ELSEVIER

Carbohydrate Polymers 43 (2000) 1–9

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

# Effect of size and shape of particulate inclusions on the rheology of guar galactomannan solutions☆

P. Rayment, S.B. Ross-Murphy*, P.R. Ellis

*Biopolymers Group, Division of Life Sciences, King's College London, Franklin-Wilkins Building, 150 Stamford Street, Waterloo, London SE1 8WA, UK*

Received 2 September 1999; received in revised form 3 November 1999; accepted 25 November 1999

**Abstract**

In our earlier work, the effects of particulate inclusions on the rheological properties of a guar galactomannan entanglement solution were studied. Filler materials varying in size and shape were investigated including a rice starch sample, chosen for its homogeneity and spherical nature. In the present paper, the work has been extended to include microcrystalline cellulose selected for its rod-like appearance and heterogeneous nature. The effects of particulate and composite properties on the apparent zero-shear viscosity and yield stress of the system were determined, and compared with previous results obtained using the more isotropic rice starch filler © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Particulate inclusions; Rheology; Guar galactomannan solutions

## 1. Introduction

Guar galactomannan is a water-soluble polysaccharide obtained from the endosperm of the Indian cluster bean *Cyamopsis tetragonoloba* (L.) Taub. The structure of this non-starch polysaccharide (NSP) consists of an essentially linear β-D-(1→4)-mannan backbone, solubilised by irregularly substituted, uncharged α-D-(1→6)-linked galactose side groups (Dea & Morrison, 1975). In previous publications (Rayment, Ross-Murphy & Ellis, 1995, 1998) we have reported the use of a yield stress modified Cross equation (1) (Cross, 1965) to describe the shear-thinning behaviour of starch particulate filled guar gum solutions

$$\eta = \eta_\infty + [\eta_{0X} - \eta_\infty]/[1 + (a\dot{\gamma})^p] + (\tau_X/\dot{\gamma}) \quad (1)$$

Here $\eta_{0X}$ and $\eta_\infty$ are limiting (Cross) viscosities, at zero and infinite shear rates, $a$ and $\dot{\gamma}$ are relaxation time and the shear rate, respectively, $p$ is an exponent and $\tau_x$ is the apparent yield stress. Recent results by Chamberlain and Rao (1999) have confirmed that this parameter compares favourably with more traditional estimates of the yield stress, such as that due to Casson (Lapasin & Pricl, 1995).

Guar galactomannan polymer chains are known to exist in solution as fluctuating 'random coils' which, at a sufficiently high molecular weight and concentration, display entanglement behaviour (Richardson & Ross-Murphy, 1987; Robinson, Ross-Murphy & Morris, 1982). Such entanglements produce an enhancement of the viscosity of the solution (Doi & Edwards, 1986; Ferry, 1980).

Dietary non-starch polysaccharides (NSP), such as guar galactomannan, are of a particular interest to nutritionists since they have significant effects on the physical properties of digesta within the gastrointestinal (GI) tract (Ellis & Morris, 1991; Ellis, Rayment & Wang, 1996). Much research has shown that the majority of the functional properties of water-soluble NSP (s-NSP) depend on their capacity to hydrate rapidly and increase viscosity in the upper gut postprandially. A number of factors will influence the behaviour of guar galactomannan in the gut. One critical factor is the contribution made by particulate components to the viscosity of digesta, which will depend on the size and shape of the particulates. Therefore, to enhance our understanding of the physical properties of digesta it is important to study model entanglement systems filled with particulates, although in vivo other mechanisms such as gastrointestinal motility and fluid secretion and absorption play a crucial role.

A number of workers have studied systems filled with spherical particles (Landel, 1958; Metzner, 1985; Poslinski, Ryan, Gupta, Seshadri & Frechette, 1988; Richardson &

☆ Presented in part at the International Hydrocolloids Conference, Sydney, 1996.

* Corresponding author. Tel.: + 44-20-7848-4081; fax: + 44-20-7848-4082.

*E-mail address:* simon.ross-murphy@kcl.ac.uk (S.B. Ross-Murphy).


PII: S0144-8617(99)00203-9

Ross-Murphy, 1987). The effects of more anisotropic or 'rod-like' particles have been less well studied however, although the work by Kitano, Kataoka and Shirota (1981) is noteworthy. When a system is filled with non-spherical particles, the type and degree of orientation of the particles can have a substantial effect on the rheological behaviour (Chow, 1980; Metzner, 1985). As the filler concentration is increased particle–particle interaction is of paramount importance. The microcrystalline cellulose samples described in this paper provide an essential insight into the behaviour of anisotropic soft filler phases in a biopolymer solution and contrasts with the (more) isotropic guar galactomannan/rice starch system which has been described previously (Rayment et al., 1995) by the Eilers (2) and Landel (3) equations. These equations are generally written in terms of the relative packing fraction ($\phi'$), which can be modified according to the size and shape of the particle in question.

$$\eta = \eta/\eta_s = [1 + 3\phi'/(4(1 - \phi')]^2 \quad (2)$$

$$\eta_r = (1 - \phi')]^{5/2} \quad (3)$$

The use of such equations to describe the behaviour of anisotropic particles will be presented in this paper and compared, albeit briefly, to that of more isotropic 'spherical' filler systems.

A number of workers have studied the non-Newtonian flow behaviour of clay suspensions and have described the tendency of such systems to flocculate due to associative forces between the particles in the suspension (Hunter & Nicol, 1968). The relevance of these types of studies has been acknowledged and the processes involved in the proposed sedimentation of particles within our system will be discussed.

## 2. Materials and methods

A guar gum sample (Meyprogat 90, intrinsic viscosity 10.5 dl $g^{-1}$) was kindly donated by Meyhall Chemicals A.G., Switzerland. The method for extraction, purification and characterisation of galactomannan is described in detail by Rayment et al. (1995).

Guar gum solutions were prepared by dissolving known weights of the purified sample in distilled water to give nominal galactomannan concentrations of 1 and 2% (w/w), respectively. The solutions were heated to 80°C for 5 min followed by continuous stirring at room temperature overnight to ensure complete hydration of the polymer.

A microcrystalline cellulose (MCC) sample (Vivacel 20) was kindly donated by Allchem International Ltd (J. Rettenmaier & Söhne GmbH, Germany). The manufacturers specifications gave an average particle size of 25 μm. In contrast to most commercial microcrystalline cellulose samples, this is free of added sodium carboxymethylcellulose dispersant. Experience showed that the sample was very difficult to disperse adequately in the guar galactomannan solutions. Therefore, the MCC sample was initially dispersed in distilled water on a magnetic stirrer for approximately 1 h. The purified guar galactomannan sample was then added to this dispersion and left overnight with continuous stirring to allow hydration to occur. The final Vivacel 20 concentrations ranged from 0 to 26% (w/w).

### 2.1. Steady shear rheological measurements

Experiments were performed at 25°C using the Rheometrics Fluids Spectrometer (RFSII, Rheometric Scientific Inc., USA) with a 25 mm diameter parallel plate configuration and a 1 mm gap. The experimental limitation of the relationship between instrument geometry and particle size of filler was highlighted by Rayment et al. (1995). Rice starch has the smallest particle size of commercial starches, whereas the MCC sample has a larger particle size. It was decided that the parallel plate should be used in this case to prevent any disproportionate effect on flow behaviour at the apex of the cone. Therefore, all cone/plate experiments with the guar galactomannan/rice starch mixtures described in Rayment et al. (1995) were repeated using the 25 mm parallel plate with a 1 mm gap to allow direct comparison of results. We considered this to be an essential precursor to the parallel plate studies of MCC. Results from cone/plate and parallel plate experiments were highly reproducible.

The transducer system measured torque in a dual range of 0.002–10 and 0.02–100 g cm, which correspond to a stress range of 0.06–3000 Pa with this geometry. Problems encountered with drying of the samples were reduced by applying a thin layer of a high-viscosity paraffin oil to the exposed surface and the use of a solvent trap. Steady shear measurements were conducted, in the main, at shear rates of 0.05–1000 $s^{-1}$ with a reduction in the rate necessary at the higher filler concentrations. The delay (equilibrium) times between each measurement and measurement times were increased as the filler concentration was increased.

### 2.2. Determination of the density ($\rho$) and maximum packing fraction, $\phi_{max}$ of the filler materials

The densities of the microcrystalline cellulose was originally determined using a specific gravity bottle, and densities were determined in both ethanol (99.7–100% v/v) and distilled water. Values obtained were then verified using a Beckman Air Comparison Pycnometer Model 930 (Beckman Instruments, Inc., USA).

The density of the microcrystalline cellulose sample was determined as $1.617 \pm 0.006$ gm $l^{-1}$ using the air comparison pycnometer and $1.516 \pm 0.093$ gm $l^{-1}$ using the specific gravity bottle. The difference presumably reflects the small voids, which remain unfilled due to capillary forces. Corresponding values for the rice starch were $1.571 \pm 0.003$ and $1.499 \pm 0.058$ gm $l^{-1}$, respectively. In both cases it was assumed that the latter value would best

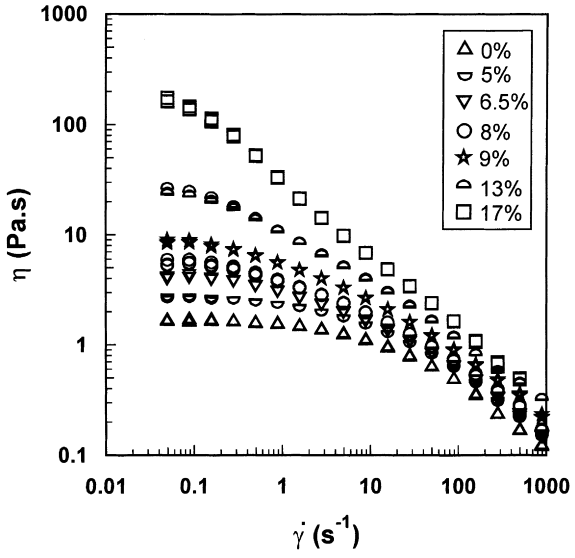


Fig. 1. Effect of increasing MCC (Vivacel 20) concentration on the viscosity-shear rate flow curve of a 1% (w/w) guar galactomannan solution. Duplicate data are displayed to show good replication of results.

describe the particles under experimental conditions and this value was subsequently taken for maximum packing ($\phi_{max}$) determination (Rayment et al., 1995). The water continuous to water-discontinuous 'phase transition' occurred at 36.8% by weight of MCC and therefore $\phi_{max}$ was determined as 0.28, which contrasts with $\phi_{max} \backsim 0.46$ for the rice starch, and reflects its greater anisotropy (Kitano et al., 1981).

### 2.3. Determination of particle size of the filler materials

#### 2.3.1. Microscopy

Both light and scanning electron microscopy were used to visualise the MCC samples. Full details and relevant images are given in Rayment (1996).

#### 2.3.2. Light scattering

The particle size of the filler materials was determined using a Malvern Diffraction Particle Sizer (focal length = 100 mm). A parallel, monochromatic beam of light (beam length = 14.3 mm) was produced by a low-power visible laser transmitter (wavelength = 633 nm). Approximately 0.5 g of each sample was sonicated in 10 ml absolute butan-1-ol for 10 min to disperse the sample evenly. The sample cell was cleaned thoroughly before use and filled with butanol. The instrument was set to zero using the solvent to establish a baseline. Approximately 2–3 drops of the sample mixture were dropped into the cell so that obscuration values fell in the range 0.15–0.2. Malvern's own non-linear least squares analysis was used to find the size distribution best fitting the diffraction pattern.

## 3. Results

The yield of purified guar galactomannan polymer extracted from the guar flour was 56 g/100 g (w/w). The moisture content was determined as 5.58 ± 0.57%. The proportions of soluble galactose and mannose residues were determined as 92.7 ± 2.3% on a wet weight basis. The ratio of galactose to mannose was 0.63 ± 0.025. This is similar to results produced by Robinson et al. (1982). The intrinsic viscosity, $[\eta]$ was determined as 10.5 dl $g^{-1}$ by extrapolation of $\eta_{sp}/C$ and $\ln \eta_r/C$ plots to zero $C$. The molecular weight of the guar galactomannan was estimated as $1.39 \times 10^6$ using the Mark–Houwink (M–H) relationship (Robinson et al., 1982). This is slightly lower than the value determined using the parameters of Beer and co-workers (Beer, Wood & Weisz, 1999) who obtained a similar M–H plot. Here, the molecular weight was determined as $1.86 \times 10^6$. The critical overlap concentration ($C_{cr}$) was calculated to be 0.24% (polymer concentration) from a double log plot of specific viscosity against the coil overlap parameter and $C^*$ determined simply as $1/[\eta] \approx 0.1\%$. Similar to other polysaccharides (Lapasin & Pricl, 1995) for $\eta_{sp} < 10$, $\eta_{sp} \approx C^{1.1}$, whereas for $\eta_{sp} > 10$, $\eta_{sp} \approx C^{4.3}$. The ratio $C_{cr}/C^*$ was $\backsim$2.4. This is close to the value reported by Robinson et al. (1982) for other guar gum solutions.

Fig. 1 shows the effect of increasing MCC concentration on the typical shear-thinning behaviour of a 1% guar galactomannan solution. The Newtonian plateau displayed at low-shear rates with low filler concentration is replaced by a more power-law behaviour as filler concentration is increased. However, this does appear to be slightly different to the behaviour shown with rice starch inclusions (Rayment et al., 1995). In Fig. 1, all the viscosity-shear rate profiles appear to 'flatten off' at low-shear rates, even at the higher filler concentration, whereas in the rice starch systems asymptotic yield stress behaviour was seen.

### 3.1. Effect of increasing/decreasing shear rates

Further steady shear experiments undertaken with the MCC filled guar galactomannan solutions revealed peculiar flow characteristics. It appeared that the way in which the test was undertaken, with respect to starting at a low-shear rate and increasing the rate or starting at a high-shear rate and reducing the rate, significantly affected the flow profiles. This ascending or descending shear rate test is described as 'direction of the test' in the ensuing discussion. Fig. 2(a) and (b) shows the effect of direction of the test on the viscosity-shear rate flow curves of a 1% guar galactomannan/17% MCC mixture. In Fig. 2(a) the test is undertaken from a low-shear rate to a high-shear rate and then reversed with the same sample loading. In Fig. 2(b) the test is carried out from a high-shear rate to a low-shear rate and reversed. There appears to be a greater difference in the viscosity profiles of the sample run from a low- to high-shear rate

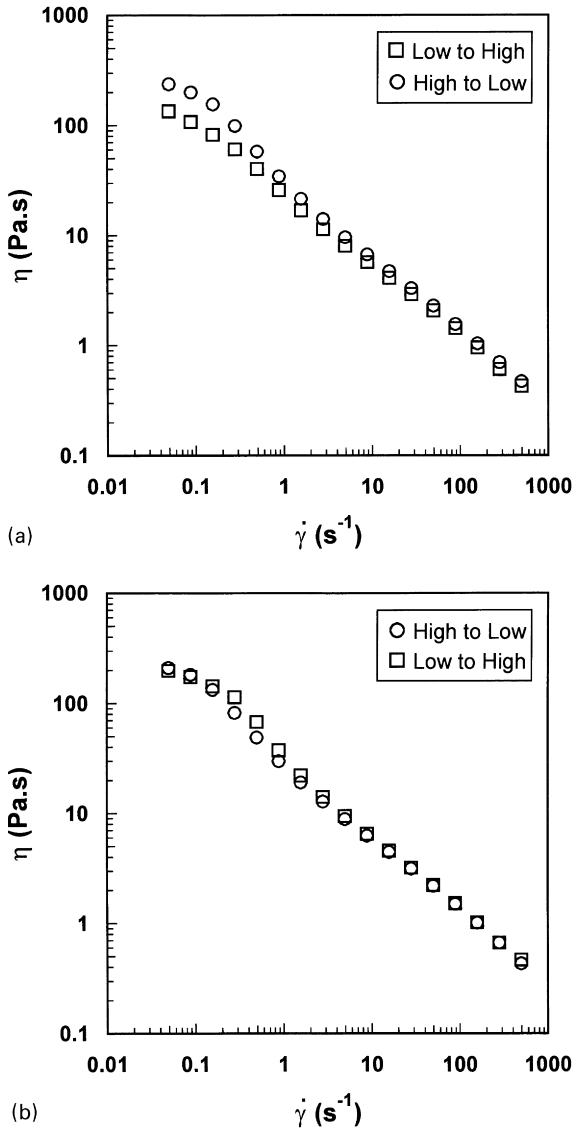


Fig. 2. Effect of direction of test on the viscosity-shear rate flow curves of a 1% guar galactomannan/17% MCC mixture: (a) low- to high-shear rate then high- to low-shear rate; and (b) high-to low-shear rate then low- to high-shear rate. Each test (a) and (b) was carried out on the same sample loading. 'Low' and 'High' represent low- and high-shear rates, respectively.

then reversed (Fig. 2(a)). It is possible that the high-shear rates generated in the initial rate sweep affected the MCC when the test is reversed. The test run from a high- to low-shear rate produced unusual viscosity-shear rate flow curves. There appears to be a 'trough' in the data at the middle shear rate regime. The direction of shear rate change does not appear to have such a pronounced effect on the results. These results may be due to sedimentation of the MCC particles in the guar galactomannan solution. However, elevated viscosities are produced when the test is performed from a high-shear rate to a low-shear rate (Fig. 2(a)). This may be due to the high-shear rates increasing the proportion of particles suspended. When the experiment is

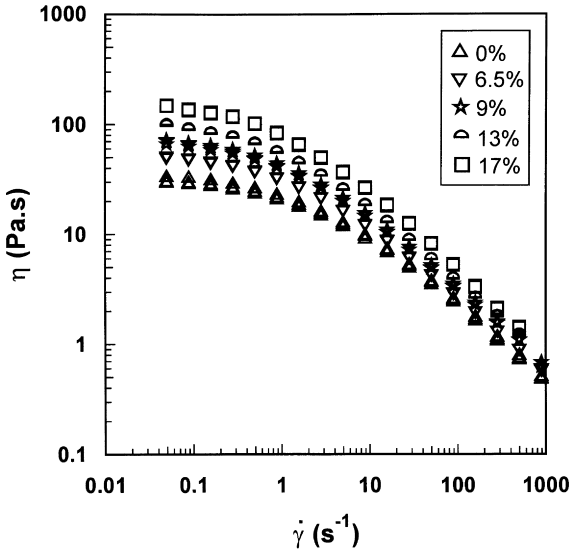


Fig. 3. Viscosity-shear rate flow curves for a 2% guar galactomannan/MCC mixture tested from a low-shear rate to a high-shear rate.

carried out at a low-shear rate to a high-shear rate the MCC particles may actually become suspended during the progression of the test to high-shear rates.

The 1% guar galactomannan solutions filled with 17% MCC produced an obvious 'power-law' behaviour during the steady shear tests. In general, more problems were encountered with drying out of the samples and particle–particle association at high filler concentration. In subsequent tests, a mixture of lower volume fraction was used, namely a 1% guar galactomannan/14% MCC system.

### 3.2. Direction of shear rotation

Another factor that must be considered is the actual direction of rotation of the fixture during the experiment. All previous experiments have been undertaken with the fixture rotating in two directions per measurement, i.e. the fixture rotates clockwise then anticlockwise per measurement. The current instrument will take a measurement in both directions and then average them. However, it is possible to set the instrument to measure one direction per measurement and, as such, the instrument will measure in a clockwise or anticlockwise direction depending on which is set. Initial observations suggested that the zero-shear viscosity increased and yield stress decreased when two directions per measurement was used regardless of the shear rate test conditions used. A possible explanation for this is the arrangement of the MCC particles between the test plates during flow. This is considered in greater detail in the following discussion.

Experiments were then carried out using a 2% guar galactomannan solution filled with varying concentrations of MCC. The fluids rheometer was fixed to operate with two directions per measurement and shear rate was set from low- to high-shear rates and vice versa.

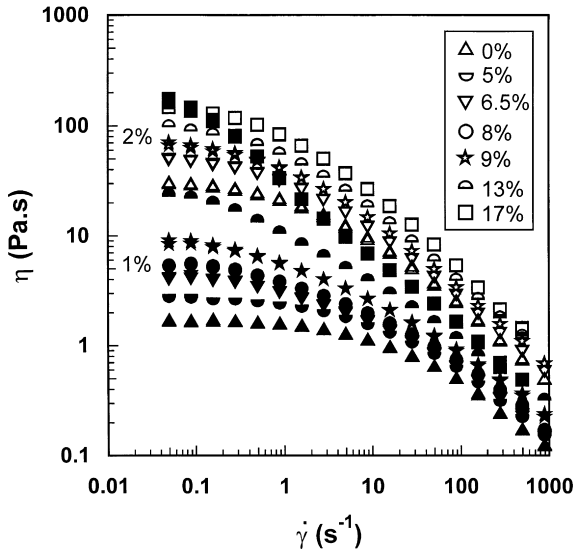


Fig. 4. Viscosity-shear rate flow curves for a 1% (solid symbols) and 2% (open symbols) guar galactomannan solution filled with MCC. Both data sets shown were tested from a low- to a high-shear rate.

Fig. 3 shows the viscosity-shear rate flow curves of a 2% guar galactomannan/MCC mixture tested from a low-shear rate to a high-shear rate. The results are similar to those displayed by the 1% guar filled systems, although the system tends to a more pronounced Newtonian plateau at low-shear rates even for the higher filler concentrations. For the samples tested from a high-shear rate to a low-shear rate results are very comparable (data not shown) with zero-shear viscosities ranging from approximately 30 Pa s for the unfilled system to 180 Pa s for the 17% (w/w) filled system, so the effect of test direction does not appear to be as significant for the 2% guar galactomannan filled system compared to the 1% filled system. This may be due to the overall stabilising effect of guar galactomannan in solution. The filler particles may have stabilised to a greater extent in the solutions of higher galactomannan concentration and thus, prevented from sedimenting.

### *3.3. Effect of guar galactomannan concentration*

Fig. 4 shows the results for both the 1 and 2% guar galactomannan filled systems when testing from a low- to a high-shear rate. The interesting point is that the 1% guar galactomannan/17% MCC (solid square) mixture shows a steep power-law behaviour and produces a measured viscosity above that of the 2% guar galactomannan/MCC mixtures. This may be due to the stabilising effect of increased guar galactomannan concentration, or the reduction of inter-particle interactions at higher solution viscosities (Metzner, 1985). If the MCC filler particle sediments too quickly in the 1% guar galactomannan solutions, this will generate the variable flow curves reported.

All the steady shear data was then fitted to the modified Cross equation using methods described previously (Rayment et al., 1995). The zero-shear viscosity and apparent yield stress parameters calculated were compared for 1 and 2% guar galactomannan/MCC data.

Fig. 5(a) shows the apparent zero-shear viscosity data for both guar galactomannan concentrations plotted against filler concentration. The data is then normalised, by dividing each value by the viscosity of the unfilled system, to show the effects more clearly (Fig. 5(b)).

Fig. 6(a) shows the effect of filler concentration on the apparent yield stress parameter for both guar galactomannan concentrations. Again the data is normalised to negate polymer concentration effect and this is displayed in Fig. 6(b).

Figs. 7 and 8 display the normalised zero-shear viscosity and yield stress respectively, fitted to the Landel and Eilers equation and compared to results for the rice starch filled system. Here, the rice starch and 2% guar galactomannan/MCC data appears to fit the Landel and straight line equation, respectively. The MCC in the 1% guar galactomannan solutions appear to have a more pronounced effect on increasing both the apparent zero-shear viscosity and yield stress parameters.

The particle size of the MCC sample, determined using the Malvern Particle Sizer, was approximately $27.5 \pm 1.5$ μm. This was close to the value of 25 reported by the manufacturer. However, microscope images suggest that the MCC is irregular in size and shape, and the size distribution is bimodal, with a large number fraction of regular 'rod-like' particles, with a length 15–25 μm and a correspondingly small number fraction of heterogeneous more rounded clumps, $\sim 10\times$ as large, many of which appear to be composed of small rod-like particles. We consider the major rheological effects must come from the smaller anisotropic particles, and the value of $\phi_{max}$ supports this. (In principle the sample could have been fractionated, but we were keen to use a sample of interest in applications).

## 4. Discussion

Steady shear experiments of MCC have revealed a number of interesting results. The effect of increasing the MCC concentration on the guar galactomannan network is, at least trivially, similar to that of the rice starch filler. As the amount of filler is increased the mixture becomes more shear rate dependent at lower shear rates. The Newtonian plateau is eventually replaced by a power-law behaviour at the highest filler concentrations. The filler particles appear to 'reinforce' the polymeric network increasing the relaxation time of the filled system.

However, the effect of the particulate inclusions on the rheological properties appears to be more pronounced in the 1% guar galactomannan solutions than in the 2% solutions. It seems that the presence of more galactomannan polymer reduces the effect of the filler properties on the system as a whole. This may be due to a number of reasons. The

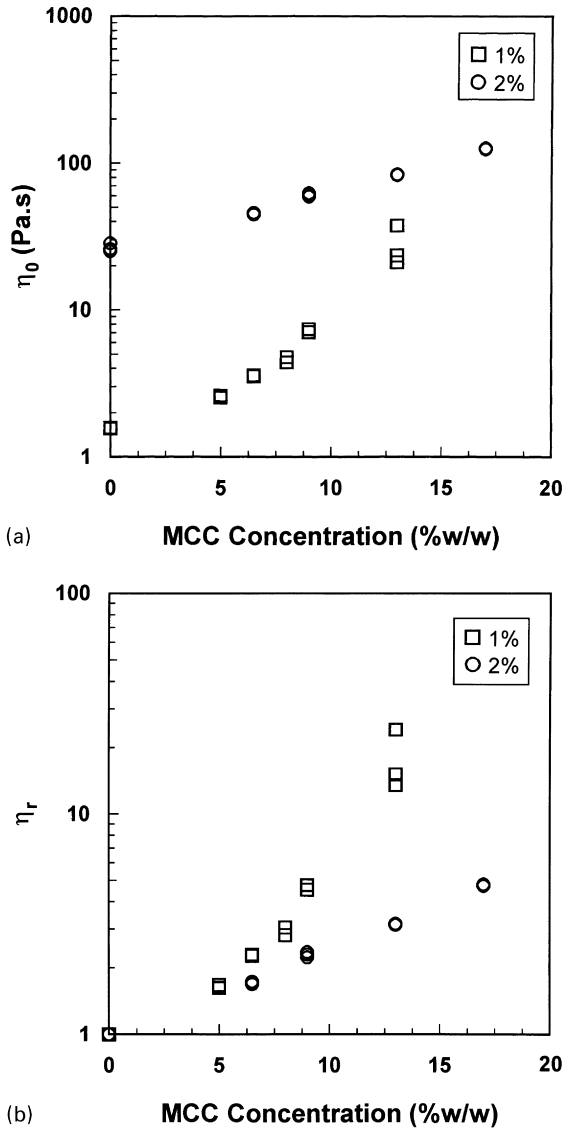


Fig. 5. (a) Relationship between apparent zero-shear viscosity and filler concentration of a 1 and 2% guar galactomannan solution. (b) Effect of filler concentration on the normalised zero-shear viscosity data for a 1 and 2% guar galactomannan solution.

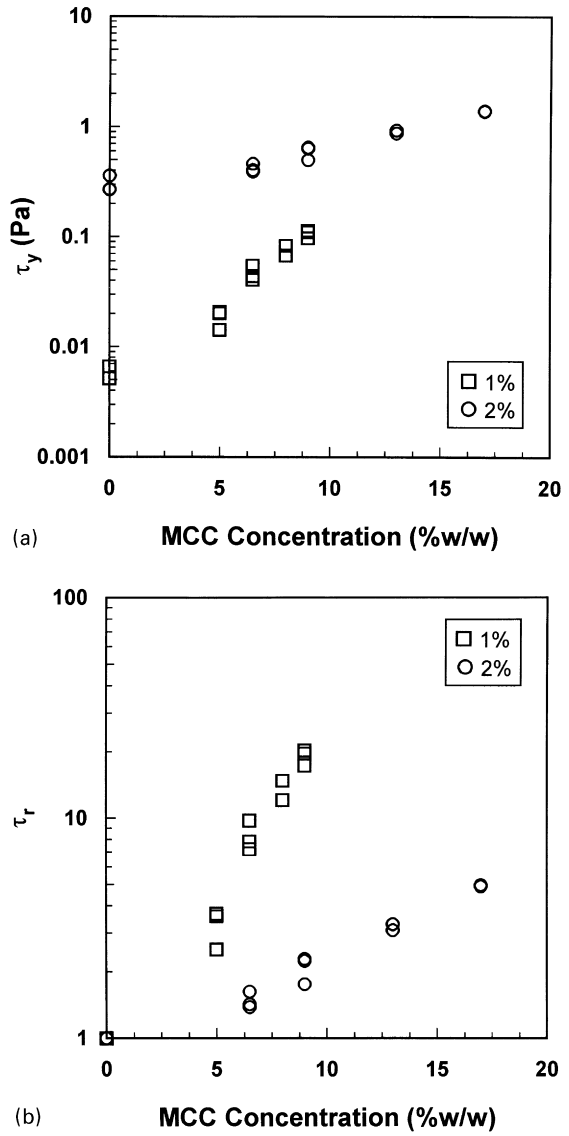


Fig. 6. (a) Relationship between apparent yield stress and filler concentration of a 1 and 2% guar galactomannan solution. (b) Effect of filler concentration on the normalised yield stress data for a 1 and 2% guar galactomannan solution.

preparation method may have resulted in reduced hydration of the galactomannan in the MCC dispersion. This would be more significant with the 2% guar galactomannan mixtures. Also, the sedimentation of the particles in the 1% guar galactomannan solutions appears to be a critical factor in the overall behaviour of the mixed system. The tendency of the 2% guar galactomannan solutions filled with high particulate concentration to a Newtonian plateau at low-shear rates was shown in Fig. 3. It is this behaviour which caused the effect shown in Fig. 7. All the rice starch mixtures produced similar zero-shear viscosity values even when the guar galactomannan concentration was varied from 1 to 3% (Rayment et al., 1995).

We feel that sedimentation is the more likely cause of the abnormal flow behaviours shown during the testing of the MCC-filled 1% guar galactomannan solutions rather than other particle–polymer associations such as depletion flocculation. In depletion flocculation, the attractive forces result from the osmotic pressure of non-absorbing polymer coils (Otsubo, 1996). This process results in phase separation caused by the depletion of polymer from a particle-poor to a particle-rich phase. If this were the case, we should expect the system with the higher polymer concentration to be effected more severely. This is not the case since this system shows greatest adherence to the models (Fig. 7). As described previously, the rice starch filled guar gum solutions with varying polymer concentration could all be superposed on the same figure, once the data was normalised to negate the polymer concentration effects (Rayment et al., 1995). Sedimentation of the MCC particles

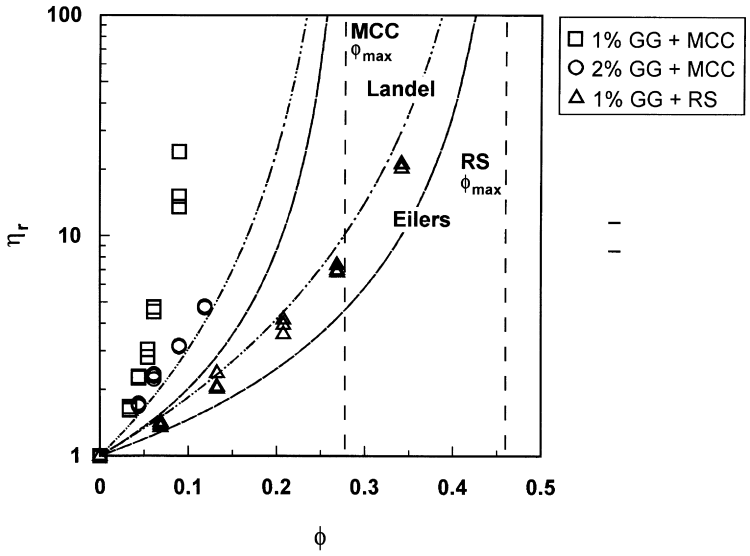


Fig. 7. Log of normalised zero-shear viscosity data for all filler systems fitted to the Landel (dot-dashed line) and Eilers (solid line) formula. The maximum packing fraction ($\phi_{max}$) of the MCC and rice starch system is represented by a dashed line.

in the 1% guar galactomannan solutions could be observed during the preparation and storage of the mixtures and after completion of the test, whilst separating the rheometer test surfaces. The concentration of polymer in the 2% guar galactomannan solution was sufficient to allow stabilisation and suspension of the MCC particles.

The size and shape of the filler particles are of paramount importance, but MCC particles are anisotropic, 'rod-like' in appearance and more heterogeneous than originally thought. A number of equations, relating to volume fraction, have been used to describe the behaviour of these suspensions of particles, but without correction to $\phi_{max}$, these predict the behaviour of spheres. There is a significant increase in zero-shear viscosity when the volume fraction of the filler approaches maximum packing fraction ($\phi_{max}$) (Fig. 7). $\phi_{max}$ of the rice starch was previously determined as 0.46, which is considerably lower than that of ideal spheres. The $\phi_{max}$ of the MCC sample was determined as 0.28. This is much lower than the rice starch which suggests a reduction in close packing produced by the anisotropic rod-like shape. Kitano et al. (1981) have shown that there is a good (negative) linear correlation between the average aspect (length to diameter) ratio (their $\bar{p}$) and $\phi_{max}$. Using $\phi_{max} \approx 0.28$, and Fig. 2 from Kitano et al., we estimate $\bar{\bar{p}} \approx$ 15–20. Inspection of microscope images (Rayment, 1996) suggest that a more realistic value for the smaller, but more numerous MCC fibrils is $\approx$ 8–10, and for the few aggregates, ca 2–3. The Kitano rule was also established using

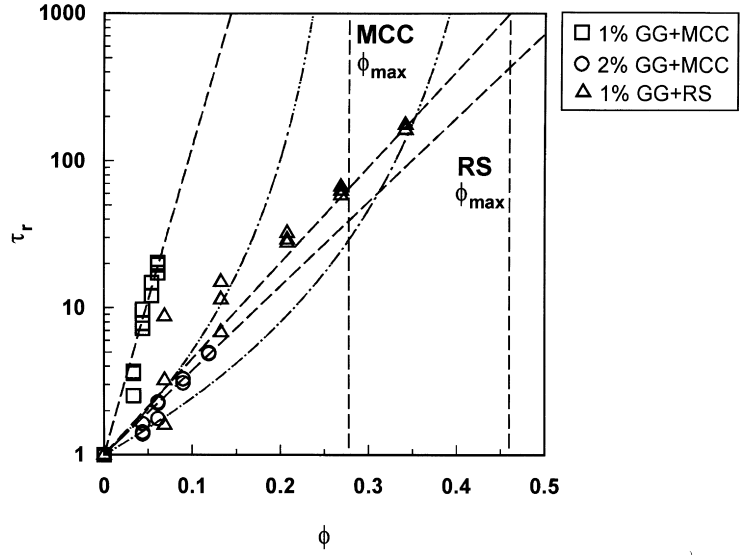


Fig. 8. Log of normalised apparent yield stress data for all filler systems fitted to the Landel (dot-dashed line) and Eilers (solid line) formula. The maximum packing fraction ($\phi_{max}$) of the MCC and rice starch system is represented by a dashed line.

model glass and carbon fibres co-extruded with polyethylene melts, which would encourage high alignment and, in turn, tend to increase the apparent $\phi_{max}$ relative to that for randomly oriented particles.

Ring and Stainsby (1982) considered the effect of volume fraction by the Kerner equation. However, they did not consider the association of water between the system constituents. The SEM was performed with a dry MCC sample so any swelling through the absorption of water is prevented. However, the mean particle size determined by the light and scanning microscopes was similar, which suggests that little absorption of water actually occurred. Recent work by Abdulmola, Hember, Richardson and Morris (1996) has shown solvent partition between gelatinised starch–gelatin phases to be important. The rice starch granules used in this work have not been gelatinised and therefore may explain the good superposition of data in this case (Fig. 7). The apparent $\phi_{max}$ is calculated on the basis that there is a distinction between filler phase and dispersant. This would not be true if swelling and water absorption took place. In our work, particle size determinations carried out using wet and dry filler samples suggests absorption of moisture is minimal.

During the test in which the fixture is rotated in two directions per measurement it can be assumed that the size and shape of MCC particles will greatly affect flow conditions. The 'rod-like' particles may begin to tessellate and 'line up' in the same direction during the test and when the direction is altered mid-test, this alignment is destroyed. The particles then may be forced to associate with their neighbours and particle–particle interactions dominate flow behaviour. This may explain the elevated apparent zero-shear viscosity values encountered in the two directions per measurement test. Such effects would be reduced as the viscosity of the medium is increased, as observed on passing from 1 to 2% guar solutions.

## 5. Conclusions

The apparent zero-shear viscosity and yield stress parameters determined for 1 and 2% guar galactomannan filled MCC systems have been studied. Sedimentation is a critical issue and at 1% guar galactomannan concentrations this can be seen quite clearly when removing the test plates after completion of the experiment. Particle interactions and topological arrangement between the fixture during the test are also critical with an anisotropic system. Chow (1980); Kitano et al. (1981) illustrated the effect of anisotropic particle shape on the mechanical properties of polymeric composites. The extent of water absorption and swelling appear not to play such an important role in this system but should be appreciated. All these points are quite critical in applications involving MCC in practical systems, but we surmise few, if any, of these factors have been considered.

## Acknowledgements

PR acknowledges the receipt of a Ministry of Agriculture, Fisheries and Food studentship and Leatherhead Food Research Association for their collaboration and financial support. The authors also acknowledge the support of the BBSRC for the purchase of the Rheometrics Fluids Spectrometer (F01033). We are grateful to the late Prof. Iain Dea of Quest International and Prof. Paul Luckham of the Department of Chemical Engineering, Imperial College, London for invaluable discussions. We are also indebted to a referee for suggesting the Kitano and Metzner references.

## References

Abdulmola, N., Hember, M. W. N., Richardson, R. K., & Morris, E. R. (1996). Application of polymer blending laws to starch–gelatin composites. *Carbohydrate Polymers*, *31*, 53–63.

Beer, M. U., Wood, P. J., & Weisz, J. (1999). A simple and rapid method for evaluation of Mark–Houwink–Sakurada constants of linear random coil polysaccharides using molecular weight and intrinsic viscosity determined by high performance size exclusion chromatography: application to guar galactomannan. *Carbohydrate Polymers*, *39*, 377–380.

Chamberlain, E. K., & Rao, M. A. (1999). Rheological properties of acid converted waxy maize starches in water and 90% DMSO/ 10% water. *Carbohydrate Polymers*, *40*, 251–260.

Chow, T. S. (1980). The effect of particle shape on the mechanical properties of filled polymers. *Journal of Materials Science*, *15*, 1873–1888.

Cross, M. M. (1965). Rheology of non-Newtonian fluids: a new flow equation for pseudoplastic systems. *Journal of Colloid Science*, *20*, 417–437.

Dea, I. C. M., & Morrison, A. (1975). Chemistry and interactions of seed galactomannans. *Advances in Carbohydrate Chemistry and Biochemistry*, *31*, 241–312.

Doi, M., & Edwards, S. F. (1986). *The theory of polymer dynamics*, Oxford, UK: Clarendon Press.

Ellis, P. R., & Morris, E. R. (1991). Importance of the rate of hydration of pharmaceutical preparations of guar gum: a new in vitro monitoring method. *Diabetic Medicine*, *8*, 378–381.

Ellis, P. R., Rayment, P., & Wang, Q. (1996). A physico-chemical perspective of plant polysaccharides in relation to glucose absorption, insulin secretion and the entero-insular axis. *Proceedings of the Nutrition Society*, *55*, 881–898.

Ferry, J. D. (1980). *Viscoelastic properties of polymers*, (3rd edition). New York: Wiley.

Hunter, R. J., & Nicol, S. K. (1968). The dependence of plastic flow behaviour of clay suspensions on surface properties. *Journal of Colloid and Interface Science*, *28*, 250–259.

Kitano, T., Kataoka, T., & Shirota, T. (1981). An empirical equation of the relative viscosity of polymer melts filled with various inorganic fillers. *Rheologica Acta*, *20*, 207–209.

Landel, R. F. (1958). The dynamic mechanical properties of a model filled system; polyisobutylene–glass beads. *Transactions of the Society of Rheology*, *2*, 53–75.

Lapasin, R., & Pricl, S. (1995). *Rheology of industrial polysaccharides—theory and applications*, . London: Blackie Academic and Professional.

Metzner, A. B. (1985). Rheology of suspensions in polymeric liquids. *Journal of Rheology*, *29*, 739–775.

Otsubo, Y. (1996). Flocculation of colloids by soluble polymers and its effect on rheology. *Heterogeneous Chemistry Reviews*, *3* (4), 327–349.

Poslinski, A. J., Ryan, M. E., Gupta, R. K., Seshadri, S. G., & Frechette, F.

J. (1988). Rheological behaviour of filled polymeric systems. I. Yield stress and shear-thinning effects. *Journal of Rheology*, *32* (7), 703–735.

Rayment, P. (1996). PhD thesis, University of London.

Rayment, P., Ross-Murphy, S. B., & Ellis, P. R. (1995). Rheological properties of guar galactomannan and rice starch mixtures—I. Steady shear measurements. *Carbohydrate Polymers*, *28*, 121–130.

Rayment, P., Ross-Murphy, S. B., & Ellis, P. R. (1998). Rheology of guar galactomannan/rice starch mixtures—II. Creep Measurements. *Carbohydrate Polymers*, *35*, 55–63.

Richardson, R. K., & Ross-Murphy, S. B. (1987). Non-linear viscoelasticity of polysaccharide solutions. 1. Guar galactomannan solutions. *International Journal of Biological Macromolecules*, *9*, 249–312.

Ring, S., & Stainsby, G. (1982). Filler reinforcement of gels. In G. O. Phillips, P. A. Williams & D. J. Wedlock, *Gums and stabilisers for the food industry: Proceedings of Food and Nutrition Science* (pp. 323–329). vol. 6. Oxford: Oxford University Press.

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.