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A comparison of the rheological behaviour of crude and refined locust bean gum preparations during thermal processing

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Abstract

The behaviour, during thermal processing, of a higher quality analytical-grade (AG) locust bean gum (LBG) was compared with a lower quality technical grade (TG) LBG. The TG material contained a substantial amount of material (40%) of dry weight, which remained insoluble after heating to 70°C. Sugar analysis suggests that this insoluble material contained high levels of arabinose. The TG material showed low viscosity throughout the heating cycle and lower levels of degradation at high temperatures, as evidenced from viscosity measurements. The reason for this could have been that, in these samples, the viscosity is dominated by the non-soluble particulates in the system; however, on removal of particulates further rheological studies, made at comparable galactomannan concentrations, also showed differences between the degradation of the AG and TG LBG. Despite the difference in behaviour through the heating cycle, at equal galactomannan levels, the AG and TG materials had similar viscosities at the end of this cycle. This may explain why, after heat processing, the TG material interacts synergistically with carrageenan in a similar way to AG locust bean gum.

Keywords: Thermal processing; Locust bean gum; Sugar analysis; Arabinose; Viscosity measurement; Galactomannan; Carrageenan

1. Introduction

Polysaccharides derived from seed gums are widely used in the food industry as thickeners in dressings, sauces and frozen products because of their cold water dispersibility, compatibility with high acidic emulsions and low cost on a viscosity basis. In addition to increasing viscosity they inhibit ice crystal formation, modify texture and control product consistency with respect to changes in temperature (Fox, 1992). The seeds of many Leguminosae contain galactomannans in the cells of the endosperm and these have been studied extensively (Dea and Morrisson, 1975).

The gum of the locust bean (LBG), *Ceratonia siliqua*, is derived from the endosperm of the seeds after removal of the testa (seed coat), and the quality of the gum is dependent on the degree of separation achieved. The structure has a linear backbone of β-1,4-D-mannose substituted to varying degrees at 1–6 with an α-D-galactose side groups (Fox, 1992). The LBG samples used in this study were a more refined analytical grade (AG) and a crude technical grade (TG).

During many food sterilisation processes, gums are subjected to high temperatures. These processes cause the polymer to solubilise, but as other research has shown, can also cause degradation resulting in a lowering of viscosity (Owen et al., 1992). Different grades of LBG are already extensively employed in heat-sterilised foods, particularly when a mixed gel with carrageenan is required. The two polysaccharides are well known to show a synergistic interaction (Morris, 1995).

The objective of the work described in this paper is to compare the composition and rheological properties during thermal processing of TG LBG with an AG LBG, which is equivalent to a refined food grade (FG) preparation.

To obtain information on the changes occurring during thermal processing, viscosities have been measured through the heat processing cycle using a Bohlin CS rheometer equipped with a high-pressure cell. This allowed the viscosity to be assessed as the 'suspension' is heated from 20 to 121°C, held at this temperature and then cooled back to ambient. The resultant profile is a reflection of several phenomena occurring simultaneously throughout the experiment. The most important is: an increase in the concentration of polysaccharide in solution with increasing temperature and thermal degradation of the galactomannan. To obtain information on the latter, the change in viscosity with time at a constant temperature was monitored. A similar approach using a slit viscometer has been used by

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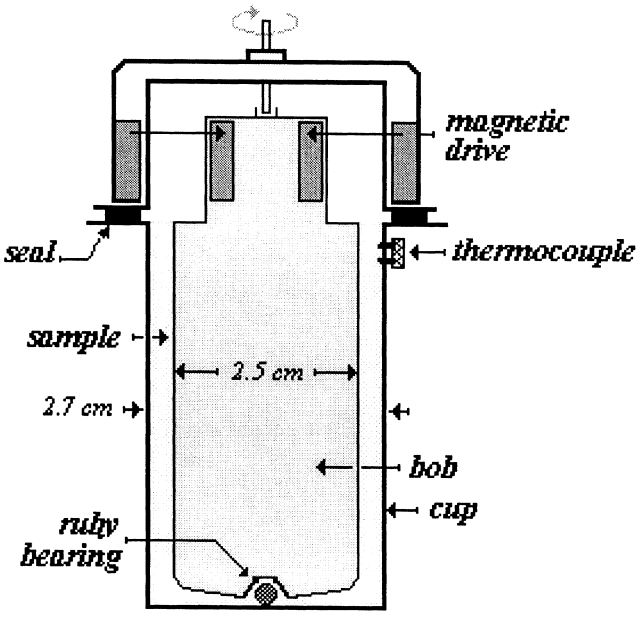

Fig. 1. Schematic of Bohlin High-Pressure-Cell (HPC).

Bradley and Mitchell (1988) to study thermal degradation. The results are related to the composition of the two materials.

2. Experimental

2.1. Materials

The galactomannans used in these studies were a refined locust bean gum (LBG) designated as sample AG (Sigma, UK) and low-grade (sample TG) LBG from a commercial source.

2.2. Composition analysis

2.2.1. Moisture, protein and fat

Moisture content of 1 g samples was obtained by drying in an oven at 105°C to constant weight. Protein analysis of 0.25 g samples was obtained using the Kjeldahl method with a conversion factor of 6.25. Fat analysis of 10 g samples was obtained by Soxhlet extraction with petroleum ether as a solvent.

2.2.2. Removal of particulates from TG material

Samples (1%) were prepared in distilled water at ambient temperature and mixed with Silverson mixer at high speed for 2 min. They were then placed in a 70°C water bath for 1 h while being stirred at low speed. After cooling and centrifugation at 18 500 × *g* for 15 min, the supernatant was decanted. Samples were oven dried overnight at 105°C. The dry weights of the supernatant and particulates were determined.

2.2.3. Sugar analysis

Neutral sugars were measured using gas-liquid chromatography (GLC) as alditol acetates following hydrolysis by sulfuric acid as described by Englyst et al. (1982). Allose was added to the sample as an internal standard prior to hydrolysis. A 0.5 μl sample was injected into a Supelco SP2330 column (30 m × 0.75 mm). The initial temperature of 200°C in the system was increased to 240°C at a rate 4°C/min. Helium was the carrier gas at a flow rate of 5 ml/min. Recoveries were expressed as the percent of the dry weight of material hydrolysed. Peak assignments were confirmed by comparison with the appropriate monosaccharide.

2.3. Measurement of viscosity

Gum suspensions 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 for 2 min. The samples were left overnight at this temperature to hydrate. They were briefly stirred with a magnetic stirrer to ensure homogeneity prior to measurement.

All measurements of viscosity were made using a Bohlin CS 10 rheometer. As the intention was to predict viscosity changes during a food sterilisation cycle, some viscosities were measured at over 100°C. This was possible due to the use of a high-pressure cell (HPC) attachment to the Bohlin CS rheometer (Fig. 1). In this cell the sample (7 ml) was completely enclosed, the bob being driven via a magnetic coupling while being supported on a ruby bearing.

2.3.1. Viscosity measured during a temperature cycle

The viscosity of 1% (w/v) for AG and 2% (w/v) for LG samples was measured at a shear stress of 5 Pa while 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.

2.3.2. Viscosity measurements at 121°C

The rotational viscosity of 1% (w/v) for AG and 2% (w/v) for LG samples was measured at a shear stress of 3 Pa with the temperature maintained constant at 121°C for 1 h using the HPC. A temperature of 121°C was reached after less than 10 min heating from ambient.

2.3.3. Effect of heat treatment on viscosity of AG and LG supernatant

Samples of AG at 2% (w/v) and LG at 4% (w/v) were prepared in the same buffer and conditions. Suspensions were solubilised in a 70°C water bath for 1 h. After cooling they were centrifuged at 18 500 × *g* for 15 min. Supernatants from the two samples, which contained approximately the same concentration of galactomannan, were decanted into 20 ml media bottles and further heat treated for 1 h at a range of temperatures from 70 to 121°C. Temperature treatments up to 100°C were achieved using a water bath,

Table 1
Gross composition of LBG samples (AG and TG).

Sample	Carbohydrate[a] (%)	Protein (%)	Fat (%)	Ash (%)	Moisture (%)	Particulate[b] (%)	Supernatant[b] (%)
AG	80.9	6.5	0.6	1.0	11.0	0	85
TG	72.0	13.5	1.3	2.7	10.5	34	51

[a] Carbohydrate determined by difference.
[b] 70°C/h solubilised, 18 500 × *g*/15 min centrifuged, supernatant was decanted and both phases dried in a 105°C oven. Results taken from duplicates and the standard error of the mean are < 5% for all. Particulate and supernatant expressed as percent of wet weight of original material.

and for temperatures above this an autoclave was used. The rotational viscosities of the samples were measured at 25°C after heating and subsequent cooling using the rheometer equipped with cone and plate (CP4/40) geometry. A shear stress of 1 Pa was used.

3. Results and discussion

3.1. Composition

Table 1 compares the composition of a typical TG preparation with an AG material. The values for the AG LBG compare favourably with expected values (Maier et al., 1993), with all the material soluble at 70°C. It can be seen that the crude preparation contains a substantial amount of a component, which remains insoluble at 70°C (termed particulates). It is tempting to associate this with the high level of arabinose and protein found in this sample. A GLC analysis of the sugar content in the non-particulate fraction (supernatant) of TG (Table 2) showed that this contained less than 2% arabinose expressed as a proportion of the total sugar, the remaining being mannose plus galactose. The GLC recovery from the particulate fraction is low. However, taken together these results suggest that in this sample the particulate phase probably contains a glycoprotein with a high arabinose content and the supernatant is primarily galactomannan with a mannose:galactose (M/G) ratio of 3.7. The range of M:G ratios found are in agreement with the literature (MacCleary et al., 1985; Gaisford et al., 1986).

3.2. Viscosity

When compared on an equal concentration basis a large difference between the initial viscosity of the preparations was observed. In general the TG materials had a much lower viscosity after solubilising at 70°C than the AG sample. This can be attributed to the lower amount of soluble material (supernatant) in the TG material as shown in Table 1.

To allow a comparison of the two materials at a similar soluble galactomannan level the behaviour, through a heat processing cycle, of 2% of TG was compared with 1% of AG (Fig. 2). Although the initial viscosity of TG is substantially lower than AG, both samples show some increase in viscosity after 45°C which peaks at a temperature of approximately 65°C. The TG also gave two other small peaks at 100 and 115°C, which suggests that there are other fractions requiring high temperatures to solubilise. There is a subsequent decline in viscosity to the maximum temperature of 121°C and then during cooling the viscosity recovers. Despite the large initial differences on viscosity prior to processing at the end of the process the viscosities are similar for the two samples. There appears to be a relationship between M:G ratio and viscosity which is also reported in other research (Fernandez et al., 1991). There is an absence of published work for viscosities of LBG treated at high temperatures. However, Fernandez et al. (1991) have reported that there was a strong temperature dependence on the kinetics of gelation for LBG samples from different sources at low temperatures.

Fig. 3 compares the change in viscosity with time for the two samples (at the same concentrations as above) when maintained constant at a temperature of 121°C following rapid heating (less than 10 min) to this temperature. It can be seen that there are very large differences in the rate of viscosity decrease between the two samples. The similar viscosities at the end of the processing cycle for the two samples, despite the large differences in initial viscosity, could be interpreted in terms of differences in the stability to degradation (Bradley and Mitchell, 1988). Another possibility is the solubilisation of polysaccharide from the particulate material.

To determine if the behaviour of the galactomannan component in the supernatant differs between the AG and

Table 2
Sugar distribution determined

Sample	Man (%)	Gal (%)	Ara (%)	Xyl (%)	Glu (%)	Recovery (%)	M:G ratio
AG	77.8	20.3	0.0	1.0	0.9	100	3.8
TG total	45.5	14.0	33.9	1.7	5.1	75	3.3
TG supernatant*	76.5	20.7	1.8	0	2.1	81	3.7
TG particulate*	40.5	11.9	39.8	7.1	1.2	35	3.4

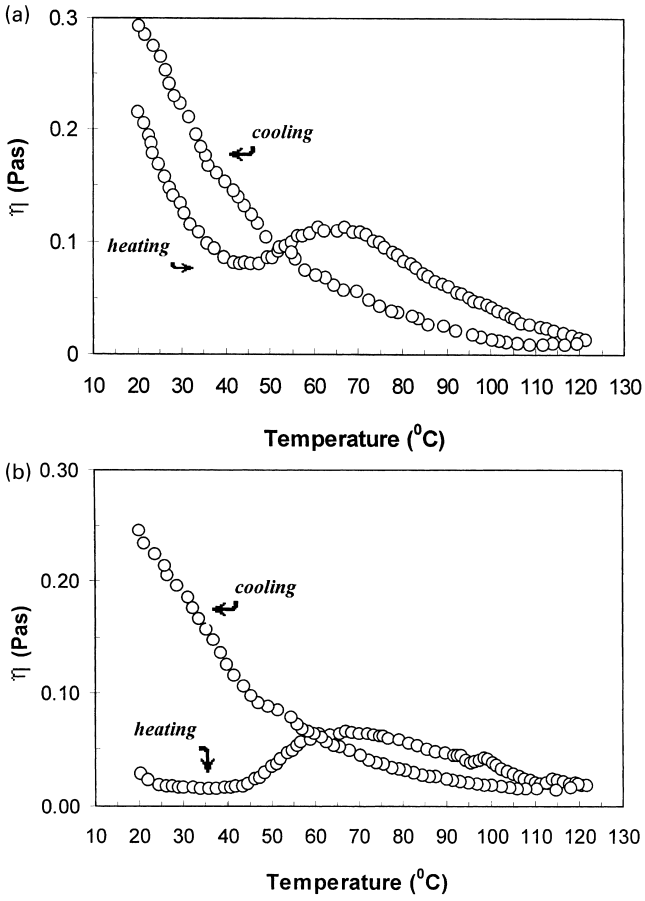

Fig. 2. Rotational viscosity of 1% (w/v) AG sample (a) and 2% (w/v) LG sample (b) measured at a shear stress of 5 Pa with temperature increasing at a rate of 1°C/min from 20°C to 121°C and immediately cooled back to 20°C at a rate of 2°C/min.

the TG sample, solutions were prepared at equal soluble galactomannan contents and heated to a range of temperatures from 70 to 121°C for 1 h, and their viscosities were subsequently measured after cooling to 25°C. The results in Fig. 4 show large differences between the two materials.

The strong dependence on temperature for the AG sample compared with the TG confirms that there are differences in the degree of sample degradation as suggested by the data in Fig. 3. We believe that this is due to the presence of materials in the crude preparation that protect the galactomannan

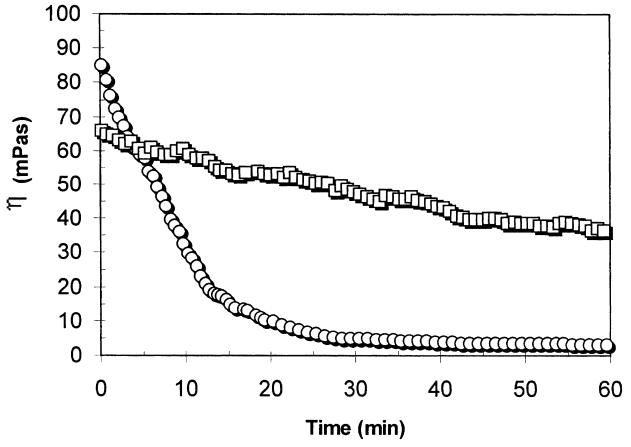

Fig. 3. Rotational viscosity of 1% AG (○) and 2% LG (□) samples measured at a shear stress of 3 Pa while the temperature was set constant at 121°C over a 1 h period.

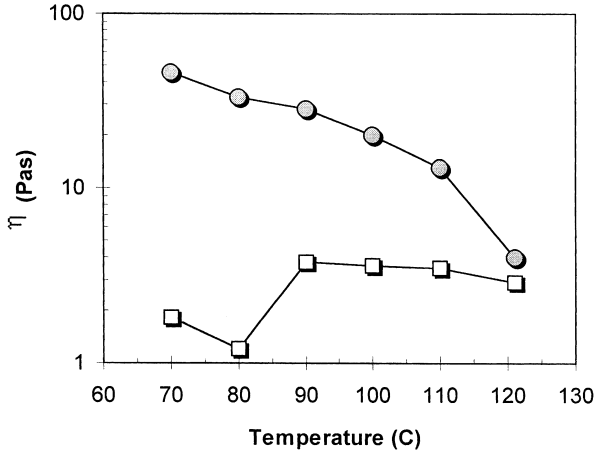

Fig. 4. Effect of heat treatment on viscosity of AG and LG supernatant approximately 2% (w/v) (for details of solution preparation see text). Treatment at 70, 80, 90, 100, 110 and 121°C for 1 hour.

from degradation. The protein component may well play an important role since amino acids are known to be effective in scavenging free radicals which are involved in degradation at neutral pH (Pilnik and McDonald, 1968; Bradley and Mitchell, 1988). We may conclude that although these crude materials have poor solubility and initially make a low contribution to viscosity, at the end of the heating cycle sufficient material has been solubilised, with the appropriate M:G ratio, to explain their functionality in mixed carrageenan LBG systems (Arnaud et al., 1989; Fernandez et al., 1991, 1994).

Our results suggest that the soluble material from the TG sample does not behave in the same way as the AG LBG in terms of viscosity (Fig. 4). The low viscosity, even of the soluble fraction, could reflect a lower galactomannan molecular weight (Turqois et al., 1992) but it may also be a consequence of some soluble non-galactomannan material. The analytical data shows the presence of some such material.

The overall viscosity response shown in Fig. 2 is a combination of solubilisation, degradation and the temperature dependence of viscosity for a system of constant composition and concentration (Kök et al., 1996). We are currently attempting to analyse this viscosity response quantitatively by first obtaining a degradation model and using it to predict the constant concentration viscosity profile. It would appear that this is applicable to the refined material but cannot explain the more complicated behaviour of the crude material. This will be the subject of a further paper.

4. Conclusions

The functionality of the samples would seem to be greatly influenced by the non-galactomannan fraction, but our preliminary studies also indicate that the thermal stability of the galactomannan fraction still differs between the refined and crude samples.

Further work is now required to establish the relationship between the composition of the low-grade (TG) material and its functionality.

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