Thermal Degradation of Guar Gum

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ABSTRACT

Information about the thermal degradation of guar gum has been obtained from the time dependence of the viscosity at high temperatures measured using a slit viscometer. The viscosity is related to the molecular weight using previously published relations between the zero shear specific viscosity and the coil overlap parameter in conjunction with the appropriate Mark–Houwink equation. Unlike anionic polysaccharides it is found that the kinetics determined by this method depend on solution concentration. This was found to be caused by thixotropic effects at the higher concentrations and degradation in flow. At the lowest concentration studied these two effects were absent and the kinetic equation obtained was $K_r = 0.51 \exp[-56330 \, (KJ/mol)/RT] \, s^{-1}$, where K_r is the rate constant. The viscosity results were supported at least in a semi-quantitative fashion by low speed sedimentation equilibrium measurements in the analytical ultracentrifuge. The relationship between the intrinsic viscosity and the measured molecular weight for the series of native/ degraded polymers could not be represented by a Mark–Houwink equation, suggesting that the molecular weight measurements were complicated by self-association. Gel permeation chromatography confirmed that self-association does occur and the elution profiles revealed a significant quantity of very low molecular weight material in the heat degraded material suggesting that thermal degradation is not a random process.

INTRODUCTION

In a previous paper we have reported a method for determining information about the degradation of polymers at high temperatures from viscosity measurements (Bradley & Mitchell, 1988). The method

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employs a slit viscometer developed by Berrington *et al.* (1987). In this paper we describe the application of this method to guar gum. The thermal stability of this material and chemically modified guar is of considerable interest particularly in the oil industry, e.g., Pat. GB 2089362A. It is well known that the rate of thermal degradation will depend on the presence of dissolved oxygen, but in order to make the results relevant to practical systems no attempt has been made to exclude oxygen or include free radical scavengers.

The viscosity measurements are supported at least in a qualitative sense by gel permeation chromatography (GPC) and determination of molecular weights using low speed sedimentation equilibrium (LSSE).

EXPERIMENTAL

Materials

The material used in this study was a commercial grade guar gum purchased from Sigma Inc. of Poole, Dorset, UK.

Sample preparation

The solutions for slit viscometry were prepared by wetting a known weight of guar with a small amount of absolute ethanol (0·5 ml ethanol per 100 mg guar) to prevent aggregation during the dispersion process. The guar was dispersed in a mixed phosphate buffer (KH_2PO_4, Na_2HPO_4) of pH 6·0 containing 0·2 M NaCl using a high shear Silverson Mixer.

The solution was then heated to 80°C over a 10 min period using a steam bath, before being cooled in an icewater bath. Vigorous stirring was maintained during both these operations.

Low speed sedimentation equilibrium measurements were carried out on portions of the solution which had been recovered from the slit viscometer after having been sheared. This solution was diluted to give a concentration of ~ 1 mg ml^{-1}, after which it was dialysed against the buffer solution for ~ 24 h. Intrinsic viscosity, $[\eta]$, and GPC measurements were also made on the material which had been treated in the slit viscometer.

Solutions for $[\eta]$ measurements were prepared by serially diluting the recovered material in buffer to give concentrations between 0·01% and 0·1% w/v. Those for GPC were diluted so that the column loading

concentration was ~ 0·3% (w/v), and the solutions were then degassed and filtered.

Experimental procedures

Slit viscometry
These experiments were carried out as previously described by Bradley & Mitchell (1988), with the addition of one new experimental feature. This consisted of measuring the solution viscosity at a constant applied wall shear stress as a function of temperature. The heating rate over the range 25–130°C is 3° min^{-1}. This leads to information on the temperature dependence of the solution viscosity and to the evaluation of the activation energy of viscous flow E_f, from the expression

$$\beta = \beta_0 \exp \left(\frac{E_f}{RT} \right) \tag{1}$$

where β is the 'consistency index' in the power law relationship

$$\tau = \beta \dot{\gamma}^n \tag{2}$$

τ being the shear stress and n the 'flow behaviour index', (e.g., Bradley & Mitchell, 1988).

In calculating rate constants for thermal depolymerisation from the viscosity changes with time the treatment is the same as previously described (Bradley & Mitchell, 1988). The Mark–Houwink equation employed was that reported for guar by Robinson *et al.* (1982).

$$[\eta] = 3 \cdot 8 \times 10^{-4} M_w^{0.723} \, dl.g^{-1} \tag{3}$$

and the dependence of the 'zero shear' viscosity η_0 on the solvent viscosity η_s and the coil overlap parameter $C[\eta]$ was taken as

$$\eta_0 = \frac{\eta_s}{10 \cdot 0} C[\eta]^{3.5} \tag{4}$$

(Doublier & Launay, 1976; 1981), C being the weight concentration (g.dl^{-1}).

Analytical ultracentrifugation
Sedimentation equilibrium measurements were performed on a Beckman Model E analytical ultracentrifuge employing Rayleigh interference optics and an RTIC temperature measurement system. The 'low' or 'intermediate' speed method as described by Creeth &

Harding in 1982 was employed. Determinations were made using either 12 mm or 30 mm optical path length cells at the lowest possible concentration (~ 0.3 mg/ml for 30 mm cells, ~ 1 mg/ml for 12 mm), to minimise possible effects of thermodynamic non-ideality and/or associative phenomena.

The partial specific volume of guar was taken to be 0.613 ml/g (Gaisford *et al.*, 1986). Whole-cell apparent weight average molecular weights, M_w^0, were extracted by using the limiting value at the cell base of a particularly directly determinable point average (the 'star' average, M* (Creeth & Harding, 1982)); an independent estimate for the initial concentration was not required.

Earlier determinations in this study were made using a conventional mercury arc ion light source but the more recent work took advantage of a recently acquired laser light source. Measurements on native guar at the start and completion of this work were in agreement.

Intrinsic viscosity
The determination of the intrinsic viscosities of the guar samples was made at a temperature of $25.0 \pm 0.1°C$ using an Ostwald Viscometer having a flow time for water of 301 s. The intrinsic viscosity was calculated from a Huggin's plot of the reduced viscosity versus concentration.

Gel permeation chromatography (GPC)
GPC studies were performed on columns packed with Sephacryl S500 gel, run at about 10 ml h^{-1}. Fractions of about 2 ml were collected using an ATTO mini collector and analysed for total sugar content by the phenol sulphuric acid method (Dubois *et al.*, 1956). All samples were filtered through Whatman 541 filter paper to remove sediment and degassed before application to the column.

RESULTS

The slit viscometer performs measurements at high wall shear rates ($1000-10000$ s^{-1}) and in this region and over the concentration ranges employed the flow curve can be described by the power law equation (2). Good linearity was found for plots of log τ_w versus log $\dot{\gamma}_{wN}$ where $\dot{\gamma}_{wN}$ and τ_w are the Newtonian wall shear rates and shear stresses respectively. This would be expected from the relationship between the viscosity and generalised shear rate reported by Robinson *et al.* (1982).

TABLE 1
Variation in the Power Law Index and Flow Activation Energy with Concentration of
Guar Gum at pH 6·0

Concentration $(g. dl^{-1})$	Temperature range of measurements (°C)	Power law index n	E_f $(kJ \, mol^{-1})$
1·0	35–105	0·317 ± 0·01	4·20
0·9	35–105	0·417 ± 0·02	5·72
0·8	30–100	0·460 ± 0·01	6·98
0·7	20–100	0·514 ± 0·01	8·20
0·6	40–115	0·520 ± 0·02	11·10
0·5	30–120	0·460 ± 0·03	11·90
0·4	30–110	0·569 ± 0·01	9·10
0·3	35–95	0·605 ± 0·03	9·10

E_f, activation energy of viscous flow.

As previously reported (Doublier & Launay, 1981) the power law index, n, found for guar was essentially temperature independent. Table 1 shows the values of n and E_f for several concentrations of guar. The 0·5% solution seems to show an anomalously low value of n and also shows a maximum of E_f.

Patel *et al.* (1987) have recently reported results on the temperature dependence of the zero shear viscosity for guar gum and when these results are interpreted using the Arrhenius equation a maximum in the activation energy of viscous flow is found at a concentration of 1·2%. This is higher than the concentration of the maximum in E_f found for the temperature dependence of the consistency index. However, the intrinsic viscosity of our material (~ 11·5 dl.g^{-1}) was considerably higher than that reported by Patel *et al.* (~ 2·5 dl.g^{-1}) although their value was obtained from a fit of the relationship between the concentration and the zero shear specific viscosity obtained at high concentrations.

It is possible that the activation energy is a maximum at concentrations about the concentration for entanglement formation (C^*) and at higher concentrations the decrease in E_f is due to a reduction in the size of the flow unit, which then becomes the distance between entanglement points as has been suggested by Patel *et al.*

A recent study (Bradley & Mitchell, 1988) has shown that the rate constants of depolymerisation of several ionic polysaccharides were independent of the polymer concentration. Figure 1 illustrates that this is not the case for guar gum: Arrhenius plots of data obtained on guar at different concentrations show different rate constants. The apparent rate constants are much greater for highly concentrated solutions than for
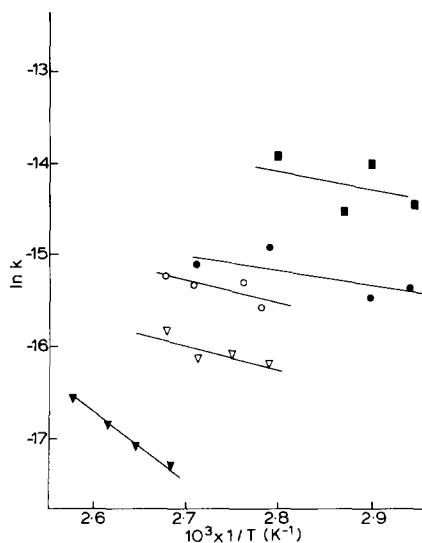
Fig. 1.   Arrhenius plots for guar gum data: ■, 0·9%; ●, 0·8%; ○, 0·7%; ▽, 0·6%; ▼, 0·5%.

dilute ones; also the temperature dependence becomes weaker with increasing concentration. At the lowest concentration employed (0·5%) the equation

$$K_r \approx 0.51 \exp[-56330\,(kJ/mol)/RT]\,s^{-1} \tag{5}$$

was obtained, where K_r is the rate constant.

There are two possible explanations for the anomalous behaviour at the high concentrations:

(i) At the higher concentrations the polymer degrades as a consequence of flow rather than heat. The shear and elongational stresses which cause depolymerisation will increase with increasing concentration. This explanation appears to be supported by Fig. 2, where it is shown that the apparent rate constants at a constant temperature of 60°C increase with wall shear stress.

(ii) Thixotropic effects exist and the reduction in viscosity with time experienced by the concentrated solutions is not entirely due to depolymerisation and thus the molecular weight reduction deduced from the change in solution viscosity overestimated the degree of depolymerisation.

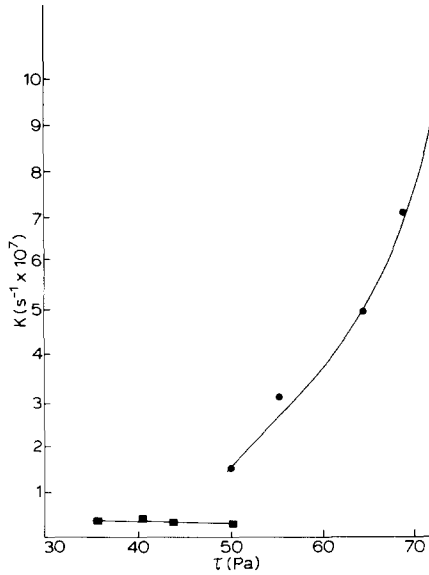To test this a series of measurements was made where the solution

Fig. 2. The effect of the applied shear stress on the apparent rate constant of depolymerisation of guar. ■, 0·5%; ●, 0·8%.

was sheared in the slit viscometer, allowed to relax for a period of time and then resheared. It was indeed found that at concentrations above 0·6%, time dependent viscosity changes were observed. Figure 3 shows thixotropic effects observed in a ~ 0·8% guar gum solution at 60°C.
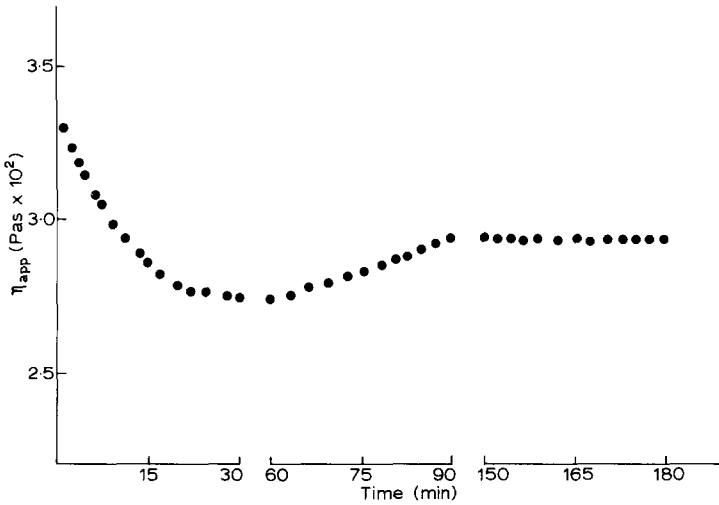

Fig. 3. Thixotropic effects observed in a 0·8% guar gum solution at a temperature of 60°C and an applied shear stress of 58 Pa.

TABLE 2
Molecular Weight and Intrinsic Viscosity Data

	A	B	C	D
M_w^0 (g.mol^{-1})	700 000 ± 100 000	160 000 ± 10 000	450 000 ± 60 000	—
$[\eta]$(dl.g^{-1})	11·51 ± 0·5	5·87 ± 0·25	6·70 ± 0·27	9·40 ± 0·38

A, native guar. B, heat treated guar 0·5%; $\tau_w = 23$ Pa; 110°C for 12 min; $\dot{\gamma}_{AV} \sim 4200$ s^{-1}. C, highly sheared guar 0·8%; $\tau_w = 58$ Pa; 60°C for 11 min; $\dot{\gamma}_{AV} \sim 5500$ s^{-1}. D, lightly sheared guar 0·8%; $\tau_w = 23$ Pa; 60°C for 11 min; $\dot{\gamma}_{AV} \sim 2500$ s^{-1}. M_w^0, whole-cell apparent weight average molecular weight from low speed sedimentation equilibrium in the analytical ultracentrifuge; τ_w, Newtonian wall shear stress; $\dot{\gamma}_{AV}$, average Newtonian wall shear rate.

Similar experiments with a Newtonian fluid (concentrated sugar syrup) and solutions of sodium carboxymethylcellulose did not show this behaviour.

In an attempt to determine the relative contributions of thermal degradation, flow degradation and thixotropic effects to the apparent rate constants, information about molecular weight changes in the slit viscometer were obtained using low speed sedimentation equilibrium.

As can be seen from Table 2, the weight average molecular weight, M_w^0, drops dramatically upon both heat and flow degradation with a corresponding drop in the intrinsic viscosity. Specifically we find:

(i) Shearing of the solution does indeed appear to cause some depolymerisation, and the intrinsic viscosity results indicate that the degree of depolymerisation increases with increasing wall shear stress.

(ii) Thermal treatment of the polymer causes extensive depolymerisation and to a degree greater than that caused by flow alone, contrary to what would be expected from the rate constants shown in Fig. 1.

The intrinsic viscosity does not appear however to be related to the molecular weight by a simple Mark–Houwink equation. This is likely to be due to a tendency of guar to self-associate in dilute solution: further, the effect of a change in conformation of the guar upon treatment cannot be excluded.

An attempt was also made to investigate change in GPC behaviour upon heat treating the guar, both in a relative sense and in a calibrated sense. Figure 4(a)–(c) gives the elution profiles for native (a), heat treated (b) and flow modified (c) guar. An increase in the level of very low
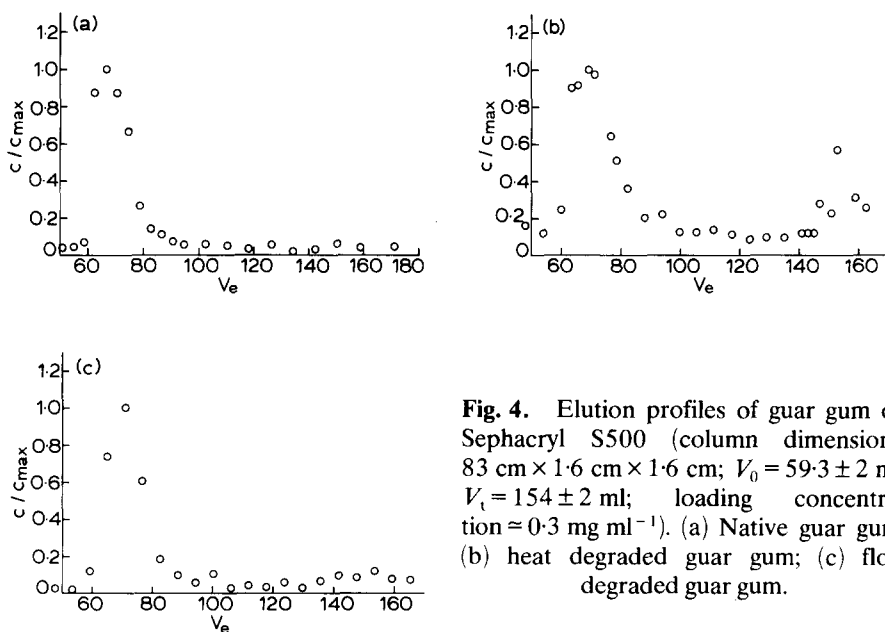
Fig. 4. Elution profiles of guar gum on Sephacryl S500 (column dimensions: 83 cm × 1·6 cm × 1·6 cm; $V_0 = 59·3 \pm 2$ ml, $V_t = 154 \pm 2$ ml; loading concentration $\approx 0·3$ mg ml^{-1}). (a) Native guar gum; (b) heat degraded guar gum; (c) flow degraded guar gum.

molecular weight material is particularly noticeable for the heat treated material.

Rechromatographing of isolated fractions of narrow bandwith clearly demonstrated a redistribution of material (Fig. 5); the shift in the peak and broadening cannot be explained in terms of simple diffusion zonal broadening phenomena. We took this as strong evidence for significant self-association phenomena and therefore attempts at calibrating the elution profile by measuring the molecular weights of isolated narrow fractions would prove futile (Ball *et al.*, 1988).
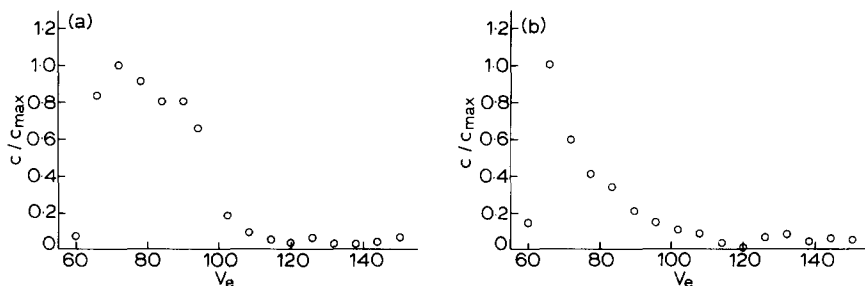

Fig. 5. Elution profiles of guar gum on Sephacryl S500 (column 81 cm × 1·6 cm; $V_0 = 59 \pm 2$ ml, $V_t = 152 \pm 2$ ml). (a) Loading concentration ∼ 1·0 mg ml^{-1}; (b) rechromatographing of fractions of $V_e = 94$–100 ml from (a).

CONCLUSIONS

(1) The use of continuous high temperature viscosity measurements to characterise the thermal degradation of guar gum fails at high concentrations because of (i) reversible time dependent viscosity changes, and (ii) degradation due to flow.

(2) At the lowest concentration employed (0·5%) these effects seem to be absent and the kinetic equation $K_r \simeq 0·51$ exp$[-56330$ (kJ/mol)/RT$]$ s^{-1} was obtained.

(3) Measurements of $[\eta]$ and the molecular weight and gel permeation chromatography show that both heat and flow cause the material to degrade considerably.

(4) Heat degradation in particular results in the production of significant quantities of low molecular weight material with a consequent large increase in polydispersity.

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