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The stability of guar gum in an aqueous system under acidic conditions

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Abstract

The stability of guar galactomannan in acidic conditions was investigated using dilute polymer solutions at temperatures of 25, 37 and 50°C. The depolymerisation of guar galactomannan was monitored by determining changes in solution viscosity, from which the viscosity-average molecular weight was estimated. The lowest pH values at which guar galactomannan remained stable were found to be 2.0, 3.0 and 3.5, respectively, at these temperatures. The acid degradation appears to be a random scission process obeying first order kinetics. The activation energy at pH 1.5, 2.0 and 3.0 were estimated to be 117.4, 118.6 and 120.5 kJ mol^{-1}, respectively. This indicates that guar gum is reasonably stable under an acidic environment. The viscosity of fully hydrated guar gum solutions at acidic pH was found to be slightly lower than it was at neutral pH even when no degradation occurred. Current results suggest that guar gum may be used in mild acidic processing conditions, particularly when excessive heat treatment is not used.

Keywords: Guar gum; Stability; Acidic degradation

1. Introduction

Guar gum, a galactomannan-rich flour extracted from the seeds of the leguminous plant *Cyamopsis tetragonoloba* (L.) Taub, is widely used as a thickening and stabilizing agents, in a range of industrial applications (Goldstein, Alter & Seaman, 1973). The study of its solution stability in acidic environment is of considerable importance to those studying its functional properties in food processing and the oil industry, and, more recently, to those interested in the physiological effects of dietary fibre (e.g. its behaviour in the human stomach) (Ellis, Rayment & Wang, 1996). Guar galactomannan and many similar polysaccharides are readily hydrolysed to monosaccharides in strong acidic conditions, such as when mixed with 12 M sulphuric acid. However, under more gentle conditions, they may either remain undegraded or be partially hydrolysed to produce a variable mixture of monosaccharides, oligosaccharides and polysaccharides with a broad range of degree of polymerisation. The kinetics of acidic hydrolysis of several polysaccharides was investigated previously (Carpron, Yvon & Muller, 1996; Ekström, 1985; Ekström, Kuivinen & Johansson, 1983; Hjerde, Kristiansen, Stokke, Smidsrod & Christensen, 1994), although galactomannans, such as guar gum, were not included in these studies. Apart from the usual physicochemical conditions, such as temperature, pH and concentration, the degradation rate of polysaccharides is also influenced by the conformation of the molecules, namely, the strandedness (Hjerde et al., 1994). It has been generally accepted that galactomannans exist in solution as random coiled single-stranded chains. For such a conformation, a non-specific degradation (random scission) can be expected, and may be described by the following equation (Tanford, 1961a):

$$\frac{1}{\bar{x}_{w,t}} = \frac{1}{\bar{x}_{w,0}} + \frac{kt}{2} \tag{1}$$

in which $\bar{x}_{w,0}$ and $\bar{x}_{w,t}$ are the weight-average degree of polymerisation at the beginning of the reaction and at reaction time t, respectively, and k is the reaction constant. This equation implies that the reciprocal of weight-average degree of polymerisation is a linear function of the reaction time.

Degradation is often followed experimentally by determining the molecular weight as a function of time, using light scattering or viscosity (usually by measuring intrinsic viscosity) as the measure of molecular weight. The former gives the weight-average molecular weight (M_w) and the latter gives viscosity-average molecular weight M_v. The magnitude of M_v is between M_w and M_n (the number-average molecular weight) and is usually closer to M_w. In the case of condensation polymers, in which there is no change

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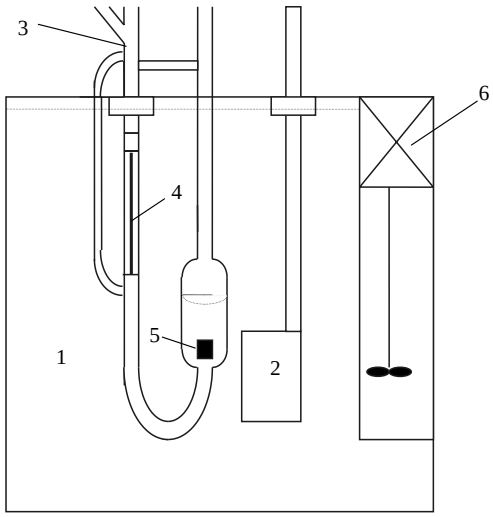

Fig. 1. Experimental rig for studying the degradation of guar gum in dilute solution: (1) water bath; (2) magnetic stirrer; (3) glass viscometer; (4) capillary; (5) stirrer; and (6) temperature control system.

in reactivity of functional groups with chain length, M_v/M_w and M_v/M_n are constants independent of molecular weight. In this case, the intrinsic viscosity $[\eta]$ can also be used to measure M_w and M_n provided calibration is carried out. However, in the present study, the approximation $M_v \approx M_w$ was made without calibration since the change in molecular weight is more important than its precise value. Since $1/\bar{x}_{w,t} \propto 1/M_w$, then $1/\bar{x}_{w,t}$ is approximately $\propto 1/M_v$, which indicates that in a random scission process the reciprocal of viscosity-average molecular weight should also follow a linear dependence on the degradation time.

The work reported here is an investigation of the stability of guar gum solution at different pH levels at 25, 37 and 50°C. A special device was designed to allow the polymer degradation process to be monitored by determining changes in viscosity. The present study was not designed to investigate the kinetics of guar gum hydrolysis per se, but the main interest was merely to find out to what extent the viscosity of guar gum solutions will change under various conditions of pH and temperature. This approach allowed the time course of hydrolysis to be followed by measuring the changes in relative viscosity without interrupting the process and also without removing aliquots of the sample from the reaction vessel. On the basis of the information obtained from the above experiments, the hydration kinetics of guar gum solution was then studied under pH conditions where the polymer is stable or readily degraded—the results of this work will be published elsewhere.

2. Experimental

2.1. Samples and preparations

All experiments were carried out using a commercial food grade guar gum flour M150 (Meyprogat range, Meyhall Chemical Company Ltd, Switzerland). The sample, which was analysed chemically by standard methods described previously (Wang, Ellis, Ross-Murphy & Reid, 1996), was found to contain 93% non-starch polysaccharides including 88% galactomannan, 3.7% protein, 1.2% lipid and 0.6% ash on a dry weight basis. The molecular weight of the sample was estimated as 2.8×10^6 by intrinsic viscosity measurement (Wang, 1997). The mean particle size, as determined by Malvern Mastersizer laser diffraction particle sizer, was 61 μm (Wang, 1997).

2.2. Hydrolysis device

The viscosity was determined by using a dilution capillary viscometer (Cannon Ubbelohde Dilution B glass viscometer, Glass Artefact Viscometers, Braintree, Essex, CM7 5JQ, UK). This was immersed in a viscometer bath, containing distilled water, to maintain the temperature at 25 ± 0.1°C. A special long-armed L-shaped magnetic stirring device (Fig. 1) was also immersed in the water bath, to allow vigorous mixing of sample solutions in the viscometer during the experiments. The stirrer was chosen carefully in order to minimise the disturbance during the measurement of viscosity. During the measurement the stirrer was suspended in the solution, inside the viscometer bulb, without touching the wall of the viscometer. All measurements were carried out at a concentration of 0.07% w/w galactomannan.

2.3. Estimation of molecular weight

Using a capillary viscometer (see Fig. 1) the relative viscosity (η_r) was measured, from which the specific viscosity was calculated ($\eta_{sp} = \eta_r - 1$). Intrinsic viscosity $[\eta]$ is normally determined by measuring reduced viscosity $\eta_{red}(= \eta_{sp}/C)$ at various concentrations in dilute solution and extrapolating to concentration $C = 0$. The concentration dependence is often expressed in terms of the following relationship (Tanford, 1961b):

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C \tag{2}$$

where K is known as the Huggins constant. For flexible polymer molecules in good solvents K is often near to 0.35, although somewhat higher values occur in poor solvents. In the present work, therefore, a value of 0.35 was adopted in Eq. (2) to calculate intrinsic viscosity by measuring specific viscosity in dilute solutions:

$$[\eta] = \frac{\sqrt{1 + 1.4\eta_{sp}} - 1}{0.7C}. \tag{3}$$

From the intrinsic viscosity, the viscosity-average molecular weight (M_v) was estimated by using the Mark Houwink equation, $[\eta] = kM_v^{\alpha}$, with $\alpha = 0.732$ and $k = 3.8 \times 10^{-4}$ (Robinson, Ross-Murphy & Morris, 1982), values close to

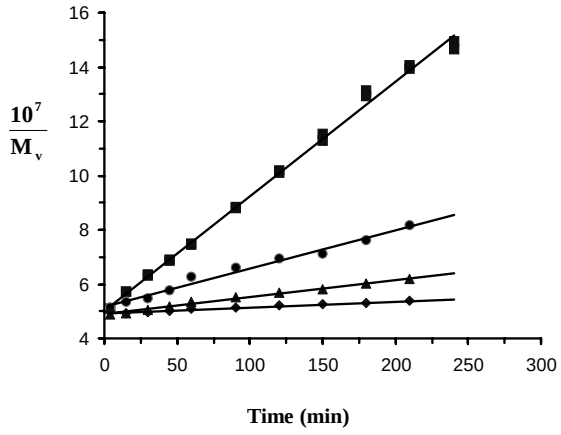

Fig. 2. Degradation process for guar gum solutions (0.07% w/w) at 50°C. $1/M_v$, reciprocal of molecular weight and t, reaction time. (■) pH 1.5; (●) 2.0; (▲) 2.2; and (◆) 2.5.

those reported in the more recent work of Beer, Wood and Weisz (1999).

3. Results

3.1. Kinetics of acidic degradation

As discussed above, assuming that the degradation reaction of guar gum under acidic conditions is a random scission process, the reciprocal of viscosity-average molecular weight ($1/M_v$) should be linearly related to the reaction time. In other words, the reaction obeys first order kinetics. The reciprocal of viscosity-average molecular weight was plotted against incubation time in Fig. 2, taking the data at a temperature of 50°C, as an example. A good linear relationship was obtained between $1/M_v$ (which is proportional to the reciprocal of degree of polymerisation) and reaction time. All the correlation coefficients (r^2) were higher than 0.98 (with estimated variance <0.05, $n \geq 8$).

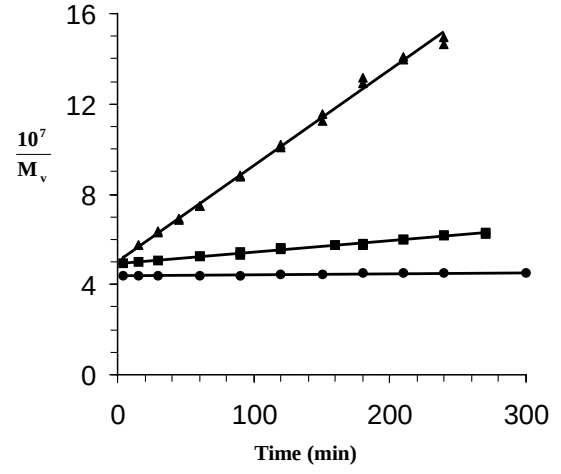

Fig. 3. Reciprocal molecular weight ($1/M_v$) against reaction time at pH 1.5: (●) 25°C; (■) 37°C; (▲) 50°C.

3.2. Effects of temperature and pH on degradation rate

Temperature had a pronounced effect on the pH-dependent degradation of guar galactomannan. For example, as shown in Fig. 3, at pH 1.5 the molecular weight decreased rapidly at 50°C, whereas at 25°C degradation was negligible. High temperature obviously accelerates the degradation process. The reaction rate constant k (i.e. two times the slope of the reaction line) at different temperatures allows an estimate of the activation energy (E) for hydrolysis according to an Arrhenius type relationship: $\ln k = \ln A - E/RT$, in which R is the universal gas constant and T is temperature in Kelvin. The plots of $\ln k$ versus $1/T$ at three pH levels gave the expected straight lines (Fig. 4). The E values calculated from these plots for pH 1.5, 2.0 and 3.0 were 117.4, 118.6 and 120.5 kJ mol^{-1}, respectively, indicating only a small change in E over the pH range studied. Although the activation energies are not strongly dependent on pH, the absolute rate constant at a given temperature increases substantially with decreasing pH as can be seen in Fig. 2 and Fig. 5. A consequence of this is that temperature has a greater effect on viscosity reduction at lower pHs. At 37°C and pH 1.5, which is the most relevant pH from a biological perspective, the degradation rate was found to be very slow. After four hours incubation under these conditions the viscosity decreased by only 11%, whereas at 50°C it decreased by 37%. The viscosity reduction was calculated as the difference between the initial relative viscosity and the relative viscosity after 4 h divided by the initial relative viscosity, a definition which has been applied in all the following text. The reductions in relative viscosity under different conditions after 4 h incubation are summarised in Table 1. At a given temperature there was a pH level above which the reduction in viscosity was negligible, as was the case at 50°C when pH $>$ 3.0.

3.3. The lowest pH that guar gum remains stable in solution

Experiments were carried out at 25, 37 and 50°C and at pH levels between pH 1.0–6.5. It was found that the viscosity of guar gum solution was always slightly lower in acidic pH than it was in neutral pH, even when no degradation occurred. For example, at 25°C the viscosity of a 1% solution at pH 3.0 was found to be 2.3% lower than that at pH 6.5. Since this difference in viscosity did not change with time (at least during the experimental periods), it was unlikely that this difference resulted from the degradation of the polysaccharides. Therefore, in the current study, guar gum was considered to be stable when the viscosity of guar gum solution was not reduced by more than 2% after 4-h incubation at a stipulated temperature. Table 2 lists the lowest pH at which guar gum was found to be stable at temperature 25, 37 and 50°C, respectively. The above results have shown that, as expected, temperature and pH had an effect on the stability of guar gum solutions, both separately, and synergistically when considered together.

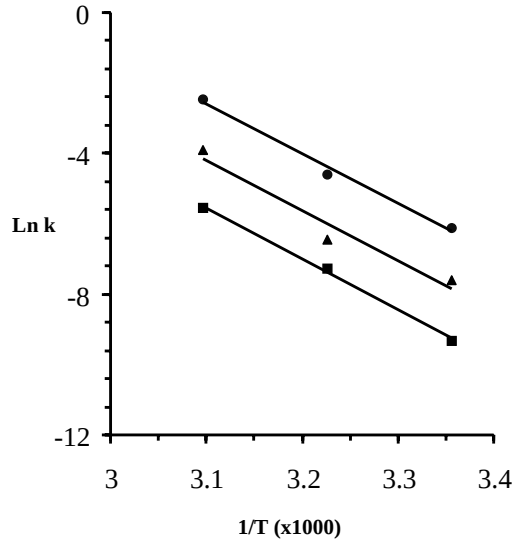

Fig. 4. Arrhenius plots for degradation of guar gum at three pH levels. k, degradation rate constant, and T is temperature in Kelvin. (●) pH 1.5, $\ln k = -14.11(1/T) + 41.14$, $r^2 = 0.991$; (▲) pH 2.0, $\ln k = -14.28(1/T) + 40.08$, $r^2 = 0.958$; (■) pH 3.0, $\ln k = -14.51(1/T) + 39.43$, $r^2 = 0.997$.

4. Discussion

The strong linear relationship observed between the reciprocal of average molecular weight and reaction time in all experiments indicates that the degradation of guar galactomannan under acidic condition is random with respect to chain cleavage. This linear relationship has been repeatedly observed for the degradation of polysaccharides with a single-stranded conformation (Hjerde et al., 1994; Rickards, Herp & Pigman, 1967). This is also consistent with the assumption that guar galactomannan has a disordered single-stranded conformation in aqueous solution. In contrast, polysaccharides with multiple-stranded conformations, such as xanthan and scleroglucan, generally exhibit an induction period with an apparently slow degradation rate at the initial stage, followed by a second stage where the apparent degradation rate is much higher (Hjerde et al., 1994). The induction period has been ascribed to the co-operative intermolecular forces within the multiple-stranded structure, which prevents strand separation during the initial reaction periods. Consequently, the apparent molecular weight does not decrease much at this stage.

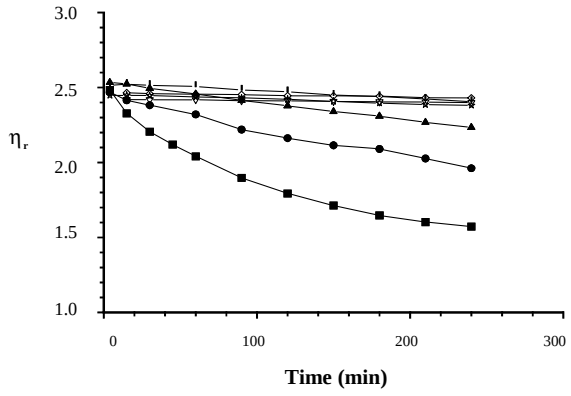

Fig. 5. The relative viscosity (η_r) changes of guar gum solutions (0.07% w/w) at different pH levels, temperature = 50°C: (■) pH 1.5; (●) 2.0; (▲) 2.2; (☆) 2.5; (▽) 3.0; (◇) 3.5; (⊥) 4.0.

Table 1
Summaries of viscosity reduction of guar gum solutions (0.07%, w/w) after 4 h incubation at different temperature and pH levels. The viscosity reduction ($\Delta\eta_r$) is calculated as the difference between the initial relative viscosity and the relative viscosity at 4 h incubation time divided by the initial relative viscosity (*—not determined)

Temperature	25°C	37°C	50°C
pH	Viscosity reduction (%)		
1.0	*	23.8	*
1.5	2.2	11.0	36.7
2.0	2.0	4.9	22.5
2.5	*	2.1	4.4
3.0	0.4	1.2	2.8

The activation energy for the degradation of guar galactomannan at acidic conditions is close to (actually slightly higher than) the values obtained for thermal degradation of schizophyllan, which is 104 kJ mol^{-1} (Zentz, Verchere & Muller, 1992) and k-carrageenan, which is 105 kJ mol^{-1} (Bradley & Mitchell, 1988). However, it is significantly higher than that reported for guar gum: 56.3 kJ mol^{-1} (Bradley, Ball, Harding & Mitchell, 1989), although their value was obtained using a much higher polymer concentration than that used in our own study. Also, Bradley et al. worked at about neutral pH and at high temperatures (~100°C). The susceptibility of degradation under these conditions to the oxygen environment suggests that free radicals are involved (Mitchell, Hill, Jumel, Harding & Aidoo, 1992). It is likely that there is a different activation energy for free radical and acid degradation. The present result indicates that guar gum may be more stable to acidic environments than previously thought. Analysis of the results strongly suggests that processing of guar gum below 50°C and at pH > ~2, does not markedly affect the Mv of the galactomannan. The slight decrease of solution

Table 2
Summary of data showing the stability of guar gum in solutions at different temperatures and pH levels. ($\Delta\eta_r$) is the viscosity reduction after 4 h incubation (calculated in the same way as in Table 1)

Temperature (°C)	25	37	50
Stable pH	2.0	3.0	3.5
($\Delta\eta_r$) (%)	2.0	1.2	1.4

viscosity seen at all levels of pH below neutral is probably not due to the degradation of galactomannan, but more likely caused by a change in water structure affecting the interaction between the water/galactomannan and galactomannan/galactomannan molecules. The weak protonation of the hydroxyl groups in the galactomannan and water molecules caused by high [H^+] may reduce the inter- and intra-molecular hydrogen bonding. It is possible that galactomannan molecules are less expanded in acidic medium because the hydrogen bonding between water and galactomannan is less prevalent. The interaction between galactomannan molecules may also be reduced, which results in less association of the molecules. Both effects tend to lead to a reduction in viscosity. It seems reasonable, in view of the discussion over, to select a viscosity reduction of about 2% as the upper limit for the stability of a guar gum solution.

The result from the current study has implications in a range of applications where low pH systems employ guar gum either as an added thickener or as dietary fibre, modifying physiological response. Although guar gum has already been widely used in food industry, it was not recommended for use in products with a final pH lower than pH 4.5, such as yoghurt drinks and salad dressing etc. (see for example, Hercules Incorporated, Fragrance and Food Ingredients Group, 1999). In these products pectins and xanthan are usually used because they are relatively stable under acidic condition. However, from the current study, it appears that guar gum could still be an alternative in such products, in particular, in the case of cultured milk products that are not subject to heat treatment after culturing, such as yoghurt. The excellent compatibility of guar gum with salt and other hydrocolloids is another advantage for this material.

Because of the relatively high stability of guar gum in mild acidic conditions, it also appears to be a good source of water-soluble non-starch polysaccharides (NSP) to produce beneficial therapeutic effects in people with diabetes and hyperlipidaemia (Ellis, 1999). The intragastric pH of human is acidic, usually not lower than $1.5 \sim 2$ after a meal (Rayding, Nelson & Basted, 1984). Since it is known that the viscosity of the soluble dietary NSP is a key factor for their use in therapy, the degradation of these polysaccharides (and thus a loss of viscosity) is not desirable. The present result suggests that significant acidic degradation of any guar galactomannan, contained in the food in the gastrointestinal tract, is unlikely.

Finally, it is worth noting that although this experiment was conducted on high molecular weight guar gum, the conclusions obtained are expected to be applicable to lower molecular weight samples. There is evidence from thermal degradation measurements of polysaccharides that the reaction rate does not depend on chain length (Zentz et al., 1992). Since the scission of guar galactomannan appears to be random, a future study might involve analysis of molecular distribution to confirm this. It might also be useful to examine other galactomannans (e.g. locust bean gum) to see if they are more or less pH stable.

5. Conclusions

The current study shows that guar gum is relatively stable under mild acidic conditions. Higher temperatures and lower pHs do reduce the stability of guar gum in solution. The lowest pH at which guar galactomannan remains stable, at temperatures 25, 37 and 50°C, was found to be 2.0, 3.0 and 3.5, respectively. The acid degradation of guar gum is likely to be a random scission process with first order kinetics. Current results suggest that guar gum may have extended uses in acidic systems.

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