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Dissolution kinetics of guar gum powders—II. Effects of concentration and molecular weight

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Abstract

This study investigated and compared the hydration rate of commercial samples of galactomannan-rich guar gum of different average molecular weights (M_w) and concentrations. An empirical logarithmic model, developed in a previous paper for describing the hydration kinetics of guar gum powders, was used for this purpose. The hydration rate was found to be dependent on the galactomannan concentration. In the intermediate galactomannan concentration range (0.5–1.2% w/v) of one of the relatively high-M_w samples, the hydration rate increased with increase in concentration. For the more concentrated systems (>1.2% w/v) of the same sample, an increase in concentration appeared to suppress the hydration process, thus reducing the hydration rate. As might be expected, molecular weight (M_w) had a significant effect on the hydration rate of guar gum. Using guar samples with a M_w range of 0.1–2.8 million, an inverse relationship between M_w and hydration rate was demonstrated. However, one high-M_w sample produced a significantly lower hydration rate than that predicted from this relationship. This apparently anomalous result can be explained by the observation that in this sample there was a variation in the M_w distribution with respect to particle size. This indicates that particle size (and distribution) and M_w are crucial factors in determining net hydration rates.

Keywords: Guar gum; Galactomannan; Dietary fibre; Hydration; Dissolution

1. Introduction

It is well known that molecular weight (M_w) influences the dissolution rate of macromolecular materials, and, in this respect, the polystyrene–toluene system has been the most commonly studied system (Ueberreiter, 1968), as it is in other aspects of polymer science. However, there is no corresponding study reported in detail on the dissolution (hydration) behaviour of guar gum, a galactomannan-rich flour produced from the leguminous plant *Cyamopsis tetragonoloba* (L). Taub. When guar galactomannan, and many other such high-M_w polysaccharides, are added to an aqueous system, they can significantly increase the viscosity of the system as the polysaccharide concentration (C) increases. This effect of viscosity on hydration rate has not been studied extensively.

The aim of the current study was to investigate to what extent the hydration rate is affected by both M_w and C for guar gum samples that are of industrial interest and those that are of use in medical and nutritional studies. In many of these studies, guar gum is known to have beneficial effects on gut function and metabolism in humans and experimental animals (Ellis, Rayment, & Wang, 1996; Ellis, Wang, Rayment, Ren, & Ross-Murphy, 2001; Juneja, Sakanaka, & Chu, 2001). For example, there are a plethora of studies showing that guar gum reduces post-prandial glycaemia and insulinaemia in healthy and diabetic human subjects (Gatenby, Ellis, Morgan, & Judd, 1996; Jenkins et al., 1976; Morgan, Tredger, Wright, & Marks, 1990). These metabolic effects are considered to be of clinical value in the dietary management of diabetes mellitus (Ellis et al., 2001; Gatenby et al., 1996; Rendell, 2000). The biological activity of guar gum is largely, but not exclusively, dependent on its capacity to increase the viscosity of digesta in the stomach and small intestine (Brennan, Blake, Ellis, & Schofield, 1996; Ellis et al., 1996;

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Ellis, Roberts, Low, & Morgan, 1995; Slaughter, Ellis, Jackson, & Butterworth, 2002). The degree of viscosity generated in the gastrointestinal tract by the guar galactomannan is determined by the M_w and C of the polymer and, of course, whether the polymer hydrates to form a molecular dispersion (Ellis et al., 1996, 2001).

In a previous paper, we described a rheological method that had been designed for determining the hydration rate of guar gum, both as a commercial flour and a purified galactomannan sample (Wang, Ellis, & Ross-Murphy, 2002). An empirical logarithmic model for describing the hydration kinetics of guar gum powder was also established and found to be reliable for predictive purposes. This current paper describes work that uses the same technique and model for investigating and comparing the hydration rate of commercial guar gum flours of different average M_w. Guar gum flours were used for each experiment without any pre-treatment except for the adjustment of moisture content. The effect of polymer C on the hydration rate was also investigated. One objective of this was to determine if the galactomannan C significantly influences the hydration rate of guar gum in the C-range normally used in clinical trials. It is envisaged that the results of this investigation will facilitate our understanding of the behaviour of guar gum in the gut lumen and also provide useful information about the types, doses and mode of administration of guar gum that should be used to optimise its therapeutic effects. At the same time, both the M_w and C are prime parameters for determining the usability and applications of guar gum (and other polysaccharide) solutions, and so the present paper has much broader interest.

2. Experimental

2.1. Materials

As in Part I of this series (Wang et al., 2002), commercial guar gum flours of different average M_w (Meyprogat series: M150, M120, M90 and M60; Rhodia Food (formerly Meyhall Chemical AG), Kreuzlingen, Switzerland) were used in this study. The moisture contents of samples were adjusted to approximately the same level before performing the hydration experiments. Thus, each sample was placed in a container and left in a sealed incubator containing saturated sodium chloride solutions (in a beaker) for about 24 h at 27 °C. It was assumed that the equilibrium moisture content (EMC) was attained after that period. For measurements of intrinsic viscosity (see Section 2.3), the guar gum samples were purified by a method described elsewhere (Rayment, Ross-Murphy, & Ellis, 1995; Wang, 1997).

2.2. Chemical analysis of guar gum

The moisture content of each sample was measured after leaving the sample in an oven at 104 °C for 16 h using AACC method 44-15A (American Association of Cereal Chemists, 1983). Lipid content was also analysed according to AACC method 30-26 (crude fat by Soxhlet method; light petroleum, bp 40–60 °C, diethyl ether extraction). Crude protein content ($N \times 5.71$) was estimated by the Kjeldahl method (Kirk & Sawyer, 1991). Ash (total minerals) content was analysed by slowly heating a 5 g sample in a muffle furnace to 525 °C and leaving for 12 h at that temperature (Kirk & Sawyer, 1991). The Englyst method (Englyst, Quigley, Hudson, & Cummings, 1992) was employed to determine non-starch polysaccharides (NSP) content, including galactomannan, by gas–liquid chromatography following acid hydrolysis and derivitisation of the carbohydrates to alditol acetates. This method was modified by increasing the hydration time of the guar gum in phosphate buffer (i.e. overnight hydration, rather than 40 min as used in the standard method) (Rayment et al., 1995). Uronic acid content was determined by a sulphuric acid–dimethylphenol colorimetric assay (Englyst et al., 1992). All measurements were done in duplicate except for the analysis of NSP, which was performed in triplicate.

2.3. Methods for physical characterisation of guar gum

As detailed in our previous paper (Wang et al., 2002), intrinsic viscosity was measured using a dilution capillary viscometer (Ubbelohde type), and viscosity-average molecular weight (M_v) was estimated through an appropriate Mark–Houwink relationship (Robinson, Ross-Murphy, & Morris, 1982). Since the published relationships are now known to be reasonably robust, we can assume that the weight-average molecular weight, $M_w \approx M_v$.

Particle size distribution and specific surface area were determined using a Malvern 2600 Laser Diffraction Sizer (Malvern Instruments Ltd, Worcs, UK) as discussed in more detail elsewhere (Wang et al., 2002). Guar gum samples were dispersed in butan-1-ol solvent and left in an ultrasonic bath for 5 min in order to break up any aggregates of particles. During measurements a magnetic stirrer was used to ensure homogenised suspension of particles. No swelling of samples was observed in this solvent when examined by light microscopy. Guar gum flours were also examined by scanning electron microscopy (SEM), to provide further information about shape and size of the guar particles. Appropriate samples were mounted on an aluminium stub with double-sided adhesive tape. The tape was first firmly attached to the stub and the sample powder was scattered carefully over its surface. The stub with the specimen was then sputter coated with a thin layer of gold (Polaron Equipment Ltd, SEM coating unit, E5100) to make the specimen conductive. The specimens were examined in a Philips SEM501B scanning electron microscope. Photographic images were recorded on Ilford FP4 film ISO 125, 220.

2.4. Hydration method

The hydration experiments were carried out according to the method described in the previous paper (Wang et al., 2002) with some minor modifications detailed below. An accurately weighed sample of guar gum was dispersed in 500 ml distilled water in a glass jar, which was then placed in a mixing box incubator and rotated end-over-end at a constant rotational velocity at 25 °C. To study the effects of M_w on hydration rate, the mixing box was set at a speed of 6 rpm. In previous work (Ellis & Morris, 1991), hydration experiments were performed on 1.0% (w/v) dispersions of guar gum prepared on a dry weight basis (i.e. solids content is constant). However, in the current study, because the galactomannan content of the different guar samples varied (Table 1), it was considered useful to repeat the hydration experiments using guar gum solutions where the galactomannan was also kept constant. Thus, two types of guar gum solution were studied, a 1.0% (w/v) dispersion based on the dry matter content of the flour samples and a 1.0% (w/v) dispersion based on the galactomannan content of the guar gum flours, which corresponded to a concentration of approximately 1.1% of dry matter. Steady shear viscosity measurements were performed on a Rheometrics Fluids Spectrometer (RFSII; Rheometric Scientific, Piscataway, NJ, USA). A plate–plate geometry (50 mm in diameter, 1 mm gap) was used for high-M_w samples including guar gum grades M150 and M120. Couette geometry (34 mm cup diameter, 32 mm bob diameter and 35 mm bob length) was used for the rest of the samples. The zero-shear viscosity was calculated as the average value of the first four shear rates starting at the lowest shear rate (five measurements were made per decade during the experiment, typically from $\sim 0.01-1000\ s^{-1}$). To obtain the 'ultimate viscosity', the sample dispersion was homogenised with an Ultra-Turrax mixer, followed by a further 3 h hydration at higher temperature (40 °C). Distilled water was added back to compensate for moisture loss during the process.

For the study of concentration effects, a medium–high M_w sample (M120) was used at different concentrations between 0.5 and 1.4% (w/v). The rotational velocity of the mixing box was 15 rpm in order to cover a wider concentration range, since at high polymer concentrations there is greater tendency for guar particles to aggregate at low mixing velocities. The viscosity was measured using a Brookfield LVTDV-II rotoviscometer (Brookfield Viscometers, Harlow, Essex CM19 5TJ, UK) with a small sample adapter (SC13R) and a range of spindles (SC4 18, 25, 31 and 34). Zero-shear viscosity was calculated as the average value of the first two points at the lowest range of shear rates used (between 0.1 and 1 s^{-1}).

In the previous paper (Wang et al., 2002), the following double logarithmic model was developed to describe the hydration process of guar gum flours:

$$\ln(1 - \eta_t/\eta_\infty) = b + k \ln t \quad (1)$$

where η_t is the zero-shear viscosity at time t and η_∞ is the ultimate viscosity of the dispersion. The hydration constants k and b can be extracted from plots of $\ln(1 - \eta_t/\eta_\infty)$ versus $\ln t$, which form a group of straight lines with slope k and intercept b. The hydration index $t_{0.8}$, which is the time that is needed for the viscosity of the dispersion to reach 80% of ultimate viscosity, was used for comparing the hydration rate of different samples. From Eq. (1) we have:

$$t_{0.8} = \left(\frac{0.2}{e^b}\right)^{\frac{1}{k}} \quad (2)$$

Table 1
Chemical composition of guar gum flours (% dry matter) and EMC under saturated NaCl solution at 27 °C. All values are means of duplicates except for the galactomannan content, which is the mean of triplicates. NSP, non-starch polysaccharides

Samples	EMC (%)	Protein ($N \times 5.7$)	Lipid	Ash	Galacto mannan	Uronic acid	Total NSP
M150	11.7	3.7	1.2	0.6	87.8	1.3	90.4
M120	10.2	3.8	1.4	0.5	91.4	2.0	93.4
M90	10.3	4.0	1.2	1.7	91.3	2.6	95.2
M60	10.1	3.2	1.3	3.1	82.1	1.6	87.0

3. Results and discussion

3.1. Characterisation of guar gum

3.1.1. Chemical composition

Chemical compositions of guar flours including galactomannan content are summarised in Table 1. The galactomannan contents of all four samples were found to be slightly different. Generally, the samples of medium–high M_w contained higher concentrations of galactomannan than the low M_w sample (M60). Apart from galactose and mannose, there were small amounts of other monosaccharides present such as glucose and arabinose, which accounted for approximately 2–5% of total NSP contents and varied in different samples. The sample of low M_w guar gum (M60) contained a lower concentration of galactomannan, attributed mainly to the presence of a larger proportion of ash than the other samples. The relatively high ash content of M60 is due to the higher salt content that is introduced as a result of the hydrolysis treatment when preparing the low M_w samples.

The EMCs of all samples after exposure to the air with saturated NaCl solution at 27 °C were close to each other (Table 1), although the EMC of M150 was slightly higher than the rest of the samples. This is possibly because of the difference in original moisture contents between these samples. At any given water activity, the EMC of a material will be greater during desorption than that during absorption at the same temperature (the so-called absorption hysteresis

Table 2
Mean particle size (d_m), specific surface area (A_{sp}), intrinsic viscosity [η] and weight-average molecular weight (M_w) of guar gum. (It is assumed that the weight average molecular weight $M_w \approx M_v$.) Values for d_m and A_{sp} are means (± standard deviation) of triplicates

Samples	$d_m \pm$ SD (μm)	$A_{sp} \pm$ SD (m^2/g)	[η] (dl/g)	$M_w \times 10^{-6}$ (g/mol)
M150	60.7 ± 1.5	0.13 ± 0.02	17.5	2.82
M120	50.9 ± 6.7	0.15 ± 0.03	15.4	2.37
M90	70.8 ± 3.7	0.13 ± 0.03	10.5	1.39
M60	54.5 ± 1.6	0.17 ± 0.04	6.8	0.75

phenomenon). Nevertheless, it is unlikely that such small differences in EMC between the samples will affect their hydration behaviour significantly.

3.1.2. Particle size, intrinsic viscosity and molecular weight

Physical characterisation revealed differences between the different grades of guar gum flours, as seen in Table 2. Thus, samples M150 and M90 had slightly larger particle size (d_m), but correspondingly lower specific surface area (A_{sp}), than those of the other samples. The distribution of particle size was also found to be different as shown in Fig. 1(a)–(d). Compared to M150, M120 has a slightly broader range of particle size distribution. The particles with mean diameter smaller than 25 μm accounted for 12.0% of the total particles in M120 (Fig. 1(b)), whereas there was only 6.5% of this fraction in M150 (Fig. 1(a)). This difference can also be seen in the SEM images, Fig. 2(a)–(d). It is clear that M120 has a greater proportion of finer particles than M150. The shapes of particles between each sample were also different from each other. For example, M90 appears to have rather more spherical particles compared to those of the M150 sample, which were more rod shaped. As will be discussed below, these differences may have effects on the hydration behaviour of these samples.

Not surprisingly, there were differences in intrinsic viscosity ([η]) and estimated M_v between the different samples. Viscosity average molecular weight (M_v) was calculated by the Mark–Houwink relationship, given as: $[\eta] = kM_v^{\alpha}$ where $k = 3.8 \times 10^{-4}$, $\alpha = 0.72$ (Robinson et al., 1982), which are essentially the same as the values reported by Picout, Ross-Murphy, Errington and Harding (2001). As indicated in Table 2, we have assumed that $M_w \approx M_v$. The intrinsic viscosity values estimated here were generally higher than would be expected. This is due to the method adopted in this analysis, where the guar gum samples were purified before measurements were taken. In the calculation of [η], the polymer concentration was estimated on the basis of the galactomannan content (determined by the method of Englyst et al. (1992)), rather than on the dry weight basis of the flour (which includes other polysaccharides and impurities) as in previous studies. It should be noted, however, that a slight underestimate of the polymer concentration may occur, because a small

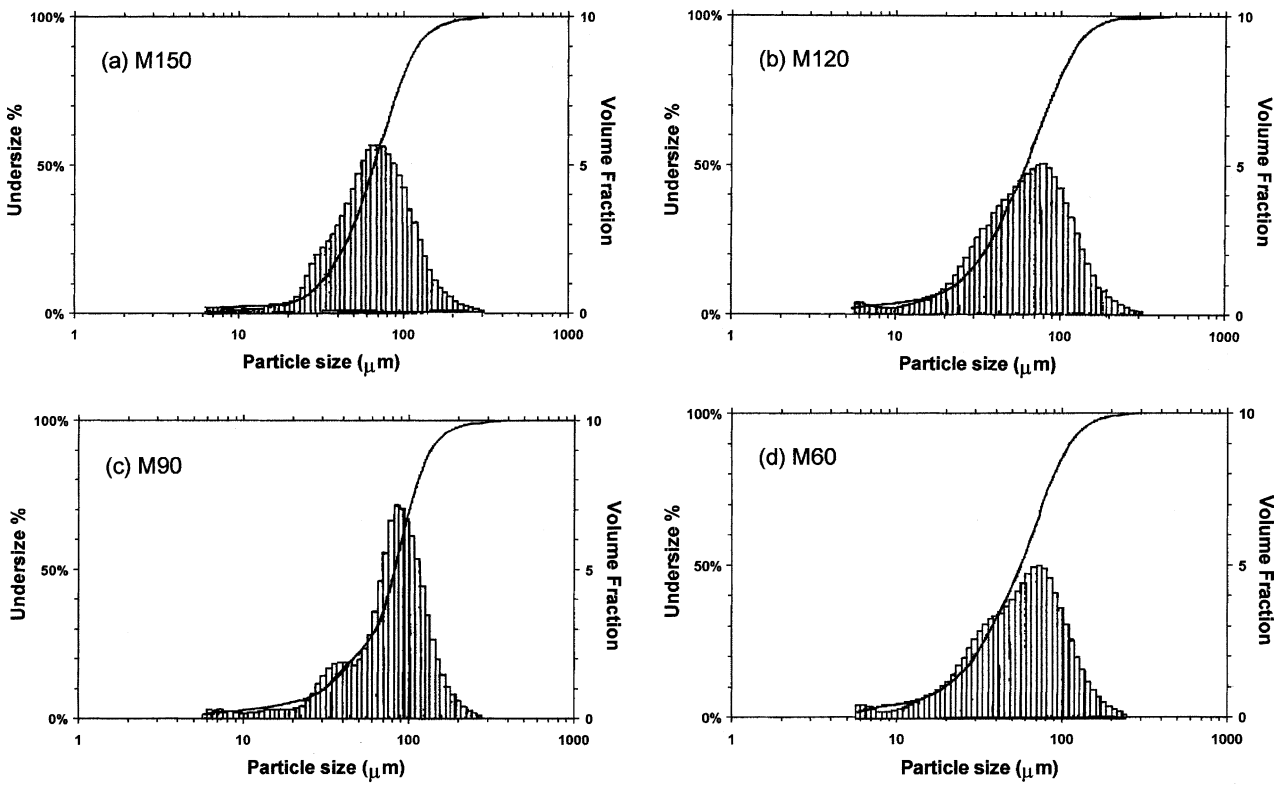

Fig. 1. Particle size distribution of guar gum flour samples of different M_w ((a) M150, (b) M120, (c) M90, and (d) M60) as measured by Malvern 2600 sizer. For chemical composition and physical properties of samples, see Tables 1 and 2.

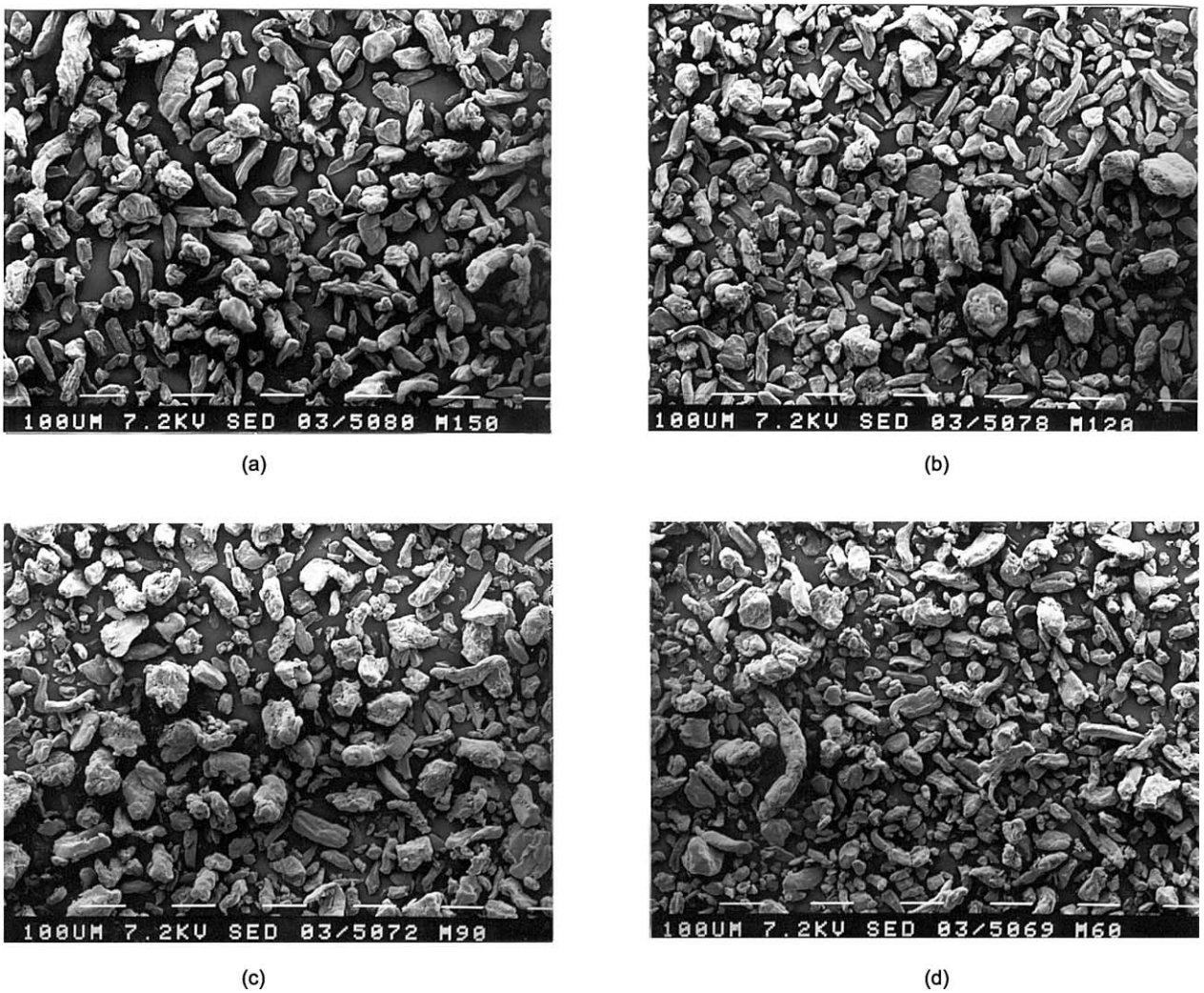

Fig. 2. Micrographs produced by SEM of guar gum flour samples of different M_w : (a) M150, (b) M120, (c) M90, and (d) M60. For composition and physical properties of samples, see Tables 1 and 2. All white scale bars = 100 μm.

amount of low-M_w polymer might be lost during the ethanol purification step (see Section 2.1). Thus, oligosaccharides with $<10-15$ monosaccharide residues are not normally precipitated in 80% ethanol (Asp, Schweizer, Southgate, & Theander, 1992), which was the ethanol concentration used to precipitate the galactomannan polysaccharide during the purification stage.

3.2. Effects of polymer concentration (C) on hydration rate

These experiments were carried out using M120 at a C range of 0.5–1.4% (w/v), corresponding to a C/C^* range of 8–22 ($C^* \approx 1/[\eta]$). Beyond this C range the viscosity was either too low or too high to measure using the Brookfield viscometer (LVTDV II). The experimental results are summarised in Table 3 and Figs. 3 and 4. As illustrated in Fig. 3, the lowest rate of increase of viscosity is for the lowest C but the behaviour does not increase monotonically. (For clarity not all concentrations are shown in this figure.) For example, both the slope k and intercept b (Eq. (1)) increase in the C range 0.5–1.2%, and there is an approximately linear relationship between k and C. However, at a polymer C of 1.2% there was an apparent change in this behaviour. When $C > 1.2\%$, which corresponds to a $C/C^* \sim 19$, both the slope and intercept of the corresponding line in Fig. 3 decrease again.

To elucidate this, we need to consider the behaviour of the hydration index $t_{0.8}$. According to Eq. (2), the corresponding values of $t_{0.8}$ would decrease with increase in k, but increase with increase in b. As shown in Fig. 4, the net result is that at these higher concentrations, at least in the range we studied, $t_{0.8}$ then decreases with increase in C. In other words, the higher the polymer concentration, the faster the hydration process is within this concentration range. The behaviour of $t_{0.8}$ with concentration is apparently parabolic. To this must be added the observation that, at least intuitively, as we approach zero concentration, when there is no polymer we could assume that $t_{0.8}$ must $\rightarrow 0$. Although at first glance this is surprising, the behaviour, taken as a whole, appears to be genuine, since Fig. 4(a)

Table 3
Hydration constants k and b, and hydration index $t_{0.8}$ obtained for different concentrations of M120 guar gum. Values are means of duplicates or triplicates

C (%w/w)	C/C^*	k	b	$t_{0.8}$ (min)
0.5	7.7	−0.38	0.32	159
0.6	9.2	−0.41	0.46	164
0.8	12.3	−0.51	0.77	106
1.0	15.4	−0.56	0.75	67
1.2	18.5	−0.60	0.84	60
1.3	20.0	−0.44	0.35	90
1.4	21.5	−0.41	0.24	97

shows duplicate (and in one case triplicate) measurements. It seems unreasonable to draw a (horizontal) line through this, and indeed this has been shown statistically to be inappropriate. Rather we have to invoke some other more appropriate explanation for this phenomenon. However, an alternative presentation clarifies this. If we, as follows from the definition of $[\eta]$, define a reduced hydration rate $t_{0.8}/C$ and plot this against C/C^* (or its equivalent $C[\eta]$) we see that there is a steady decrease in the reduced hydration rate until we reach the semi-dilute regime, with $C[\eta] \sim 15$, where there appears to be a plateau regime. Using this alternative approach, we also see that a newly defined intrinsic hydration rate, here given by $[t_{0.8}/C]_{C\to 0}$, appears to be finite and to have a value ~600 (Fig. 4(b)). This gives a more appropriate limit result.

From the results obtained for M120, it is helpful to consider how the relationship between hydration rate and polymer C varies with respect to the C regime, namely, dilute ($C < 0.5\%$), transitional (0.5–1.2%) and semi-dilute solution regimes ($C > 1.2\%$). The corresponding values for C/C^* are found in Table 3. Unfortunately, the results of the present experiment did not provide sufficient evidence to illustrate the first regime, due to the technical limitations of measuring the hydration rate of the polymer at low C. Nevertheless, from consideration of theory, there may be a number of possible explanations of these results. One of these is that the hydration rate is independent of the polymer

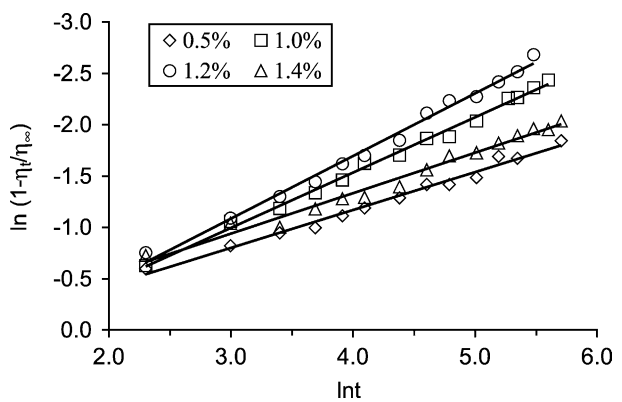

Fig. 3. Examples of hydration curves of M120 guar gum flour at different galactomannan concentrations (0.5–1.4%) according to Eq. (1). Each experimental point is the mean of duplicate values.

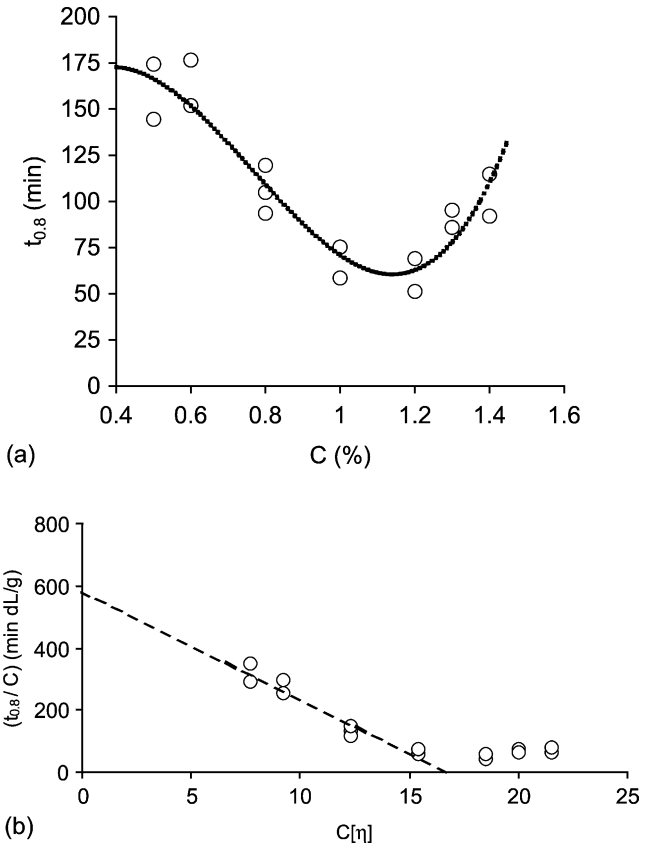

Fig. 4. (a) Hydration index $t_{0.8}$ (min) versus galactomannan C (%) for M120 guar gum flour. The broken line is the polynomial regression (quadratic) of the experimental data ($r^2 = 0.90$). Intrinsic hydration rate plotted versus 'overlap parameter', c[η]

concentration in the dilute regime, but is determined only by the hydration rate of each single particle. In this case, hydration is achieved mainly through the diffusion process of the polymer molecules, since the difference in the concentration between the swollen layer of particle surface and the bulk solution is large and the deposition of the polymer molecules from the solution to the particle surface is likely to be limited (Abdou, 1989). However, because the increase in concentration will stimulate the deposition process of the polymer molecules onto the surface of swollen particles, and the concentration gradient will also be decreasing, at some stage it must be assumed the hydration rate will decrease with the increase in concentration. Indeed we observed this effect at the highest particle concentrations ($C > 1.2\%$), which exhibited increases in the $t_{0.8}$ index, reflecting an attenuation in the hydration rate.

In the transitional concentration regime (0.5–1.2%), however, the data clearly shows that the hydration rate increases with increasing concentration, which at first sight appears difficult to interpret. Generally the hydration rate increases with an increase in the 'effective' specific surface area of the sample. Thus, contrary to the results of the present study, in the C range 0.5–1.2% an increase in hydration rate is not expected, because the initial specific surface area scarcely changes with concentration. One

plausible explanation for this behaviour is that as the concentration of guar particles increases in the range 0.5–1.2%, there is likely to be a concomitant increase in particle–particle collisions, thereby contributing to surface abrasion (i.e. the so-called ball-mill effect). This mechanism would probably play a role only in the early stages of hydration, when the development of viscosity is still relatively low (i.e. the dilute regime).

An alternative explanation, which is not mutually exclusive from the first, is that the shear stresses due to the rotation of the mixing box play a more significant role in the C range 0.5–1.2%. As was described in the previous paper, the individual particles of flour form a swollen 'gel layer' during the hydration process. The deformation of this layer would depend on the viscosity ratio η_{gel}/η_{sol}, where η_{gel} is the viscosity of this gel layer and η_{sol} is the viscosity of the continuous medium, i.e. the solution. By analogy with the flow of emulsion droplets, deformation of this layer at a given shear rate would only occur when this ratio is lowered (Tolstoguzov, Mzhel'sky, & Gulov, 1974). In the current experiment, deformation of the gel layer is unlikely to have occurred in dilute solutions because of the high viscosity ratio (i.e. small η_{sol}). As the polymer concentration increases this viscosity ratio decreases because of the increase in solution viscosity (i.e. high η_{sol}). Moreover, in some concentration range, the deformation would be expected to increase with the increase in concentration. This facilitates the removal of the polymer molecules from the particle surface, and may also increase the surface area, which further enhances the hydration process. However, further speculation is probably inappropriate, for example, the transport behaviour of polymer solutions is itself rather complex. In addition there are a number of differing contributions, including the effect of the so-called co-operative diffusion mechanism (Brown, 1993; de Gennes, 1979). All involve both strong and weaker concentration dependent terms.

3.3. Effects of molecular weight (M_w) on hydration rate

The initial objective of this experiment was to investigate the differences in the hydration rate of guar gum flours of different M_w. One point that needs to be borne in mind is that many of the physical parameters that are known to influence hydration, such as particle size and shape, surface properties and density, etc. are not identical for the different samples of guar gum. Thus, it is difficult to distinguish between the effects of M_w and all the other physical parameters that are likely to influence hydration. However, for the samples used in the current study, the differences in molecular weight are substantial, and the contribution made by the other physical parameters to the rate of hydration is likely to be of much less importance.

This experiment was performed on two groups of samples in order to take into account the differences in the galactomannan contents of selected grades of guar gum (Table 1). Thus, the hydration rates of different samples were compared at the same concentration, at 1.0% (w/v) on the basis of galactomannan content (group 1) and at 1.0% (w/v) on the basis of the dry matter content (group 2).

Nevertheless, the logarithmic model for hydration was found to fit the hydration curves of all the guar gum samples studied. Fig. 5 is an example of the hydration profiles for M150, M120, M90 and M60 (all 1.0% solutions based on galactomannan content) when plotted according to Eq. (1). The hydration index, $t_{0.8}$, which was calculated for each of the four guar gum samples and summarised in Table 4, was found to be strongly influenced by M_w (Fig. 6). Thus, low M_w samples hydrated more rapidly than those of high M_w, using a concentration (~1.0%, w/v) based either on the same polymer weight or the same solids (dry matter) content. For example, the 1.0% dispersion of M150 calculated on a polymer weight basis required ~10 times longer to achieve 80% ultimate viscosity compared to M60 of the same polymer concentration. When the comparison was made on these two samples for 1.0% dispersions on a dry weight basis, the $t_{0.8}$ value of M150 was ~14 times larger than that of M60. Given the variations in estimating $t_{0.8}$, the predicted values, whether estimated on a polymer weight or on a dry weight basis, showed good agreement for the different samples. The results of preliminary experiments using lower M_w grades of guar gum, M30 and M7 (M_w : 3.7×10^5 and 1.1×10^5, respectively) showed that these samples hydrated more rapidly than the higher M_w grades (Wang, 1997), confirming there is an inverse relationship between M_w and hydration rate. However, the data obtained for M120 did not fit this relationship as well as the rest of the data. Thus, despite the lower average M_w of this sample compared with the native guar gum (M150), the hydration rate was somewhat slower than we would have predicted from the trend. Indeed, as shown in Fig. 6 and Table 4, the difference in hydration rate between M120 and M150 was not significantly different.

However, it is not difficult to explain the 'apparent' abnormal hydration behaviour of M120 when compared to

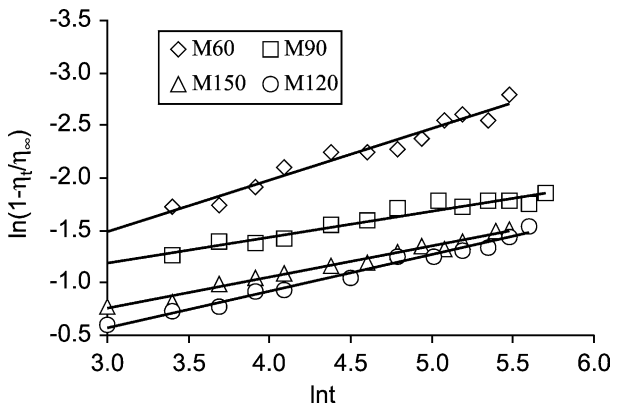

Fig. 5. Examples of hydration curves of different guar gum flour samples (1% solutions, based on galactomannan content, of M150, M120, M90 and M60) according to Eq. (1). Each experimental point is the mean of duplicate values.

Table 4
Hydration indices ($t_{0.8}$) of guar gum samples of different M_w, calculated from Eq. (2) using hydration constants k (slope) and b (intercept) estimated from linear regression lines in Fig. 5. The $t_{0.8}$ values (min) are means (± SD) of triplicates. Statistical analysis data of linear plots in Fig. 5 also included. P levels of all r^2 values are <0.001). GM, galactomannan content of samples taken from Table 1

Samples	Polymer weight basis		GM (%)	Dry weight basis	
	$t_{0.8}$ ± SD (min)	r^2		$t_{0.8}$ ± SD (min)	r^2
M150	307 ± 34	0.94	88	359 ± 65	0.93
M120	363 ± 62	0.97	91	363 ± 62	0.97
M90	103 ± 11	0.90	91	103 ± 11	0.90
M60	29 ± 5	0.89	82	26 ± 6	0.90

M150. Firstly, although M120 is produced from M150 by hydrolysis (directly in powder form without dissolving in water: W.C. Weilinga, Rhodia Food, Personal Communication), the difference in M_w between M120 and M150 is still relatively small (less than 16%, Table 2). Secondly, as mentioned previously, M120 contains a larger fraction of fine particles ($D_v < 25$ μm) compared to M150. It is likely that most of these fine particles were produced during the hydrolysis treatment and contained therefore mainly low-M_w galactomannan. If this were the case, then during the hydration process the molecules from this fraction would hydrate rapidly, but would contribute less to the overall viscosity of the solution because of their relatively low M_w. In contrast, the fractions with large particle size would tend to hydrate slowly, but make a larger contribution to the solution viscosity because of the relatively higher M_w of the galactomannan.

In order to test whether there is a difference in M_w between different particle size fractions of M120, the intrinsic viscosity of some fractions of these, separated by sieving, were measured. Fraction 1 accounted for 37% of the total M120 samples (by weight) and consisted of particles <45 μm. Fraction 2 accounted for 40% of the total sample, and consisted of particles >63 μm. The [η] for Fraction 2 was found to be 17.0 dl/g, which is very close to the intrinsic viscosity of M150, which is 17.5 dl/g, whereas [η] for Fraction 1 was 14.9 dl/g, which is somewhat lower than that obtained for the original M120 flour (see Table 2). This substantiates our original view that the lower particle size fraction of M120 contained a larger proportion of hydrolysed and therefore low-M_w galactomannan.

Finally, the polymer concentration of the high M_w fraction of M120 was actually lower than the proposed concentration (i.e. 1.0% on galactomannan basis or on dry weight basis) and therefore lower than that used for M150. For instance, if the low M_w fraction accounts for 10% of the total weight of the sample, a 1.0% solution based on total sample weight is actually a 0.9% solution based on the high M_w fraction. In the concentration experiments using M120, we observed that when the polymer concentration was <1.2%, the hydration rate of M120 decreased in proportion to a decrease in C. Thus, the galactomannan concentration may also be an important factor in contributing to the low hydration rate of M120.

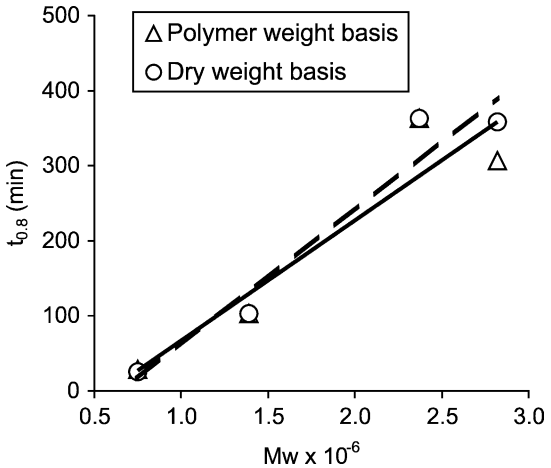

Fig. 6. Hydration index $t_{0.8}$ (min) versus molecular weight (M_w) of guar gum flour. Unbroken (polymer weight basis) and broken lines (dry weight basis) suggest a linear relationship, with $r^2 = 0.88$ and 0.95 ($P < 0.05$), respectively.

4. Conclusions

The hydration rate of guar gum was found to be strongly dependent on the galactomannan concentration. At intermediate polymer concentrations, the hydration rate increases with increase in concentration. For more concentrated systems, an increase in concentration will suppress the hydration process, thereby reducing the hydration rate. Although this mechanism is currently based on the results obtained from M120 guar sample, this explanation can probably be applied to other grades of guar gum and other similar polymers.

As might be expected, M_w had a significant effect on the hydration rate of the guar gum samples studied, and the results show that there is an inverse relationship between M_w and hydration rate. Although the hydration rates of M120 and M150 samples were not found to be significantly different, this was thought to be due to the variation in the M_w distribution of the M120 and especially with respect to the particle size.

It is clear from the preceding discussion that there are still some significant uncertainties. Indeed, if we were to start a more extensive study, it would be far better to start with a single sample and fractionate. However, we were driven by an interest and desire to examine commercial samples and to make measurements that are of interest and application to industry, and in these respects, the study we describe here seems the most appropriate.

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