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Viscosity of galactomannans during high temperature processing: influence of degradation and solubilisation

M.S. Kök, S.E. Hill*, J.R. Mitchell

Division of Food Sciences, School of Biological Sciences, University of Nottingham, Sutton Bonington Campus, Loughborough LE12 5RD, UK

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Abstract

The rheological properties of guar gum (GG) and locust bean gum (LBG), in response to high temperature treatments, were measured using a rheometer equipped with a high pressure cell. This has allowed the viscosity to be assessed at temperatures above 100°C and as the polymer suspension is heated from 20 to 121°C and then cooled back to ambient temperature to simulate a food sterilisation cycle. Activation energies for depolymerisation estimated from viscosity changes with time at a series of constant temperatures were estimated as 63 kJ/mol for GG and 98, 104, 110 kJ/mol for three different samples of LBG. A model was developed to interpret the viscosity change through the simulated sterilisation cycle. This took into account the degradation of the polysaccharide and the change in viscosity due to thermal motion. Estimations of molecular weight changes during the heating process suggest that GG is more susceptible to thermal degradation than LBG. It is suggested that this is due to the greater ability of the latter to associate in solution. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Galactomannans; Solubilisation; Guar gum; Locust bean gum

1. Introduction

Galactomannans are water soluble polysaccharides found in the seed endosperm of a variety of legumes and consist of a (1–4) linked β-D-mannopyranosyl backbone partially substituted with (1–6) linked α-D-galactopyranosyl substituents. The industrially most important galactomannans are guar gum (GG) and locust bean gum (LBG) which have a mannose to galactose ratio of about 1.8 and 3.5, respectively (Dea & Morrison, 1975; Fox, 1992). This difference in the degree of galactose substitution causes differences in water solubility. GG is cold water soluble whereas LBG shows low solubility at ambient temperatures and heat treatment is required for maximum solubility (Gaisford, Harding, Mitchell & Bradley, 1986; Hui & Neukom, 1964; Maier, Anderson, Karl, Magnuson & Whistler, 1993).

An important application of these materials is as thickeners in food products that are subjected to heat sterilisation (Fox, 1992). For in-container sterilisation, temperatures up to 125°C can be reached whereas in aseptic processes temperatures as high as 140°C are encountered (Brennan, Butters, Cowell & Lilly, 1990). The stability of galactomannans to high temperatures is also of importance in oil well drilling applications where modified GG is used as a component of drilling muds (Maier et al., 1993). Thermal stability of polysaccharides has been quite extensively studied (e.g. Franz & Feuerstein, 1997; Khomutov, Ptichkina, Sheenson, Lashek & Panina, 1994; Pilnik & McDonald, 1968; Rao, Walter & Cooley, 1981). Degradation mechanisms include acid hydrolysis, oxidative reductive depolymerisation (ORD) and β-elimination. Since galactomannans can be protected from degradation by the addition of antioxidants (Mitchell et al., 1992; Rodriguez, 1985) it appears that they are particularly susceptible to ORD. Only at ambient temperatures and low moisture contents are they stable against depolymerisation on storage (Franz & Feuerstein, 1997). A value for the activation energy for thermal depolymerisation of GG of 56 kJ/mol has been reported by Bradley, Ball, Harding and Mitchell (1989). This is low compared with other polysaccharides with the exception of sodium alginate which is very thermally labile and has a reported activation energy for degradation of 51 kJ/mol (Bradley & Mitchell, 1988). Axelos and Branger (1993) have obtained values of 68 and 93 kJ/mol for pectins with different degrees of polymerisation where at neutral pH degradation by β-elimination dominates. Values of 104 and 105 kJ/mol have been reported for schizophyllan and carrageenan, respectively (Bradley & Mitchell, 1988; Zentz, Verchere & Muller, 1992).

The objective of the work described in this paper is to

* Corresponding author. Tel.: +44-115-951-6145, fax: +44-115-951-6142.

E-mail address: sandra.hill@nottingham.ac.uk (S.E. Hill)

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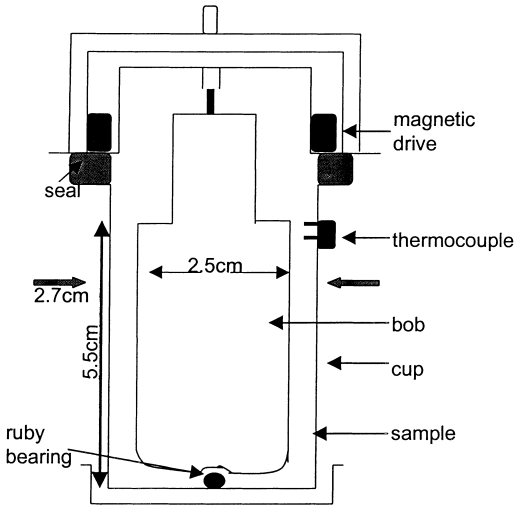

Fig. 1. Schematic of high pressure cell. Sample size is approximately 7 ml.

obtain the activation energy for depolymerisation for three LBG samples and a sample of GG. This data will then be used to interpret the viscosity changes occurring as dispersions of the polysaccharides, which are heated to 121°C and cooled to ambient to simulate a food sterilisation process. A rheometer equipped with a pressure cell was used to obtain viscosity measurements above 100°C. A preliminary account of some aspects of this work was presented at the conference on Polysaccharide Biotechnology held at the University of Nottingham in September 1997 (Kök, Hill & Mitchell, 1999).

2. Materials and methods

2.1. Materials

The galactomannans used in these studies were; GG and three LBG samples (AG), purchased from Sigma, UK, and two food-grade (FG1 and FG2) LBGs from other commercial sources.

2.2. Experimental

2.2.1. Sample preparation

Gums were prepared by adding a known weight to a volume of 100 mM sodium phosphate buffer, pH 7.0, at ambient temperature using a high shear Silverson mixer. The samples were left overnight to hydrate. Preliminary experiments showed that 1% GG reached its highest viscosity after 2 h at ambient temperature, whereas 1% AG LBG took at least 12 h to achieve a maximum level of viscosity.

2.2.2. Measurement of viscosity

All measurements of viscosity were made using a Bohlin CS 10 rheometer. For experiments utilising temperatures of 90°C and below a concentric cylinder C25 geometry was used. To determine viscosities above 90°C, or to follow viscosity changes during heating up to 121°C, a high pressure cell (HPC) attachment was fitted to the Bohlin (Fig. 1). In this cell, a 7 ml sample was completely enclosed; the bob being driven via a magnetic coupling and supported on a ruby bearing. In calculating shear rates, the rheometer software takes into account the finite gap between the cylinders, assuming Newtonian flow behaviour. Although this is not correct, the error will be small for small gaps.

2.2.2.1. Rotational viscosity measured during a temperature cycle. The rotational viscosity of 1% (w/v) samples was measured at a shear stress of 5 Pa while the temperature was increased at a rate of 1°C/min from 20 to 121°C and immediately cooled back to 20°C at a rate of 2°C/min.

2.2.2.2. Effect of heat treatment on viscosity, subsequently measurement at 25°C. Samples were prepared at a concentration of 0.8% (w/v) stored overnight and canned. The metal cans of 7.5 cm diameter and 6 cm in height were completely filled eliminating any headspace and sealed. Samples were heated for 30 min at 20, 40, 60, 80, 100°C in a water bath and also for 30 min in a pressure cooker at 121°C. Viscosity of the samples was measured at 25°C before and after heat treatment, over the shear stress range of 1–20 Pa and the results reported at a stress of 1 Pa.

2.2.2.3. Rotational and complex viscosity measurements while samples are kept at constant temperatures. The rheometer software corrects for measurement geometry inertia. There is no fundamental significance in the different frequencies used but the higher frequency employed for low viscosity LBG solutions improved the magnitude and quality of the stress signal at the target strain. Samples (1%, w/v) were held at a specific temperature in the range 70–121°C over a 2 h period. Measurements were made in oscillation at a frequency of 0.2 Hz for GG and 1 Hz for LBG and strain set at 0.5 for both gums. C25 geometry for temperatures up to and including 90°C was used. For higher temperatures rotational viscometry at a shear stress of 5 Pa was performed using the HPC geometry. We found it difficult to obtain reproducible data in oscillation for these systems at high temperatures using the HPC.

2.2.3. M_w determination using SEC/MALLS system

LBG samples (0.5%) were suspended in phosphate buffer at room temperature and left overnight. The sample was then heated to 70°C for 1 h. During the first 15 min of this heating period rapid agitation was carried out with a Silverson mixer. The procedure for preparing the GG solution was similar except that a temperature of 40°C was used for the heating stage. Samples were centrifuged and filtered before adding to the size exclusion columns. The SEC/MALLS system consisted of a Waters 590 Solvent Delivery module (Waters, Millipore, Watford, UK), a Rheodyne injection loop, a guard column and two analytical columns (PSS

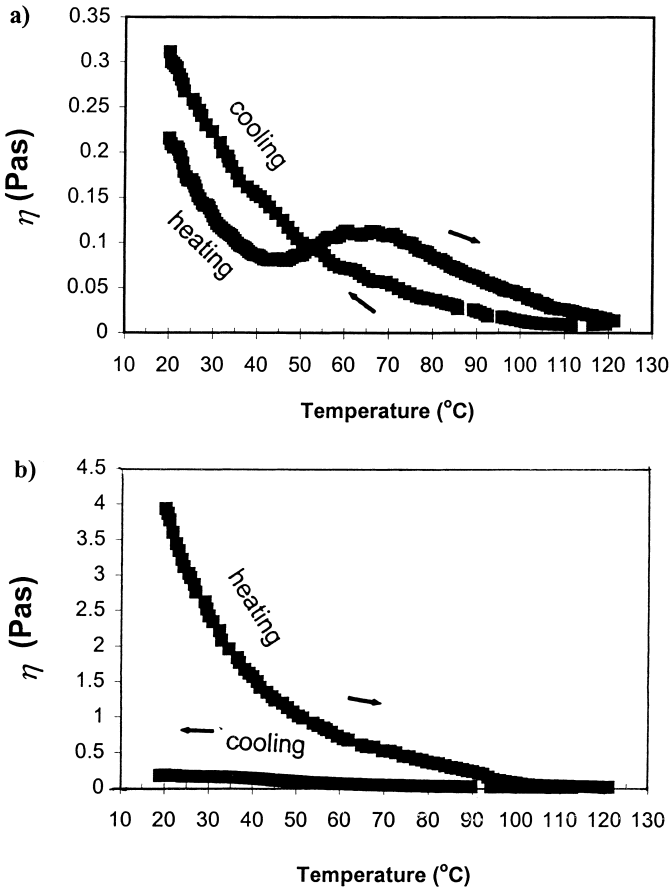

Fig. 2. Viscosity change during a heating and cooling cycle of (a) LBG and (b) GG. Measurements made at shear stress of 5 Pa. Heating rate 1°C/min and cooling rate 2°C/min.

Hema-Bio Linear + PSS Hema-Bio 40, PSS GmbH, Mainz, Germany). Scattered light intensities and concentrations were, respectively, measured using Dawn F multiangle light scattering and an Optilab 903 (Wyatt, Santa Barbara, US) interferometric refractometer. The eluents were pumped at a flow rate of 0.8 ml/min at room temperature.

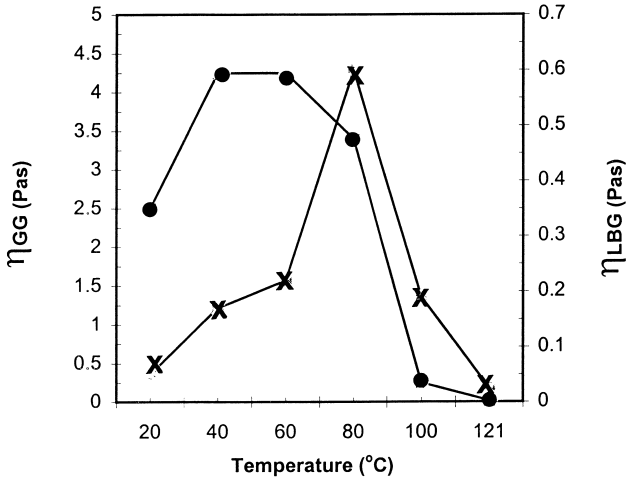

Fig. 3. Viscosity measured at shear stress of 1 Pa and a temperature 25°C for samples of AG LBG (X) and GG (●) following heat treatment for 30 min at 20, 40, 60, 80, 100 and 121°C.

3. Results and discussion

3.1. Change in viscosity during heat processing

Fig. 2a and b compares the viscosity during a heating and cooling cycle corresponding to a typical sterilisation process for LBG (sample AG) and GG. The two other LBG samples showed a similar profile to AG.

The viscosity will be governed by three factors:

(i) a reversible decrease in viscosity with increasing temperature due to increasing macromolecular motion;
(ii) increase in viscosity due to increased solubilisation;
(iii) loss of viscosity due to decreasing molecular weight as a result of thermal degradation.

For AG LBG there is a marked increase in viscosity at temperatures above 50°C and this corresponds to solubilisation of the polymer. In excess of 80°C degradation effects outweigh any further increase in solubilisation. On cooling, LBG recovers viscosity to levels exceeding the initial

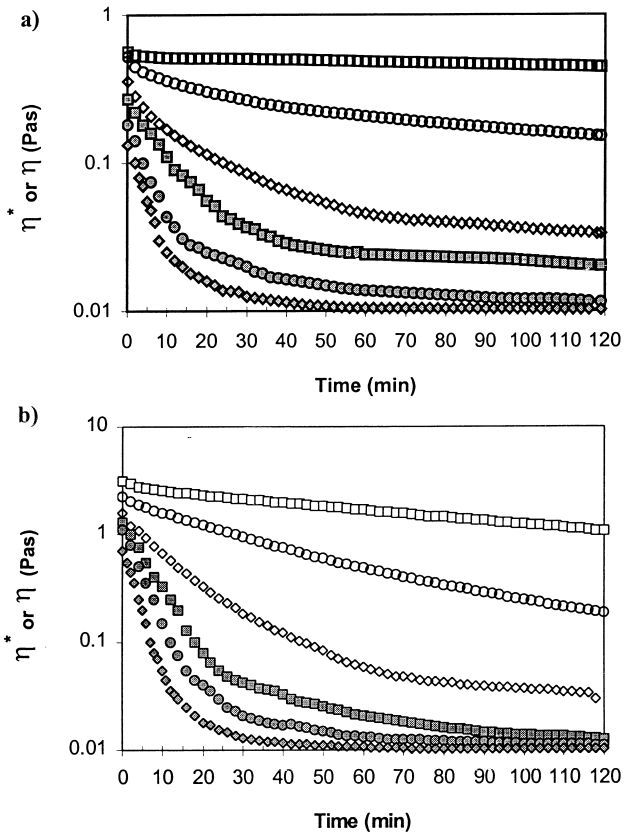

Fig. 4. Viscosity changes with time for samples of (a) AG LBG and (b) GG held at a series of temperatures. Viscosities at temperatures up to including 90°C are dynamic viscosities obtained at a frequency of 0.2 Hz for GG and 1 Hz for LBG. A strain of 0.5 and C25 geometry was employed. At higher temperatures the viscosity was measured in continuous rotation at a shear stress set at 5 Pa using the HPC. (□ 70°C, ○ 80°C, ◇ 90°C, ■ 100°C, ● 110°C, ◆ 121°C).

viscosity. The profile for GG is different. The initial viscosity is much higher and there is no peak due to solubilisation. It is recognised that whereas typically 80% of GG is soluble at ambient temperature, only 35% of LBG is cold water soluble at ambient temperature. At 80°C maximum solubilisation of LBG has occurred (Gaisford et al., 1986; Hui & Neukom, 1964).

Somewhat similar information on the relative importance of solubilisation and degradation can be obtained from the change in the viscosity measured at ambient temperature for samples that have been previously heated at different temperatures for 30 min (Fig. 3). For GG preheating to 40 and 60°C gave the maximum viscosity at all shear stresses. Treatment at higher temperatures showed decreases in viscosity almost certainly as a result of macromolecular degradation. In comparison, AG LBG showed maximum viscosity at higher temperatures due to additional material being solubilised at these higher temperatures. The viscosity of the preheated LBG solutions decreased in the following order of heating temperatures $80 > 60 > 100 > 40 > 20 > 121$°C.

It is of interest to obtain a more quantitative understanding of the viscosity data shown in Fig. 2. If the concentration is above the coil overlap (c^*) the dependence of the zero shear viscosity on the coil overlap parameter ($[\eta]c$) will approximate to $([\eta]c)^4$ (Lapasin & Pricl, 1995). If it is assumed that the viscosity measured shows a similar concentration dependence to the zero shear viscosity then the measured viscosity at any time during a heat processing cycle will be given by an equation of the form:

$$\eta = k(c(t)[\eta](t))^4 \exp\left[\frac{E_T}{RT}\right] \quad (1)$$

where E_T is the activation energy determining the temperature dependence of viscosity and k is a constant. For LBG the concentration c and the intrinsic viscosity ($[\eta]$) will be a function of the time (t) during the heating cycle. The former because of increasing solubilisation with temperature, the latter because of increasing degradation. In this paper, we estimated the activation energy for degradation from measurements at constant temperature. If a value for E_T is assumed we can predict viscosity temperature relationships for the fully solubilised material and compare the predicted results for different rate constants for degradation with the experimental results. We make the additional assumption that degradation does not occur until full solubilisation takes place.

3.2. Degradation kinetics

Information has been obtained about the kinetics of degradation from viscosity measurements at constant temperature. The data has been analysed using the method of Bradley & Mitchell (1989).

The activation energy for degradation (E_d) can be defined by an Arrhenius equation:

$$k_d = k_{do} \exp\left(\frac{-E_d}{RT}\right) \quad (2)$$

where k_d is the rate constant for the degradation process at temperature T (K) and k_{do} is a constant.

The change in molecular weight due to degradation is assumed to follow Eq. (3) (Bradley & Mitchell, 1988):

$$\frac{1}{M_t} = \frac{1}{M_0} + \frac{k_d t}{2L} \quad (3)$$

where M_0 is the weight average molecular weight at time zero, M_t at time t, and L is the weight of a monomer unit.

If it is assumed that the exponent α in the Mark–Houwink equation for the galactomannans

$$[\eta] = KM^{\alpha} \quad (4)$$

is close to the value of 0.723 obtained by Robinson, Ross-Murphy and Morris (1982) for GG then if the viscosity depends on $(c[\eta])^4$ as implied by Eq. (1) then the dependence of viscosity (η) on the molecular weight will be very close to $\eta \propto M^3$. It follows that if Eq. (3) holds a plot of $1/3\sqrt[3]{\eta}$ against time should be linear with an initial slope (k_s)

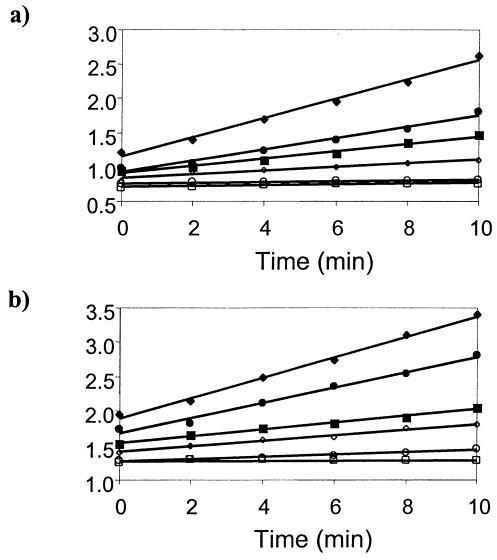

Fig. 5. Examples of linearisation of thermal degradation curves obtained from η measurements over time by plotting $1/\sqrt[3]{\eta}$ against time for (a) AG LBG and (b) GG for temperatures of (□ 70°C, ○ 80°C, ◇ 90°C, ■ 100°C, ● 110°C, ◆ 121°C).

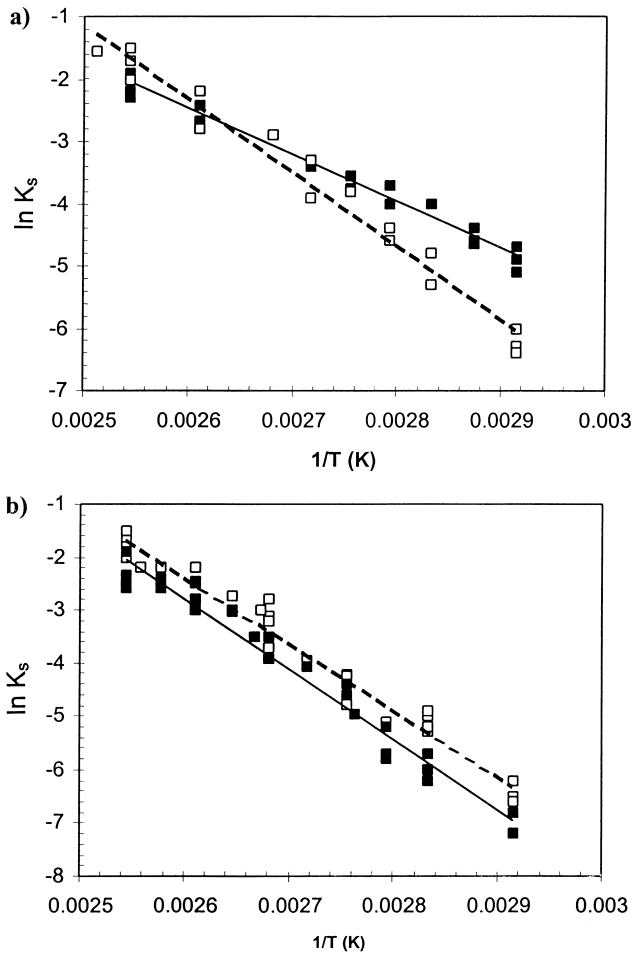

Fig. 6. Logarithmic plot of slopes K_s from Fig. 5, against the inverse of temperature ($1/T$ (K)) for (a) GG (■), AG LGB (□), (b) FG1 LBG (□), FG2 LBG (■). Line of best fit is shown.

that is proportional to the rate constant for degradation. The activation energy E_d can then be obtained from the slope of an Arrhenius plot, where $\ln k_s$ is the ordinate.

Fig. 4 displays the change in viscosity with time for GG and LBG (AG). At temperatures up to and including 90°C as previously mentioned the viscosities are dynamic viscosities at a frequency of 1 Hz. At the higher temperatures steady shear viscosities obtained from the HPC are used.

Representative plots of $1/3\sqrt[3]{\eta}$ against time for the galactomannans are shown in Fig. 5. Straight lines have been fitted to the first 10 min of the degradation curves. The response of initial linearity gives some justification to the assumed dependence of the viscosity on $(c[\eta])^4$. If the heating period is extended, there is a more appreciable loss of linearity especially for the curves relating to the higher temperatures.

The initial slopes are proportional to a rate constant for degradation and therefore E_d can be obtained from an Arrhenius plot. These plots are shown in Fig. 6 and indicate a linear relationship with r^2 values of greater than 0.96. The reasonably good linearity gives some justification for combining experimental information obtained from dynamic and continuous rotation measurements. Whereas the former can in our view be equated to a zero shear viscosity through the Cox–Merx rule the latter obtained at higher shear rates will probably be significantly lower than the zero shear viscosity. Our data would suggest that the time dependence during heat degradation is similar.

The E_d values calculated clearly show differences between GG at 63 kJ/mol (which is in reasonable agreement with the value of 56 kJ/mol reported by Bradley & Mitchell, 1988) and the LBG samples which have values of 98 kJ/mol (AG), 104 kJ/mol (FG1) and 110 kJ/mol (FG2). Values for the activation energy of the acid hydrolysis of sucrose of 103 kJ/mol have been obtained by Rhim, Nunes, Jones and Swartzel (1989) from an analysis of data obtained using a linear increasing temperature. All the values obtained for E_d are significantly different ($p < 0.05$) from one another.

Fig. 7 shows a comparison between the calculated and measured changes in viscosity for the four samples where the value for the rate constant k_d which gives the best fit is taken. This curve was obtained using the following assumptions.

(i) Locust bean gum was fully solubilised at a temperature of 70°C and GG at 40°C, but no degradation had taken place until full solubilisation had taken place. The initial weight average molecular weight was therefore the measured value from SEC-MALLS shown in Table 1.
(ii) The value obtained by Lopes da Silva, Goncalves and Rao (1994) for E_T has been taken as 29 kJ/mol in all cases.
(iii) The constants in the Mark–Houwink equation were that of Robinson et al. (1982) for GG for all samples.

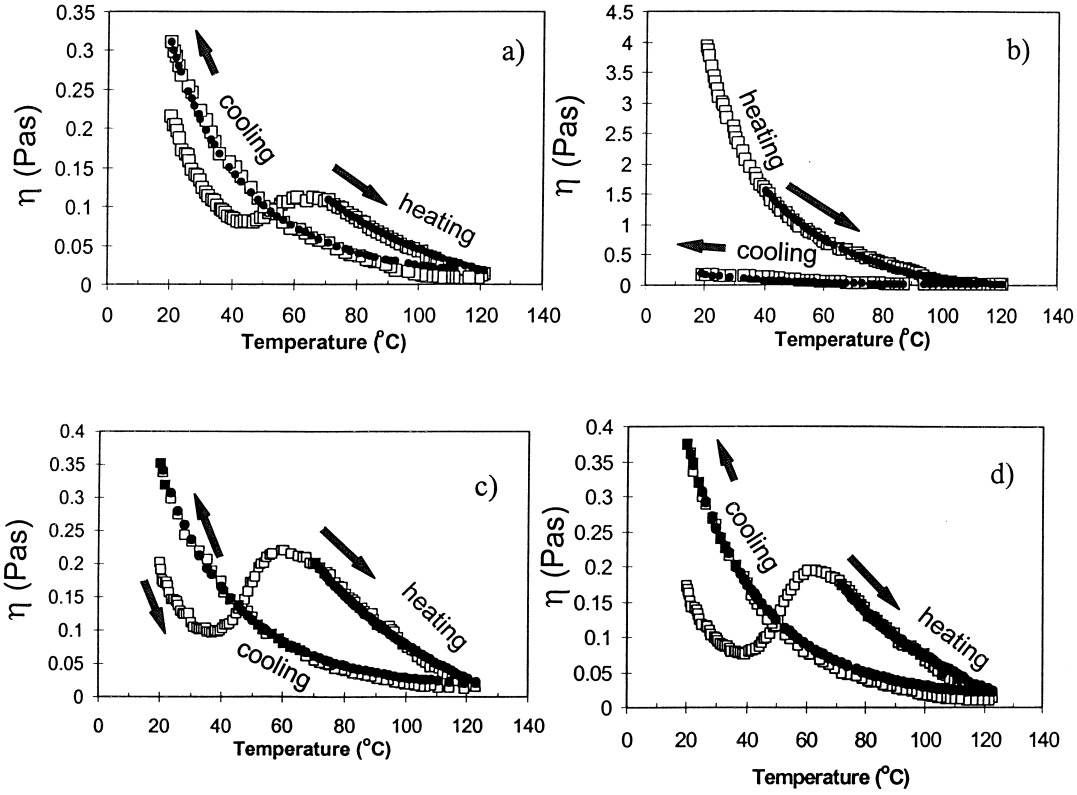

Fig. 7. Measured (□) and calculated (filled symbols) rotational viscosities (η) for (a) AG, (b) GG, (c) FG1 LBG and (d) FG2 LBG. Heating and cooling rates are 1 and 2°C/min, respectively. Viscosities were calculated from Eq. (1) as described in the text.

The above three assumptions allow a value for k in Eq. (1) to be obtained by equating the measured viscosity at 70°C (LBG) and at 40°C (GG) and the calculated value of $(c[\eta](t))^4 \exp[-E_d/RT]$. It is assumed that c is 10 g/l in all cases.

The change in molecular weight with time during the subsequent heating and cooling cycle was calculated for a range of values for the parameter k_{do}. From this molecular weight the viscosity through the simulated process could be calculated using Eq. (1).

The values for k_{do} that gave the best fit to the experimental data and were therefore used to obtain the calculated result in Fig. 7 are displayed in Table 1. Also displayed are the activation energies and initial molecular weights obtained from SEC-MALLS. The consequence of the different degradation parameters (k_{do} and E_d) for GG and LBG in terms of the rate constants, in the temperature range of interest, and molecular weight change during the heat process are shown in Figs. 8 and 9.

Our results demonstrate that there are significant differences between GG and LBG in terms of the degradation profile as well as solubility. GG has a relatively low activation energy for depolymerisation, but high rate constants in the temperature range of interest. It is recognised that LBG associates in solution and at high concentrations this can

Table 1
The values, which have been used in the model for the four polysaccharide samples studied

Samples	M_w[a] (Da)	E_d (kJ/mol)	k_{do} (min^{-1})
AG LBG	7.4E + 5	98	1.8E + 7
FG1 LBG	8.3E + 5	104	6.8E + 8
FG2 LBG	7.6E + 5	110	2.9E + 9
GG	1.1E + 6	63	1.1E + 3

[a] Measured by SEC-MALLS.

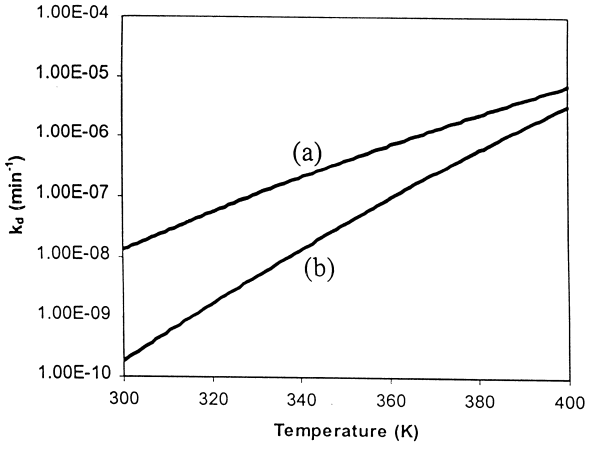

Fig. 8. Dependence of rate constants for degradation on temperature for (a) GG and (b) AG LBG, predicted from Eq. (2) and Table 1.

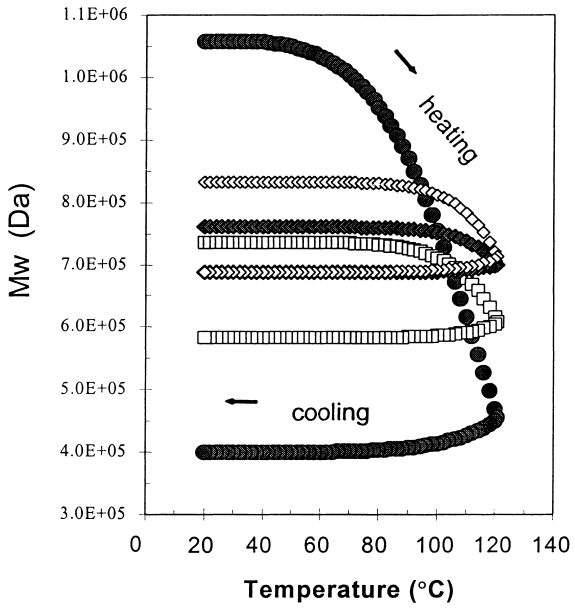

Fig. 9. Calculated change in weight average molecular weight (M_w) of AG LBG (□), FG1 LBG (◇), FG2 LBG (◆) and GG (●) during the heating and cooling cycle.

lead to gelation (Richardson & Norton, 1998). This association in solution leads to a higher intrinsic and concentrated solution viscosity than would be expected on the basis of the molecular weight of the polysaccharide (Goycoolea, Morris & Gidley, 1995; Richardson, Willmer & Foster, 1998). It is recognised that association will protect a polymer against degradation (Stokke, Christensen & Smidsrod, 1992) although it is less clear as to whether this reflects a decrease in the number of breaks or is simply due to the ability of degraded material to hold together through the association resulting in a reduced change in viscosity on degradation. The higher activation energy shows a greater dependence for the thermal degradation rate as evidenced by the viscosity data. This could be due to a decrease in LBG association with increasing temperature and hence a reduction in the protective effect. Such a view would contradict the simple molecular weight based interpretation used here. It would not, however, invalidate the general conclusion that the change in viscosity when LBG is subjected to a heat sterilisation process is completely different to that encountered with GG, which is of practical significance.

4. Conclusions

When degradation is monitored by viscosity changes during heating LBG shows less degradation during heat sterilisation at neutral pH compared with GG. The activation energy for locust bean degradation for the three samples measured is in the range 98–110 kJ/mol compared with the values of 56 and 63 kJ/mol found for GG. It is suggested that the difference in activation energy and overall degradation rate is due to the greater ability of LBG to associate in solution compared with GG.

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References

Axelos, M. A. V., & Branger, M. (1993). The effect of the degree of deesterification on the thermal stability and chain conformation of pectins. *Food Hydrocolloids, 7*, 91–102.

Bradley, T. D., & Mitchell, J. R. (1988). The determination of the kinetics of polysaccharide thermal degradation using high-temperature viscosity measurements. *Carbohydrate Polymers, 9*, 257–267.

Bradley, T. D., Ball, A., Harding, S. E., & Mitchell, J. R. (1989). Thermal degradation of guar gum. *Carbohydrate Polymers, 10*, 205–214.

Brennan, J. G., Butters, J. R., Cowell, N. D., & Lilly, A. E. V. (1990). *Food engineering operations*, 3 (pp. 295–335). Barking: Elsevier.

Dea, I. C. M., & Morrison, A. (1975). Chemistry and interactions of seed galactomannnans. *Advances in Carbohydrate Chemistry and Biochemistry, 31*, 241–242.

Fox, J. E. (1992). In A. Imeson (Ed.), *Thickening and gelling agents for food* (pp. 153–169). London: Chapman & Hall.

Franz, G., & Feuerstein, U. (1997). Chemical stability of some model polysaccharides. *Macromolecular Symposia, 120*, 169–181.

Gaisford, S. E., Harding, S. E., Mitchell, J. R., & Bradley, T. D. (1986). A comparison between the hot and cold water-soluble fractions of two locust bean gum samples. *Carbohydrate Polymers, 6*, 423–442.

Goycoolea, F. M., Morris, E. R., & Gidley, M. J. (1995). Viscosity of glactomannans at alkaline and neutral pH—evidence of hyperentanglement in solution. *Carbohydrate Polymers, 27*, 69–71.

Hui, P. A., & Neukom, H. (1964). Properties of galactomannans. *Tappi, 47*, 39–42.

Khomutov, L. I., Ptichkina, N. M., Sheenson, V. A., Lashek, N. A., & Panina, N. I. (1994). Thermal degradation of polysaccharides. *Russian Journal of Applied Chemistry, 67*, 574–577.

Kök, M. S., Hill, S. E., & Mitchell, J. R. (1999). A comparison of the rheological behaviour of crude and refined locust bean gum preparations during thermal processing. *Carbohydrate Polymers, 38*, 261–265.

Lapasin, R., & Pricl, S. (1995). *Rheology of industrial polysaccharides—theory and applications* (pp. 312–325). London: Chapman & Hall.

Lopes da Silva, J. A., Goncalves, M. P., & Rao, M. A. (1994). Influence of temperature on the dynamic and steady-shear rheology of pectin dispersions. *Carbohydrate Polymers, 23*, 77–87.

Maier, H., Anderson, M., Karl, C., Magnuson, K., & Whistler, R. L. (1993). Guar, locust bean, tara and fenugreek gums. In R. L. Whistler & J. N. BeMiller (Eds.), *Industrial gums* (pp. 205–215). San Diego: Academic Press.

Mitchell, J. R., Hill, S. E., Jumel, K., Harding, S. E., & Aidoo, M. (1992). The use of antioxidants to control viscosity and gel strength loss on heating of galactomannan systems. In G. O. Phillips & P. A. William & D. J. Wedlock (Eds.) (pp. 303–309). *Gums and stabilisers for the food industry*, 6. Oxford: IRL Press.

Pilnik, W., & McDonald, R. A. (1968). The stability of some hydrocolloids. *Gordian, 12*, 531–535.

Rao, M. A., Walter, R. H., & Cooley, H. J. (1981). Effect of heat treatment

on the flow properties of aqueous guar gum and sodium carboxymethylcellulose (CMC) solutions. *Journal of Food Science*, *46* pp. 896–899, 902.

Rhim, J. W., Nunes, R. V., Jones, V. A., & Swartzel, K. R. (1989). Determination of kinetic-parameters using linearly increasing temperature. *Journal of Food Science*, *54*, 446–450.

Richardson, P. H., & Norton, I. T. (1998). Gelation behaviour of concentrated locust bean gum solutions. *Macromolecules*, *31*, 1575–1583.

Richardson, P. H., Willmer, J., & Foster, T. J. (1998). Dilute solution properties of guar and locust bean gum in sucrose solutions. *Food Hydrocolloids*, *12*, 339–348.

Robinson, G., Ross-Murphy, S. B., & Morris, E. R. (1982). Viscosity molecular-weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan. *Carbohydrate Research*, *107*, 17–32.

Rodriguez, P. (1985). US Patent no 4,514,318.

Stokke, B. T., Christensen, B. E., & Smidsrod, O. (1992). Degradation of multistranded polymers—effects of interstrand stabilization in xanthan and scleroglucan studied by a Monte-Carlo method. *Macromolecules*, *25*, 2209–2214.

Zentz, F., Verchere, J. F., & Muller, G. (1992). Thermal denaturation and degradation of schizophyllan. *Carbohydrate Polymers*, *17*, 289–297.