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Rheological properties of guar galactomannan and rice starch mixtures—
I. Steady shear measurements

Phillippa Rayment, Simon B. Ross-Murphy* & Peter R. Ellis

Biopolymers Group, Division of Life Sciences, King's College London, Campden Hill Road London, W8 7AH, UK

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The effect of particulate inclusions, or 'fillers', on the rheological properties of a typical polysaccharide entanglement solution (guar galactomannan/water) have been studied. A number of equations have been proposed to describe the shear-thinning behaviour of 'random-coil' polysaccharides such as guar gum. However, on increasing particulate concentration the system becomes more rate-dependent at low shear rates and there is evidence of an apparent yield stress associated with this increase in particulate inclusions. In the present paper, this flow behaviour has been described with reasonable accuracy, by a yield stress modified Cross equation:

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

The use of such a model can lead to a prediction of the rheological behaviour of similar systems when the proportion of the relative components is known. The present study determines the effect of particulate and composite properties on the apparent zero-shear viscosity and yield stress of guar galactomannan and rice starch mixtures.

INTRODUCTION

Guar galactomannan, obtained from the Indian cluster bean *Cyamopsis tetragonoloba (L.)Taub.*, is a water-soluble polysaccharide with an essentially linear β-D-(1→4)-mannan backbone and irregularly substituted, uncharged α-D-(1→6)-linked galactose side groups (Dea & Morrison, 1975). In the present work, aqueous solutions of guar gum, well recognised to be model entanglement network systems (Doublier & Launay, 1981; Robinson *et al.*, 1982; Richardson & Ross-Murphy, 1987), were measured in steady shear. The Cross equation (1) is often used to describe the shear-thinning behaviour of guar gum dispersions (Cross, 1965) and has been used in a number of scientific publications (Sharman *et al.*, 1978; Doublier & Launay, 1981).

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

η_{0X} and η_∞ are limiting (Cross) viscosities, at zero and infinite shear rates, a and $\dot{\gamma}$ are relaxation time and the shear rate, respectively, whilst p is an exponent. Although other equations exist in the literature (Launay *et al.*, 1986) this is, as described by Cross, the simplest possible equation which relates viscosity to the *p*th power of the shear rate and which reduces to η_0 when $\dot{\gamma} = 0$ and to η_∞ when $\dot{\gamma} = \infty$.

However, the effect of particulate material (i.e. filler) on the rheology of an entangled network, such as guar galactomannan solution, has been much less studied. The development of a suitable mathematical model to describe the behaviour of dispersions of a soft filler phase in a biopolymer solution would be of considerable value in studies of food systems. For example, such models would be of fundamental importance in describing the rheological behaviour of water-soluble, non-starch polysaccharide components of plant foods in the gastrointestinal tract of humans and other mammals (Ellis, 1994).

For the current study, a rice starch filler, selected for size and homogeneity of starch grain, was then added to the guar galactomannan solutions in small increments and the system was measured in steady shear. As the amount of filler is increased, we would expect that the dispersion would begin to develop some additional features.

A number of studies have been undertaken to determine the effect of phase volume, size and shape of the filler on the rheological properties of a polymer

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*Author to whom correspondence should be addressed.

network (Landel, 1958; Chow, 1980; Richardson *et al.*, 1981; Ross-Murphy & Todd, 1983). The filler may interact with the polymer and result in a composition that exhibits an increased shear modulus such as the reinforcement of a gelatin gel by swollen pea starch reported by Ring & Stainsby (1982). They showed that the extent of reinforcement depended mainly on the volume fraction of the filler although size and shape were also important factors. The extent of reinforcement is often related to the volume fraction, ϕ, of the filler by Kerner's equation (2):

$$R = (2 + 3\phi)/2(1-\phi) \qquad (2)$$

However, this equation is only applicable when particle interaction forces are reduced, at low filler concentrations, since at higher volume fractions the relative strength of the polymer–particle and the particle–particle interactions dominate the reinforcement.

The simplest model to describe small non-interacting spherical particles in a low viscosity solution is that due to Einstein (3),

$$\eta = \eta_s(1 + K\phi) \qquad (3)$$

where η is the viscosity of the mixture, η_s is the viscosity of the pure solution and K is 2.5 for spheres. However, a number of equations have been proposed to describe the rheological behaviour of mixtures with higher particulate concentrations. The majority of these describe the relative packing fraction, ϕ', which is the volume fraction divided by the maximum packing fraction. Our results will be interpreted using both the Eilers (4) and Landel (5) formulae (Ross-Murphy, 1984), although neither of these equations, in themselves, reflect the non-Newtonian nature of such dispersions since they have no shear rate dependent terms.

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

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

The Landel equation (5) can be generalised by replacing the exponent $-5/2$ by q to give equation (6).

$$\eta_r = (1-\phi')^q \qquad (6)$$

It has been known for some time that one of the major effects of increasing particle volume fraction is to modify the overall shear rate–viscosity profile. For filled Newtonian fluids, a more 'power law' like $\eta(\dot{\gamma})$ profile is seen, with an apparent upswing at the lowest shear rates. This could be related to an apparent yield stress developing at lower (zero) shear rates. However, we are not aware of any work in which the behaviour of small particles in non-Newtonian (pseudoplastic) fluids, such as polysaccharide gum solutions, have been studied rigorously.

Such a system would require, for example, the Cross equation to be modified to include a yield stress term, converting equation (1) to equation (7).

$$\eta = \eta_\infty + [\eta_{0X} - \eta_\infty]/[1 + (a\dot{\gamma})^p] + (\tau_X/\dot{\gamma}) \qquad (7)$$

An 'apparent' yield stress can then be determined by extrapolating the flow data back to zero-shear rate using a mathematical model. Such a yield stress modified Cross equation might be expected to perform with reasonable precision at lower filler concentrations, but perhaps to predict yield stress less reliably at higher filler concentrations. A similar modification has previously been suggested independently by Doublier and co-workers in their studies of certain protein dispersions (Castelain *et al.*, 1986).

MATERIALS AND METHODS

A guar gum sample (Meyprogat 90) was kindly provided by Meyhall Chemicals, A.G., Switzerland (Rhône-Poulenc Group). The sample was purified using a modified isolation procedure devised by Girhammar & Nair (1992). Approximately 10 g of the guar flour was boiled with 40 ml of 70% ethanol for 1 h under reflux. The sample was filtered, washed with 95% ethanol and stored in a dessicator until required. The sample was then hydrated in distilled water at 80°C for 5 min and then cooled to room temperature. The pH was adjusted to 7.5 using 1 M sodium hydroxide. A digestion stage was carried out by adding pancreatin (from porcine pancreatin, Sigma P1750) at a concentration of 20 mg/100 ml extract. Pancreatin contains many enzymes, including those with amylase, lipase and protease activity. Sodium azide was then added to inhibit microbial activity and the pH was adjusted to 7.5 if necessary. The aqueous sample was then incubated at 34°C overnight on a mechanical shaker (Gallenkamp Orbital Incubator) to allow enzyme digestion and complete hydration of the polymer to occur. The solution was centrifuged at 6500 g for 20 min (MSE High Speed 18). The supernatant was removed and precipitated by mixing the sample with absolute alcohol to give a final concentration of 80% ethanol. The precipitated polymer was filtered and freeze-dried (Edwards Freeze Dryer Super Modulyo) for 24 h under a nitrogen atmosphere.

Relative proportions of mannose and galactose were determined by acid hydrolysis and gas chromatography of the alditol acetates (Englyst *et al.*, 1992). Two portions, (a) and (b), of each test sample are required to obtain separate values for total and water insoluble non-starch polysaccharides (NSP), respectively. Water soluble NSP is determined as the difference. The insoluble fraction was hydrated overnight in phosphate buffer, as opposed to the 40 min suggested by Englyst *et al.* (1992), in order to allow complete hydration of any soluble NSP. This method produced a significantly lower concentration of insoluble NSP than the standard technique. The acid hydrolysates produced were derivatised to alditol acetates and analysed by gas chromatography using a fused silica, bonded phase column (SGE Code: 12QC3/BPX70 (very polar) 0.2). The uronic acid content was determined by a sulphuric acid–dimethylphenol colorimetric assay.

At low polymer concentrations, zero-shear viscosity (η_0) increases linearly with increasing concentration in a double logarithmic plot. However, above a certain concentration there is a marked increase in the gradient of this plot. Here individual macromolecules so interpenetrate each others' domains that there is a rather sudden change in flow properties, exemplified by more pronounced increases in both the zero-shear viscosity and shear rate dependence of viscosity. It is now accepted that the concentration at which polymer coils totally fill the available volume is denoted C^*, here defined as $1/[\eta]$. Concentrations below C^* are termed 'dilute', and those well above C^* are termed 'semi-dilute' As is well known, in the dilute regime, and in steady shear measurements, specific viscosity $\eta\text{sp}\approx C^{1-1.5}$, whereas when $C[\eta] > \sim 10$, well into the semi-dilute or entangled regime, $\eta\text{sp}\approx C^{3.5-5}$ (Ross-Murphy, 1994; Chapter 7). The transition in viscosity slope occurs at a concentration, Ccr where $C\text{cr}\sim 2\text{–}8\ C^*$.

The intrinsic viscosity was determined by dilute solution viscometry using a Cannon Ubbelohde Dilution B glass viscometer (Size 50, 0.8–4.0 cSt; Glass Artefact (Viscometers), UK) suspended in a constant temperature water bath at 25±0.05°C. The molecular weight was calculated from the Mark–Houwink equation using K' and α values from Robinson *et al.* (1982). The critical overlap concentration (Ccr) was determined from the variation of specific viscosity with degree of coil overlap, characterised by $c[\eta]$, in a double log plot.

Guar gum solutions were prepared by dissolving a known weight of the dried material in distilled water to give nominal polymer concentrations of 1, 2 and 3%, respectively. The solutions were heated to 80°C for 5 min followed by stirring at room temperature overnight to ensure complete hydration of the polymer. An insoluble, cosmetic rice starch sample was kindly provided by Cairn Foods (Remy Industries, S.A., Belgium). The rice starch was then added to the guar solutions so that the galactomannan concentration in the aqueous medium was kept constant while the starch filler concentration was varied from 0 to 41% (w/w).

Steady shear rheological measurements

Experiments were performed at 25°C using a Rheometrics Fluids Spectrometer (RFSII, Rheometrics Inc., USA) with a 25 mm diameter cone and plate configuration and a cone angle of 0.02 radians. The transducer system measured torque in a dual range of 0.002–10 g.cm and 0.02–100 g.cm, which correspond to a stress range of 0.006–300 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 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. This allowed for relaxation in the more complex polymer–filler matrix which was produced on increasing the particulate inclusion concentration.

One experimental limitation in this area is the relationship between instrument geometry and particle size of filler in the test solution. For steady shear measurements it is obligatory to employ cone and plate geometry since the shear rate approaches constancy throughout the sample. However, the truncation of the cone tip is usually very small ($\approx 50\,\mu$m) and, as rule of thumb, the particle size should be $<\approx 1/5$ of the gap truncation. However, it is not clear that some earlier workers have appreciated this limitation. This is one of the main reasons we have employed rice starch, which has the smallest particle size of commercial starches, in the present study.

Determination of the density (ρ) of the rice starch

The density of the rice starch was determined using a specific gravity bottle. The density was determined in ethanol and water, giving values of 1.571 and 1.432±0.005 g ml^{-1}, respectively. The relative density of the rice starch particles in water was the value utilised for further calculations.

Determination of the maximum packing fraction, $\phi_{\max}$

A 40% (w/w) solution of rice starch in distilled water was taken and rice starch was added until it could no longer be wetted. The transition from a smooth paste (water continuous) to a water discontinuous powdery system occurred over quite a narrow range of added starch powder. $\phi_{\max}$ was calculated using the density value 1.432 g ml^{-1} given above.

Determination of particle size of rice starch granules by microscopy

The rice starch was dispersed on a microscope slide in a 1:1 (v/v) glycerol–water mixture to minimise evaporation and granule movement during observation. The starch granules were dispersed uniformly by applying pressure to a coverslip but care was taken to prevent fracturing and maintain granule integrity. The rice starch sample was observed under a light microscope (Leitz DIALUX 22 EB) at a magnification of ×400. The starch granules were photographed using a Wild Photoautomat MPS45 camera system and an exposure time of 1/30 s (Ilford 100 Delta DX135 24 film). An estimate of particle size was made.

RESULTS

The soluble galactose and mannose content of purified guar gum was found to be 92.7±2.3%. The ratio of galactose to mannose was 0.63±0.025. There were other sugars present, which we believe to be a contamination, such as arabinose and glucose amounting to 2.68%. It is possible to purify the polymer during the isolation procedure by way of copper complexes (Dea & Morrison, 1975) but the purification process may result in low molecular weights of galactomannans as a result of chain scission.

The intrinsic viscosity, $[\eta]$ was determined as 10.5 dl g^{-1} by extrapolation of $\eta sp/C$ and $\ln \eta r/C$ vs C plots to zero C. The molecular weight of the guar galactomannan was then determined as 1.39×10^6 using the Mark–Houwink relationship. The critical overlap concentration (Ccr) 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 $1/[\eta] \approx 0.1\%$. For $\eta sp < 10$, $\eta sp \approx C^{1.1}$ whereas for $\eta sp > 10$, $\eta_{sp} \approx C^{4.3}$. This is similar to other polysaccharides studied by Morris *et al.* (1981). The ratio Ccr/C^*, defined earlier, was ~2.4. This is close to the value reported by Robinson *et al.* (1982) for other guar gum solutions. The maximum packing fraction ($\phi_{\max}$) of the starch powder was determined as 0.474 (47.4% w/w). The rice starch particle size was found to range between 6–10 μm (Fig. 6), in agreement with published data (Juliano, 1984).

Figure 1 shows the typical shear-thinning behaviour of a pure 1% guar galactomannan solution. Steady shear measurements of such a system show a Newtonian plateau at low shear rates followed by increasing shear rate dependence at high shear rates. At low shear rates, the torque generated is well within the specifications of the transducer used. The shear stress developed in the sample can be seen to be a function of the increasing strain applied. As the amount of filler is increased (Fig. 2), the dispersion begins to develop some additional features. The effect of particulate inclusions in the guar galactomannan/rice starch mixture is, primarily, to increase the steady shear viscosity above that of the pure galactomannan system. The initial Newtonian flow properties of the pure system at low shear rates become more rate-dependent on increasing particulate concentration; the so-called 'power law' behaviour. From the flow data obtained for the rice starch/guar galactomannan mixtures, there was evidence for an extra term, here denoted the yield stress*, especially for the higher concentration range studied.

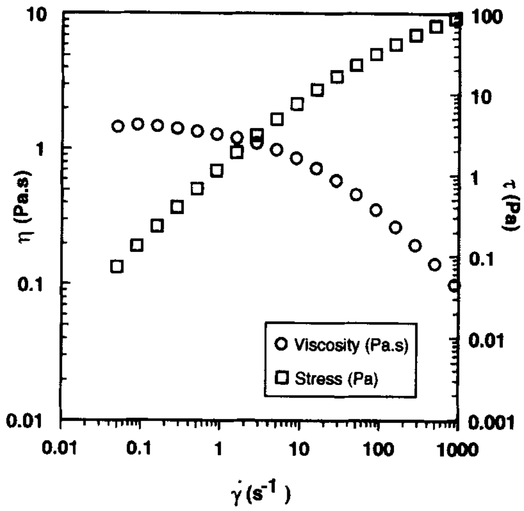

Fig. 1. Shear rate dependence of viscosity (○) and shear stress (□) in a 1% aqueous solution of guar galactomannan.

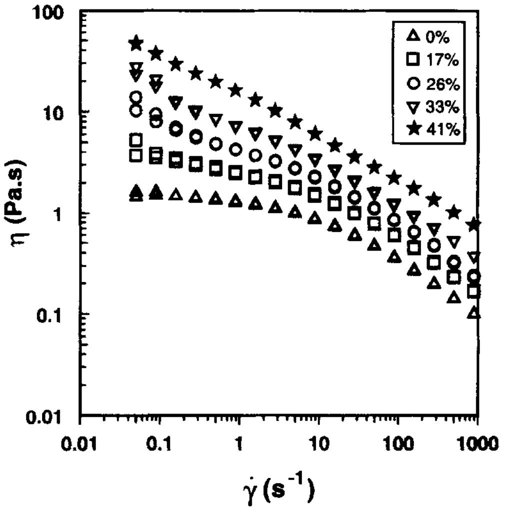

Fig. 2. Effect of increasing rice starch concentration on the viscosity–shear rate flow curve of a 1% guar galactomannan solution. Duplicate data are displayed to show good replication of results.

The yield stress modified Cross equation (7) was used to determine zero-shear viscosity (η_{0x}) and apparent yield stress (τ_x) of all flow data. Least squares fitting to the model was accomplished using Fig P for Windows (Biosoft, Cambridge, UK), which employs a modified Marquardt non-linear search algorithm.

Figure 3a shows the viscosity–shear rate flow data for a 2% guar galactomannan solution with 26%(w/w) rice starch filler interpreted in terms of the yield stress modified Cross equation. The fit obtained was good with a calculated apparent yield stress of 1.52 Pa (the

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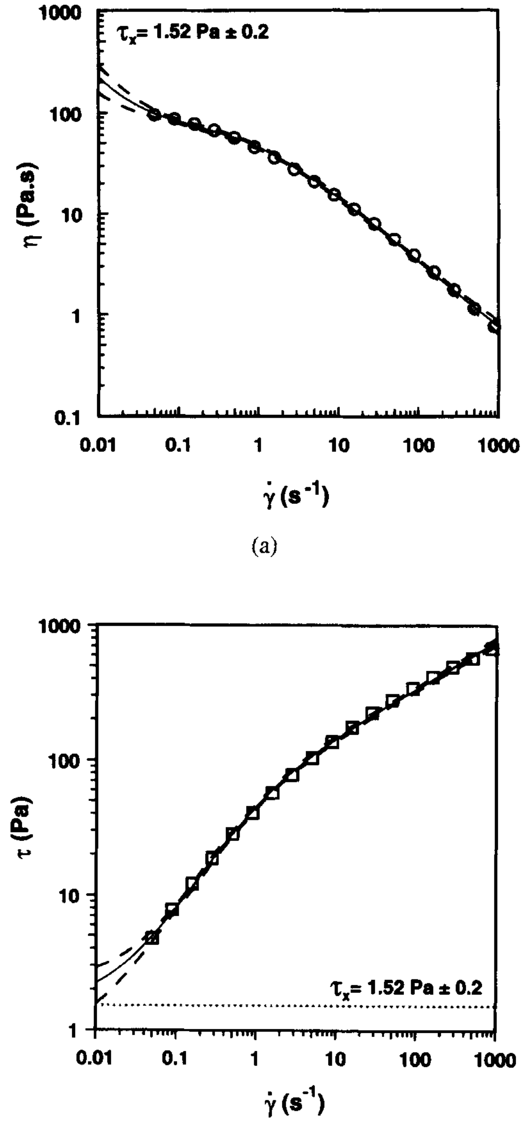
*The yield stress evaluated is a feature of the model employed and its use is not intended to suggest that a real yield stress occurs in this system.



(a)

(b)

Fig. 3. (a) Viscosity–shear rate profile of a 2% guar galactomannan/26% rice starch mixture interpreted in terms of a yield stress modified Cross equation. The dashed line represents 95% confidence limits. (b) As Fig. 3a, but replotted in terms of shear stress and shear rate, to show the apparent yield stress asymptote at low shear rates (see Fig. 1). The dashed line represents 95% confidence interval bounds and the dotted line corresponds to the value of τ_X.

dotted line represents 95% confidence interval bounds). Fig. 3b shows the same data interpreted in a shear stress–shear rate profile. The least squares fitted apparent yield stress was essentially identical to that displayed in Fig. 3a when equation (7) was recast in terms of stress and strain rate. This figure clearly displays the minimum stress measured and, interpreted in terms of the yield stress modified Cross equation, an apparent yield stress value may be determined. The value of the apparent yield stress (τ_X) is indicated by the horizontal line.

Another equation describing shear-thinning behaviour with a yield stress value is the Casson equation (8).

$$\tau^{1/2} = \tau_{CA}{}^{1/2} + \mu_{CA}{}^{1/2}\dot{\gamma}_{CA}{}^{1/2} \qquad (8)$$

where τ_{CA} and μ_{CA} are the Casson yield value and the Casson viscosity, respectively. This equation is often used to interpret rheology in the chocolate industry. The Casson yield value is considered to be an apparent yield stress similar to the Bingham yield value, τ_B. The same data is interpreted in terms of the Casson equation. However, the data points at low shear rates do not fit this equation. The extrapolated Casson yield value is $\tau_{CA} = 14.0$ Pa, whereas a more realistic estimate of yield stress (i.e. the lowest stress at which movement appears to be detected) is approximately 1.52 Pa. The extrapolated Casson yield value obtained is very much higher than the value obtained from the modified Cross equation. In our view this reflects the inadequacy of the Casson model.

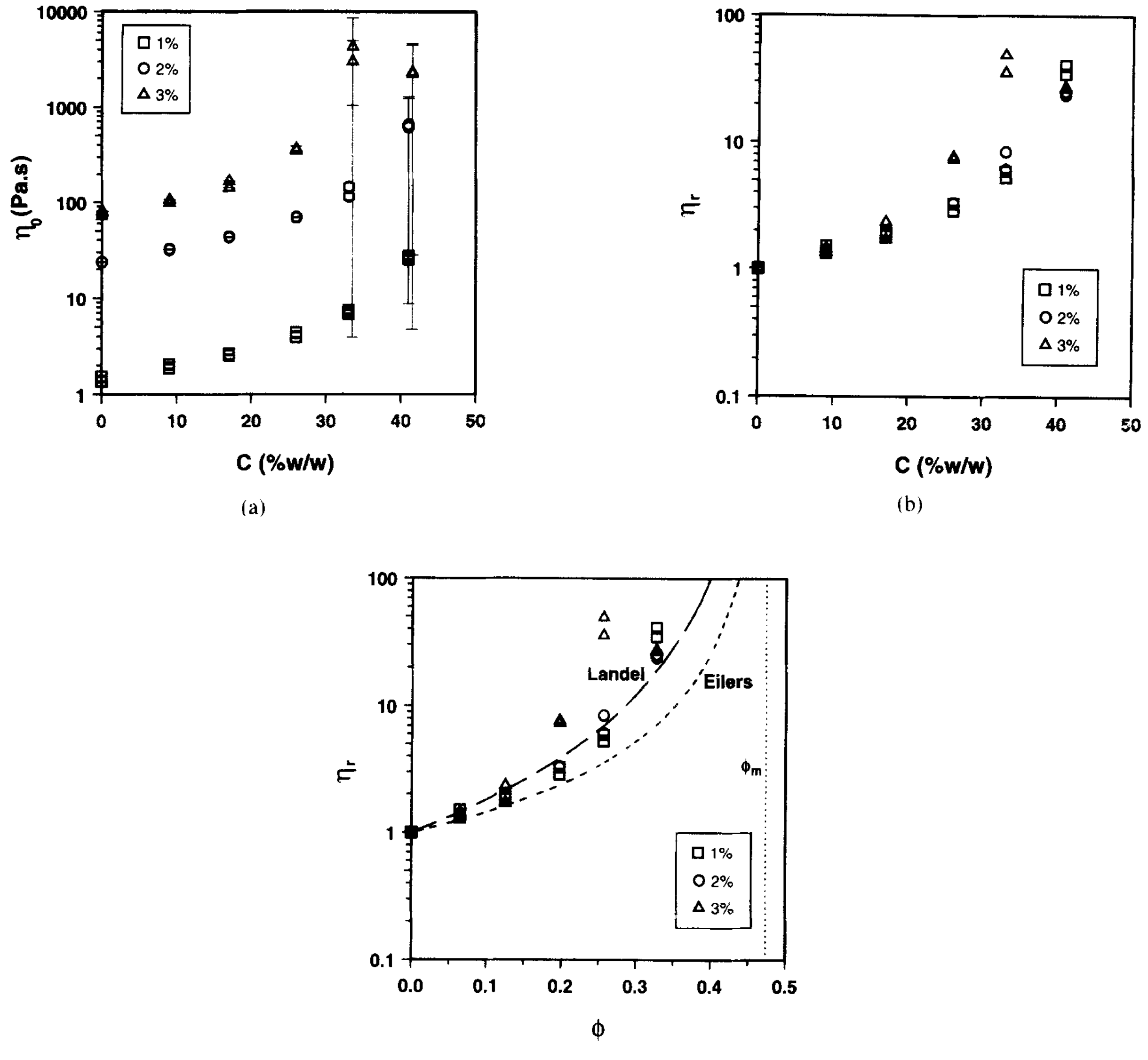
The effect of increasing filler concentration on apparent zero-shear viscosity is displayed in Fig. 4a. The data for all guar galactomannan concentrations studied are shown and the influence of particulate inclusions can be observed easily. The standard error(s) of the mean (SEM) is plotted for the high concentrations of starch filler to show the increasing unreliability of the estimated parameters from the modified Cross equation at the high particulate inclusion end. The SEM calculated for the filler concentrations from 0 to 26% (w/w) were smaller than the SEM between duplicate results and so are not shown.

Figure 5a shows the influence of increasing the concentration of particulate inclusions on the apparent yield stress parameter. The SEM are small at low filler concentrations and become larger at the higher filler concentration regime.

The effect of particulate inclusions on zero-shear viscosity and apparent yield stress is displayed more clearly by normalisation of the data (Figs 4b and 5b).

DISCUSSION

Guar galactomannan solutions are now well recognised to be model entanglement network systems (Morris & Ross-Murphy, 1981; Robinson *et al.*, 1982; Richardson & Ross-Murphy, 1987). Polymeric systems of sufficiently high molecular weight and concentration display entanglement behaviour. Ferry (1980) has described slow system relaxation processes caused by the restriction of movement of molecules in a system due to the close proximity of neighbouring molecules. A number of models have been proposed to describe the movement of molecules in such a system including de Gennes (1971), who introduced the concept of reptation of a polymer chain confined in a ‘tube-like’ region, and

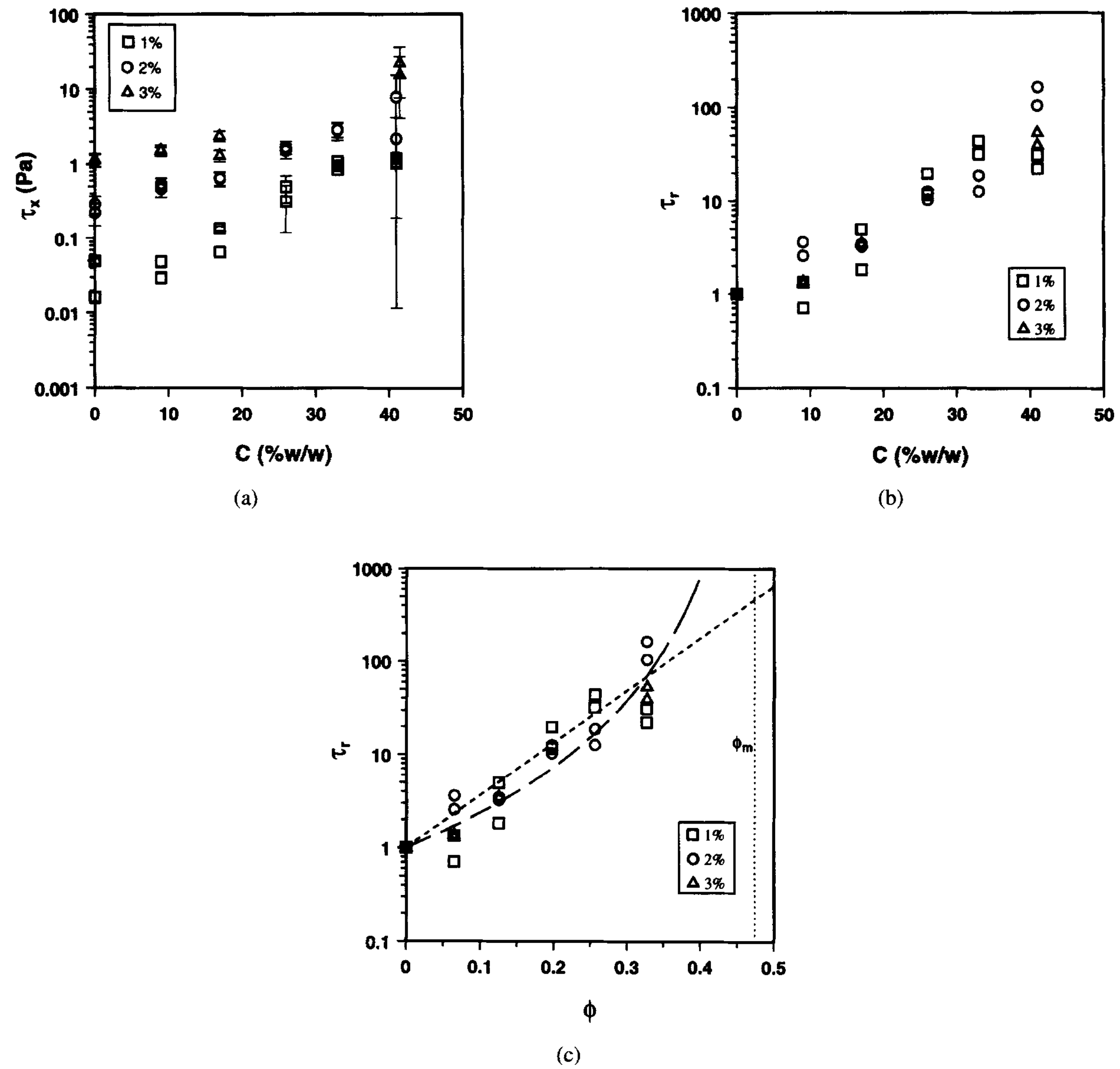


(a) (b) (c)

Fig. 4. (a) Relationship between apparent zero-shear viscosity and starch concentration for all guar galactomannan solutions studied. Data produced demonstrate the filler concentration dependence of zero-shear viscosity. The error bars represent the standard error of the mean (SEM). (b) Effect of starch filler concentration on the normalised zero-shear viscosity data of 1, 2 and 3% guar galactomannan solutions. (c) Log of normalised zero-shear viscosity data fitted to the Landel and Eilers formula. The dotted line represents the ϕ_{max} of the system.

Graessley (1967) who discussed segmental frictional coefficients. Doi & Edwards (1978) also used a 'tube' to mimic the constraints imposed by the surrounding macromolecules and introduced the slip-link network model to describe the molecular motion of concentrated polymeric systems under flow. The longest relaxation time (τ_d) corresponds to the disengagement of the polymer chain from the tube by the reptation process. At low shear rates the polymer chains are free to move though the system unperturbed by their neighbours, i.e. no 'tube' is present. The system has a short relaxation time resulting in no net change in the extent of entanglements and, therefore, no effect on the viscosity of the system. This corresponds to the Newtonian region of the viscosity–shear rate flow curves. However, as the rate of deformation is increased, the polymer chains are 'forced' to associate with their neighbours, i.e. the polymer chain is confined to a 'tube-like' region. Shear-thinning occurs at increased shear rates when the relaxation time of the 'tube' is longer than that of the polymer chain.

The shear-thinning nature of guar galactomannan solutions is well documented (Doublier & Launay, 1981; Morris, 1990; Richardson & Ross-Murphy, 1987) and is displayed in our flow curves of the pure polysaccharide system. However, 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. We suggest that the filler serves to



(a) (b) (c)

Fig. 5. (a) Relationship between apparent yield stress and starch concentration for all guar galactomannan solutions studied. Apparent yield stress data were determined in terms of the yield stress modified Cross equation and demonstrate the concentration dependence of apparent yield stress. The error bars represent the standard error of the mean (SEM). (b) Effect of starch filler concentration on the normalised apparent yield stress data of 1, 2 and 3% guar galactomannan solutions. (c) Log of normalised apparent yield stress data fitted to the modified Landel formula and a straight line equation. The dotted line represents the ϕ_{max} of the system.

reinforce the 'tube' thus increasing the relaxation time of the system.

Our reason for adopting the Cross model as opposed to other viscosity–shear rate equations, such as the Carreau or Suttersby models (Povolo, 1992), is that our own observations (unpublished) agree entirely with the conclusions of Launay *et al.* (1986) that the Cross equation is (statistically) the best empirical model for describing the flow behaviour of semi-dilute polysaccharide solutions.

Although, as already mentioned, there are countless studies of filled Newtonian fluids, there have been relatively few efforts to investigate the behaviour of disperse materials in non-Newtonian materials and these seem to be almost exclusively devoted to studies of essentially spherical particles (glass and TiO_2) in polymer melts. To our knowledge, this paper is the first attempt to relate disperse phase volume to viscosity (and more particularly non-Newtonian viscosity) in such biopolymer solutions. As far as the limited earlier work is concerned, that of Minagawa & White (1976) has attempted to model flow properties using an empirical polynomial expansion in shear rate and volume fraction. The more recent paper by Poslinski *et al.* (1988) is more interesting. In many ways the approach they have adopted is very similar to ours, in that they employ a yield stress modified Bird–Carreau model and relate the apparent viscosity to relative

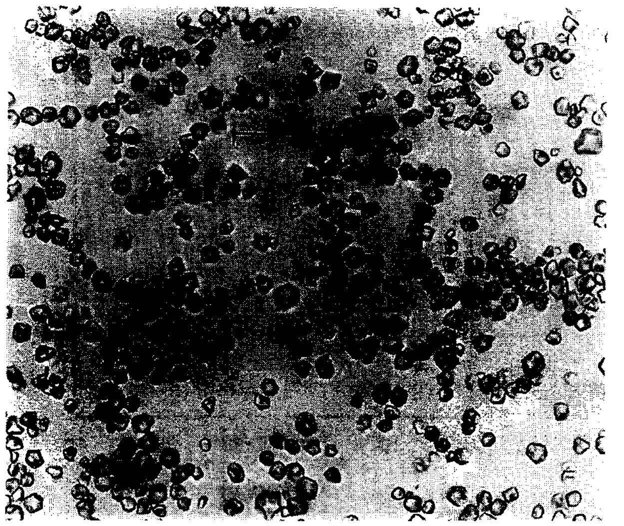


Fig. 6. Light microscopy of rice starch, ×400.

volume fraction. They adopt a semi-empirical model for the apparent yield stress, but this explicitly assumes that the apparent yield stress diverges at maximum packing. It is not clear that this is a realistic assumption and, indeed, we regard this as an open question.

The curvatures of data shown in Fig. 4a for each guar galactomannan solution are similar and, following the approach already suggested by equations (4) and (5), can be displayed more clearly by normalisation of the data (i.e. dividing each value by the viscosity of the unfilled systems (Fig. 4b)). The 1 and 2% guar galactomannan data are superimposable whilst the 3% data only deviate at higher filler concentrations. The normalised zero-shear viscosity can be seen to increase significantly as the filler concentration approaches the maximum packing fraction of the system. We make the reasonable assumption that zero-shear viscosity tends toward infinity and would become too large to measure at a certain critical concentration (volume fraction), i.e.: $\eta_0 \rightarrow \infty$ as $\phi \rightarrow \phi_{\max}$

The normalised zero-shear viscosity data are fitted to the Landel and Eilers formulae (Fig. 4c) using the previously estimated value for maximum packing fraction ($\phi_{\max} = 0.474$). The data give a good fit to the Landel formula with an exponent q of 2.5. Overall the data are in good agreement with the graph of η/η_s plotted against volume fraction of filler, ϕ for the Landel and Eilers equations (Ross-Murphy, 1984). Using this approach we could now predict η_0 for any concentration (above C^*) and at any volume fraction, say $\phi/\phi_{\max} < 0.7$.

Normalisation of the apparent yield stress data produces a superimposable effect of filler concentration for all guar galactomannan concentrations studied (Fig. 5b). However, the occurrence of a yield stress on increasing the filler concentration appears to be more gradual than the effect of filler concentration on zero-shear viscosity. We have attempted to fit the data to a straight line equation and to the modified Landel formula (equation (6)) (Fig. 5c). The data appear to give a reasonable fit to the modified Landel model ($q = 3.63$) although we might not expect the yield stress to diverge at $\phi_{\max}$

It is clear that above $\phi_{\max}$, the zero-shear viscosity must become very large since the disperse and dispersion phases (starch/guar solution) must invert. However, as mentioned earlier, the same is not necessarily true of the apparent yield stress parameter. This aspect appears not to have been addressed before, but the starch continuous powder will also have a finite yield point. Whether this is in any way related to the parameter found in the fluid phase system remains to be established. Dynamic viscosity measurements will prove more revealing here because, in the small strain limit, they could be made much closer to (and even slightly above) $\phi_{\max}$. Although the quality of fit for the two models of Fig. 5c is approximately the same, we tend to favour the straight line model where $\log(\tau_X) \propto \phi$. Hopefully, further investigations should clarify this issue.

We have established that volume fraction is important when determining the effect of particulate inclusions on the rheological properties of our system. The significant increase in zero-shear viscosity when the volume fraction of filler approaches maximum packing fraction ($\phi_{\max}$) has been shown. The maximum packing of monodisperse spheres depends markedly upon the precise geometry. For simple cubic packing $\phi_{\max}$ is 0.52, whereas for rhombohedral packing it is around 0.74. For random packing the theoretical value is 0.637, but experimentally values have been observed to fall in the range 0.55–0.64 (Maron & Pierce, 1956; Nielsen, 1977). A variation in sphere sizes (polydispersity) also affects $\phi_{\max}$ since smaller spheres can occupy 'void' volumes and, therefore, increase $\phi_{\max}$. We determined $\phi_{\max}$ as 0.474 which is lower than that of ideal spheres. This suggests a more anisotropic particle shape and corresponds well with the microscopy of the rice starch granules (Fig. 6).

Previous work by Ring & Stainsby (1982) considered the effect of volume fraction by the Kerner equation. However, it did not consider the association of water between the system constituents. When starch granules are dispersed in cold water, they absorb small quantities of water and swell slightly. This obviously removes a small amount of the available water from the polymer solution. We have also neglected this effect, but in view of the good fit obtained in Fig. 4c, the effect is presumably quite small.

CONCLUSION

The addition of rice starch as a 'filler' has significant effects on the rheological properties of a guar galactomannan solution. The effects have been shown by determination of zero-shear viscosity and an apparent yield stress through the use of a yield stress modified Cross equation. The use of such a formula can allow the prediction of the rheological properties of such a system when the component proportions are known. By fitting of the data to mathematical models which incorporate volume fraction parameters, we have produced a new master curve that may be applied to a number of semi-dilute dispersions and which has implications for a wide range of food systems of biological and industrial interest. In future work, we intend to investigate such systems in a controlled stress instrument.

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REFERENCES

Castelain, C., Lefebvre, J. & Doublier, J.L. (1986). Rheological behaviour of BSA–cellulose derivative mixtures in neutral aqueous medium. *Food Hydrocoll.*, **1**, 141–151.

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

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

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

de Gennes, P.G. (1971). Reptation of a polymer chain in the presence of fixed obstacles. *J. Chem. Physics*, **55**, 572–579.

Doi, M. & Edwards, S.F. (1978). Dynamics of concentrated polymer systems. *J. Chem. Soc. Faraday Trans. II*, **74**, 1802–1817.

Doublier, J.L. & Launay, B. (1981). Rheology of galactomannan solutions: comparative study of guar gum and locust bean gum. *J. Texture Studies*, **12**, 151–172.

Ellis, P.R. (1994). Polysaccharide gums: their modulation of carbohydrate and lipid metabolism and role in the treatment of diabetes mellitus. In *Gums and Stabilisers for the Food Industry 7*, eds G.O. Phillips, P.A. Williams & D.J. Wedlock. Oxford University Press, Oxford, pp. 207–216.

Englyst, H., Quigley, M.E., Hudson, G.J. & Cummings, J.H. (1992). Determination of dietary fibre as non-starch polysaccharides by gas–liquid chromatography. *Analyst*, **117**, 1707–1714.

Ferry, J.D. (1980). *Viscoelastic Properties of Polymers*, 3rd edition. John Wiley, New York.

Girhammar, U. & Nair, B.M. (1992). Isolation, separation and characterization of water soluble non-starch polysaccharides from wheat and rye. *Food Hydrocoll.*, **6**(3), 285–299.

Graessley, W.W. (1967). Viscosity of entangling polydisperse polymers. *J. Chem. Physics*, **47**(6), 1942–1953.

Juliano, B.O. (1984). Rice starch: production, properties and uses. In *Starch: Chemistry and Technology*, 2nd edition, eds R.L. Whistler, J.N. BeMiller & E.F. Paschall. Academic Press Inc., London.

Landel, R. (1958). The dynamic mechanical properties of a model filled system: polyisobutylene–glass beads. *Trans. Soc. Rheol.*, **II**, 53–75.

Launay, B., Doublier, J.L. & Cuvelier, G. (1986). Flow properties of aqueous solutions and dispersions of polysaccharides. In *Functional Properties of Food Macromolecules*, eds J.R. Mitchell & D.A. Ledward. Elsevier Applied Science Publishers, Barking, pp. 1–78.

Maron, S.H. & Pierce, P.E. (1956). Application of Ree–Eyring generalized flow theory to suspensions of spherical particles. *J. Colloid Sci.*, **11**, 80–95.

Minagawa, N. & White, J.L. (1976). The influence of titanium dioxide on the rheological and extrusion properties of polymer melts. *J. Appl. Polym. Sci.*, **20**, 501–523.

Morris, E.R. (1990). Shear-thinning of 'random-coil' polysaccharides: characterisation by two parameters from a simple linear plot. *Carbohydr. Polym.*, **13**, 85–96.

Morris, E.R., Cutler, A.N., Ross-Murphy, S.B., Rees, D.A. & Price, J. (1981). Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions. *Carbohydr. Polym.*, **1**, 5–21.

Morris, E.R. & Ross-Murphy, S.B. (1981). Chain flexibility of polysaccharides and glycoproteins from viscosity measurements. *Techniques in Carbohydrate Metabolism*, **B310**, 1–46.

Nielsen, L.E. (1977). *Polymer Rheology*. Marcel Dekker Inc., New York, Chapter 7.

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. *J. Rheol.*, **32**(7), 703–735.

Povolo, F. (1992). Fitting of experimental log viscosity against log shear rate curves to constitutive equations. *Polymer J.*, **24**(6), 497–508.

Richardson, R.K., Robinson, G., Ross-Murphy, S.B. & Todd, S. (1981). Mechanical spectroscopy of filled gelatin gels. *Polym. Bull.*, **4**, 541–546.

Richardson, R.K. & Ross-Murphy, S.B. (1987). Non-linear viscoelasticity of polysaccharide solutions. 1: Guar galactomannan solutions. *Int. J. Biol. Macromol.*, **9**(5), 249–312.

Ring, S. & Stainsby, G. (1982). Filler reinforcement of gels. In *Gums and Stabilisers for the Food Industry 6*, eds G.O. Phillips, P.A. Williams & D.J. Wedlock. Oxford University Press, Oxford, pp. 323–329.

Robinson, G., Ross-Murphy, S.B. & Morris, E.R. (1982). Viscosity–molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan. *Carbohydr. Res.*, **107**, 17–32.

Ross-Murphy, S.B. (1984). Rheological methods. In: *Biophysical Methods in Food Research. Critical Reports on*

Applied Chemistry, Vol. 5, ed. H.S. Chan. Blackwells, Oxford, pp. 138–199.

Ross-Murphy, S.B. (1994). Rheological methods. In *Physical Techniques for the Study of Food Biopolymers*, ed. S.B. Ross-Murphy. Blackie Academic and Professional, Glasgow, UK, Chapter 7.

Ross-Murphy, S.B. & Todd, S. (1983). Ultimate tensile measurements of filled gelatin gels. *Polymer*, **24,** 481–486.

Sharman, W.R., Richards, E.L. & Malcolm, G.N. (1978). Hydrodynamic properties of aqueous solutions of galactomannans. *Biopolymers*, **17,** 2817–2833.