Understanding factors affecting depolymerisation of galactomannans at elevated temperatures; using rheological measurements

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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 Bohlin CS10 rheometer. Our results confirm that the antioxidants provide both gums with stability at higher temperatures. This suggests that it is the action of free radicals at higher temperatures that causes degradation.

Keywords

Galactomannan; Guar Gum; Locust bean gum; Depolymerisation; pH; Antioxidant.

INTRODUCTION

Structural characteristics

Galactomannans are water-soluble polysaccharides found in the seed endosperm of a variety of legumes and consist of a 1-4 linked β-Dmannopyranosyl backbone partially substituted with 1-6 α-D-galactopyranosyl side groups[1] (see Fig. 1).

Seed gums are widely used in the food industry as a thickener because of their cold water dispersibility, compatibility with acidic emulsions and low cost on a viscosity basis. They are able to bind and immobilise a large amount of water thus increasing viscosity, modifying texture and stabilising product consistency to changes in temperature[2].
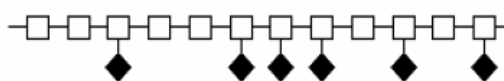

Figure1. Schematic presentation of galactomannans by Theander[3]. (□) D-mannose, (◆) D-galactose.

Locust Bean Gum

The locust bean (*Ceratonia siliqua*) is indigenous to the Middle East. The gum is obtained by first removing the testa (husk) by roasting and then grinding the endosperm[2].

Guar Gum

Guar gum is obtained from the seeds of *Cyamopsis tetragonobulus*, which is indigenous in NW India and Pakistan. The plant is an annual legume and seeds can be produced by conventional farming practices making it more economical[4].

The viscosity of galactomannans in aqueous solutions depends on time, concentration, pH, ionic strength and degree of mechanical dispersion in preparation. The measurement of viscosity for solutions of different galactomannans also depends on the shear rate or shear stress and the temperature at which the assessment is made.

The degree of solubility of the polysaccharide and the extent of degradation due to endogenous enzymes, bacterial

contamination, acid hydrolysis, β-elimination or oxidative reductive depolymerisation will also affect viscosity[5].

The chemical degradation is important to polymer functionality and the whole system needs to be considered when studying the thickening and gelation behaviour in heat processed foods. In this research the effects of changing pH and the presence of antioxidants were investigated at elevated temperatures (121 ^{0}C) which are the real reflection of the retorting process such as canned foods and often ignored.

MATERIALS & METHODS

Sample Preparation

Guar gum G-4129 Lot 80HO34 Sigma Inc., UK, Locust bean gum G-0753 Lot 82HO724 Sigma Inc., UK.

Analytical grade (AG) 1 % (w/v) gum samples were prepared in 100 Mm Sodium Phosphate Buffer, pH 7.0 (except for pH experiment), at ambient temperature using a high shear Silverson mixer for2 min.

Sodium phosphate buffer was prepared from the stock solutions of Na_2HPO_4 and NaH_2PO_4 at 0.5 M concentration. The stock solutions were diluted to 100 Mm concentration and pH was adjusted to 7.0 ± 0.1 by adjusting the mixture appropriately. pH was measured using a WPA Linton CD620 (Cambridge, UK) digital pH meter at 25 ^{0}C.

Standard sample solubilisation

Solubilisation conditions were defined as an hour at 70 ^{0}C for LBG samples and 30 min at 40 ^{0}C for GG samples. This was achieved using a water bath with samples being continuously stirred by a bench mixer (Griffin and George Ltd., UK) at low speed. These conditions were chosen, as they were thought not to cause significant degradation.

Heat treatments

Heat treatments were carried out using the same equipment as that used for solubilisation, the exception being for those retorted. A small autoclave (Benchtop-50, Harvard/LTE Ltd., England) was used to achieve high temperature treatment up to 121 ^{0}C. Samples were contained in media bottles (20 ml or 250 ml) or cans (250 ml or 500 ml). Time and temperature of heat treatments varied according to the experiment being conducted.

Standard Measurement of Viscosity

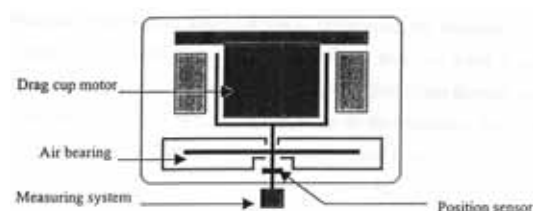All measurements of viscosity were made using a Bohlin CS 10 Rheometer (see Fig. 2).

Figure 2. Schematic diagram of Bohlin CS Rheometer

A coaxial cylinder (cup and bob) C25 geometry and oscillation technique has been used (see Fig. 3). C25 is a coaxial cup and bob geometry having a 25 mm diameter bob. The diameter of the cup is in proportion to the bob size as defined by the DIN Standard
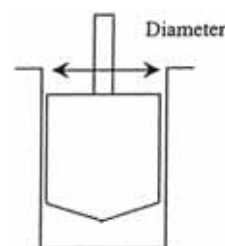

Figure 3. C25 is a coaxial cup and bob geometry.

These types of geometries require relatively large sample volumes, up to 13 ml

for C25, and are more difficult to clean.

They usually have a large mass and large inertia and so produce inertial problems when performing high frequency measurements. Shear rate and shear stress also vary slightly over the gap.

Their advantage comes from being able to work with low viscosity materials and mobile suspensions. Their large surface area gives them a greater sensitivity and so they will produce good data at low shear rates and viscosities. In addition, they are tolerable to material containing particulates, not critical on eccentricity and misalignment. Their temperature control is easy and gives good data repeatability. Therefore this geometry is most suitable for temperature sweep experiments.

For oscillatory measurements at high frequencies on low viscosity materials, the C25 cup and bob geometry with a small gap will produce the optimum test conditions.

Before all experiments the linear-viscoelastic-region (LVER) was established using Stress Sweep techniques at different frequencies. LVER was used to define a target strain for the oscillation experiments.

Effect of pH on Degradation

GG and LBG (300 ml) samples were prepared at 1 % (w/v) in 100 mM sodium phosphate buffer at pH 5.0, 6.0, 7.0, 8.0 and 9.0 and left over night.

The pH was established using the buffers of 100 mM Na_2HPO_4 (pH: 9.15) and NaH_2PO_4 (pH: 4.7). Duplicate samples were heated for 30 min at 100 ^{0}C and left over night. Oscillation tests were conducted at 25 ^{0}C using C25 geometry, the target strain set at 0.5 for both gums and frequency range studied was 0.1 to 10 Hz.

Effect of Antioxidants on Degradation

GG and LBG samples (1 % w/v) were prepared in 100 mM sodium phosphate buffer at pH 7. The antioxidant sodium sulfite was added at two concentrations of 1000 ppm and 30 ppm to GG; 2000 ppm and 30 ppm to LBG.

The antioxidant propyl gallate was added at concentration of 600 ppm and 20 ppm to GG; 500 ppm and 20 ppm to LBG and left overnight.

Controls without antioxidant were prepared in a similar manner. Samples were heated in a rotating autoclave or a water bath for 30 min at 80 ^{0}C and 100 ^{0}C and a sample was also autoclaved at 121 ^{0}C for 5 min. Additional samples with and without antioxidant were held at ambient temperature.

Viscosity was measured by the Oscillation (frequency of 1 to 10 Hz) and Constant Rate methods (shear strain of 1 to 50 s^{-1}) using C25 geometry measuring device.

RESULTS AND DISCUSSION

The chemical degradation is important to polymer functionality and the whole system needs to be considered when studying the thickening and gelation behaviour in heat processed foods.

In this research the effects of changing pH and the presence of antioxidants were investigated.

Polymers are susceptible to degradation by oxidative reductive depolymerisation (ORD) reactions, which causes viscosity to be lost.

The antioxidants propyl gallate and sodium sulfite are both permitted food additives and there is a strong synergistic interaction between them which seems to be particularly effective with galactomannans[6].

Effect of pH

Galactomannans are not charged (neutral) and should not be expected to change viscosity in a range of buffers except at very high pHs where it has been reported that hyperentanglements are suppressed[7]

This behaviour was confirmed when suspensions were prepared at a range of pH

values, from 5.0 to 9.0 at ambient temperature. However, heat treatment at 100 ^{0}C for 30 min with the same range of pH values did show differences in degradation (see Fig.4). These results are in agreement with similar work conducted by Pilnik et al.[8] on guar and locust bean gum.
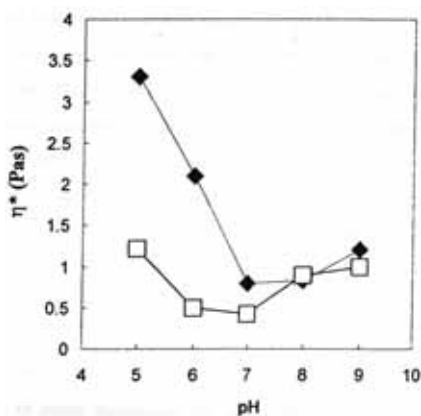

Figure 4. Effect of pH on complex viscosity for GG (◆) and LBG (□) at pH ranging from 5 to 9. Solutions prepared at 1 % in 100 mM phosphate buffer at appropriate pH and heated at 100 ^{0}C for 30 min. Measurements made at 25 ^{0}C and frequency of 0.1 Hz using C25 geometry.

Figure 4 shows minimum viscosity and therefore probable maximum degradation at pH 7.0. This may be indicative of free radical attack being optimum at this pH or perhaps induction of a naturally occurring enzyme. The latter seems less probable due to the high temperature involved and because storage at lower temperature does not seem to show degradation in the buffer.

Bradley et al.[9] have shown that the effect on non-Newtonian flow behaviour, of 0.5 % guar gum solution above 90 ^{0}C, is more shear thinning in acid than in neutral conditions. Although there is not much change in shear thinning between pH 5.0 and 6.0, at pH 7.0 the calculated activation energy is higher showing thermal stability to

be greater. This can be explained as greater depolymerization at the lower pHs.

In work by Mitchell et al.[10] an interaction between temperature and pH is found in the rate of depolymerization of galactomannans. Heat treatment of 120 ^{0}C for 10 min at neutral pH gave only 10 % loss of viscosity, however at lower pH (below 4.5) loss of viscosity is almost 90 %.

The pH effect on galactomannans is itself affected by the addition of sodium sulphite and propyl gallate which suggest that oxidative reductive depolymerization is the dominant mechanism.

The Effect of Antioxidants

Polymers are susceptible to degradation by oxidative reductive depolymerisation (ORD) reactions. This causes viscosity to be lost. The rate of loss will be dependent on the temperature and pH. Most research to date on ORD reactions has been in the area of polymers used in oil field applications[11].

The use of antioxidants in the food industry is common for the prevention of lipid oxidation, but little work has been reported on the reduction or elimination of thermal degradation of polysaccharides.

Experiments were conducted with the antioxidants propyl gallate and sodium sulfite, which are both permitted food additives and have been used in previous experimental work with galactomannans.

Typically the sulfite is thought to act as an oxygen scavenger, removing dissolved oxygen and so reducing the production of free radicals. Propyl gallate however acts as a free radical terminator and there is strong synergistic interaction between the two which seems particularly evident with galactomannans[6].

The samples that had the low amount of antioxidant (20 ppm propyl gallate and 30 ppm and sodium sulfite) added showed little difference in viscosity from those without antioxidants. At ambient temperature viscosity change is not observed on addition of antioxidants even at high concentrations,

this is as expected. When the addition of antioxidants was increased to high levels there is an improvement in viscosity on addition of antioxidants to both gums.

This result is more significant for guar which shows a greater difference in viscosity and therefore increased susceptibility to degradation. At higher temperatures of 100 ^{0}C and 121 ^{0}C the degree of protection for both gums are greater (see Fig. 5).
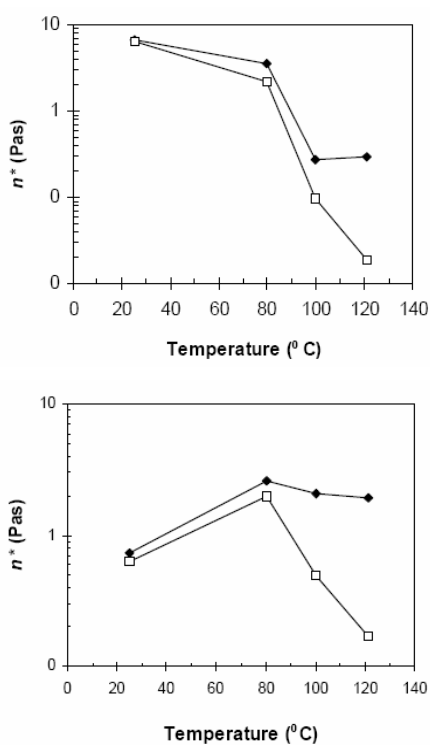

Figure 5. Effect of antioxidants on complex viscosity of 1 % GG (top) and 1 % LBG (bottom) after heat treatment. Samples heated for 30 min in a water bath at temperatures ranging from 25 ^{0}C to 121 ^{0}C with (◆) and without (□) antioxidants. Antioxidants used were sodium sulfite at 1000 ppm and propyl gallate 500 ppm. Measurements were made at 25 ^{0}C and frequency of 0.1 Hz using C25 geometry.

The antioxidants provide both gums with stability at higher temperatures. This suggests that it is the action of free radicals at higher temperatures that causes degradation. However other forces come into play as even at saturated levels of antioxidant addition, the degradation of gums can be prevented only to an extent.

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