilization of the HPG gum becomes quite slow even at high temperatures: a very alkaline medium seems to favour chain–chain interactions compared with chain–solvent interactions.

TABLE 3
Setting Time (min) at 120°C as a Function of pH for Guar and HPG

pH	*8·2*	*8·7*	*9·1*	*9·55*	*9·8*	*10·2*	*10·5*	*12*	*13*
Guar (70 g litre^{-1})								0	15
HPG (70 g litre^{-1})	0	1	8	12	25	35	30	30	110

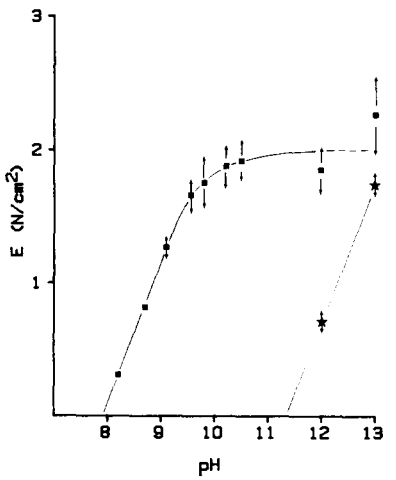

Fig. 3. pH dependence of the Young's modulus. ■ HPG (70 g litre^{-1}); ★ Guar (70 g litre^{-1}).

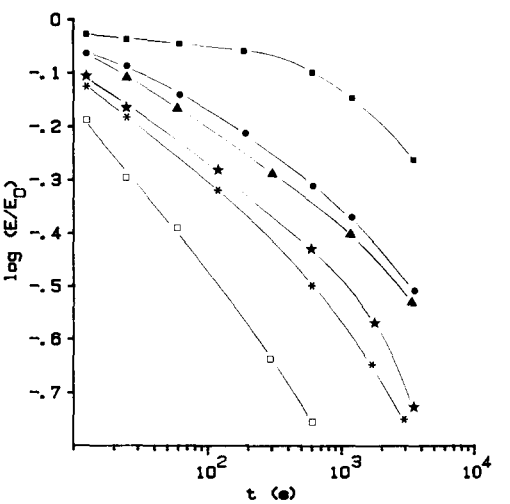

Fig. 4. pH dependence of stress relaxation behaviour for HPG (70 g litre^{-1}). ■ 0·1 M NaOH, pH = 13; ● KCl + NaOH buffer, pH = 12; ▲ $NaHCO_3 + Na_2CO_3$ buffer, pH = 9·8; ★ $KHCO_3 + K_2CO_3$ buffer, pH = 9·1; * diethanolamine + HCl buffer, pH = 8·7; □ 0·01 M $NaHCO_3$, pH = 8·2.

Figure 3 shows that the gelation phenomenon only occurs above a certain pH value. This threshold value is close to 8 for the HPG gels, although to obtain the optimum modulus requires a pH above 10. For the natural guar gum, these respective values of pH are higher and close to 11 and 13. This result has been confirmed by a few tests on other commercial gums.

Relaxation curves (Fig. 4) for HPG gums show a global showing of the relaxation phenomena when the pH increases. An analysis of some of these relaxation curves has been performed (Table 4). The agreement between the theoretical and experimental curves is very good for $t > 100$ s.

The value of the first relaxation time τ_1 is very close in the three cases (about 140 min). This could mean that, whatever the pH, the same gelation mechanism takes place (the same type of crosslinks are involved). The difference in shape of the relaxation curves can be explained by the relative importance of the different moduli, the strong domination of the first term at high pH weakens progressively as the pH falls.

The Young's moduli and relaxation results can be explained as a progressive reinforcement of the contact zones present between the chains in these concentrated media, leading to semi-permanent junction zones. At a macroscopic level, an evolution from a paste without elastic properties in neutral media to a strong gel in very alkaline media demonstrates this reinforcement.

Complementary experiments tend to show that the ionic strength of the solutions has a smaller influence than the pH on the rheological properties of these gels.

Polymer concentration dependence

Concentrations of HPG gum in the range 40–80 g litre^{-1} were prepared in a buffer solution (NaOH, KCl) of pH 12 and 0·06 ionic strength (Bates

TABLE 4
Mathematical Analysis of Relaxation Curves for HPG (70 g litre^{-1}) in Alkaline Medium

pH	*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 (%)
13	84·5	8400	8·3	327	0		7·2
12	47·0	8480	17·5	482	14·4	112	21·1
9·8	44·0	8450	22·0	347	0		34·0

& Bower, 1956). The mechanical properties of the gels formed are shown in Figs 5 and 6.

Figure 5 shows a linear relation between log E and log C with a slope of $1{\cdot}9 \pm 0{\cdot}2$. Such a result agrees with the dependence on C^2 of the shear modulus G, proposed for concentrations well above the critical gelation concentration C_0 (Clark & Ross-Murphy, 1985, 1987). Such a dependence has also been theoretically predicted recently for 'rigid' gels (Marques & Joanny, pers. comm.).

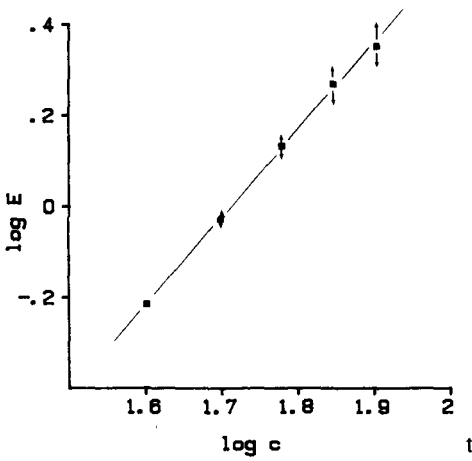

Fig. 5. Concentration dependence of the Young's modulus (HPG in buffer pH 12).

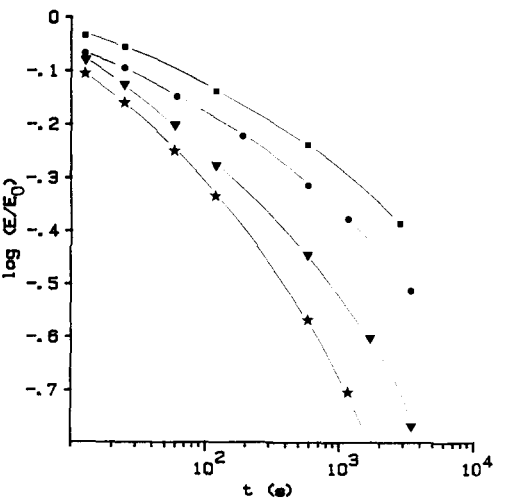

Fig. 6. Concentration dependence of stress relaxation behaviour (HPG at pH 12). ■ 80 g litre^{-1}, ($E_0 = 2{\cdot}18$ N/cm^2); ● 70 g litre^{-1}, ($E_0 = 1{\cdot}92$ N/cm^2); ▼ 50 g litre^{-1} ($E_0 = 0{\cdot}85$ N/cm^2); ★ 40 g litre^{-1} ($E_0 = 0{\cdot}57$ N/cm^2).

Relaxation curves (Fig. 6) clearly show that the relaxation phenomena are dependent on the Young's modulus of the gel. This observation will become important when a comparison with ion-crosslinked gels is performed (only gels with similar modulus can be compared).

CONCLUSION

The results obtained clearly demonstrate the possibility of preparing gels from guar gum or hydroxypropylguar gum in alkaline media. At these pHs a chain self-association mechanism almost certainly occurs. This can be regulated with the use of substituted gums for which gelation takes place at lower pHs.

ACKNOWLEDGEMENTS

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

REFERENCES

Albersheim, P., Nevins, D. J., English, P. D. & Karr, A. (1967). A method for the analysis of sugars in plant cell-wall polysaccharides by gas-liquid chromatography. *Carbohydr. Res.*, **5**, 340–5.

Arakawa, K. (1961). Rheological properties of hydrogels of agar-agar. *Bull. Chem. Soc. Japan*, **34**, 1233–5.

Bates, R. G. & Bower, V. E. (1956). Alkaline solutions for pH control. *Anal. Chem.*, **28**, 1322–4.

Black, H. N. & Melton, L. L. (1966). Temporary well plugging agent with a predetermined life. US Patent No. 3 327 212.

Chrisp, J. D. (1967). Gelled compositions containing galactomannan gums. US Patent No. 3 301 723.

Christianson, D. D., Casiraghi, E. M. & Bagley, E. B. (1985). Uniaxial compression of bonded and lubricated gels. *J. Rheology*, **29**, 671–84.

Christianson, D. D., Casiraghi, E. M. & Bagley, E. B. (1986). Deformation and fracture of wheat, corn and rice starch gels in lubricated and bonded uniaxial compression. *Carbohydr. Polym.*, **6**, 335–48.

Chudzikowski, R. J. (1971). Guar gum and its applications. *J. Soc. Cosmet. Chem.*, **22**, 43–60.

Clark, A. H. & Ross-Murphy, S. B. (1985). The concentration dependence of biopolymer gel modulus. *Brit. Polymer J.*, **17**, 164–8.

Clark, A. H. & Ross-Murphy, S. B. (1987). Structural and mechanical properties of biopolymer gels. *Adv. Polym. Sci.*, **83**, 57–192.

Comby, S., Doublier, J. L. & Lefebvre, J. (1986). Stress-relaxation study of high-methoxyl pectin gels. In *Gums and Stabilisers for the Food Industry 3*, ed. G. O. Phillips, D. J. Wedlock & P. A. Williams. Elsevier Science Publishers, London and New York, pp. 203–12.

Dea, I. C. M. & Morrison, A. (1975). Chemistry and interactions of seed galactomannans. *Adv. Carbohydr. Chem. Biochem.*, **31**, 241–312.

Dea, I. C. M., Clark, A. H. & McCleary, B. V. (1986). Effect of galactose-substitution-patterns on the interaction properties of galactomannans. *Carbohydr. Res.*, **147**, 275–94.

Deuel, H., Neukom, H. & Weber, F. (1948). Reaction of boric acid with polysaccharides. *Nature*, **161**, 96–7.

Doublier, J. L. (1975). Propriétés rhéologiques et caractéristiques macromoléculaires de solutions aqueuses de galactomannanes, Thèse de Docteur-Ingénieur, Paris VI University, n° CNRS A.O. 10919.

Ferry, J. D. (1980). *Viscoelastic Properties of Polymers*, 3rd Edition, John Wiley and Sons, New York, pp. 33–55.

Gey, C., Noble, O., Pérez, S. & Taravel, F. R. (1988). Complexes of borate ions with guar D-galacto-D-mannan polymer and related model compounds. *Carbohydr. Res.*, **173**, 175–84.

Horner, V. V. & Walker, R. E. (1965). Gels for plugging oil and gas boreholes. US Patent No. 3 208 524.

Inokuchi, K. (1955). Rheology of surface films. IV. Viscoelastic properties of 6-nylon films at air/water interface. *Bull. Chem. Soc. Japan*, **28**, 453–65.

Lin, K. S. C. & Aklonis, J. J. (1980). Evaluation of the stress-relaxation modulus for materials with rapid relaxation rates. *J. Appl. Phys.*, **51**, 5125–30.

Loewus, F. A. (1952). Improvement in anthrone method for determination of carbohydrates. *Anal. Chem.*, **24**, 219.

Morris, D. L. (1948). Quantitative determination of carbohydrates with Dreywood's anthrone reagent. *Science*, **107**, 254–5.

Noble, O. & Taravel, F. R. (1987). Nuclear magnetic resonance evidence of the guar-borate interaction. *Carbohydr. Res.*, **166**, 1–11.

Richardson, R. K. & Ross-Murphy, S. B. (1987). Non-linear viscoelasticity of polysaccharide solutions. 1: Guar galactomannan solutions. *Int. J. Biol. Macromol.*, **9**, 250–6.

Seaman, J. K. (1980). Guar gum. In *Handbook of Water-Soluble Gums and Resins*, ed. R. L. Davidson. McGraw-Hill, New York, Chapter 6, pp. 1–19.

Smith, T. L. (1979). Evaluation of the relaxation modulus from the response to a constant rate of strain followed by a constant strain. *J. Polymer Sci., Polymer Physics Ed.*, **17**, 2181–8.