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Small strain deformation measurements of konjac glucomannan solutions and the influence of borate cross-linking

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ABSTRACT

The dynamic rheology of aqueous solutions of konjac glucomannan has been evaluated over a range of concentrations up to 2.35%, and the effect of borate cross-linking of such solutions evaluated in the range 0.02–40 mM borate. In preliminary work, conventional parallel plate geometries were employed and in situ cross-linking was investigated. For borate cross-linked samples a superior method, however, was found to be measurement of pre-formed cores of cross-linked polymer into which a four-bladed vane geometry was introduced. In order to compare with other associating polymer systems, rheological data were analysed by defining plateau moduli, corresponding relaxation times and zero shear viscosities and the scaling behaviour of these parameters with polymer and cross-linker concentrations was established. Maxwell fits and time–concentration superposition procedures were investigated. The rheological properties of the cross-linked polymer were shown to be the result of both increased network connectivity and retarded network dynamics.

1. Introduction

Konjac glucomannan (KGM) is an important and long established food ingredient in Japan and is sourced in abundance from tubers of *Amorphophallus konjac* C. Koch. It is a polysaccharide comprising D-glucosyl and D-mannosyl monomers linked by β-(1→4) glycosidic bonds (Smith & Srivastava, 1959). The ratio of mannose to glucose is generally reported to be of the order 1.6:1 with the distribution being either random (Cescutti, Campa, Delben, & Rizzo, 2002) or else complex but non-random (Katsuraya et al., 2003). There is some evidence that the backbone itself exhibits some light branching (Kato & Matsuda, 1973; Maeda, Shimahara, & Sugiyama, 1980; Shimahara, Suzuki, Sugiyama, & Nisizawa, 1975; Smith & Srivastava, 1959), possibly through β-(1→6) glucosyl units (Katsuraya et al., 2003) and there are also acetyl groups periodically along the backbone (Cescutti et al., 2002; Dea et al., 1977; Maekaji, 1978). The presence of the acetyl groups and branches is believed to explain the water solubility of KGM. A comprehensive review by Nishinari, Williams, and Phillips (1992) summarises the body of characterisation work undertaken to that date. The konjac flour obtained from the dried tuber is traditionally employed in the manufacture of noodles and jellies. There has been increased interest in KGM in the West recently, where the potential of the material as a texture modifier and thickener has been realised.

Owing to the important role of KGM as a gelling agent and rheology modifier there have been a number of previously published studies on the rheological characterisation of the material. These have included measurements of aqueous solutions of the polysaccharide, and gels formed by facilitating chain association through deacteylation of the polymer or salting out effects. In common with the structurally similar galactomannans such as guar gum – and also synthetic polyols well represented by poly vinyl alcohol, PVA – KGM can be cross-linked successfully by certain inorganic salts, typified by sodium tetraborate.

Small strain oscillation measurement is also sometimes described as mechanical spectroscopy, a definition which well illustrates the notion of the probing of a sample at a series of length/time scales. Analysis of such data is very informative in revealing sample microstructure and how it responds to external forces. This study examines the microstructure of aqueous KGM solutions of concentrations in the range 0.047–1.88% (w/w) and how this is affected by cross-linking with borax (disodium tetraborate).

Early small deformation measurements of KGM (0.3–1.49%) over a very limited range of frequencies (Jacon, Rao, Cooley, & Walter, 1993) revealed a deviation for higher polymer concentrations between steady shear and oscillation data when superimposed in the classic ‘Cox Merz’ plot. Dave, Sheth, McCarthy, Ratto, and Kaplan (1998) performed dynamic measurements of

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KGM solutions ranging from 3 to 12% w/w over three decades of frequency. The storage and loss moduli displayed a slight frequency dependence which was cited as evidence that these systems were weak – as opposed to strong – gels.

Monitoring evolution of storage and loss moduli with time has been exploited as a means of following the gelation of KGM, particularly under alkaline conditions (Williams et al., 2000; Yoshimura & Nishinari, 1999; Zhang et al., 2001) or in the presence of sulphate salts (Yin, Zhang, Huang, & Nishinari, 2008). For the un-gelled polysaccharide a linear relationship was observed between the log of the storage and loss moduli and the temperature, with the loss moduli showing a greater temperature dependence (Williams et al., 2000). Measurement of dynamic data for both 0.8% aqueous KGM at 25 °C and 50 °C (Yang, Zhu, & Yan, 2006) and 0.4–1.2% aqueous KGM with milk powder at 20–40 °C (Yang & Zhu, 2006) demonstrated that KGM solutions obey time–temperature superposition, TTS. A recent study (Yang & Zhu, 2010) fitted the frequency dependence of storage and loss moduli over three decades for KGM (0.6–2.0%) to a five element Maxwell model.

The ability of borate to gel certain polyols and polysaccharides by transient interchain cross-linking was well documented by the middle of the last century (Deuel, Neukom, & Weber, 1948; Zittle, 1951). By this point, the classic features characterising such interactions had been established, for example necessity of *cis*-hydroxyl sites on the polymer, and reversibility upon addition of monosaccharides bearing *cis*-diols (e.g. mannitol), or acidic species. Furthermore, Deuel et al. (1948) attributed the mechanical properties of the gels (ropiness, plasticity) to cross-links that were “not fixed but perpetually destroyed and rebuilt”. Zittle (1951) reports gel formation with a number of different mannans and galactomannans. More recent contributions to the literature in this field – reviewed below – largely confirm the postulates of these early workers.

A number of studies have evaluated the rheology of borate cross-linked polymers by use of capillary, flow-loop or rotational viscometers, including those on PVA (Kurokawa, Shibayama, Ishimaru, Nomura, & Wu, 1992; Murakami, Fujino, Ishikawa, & Ochiai, 1980; Nickerson, 1971; Ochiai, Fujino, Tadokoro, & Murakami, 1982; Ochiai, Kurita, & Murakami, 1984; Savins, 1968; Wise, 1995), Guar gum and hydroxypropyl guar gum, HPG (Harris, 1993) and KGM (Murakami & Motozato, 1992).

The superiority of small strain oscillation measurements in rheological characterisation of borate cross-linked polymers over rotational viscometry were recognised by Schultz and Myers (1969), who employed a bob and cup geometry to measure borate (ca. 2.5–22 mM) cross-linked PVA ‘gels’ between 0 and 74 °C. TTS employing both horizontal and vertical shift factors yielded a master curve spanning 3 decades of frequency. PVA – borate gels with borate concentrations up to 50 mM were subsequently characterised using a torsion pendulum (Cheng & Rodriguez, 1981). PVA solutions, 1–2% cross-linked with up to 79 mM borate were studied by Maerker and Sinton (1986) as model associating polymer systems. Using a cone and cup configuration, they recorded the loss and storage moduli over 3.5 decades of frequency, observing the characteristic $G'G''$ crossover and G'' minimum. The dynamic rheological properties of guar galactomannan–borax ‘gels’ were systematically mapped with variations in borax (1.4–3.2 mM) and polymer concentration (0.4–1.1%), pH (8.7–11) and temperature (10–55 °C) using a cone and plate geometry (Pezron, Ricard & Leibler, 1990). Rheological measurements of guar gum up to 0.75% cross-linked with borate between 0.05 and 0.5% utilising a cone and plate geometry form part of a study by Carnali (1992). Guar gum and hydroxypropyl guar gum, HPG (0.48%) solutions cross-linked with borate, 0.12% were also evaluated over a range of temperatures (15–65 °C) and pHs (6.5–9.5) using a ‘bob and cup’ geometry (Kesavan & Prud’homme, 1992). TTS facilitated generation of master curves representing the dynamic moduli over 5 decades of frequency; for samples with pH over 8, a similar master curve resulted from a process of time–pH superposition.

A number of further studies were undertaken using the cone and plate geometry. Three examined the effect of polymer molar mass on the dynamic rheology of borate cross-linked PVA. Inoue and Osaki (1993) compared 3.0% and 1.8–2.0% solutions of low and high molar mass PVA at 5, 15 and 25 °C and borate concentrations of 3.2–31 mM; Takada and Nemoto (1997) and Takada, Nishimura, Koike, and Nemoto (1998) used 5 PVA samples having degrees of polymerisation between 350 and 3250. Whereas for all previously mentioned studies cross-linking was essentially instantaneous, dynamic time sweep experiments with borate (2.5–14 mM) cross-linked schizophyllan solution (Grisel & Muller, 1996) demonstrated much slower gelation kinetics. The effects of variation in salinity (0.25–2.0 M) and pH (9–11) on borate cross-linked 0.3–0.6% schizophyllan solutions were also determined. Further studies into the pH dependence of borate cross-linked modified guar gums include those by Power, Rodd, Paterson and Boger (1998) who documented the effect of pH between 6.25 and 11.29 on the cross-linking of HPG (up to 1.5%) with boric acid (0.036% and 5%). More recently Ratcliffe, Williams, English, and Meadows (2004) employed a vane rheometer to measure the frequency dependence of borate (0.1–20 mM) cross-linked KGM transient ‘gels’ over 5 decades of frequency for polymer concentrations up to 2.5% (w/w). Saffour, Viallier, and Dupuis (2006) generated a master curve covering 7 decades of frequency for partly hydrolysed guar gum, 2% in combination with boric acid, 0.57% by time-pH superposition of dynamic data recorded at five pHs between 5.5 and 11.8.

Of most relevance to this study is a study of KGM (0.5–1.5%) cross-linked with borax (2.36–47.2 mM) undertaken with a parallel plate rheometer over 4 decades of frequency (Gao, Guo, & Nishinari, 2008). Master curves were generated using time–concentration superposition (with respect to borax concentration) and by TTS for measurements made between 10 and 55 °C.

The aim of this study is to undertake small strain oscillation measurements to systematically investigate the microstructure of aqueous konjac glucomannan solutions and transient ‘gels’ formed by the addition of various concentrations of sodium tetraborate. In particular it will employ a vane geometry in order to overcome sample loading issues associated with the use of more conventional geometries when measuring such complex fluids, and so extend the range of polymer/cross-linker concentrations that can be studied. Earlier work reported by the authors (Ratcliffe et al., 2004) is herein expanded to include consideration of small strain oscillation measurements of the native polymer, and also a more thorough treatment of the rheology of the cross-linked polysaccharide ‘gels’ formed.

2. Materials and methods

2.1. Materials

KGM (commercial grade CHSM) originating from the Gunma Prefecture, Japan was a gift from Chesham Chemicals Ltd., Harrow, UK. The characterisation of this material has been reported previously (Ratcliffe, Williams, Viebke, & Meadows, 2005). Sodium chloride 99.5% “Goldbrand” was purchased from M56 Chemicals, Sutton Weaver, U.K. Boric acid 99.5% was purchased from FSA Laboratory Supplies, Loughborough, UK. Magnesium oxide AR was purchased from Fisher Scientific, Loughborough, UK. Silicone oil–poly(dimethylsiloxane) 200 fluid, 10 cS was purchased from Aldrich Chemical Co. Inc., Milwaukee, WI, USA. Sodium azide and di-sodium tetraborate, Analar. were purchased from BDH

Chemicals Ltd., Poole, UK. All materials were used as supplied without further purification.

2.2. Methods

2.2.1. Preparation of KGM solutions

KGM stock solutions 0.94% (w/w) and 1.88% (w/w) were prepared by a vortex addition method described previously (Ratcliffe et al., 2005). Briefly this entailed dispersion of KGM powder into distilled water, making addition into the vortex created by an electrically driven twin-bladed paddle. A 30 min mix at ambient temperature preceded a 2 h mix at 80 °C, finally cooling and adding water to compensate for evaporative loss. Dilution of the stock solutions enabled preparation of the following concentrations: 0.047, 0.094, 0.19, 0.28, 0.38, 0.47, 0.71, 1.18, 1.41 and 1.65% (w/w). Finally solutions were mixed on a roller mixer, preserved with sodium azide (at 0.02%) and refrigerated. Measurements were made within five days of sample preparation.

2.2.2. Small deformation measurements – KGM solutions

Oscillation measurements of KGM solutions 0.047–1.88% (w/w) were carried out using a combination of controlled stress and controlled strain rheometers: AR500 and CSL500 (TA Instruments, New Castle, DE, USA) and ARES (Rheometrics Scientific, Piscataway, NJ, USA). Geometries employed were double concentric cylinder, single concentric cylinder, 50 mm diameter cone and 40 mm diameter cone for concentrations 0.047–0.094, 0.19–0.47, 0.71–1.65 and 1.88% respectively. The samples were loaded by pouring an appropriate aliquot onto the lower geometry member, or where appropriate using a wide bore plastic Pasteur pipette with the tip cut off. For solutions having a representative range of concentrations the extent of the linear viscoelastic region, LVR was ascertained at 25 °C by performing strain sweep measurements (0.1–500%) at a frequency of 1 rad s^{-1}. Frequency sweep experiments ($80–1 \times 10^{-3}$ rad s^{-1}) were then undertaken for each sample at 25 °C within the LVR defined by the previous experiments, typically at 2% strain.

2.2.3. Preparation of KGM/boric acid/borate transient gels

A method largely similar to that described in Section 2.2.1 was employed, with appropriate modifications. Aqueous sodium chloride, 0.05 M was employed to disperse the KGM in place of water, to lessen ionic strength effects arising from changes in the borate concentration. A stainless steel four blade impeller was used to mix solutions. Before addition of distilled water to compensate for evaporative loss was added borax 0.05 M, 5.0 g OR a predefined volume of boric acid 0.1 M as appropriate.

2.2.4. Rheology measurement: optimisation of small strain oscillation procedure

Rheology measurements were conducted at 25 °C using a controlled stress AR500 rheometer (TA Instruments, New Castle, DE) initially using a 40 mm diameter stainless steel parallel plate, and subsequently a 28 mm diameter 4-blade stainless steel vane coupled with a 30 mm diameter couette.

2.2.5. Parallel plate geometry

The rigidity of borate cross-linked polymers hampers their proper loading onto conventional cone and plate or parallel plate geometries, and essentially precluded the study of samples with all but the lowest polymer and borate concentrations.

2.2.6. In situ gelation

The first approach conceived to overcome these restrictions was to cross-link the KGM solution in situ in the parallel plate geometry. Inspired by fracturing fluid technology used in enhanced oil recovery (U.S. Patent No. 3,974,077 (1976)) this entailed doping the KGM sol with boric acid, which does not significantly cross-link the polymer at low pH. At the point of use an appropriate amount of a solid, sparingly soluble base was added; the slow dissolution of the base in the matrix effecting pH increase and the conversion of boric acid to borate according to Eq. (1).

$$B(OH)_3 + H_2O \Leftrightarrow B(OH)_4{}^- + H^+ \quad pK_a = 9.25 \tag{1}$$

Cross-linking thus ensued. In this study, magnesium oxide was employed as the sparingly soluble base. When employing this technique it was necessary to ensure that the cross-linking process had reached equilibrium before undertaking a frequency sweep. In practice this was achieved by performing a time sweep experiment – adopting a frequency of 1 rad s^{-1} and sampling time of 5 min – the occurrence of a plateau in G' indicating that gelation was complete. The time required to achieve a plateau in G' and the ultimate value of the storage modulus itself were greater the higher the polymer and cross-linker concentrations. In practical terms, this meant that for some samples over 24 h had to be allowed for sample equilibration on the rheometer before the frequency sweep experiment could be commenced. Evaporation was prevented by application of a light silicone oil. Whilst use of the 'in-situ' cross-linking procedure enabled initial characterisation of KGM (0.1–1.88%, w/w) cross-linked with borate (2–20 mMolal) – not reported herein – a number of shortfalls were apparent. One such was the difficulty of regulating the pH owing to the very small amounts (typically 0.8 mg) of magnesium oxide solid employed to liberate monoborate anions from boric acid. Further to this there were concerns regarding both the homogeneity of the sample (dependent upon the even dispersion of MgO solid) and the possibility of side reactions indicated by occasional purple colouration of the sample.

2.2.6.1. Vane geometry mixer method. In an attempt to overcome the demands on instrument time of the preceding method, trials were conducted using KGM solutions prepared as in Section 2.2.3 but without addition of boric acid or borate. This solution was contained within the rheometer couette and cross-linked by the injection of borax solution from a syringe whilst mixing with a rotating four-bladed vane geometry. This method might have been adopted had it not been for the restrictions imposed upon the levels of polymer and borate. Thus above a certain polymer concentration it was impossible to ensure homogeneous dispersion of the cross-linker, whilst the cross-linker concentration itself was limited by the relatively low solubility of borax, given the restricted volume that could sensibly be injected.

2.2.6.2. Measurement of 'pre-gelled' samples using a vane geometry. Unlike permanently cross-linked chemical gels, polymers with borate cross-links are more appropriately described as transient networks. These self-healed when cut, allowing insertion of a vane geometry into a 'pre-gelled' sample, with subsequent relaxation of the 'gel' around the geometry.

Following calibration of the geometry for small deformation work, in a method reported elsewhere, an experimental protocol was developed which would allow reproducible measurement of borate cross-linked KGM solutions over a wide range of cross-linker and polymer concentrations.

2.2.7. The effect of varying polymer concentration with fixed cross-linker concentration

Using the procedure outlined in Section 2.2.3. KGM solutions, 0.47, 0.71, 0.94, 1.17, 1.41, 1.65, 1.88, 2.12 and 2.35% (w/w) were prepared, each cross-linked with 5 mM borate. After overnight refrigeration each solution was centrifuged in 30 cm^3 plastic blood tubes at 25 °C, 2500 rpm for 20 min and transferred to the rheometer couette. The vane geometry was slowly lowered into the sample

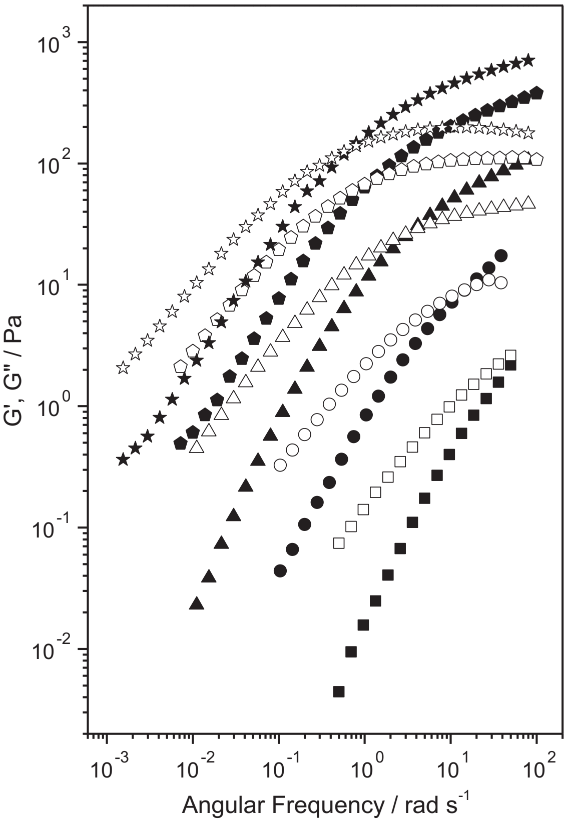

Fig. 1. Frequency sweeps for 0.19–1.65% (w/w) konjac glucomannan. 0.19% (■), 0.38% (●), 0.71% (▲), 1.18% (⬟), 1.65% (★). Solid symbols – G', open symbols – G''.

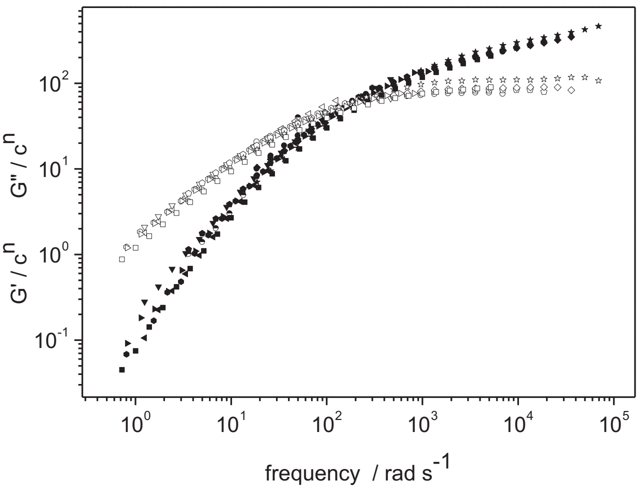

Fig. 2. Master curves of the reduced storage and loss moduli for KGM from time–concentration superposition relative to the reference data set, 0.09% (w/w). 0.09% (■), 0.19% (◄), 0.28% (⬢), 0.38% (▼), 0.47% (►), 0.71% (■), 0.94% (●), 1.18% (▲), 1.41% (⬟), 1.65% (♦), 1.88% (★). Solid symbols – G', open symbols – G''.

and the latter was carefully trimmed. A custom-made moisture trap was placed over the sample to prevent desiccation. Following equilibration at 25 °C (2 h) a frequency sweep (100–1 × 10^{-3} rad s^{-1}) was recorded at an appropriate fixed strain. The latter was determined by means of strain sweep measurements (0.1–500%) at a frequency of 1 rad s^{-1} performed on duplicate samples from within the concentration range above.

2.2.8. The effect of varying cross-linker concentration with fixed polymer concentration

The procedure outlined in the previous section was repeated using a fixed 0.94% polymer concentration but varying the volume of aqueous borax added to give samples with borate concentrations of 0.02, 0.1, 0.2, 1.0, 2.0, 5.0, 10, 15, 20, 30 and 40 mM.

3. Results and discussion

3.1. Konjac glucomannan solutions

Preliminary oscillatory shear experiments (results not shown) indicated that across the concentration range considered the LVR extends to at least 3% strain, and in some cases at least 10% strain.

The frequency dependence of the storage and loss moduli for representative examples of KGM solutions in the range 0.09–1.88% (w/w) – illustrated in Fig. 1 – essentially resembles that reported for other similar polysaccharides, for example guar gum (Robinson, Ross-Murphy, & Morris, 1982). Consequently there is remarkable similarity between the time–concentration superposition master curves reported by these authors and those presented herein, Fig. 2. The procedure employed to produce these curves entailed division of the storage and loss moduli by the solution concentration raised to a certain power, i.e. G'/c^n, G''/c^n in addition to a horizontal shift based on an arbitrary shift factor. The latter exhibited a power law scaling with polymer concentration, with an exponent of 2.3 (graph not shown). The viscoelastic response represented by the master curve is compared to that predicted using a single element Maxwell model. The classic Maxwellian response is characterised by (i) a high frequency region where elastic behaviour dominates, described by frequency independence of G' and a minimum in G'', and (ii) a low frequency region where viscous behaviour is increasingly important and thus a G'' maximum is observed concurrent with a fall in G' (Ferry, 1980). Clearly this model is not appropriate to describe the behaviour, the most significant departure being a plateau in the loss modulus at high frequencies for the KGM, in contrast to the steady decrease in the loss modulus with frequency in this regime predicted by the Maxwell model. Additionally it is noted that the gradients of $G'(\omega)$ and $G''(\omega)$ in the low frequency (terminal) regime are much less than those predicted by the model. This differs somewhat from reports for guar gum, which showed better agreement with the Maxwell model (Richardson & Ross-Murphy, 1987). The explanation for this is probably that the guar gum samples were partially fractionated, and hence less polydisperse. Ferry (1980) acknowledges significant broadening of both $G'(\omega)$ and $G''(\omega)$ in the terminal region over extended frequency ranges with polydisperse samples. The inadequacy of a single element model to fully describe the dynamic rheology is not surprising in light of the employment of a five element Maxwell model for KGM reported recently (Yang & Zhu, 2010).

Whereas for guar gum, studies reveal a low frequency plateau in the storage modulus (Gittings et al., 2001; Wientjes, Duits, Jongschaap, & Mellema, 2000) no such phenomenon was recorded for KGM. As the plateau is tentatively attributed to associations between un-substituted stretches of mannose chain segments one may have expected that KGM could also demonstrate such an effect. The evidence for KGM freeze thaw gels – presumably arising out of the same kind of associations – is also scant so it may be that the long side chains and/or acetyl substituents discourage such an effect. Furthermore, in light of an earlier discussion regarding the effects of polydispersity it may be that the plateau in the polydisperse KGM is shifted to experimentally unobtainable frequencies. Additionally, Wientjes et al. (2000) demonstrate that the plateau is much less pronounced at lower temperatures, although Gittings et al. (2001) recorded clearly defined plateaus at 25 °C.

Whereas each individual frequency sweep experiment is informative about the visco-elastic response of the material at that

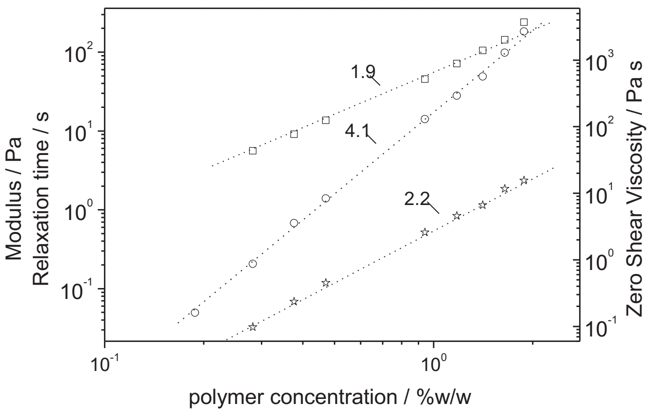

Fig. 3. The dependence of the plateau moduli (□) and relaxation time at *G′G″* crossover (☆) and the zero shear viscosity (○) on the polymer concentration of a KGM solution.

specific concentration, it is usual to identify some key parameters from each which may be used as reference points when comparing with other results. Two such useful parameters are the modulus at the point of equivalence of the storage and loss moduli – referred to hereafter as the *G′G″ crossover* and the *relaxation time*, being the reciprocal of the frequency at this crossover. The influence of polymer concentration on the rheology of KGM has been summarised in Fig. 3 by considering the scaling behaviour of the plateau modulus and relaxation time (both being determined at the *G′G″* crossover) and the zero shear (complex) viscosity, η_0 calculated from the oscillation measurements. The latter was performed using Rheometrics Orchestrator software version 6.5.5, applying an Ellis model fit to the generated complex viscosity data. In each case, the scaling is well described by a power law, allowing characterisation of the behaviour simply by a power law exponent. The exponents are in reasonable agreement with those reported for guar gum by Wientjes et al. (2000): G'_p: 1.8; τ: 2.6–2.8; η_0: 3.7–5.3. Increase in viscosity in KGM solutions with increasing concentration is clearly attributable to both slowed dynamics (τ increasing) and enhanced connectivity ($\sim G'_p$).

Agreement between the exponent noted for the relaxation time and that of the horizontal scaling factor in the time–concentration superposition experiment demonstrates that the horizontal shift simply takes account of the change in the relaxation time with variation in polymer concentration.

The Cox-Merz relationship has long been employed by rheologists to estimate steady shear viscosity data from small strain oscillation measurements. In addition there is a history of use by workers in the field to test for association between polymer chains, when deviation from the empirical relationship proposed by Cox and Merz (1958) may be observed. The process typically involves superimposing the shear rate dependencies of the shear viscosity and frequency dependencies of the dynamic viscosity on common axes. Such an approach for KGM is illustrated for small strain oscillation data from this study and shear flow data from previously reported work (Ratcliffe et al., 2005) in Fig. 4. In accordance with literature on KGM, and structurally similar galactomannans guar gum and LBG, the data reported here for KGM fails to obey the Cox-Merz ‘rule’, notably at higher polymer concentrations. The higher value of the dynamic data, particularly in the high frequency/shear rate regime agrees with that observed by Jacon et al. (1993) and is generally attributed to the presence of non-specific segment–segment interactions. It is of note that the literature is not entirely conclusive on this subject, for example Richardson and Ross-Murphy (1987) illustrated adherence to the Cox-Merz principle for 3% guar gum. A study by Yin et al. (2008) demonstrated near perfect superimposition for shear and dynamic viscosity for 0.8% KGM.

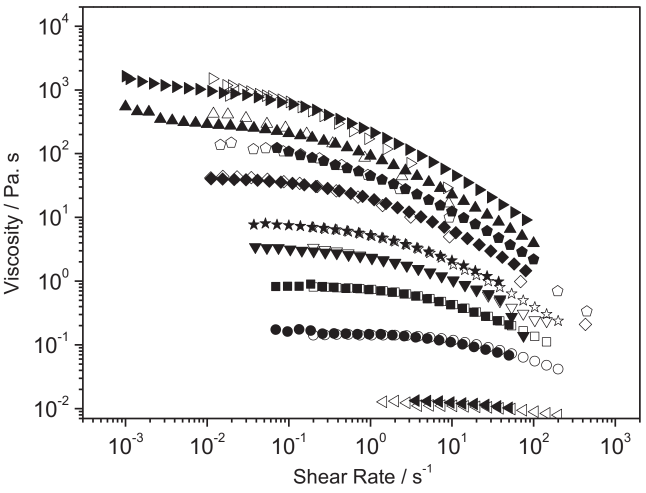

Fig. 4. Cox-Merz plots for 0.09–1.65% (w/w) konjac glucomannan. 0.09% (◂), 0.19% (●), 0.28% (■), 0.38% (▾), 0.47% (★), 0.71% (♦), 0.94% (⬟), 1.18% (▲), 1.65% (▸). Solid symbols – dynamic data; open symbols – shear flow data.

3.2. *Probing the microstructure of a range of borate cross-linked networks*

The effects on the frequency dependence of the storage and loss moduli of changing the polymer concentration with a fixed borate concentration and variation of the borate concentration with fixed polymer concentration have been published in earlier work (Ratcliffe et al., 2004).

Further interpretation of data from these experiments will entail amongst other things consideration of the influence of polymer and cross-linker concentration on the relaxation time, τ. The three methods of measuring relaxation time employed in this study are illustrated in Fig. 5. Thus in addition to that determined at the crossover point, one can measure a relaxation time at both the maximum and minimum of the loss modulus.

It is useful to compare the frequency dependence of such a cross-linked network with that of the parent polymer, also presented

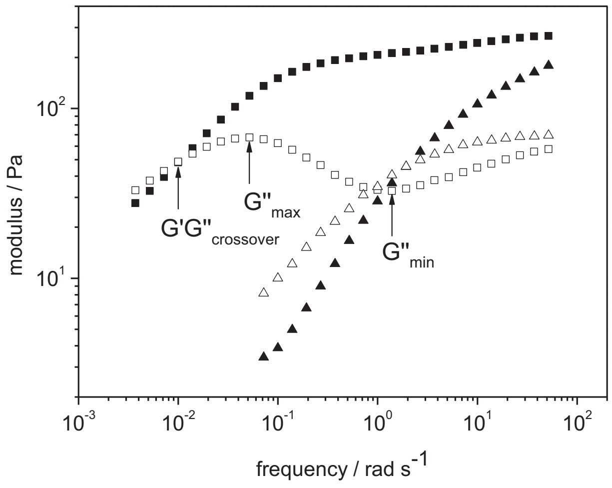

Fig. 5. The frequency dependence of the storage and loss moduli for KGM (0.94%) without borate (▲) and cross-linked with 10 mM borate (■) indicating with respect to the latter, definition of reference points according to maxima or minima in the loss modulus or the crossover point. Solid symbols – storage moduli; open symbols – loss moduli.

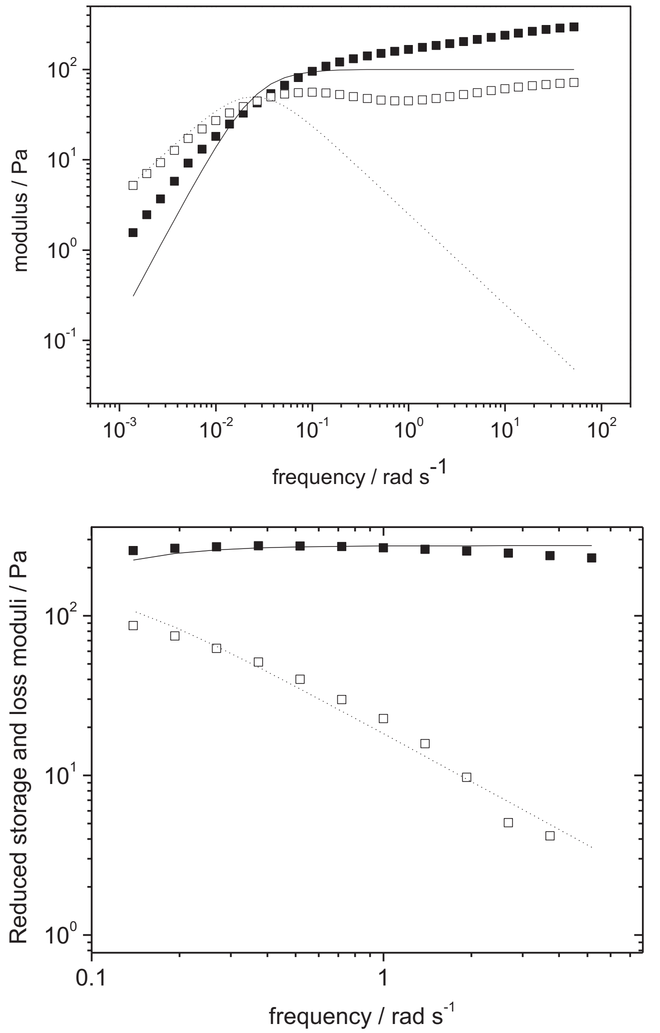

Fig. 6. Evaluation of a single element Maxwell model to describe (top) the frequency dependence of the storage (■) and loss (□) moduli of KGM 0.94% crosslinked with borate, 5 mM and (bottom) the frequency dependence of the *reduced* storage (■) and loss (□) moduli of KGM 0.94% crosslinked with borate, 20 mM. (—) G'_{Maxwell} (—) G''_{Maxwell}.

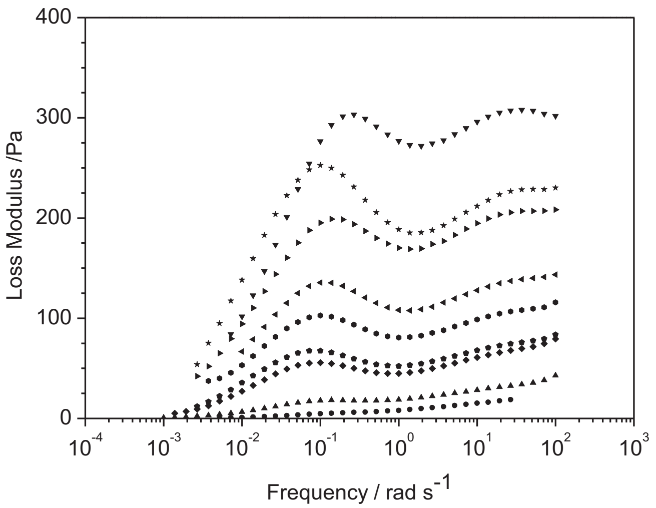

Fig. 7. The frequency dependence of the loss moduli of KGM, 0.47% (●), 0.71% (▲), 0.94% (♦), 1.17% (⬟), 1.41% (⬢), 1.65% (◄), 1.88% (►), 2.12% (★) and 2.35% (▼), cross-linked with borate, 5 mM.

in Fig. 5. In the case of cross-linked KGM samples the distinctive maxima and minima observed in the loss modulus curve were pronounced for examples with high borate concentration. These features, plus the ‘quasi plateau’ observed at high frequency in the storage modulus bear resemblance to literature examples of simple linear polymers such as a monodisperse polybutadiene (Ruymbeke, Liu, & Bailly, 2007) and poly(n-octyl methacrylate) (Ferry, 1980, p. 369). In the case of polybutadiene the ‘quasi plateau’ is attributed to the existence of entanglements. Interpretation of the frequency response of simple monodisperse polymers such as polystyrene and polybutadiene, and their polydisperse/bidisperse analogues has been reviewed by van Ruymbeke et al. (2007). The various models employed are rooted either in the Doi and Edwards’ reptation approach (Doi, 1981, 1983; Doi & Edwards, 1986; Doi, Graessley, Helfand, & Pearson, 1987; Graessley, 1982) or a variant proposed by Milner and McLeish (1997). With respect to the literature on borate cross-linked polysaccharide rheology it is the Maxwell model that has most frequently been employed. As illustrated in Fig. 6 for KGM 0.94% cross-linked with borate, 5 mM the frequency dependence of the storage and loss moduli cannot adequately be described by a single element Maxwell model, suggesting that the relaxation process is more complex. A further indication of this complexity is the inability to produce master curves from frequency sweep data (varying borate with fixed polymer concentration and vice versa) by a time concentration superposition operation (not illustrated). Indeed for borate cross-linked PVA an eleven element Maxwell model was required to obtain a good fit to experimental data (Robb & Smeulders, 1997). In an attempt to resolve the relaxation behaviour of borate cross-linked guar gum/HPG Kesavan and Prud’homme (1992) subtracted the values of the moduli for the polymer alone from those of the cross-linked polymer. The reduced moduli demonstrated a good fit to a single element Maxwell model. Such an approach has been undertaken herein for KGM 0.94% cross-linked with 0.02–40 mM borate. For samples with a borate level of 5 mM or above a reasonable fit to a single element Maxwell model was found; the lower graph of Fig. 6 illustrates a typical example. It is assumed that the reduced data describe the relaxation of the borate cross-links. The mathematical operation unfortunately precluded inclusion of data from higher frequencies as in this regime the reduced moduli were negative and could not be represented on a log scale, whilst reduced data at low frequencies were unavailable owing to lack of data at long times for the reference un-cross-linked polymer.

Close inspection of the frequency dependence of the loss moduli of borate cross-linked KGM, for example as in Fig. 6, reveals perceptible high frequency maxima. These are seen more easily by re-plotting the data on semi-logarithmic axes, Fig. 7. A response demonstrating two loss modulus maxima is anticipated for reversible networks in the model of Leibler, Rubinstein, and Colby (1991). Specifically the model predicts a low frequency maxima occurring at the reciprocal of T_d, the longest relaxation time and a high frequency maxima occurring at the reciprocal of τ, the lifetime of an association. Evaluation of the latter using the data of Fig. 7 gives for cross-linked 2.12 and 2.35% (w/w) KGM values of 19 and 27 ms respectively. Whilst these values are substantially longer than 1 ms reported from ^{11}B NMR experiments by Kramer (as cited in Prud’homme, Constein, & Knoll, 1989) it is to be remembered that they are influenced by such variables as solution pH (Pezron et al., 1990).

It is interesting that the high frequency maxima noted in Fig. 7 were not observed for un-cross-linked KGM yet were not particularly enhanced by increased borate concentration. It is proposed that – in light of the sensitivity of these maxima to the polymer concentration – they may in fact have their origin not in borate cross-links but instead specific segment–segment interactions of the polymer. It is conceivable that whereas for the native polymer the relaxation times of these may have been outside the experimental window, the dynamics of the cross-linked polymer is sufficiently slowed to allow them to be seen.

3.3. Scaling of zero shear viscosity, plateau moduli and relaxation times with polymer concentration

Before addressing the scaling of viscosity with the polymer concentration it is appropriate to consider the 'coil occupancy' over the relevant concentration range. There are a number of ways in which this may be assessed.

Whilst the critical overlap concentration for the polymer, c^* demarks the onset of the interpenetration of polymer coils, entanglements are not generally considered to be elastically effective until the concentration is 5–10 times c^* (Colby, Rubinstein, & Daoud, 1994; Graessley, 1980). For KGM c^* was determined to be 0.08 g dL^{-1} (Ratcliffe et al., 2005) thus entanglements could be expected to be significant at concentrations of 0.4–0.8% (w/w) and above.

Another approach to examining the coil occupancy is to consider the effective volume fraction of the polymer, $(2/5)c[\eta]$. The value of this parameter at a nominal 1.0% (w/w) concentration is approximately 8, indicating that entanglement can certainly be considered to be significant at and above this concentration.

Finally the entanglement has been assessed in terms of calculation of the number of elastically active strands, ν_{eff} from the measured plateau moduli (Eq. (2)) according to the affine network model (Wall & Flory, 1951), where k_B is the Boltzmann constant, and T is the absolute temperature. In this instance values for the plateau moduli were taken at the $G'G''$ crossover and in addition estimated employing Rheometrics 'Plateau Modulus Calculation' software based upon Eq. (3):

$$G'_p = \nu_{eff} k_B T \tag{2}$$

$$G'(\omega) = G'_{p\ \mathrm{model}} + \left(\frac{c_1}{\omega^{c_2}}\right) \tag{3}$$

where c_1 and c_2 are constants. The concentration dependence of ν_{eff}/N_c, the effective number density of elastically active strands for KGM, was plotted using values calculated from both $G'_{p\,\mathrm{crossover}}$ and $G'_{p\,\mathrm{model}}$ (not shown). Whereas for the former ν_{eff}/N_c did not exceed 3 for concentrations up to 2.0% w/w, values determined from $G'_{p\,\mathrm{model}}$ were 10 or greater for the higher concentrations.

The three treatments employed imply that aqueous solutions of KGM may be considered to be entangled for concentrations above say 0.4–1.0% (w/w).

Fig. 8 explores the polymer concentration dependence of the zero shear viscosity, relaxation time and plateau moduli of KGM solutions cross-linked with 5 mM borate. Power law fits to the data indicated on the figures by broken lines allow comparison with similar treatments in the literature and suggest that the concentration range studied comprises two power law regimes. The 'critical' concentration demarking the boundary between the two regimes corresponds to a polymer concentration of approximately 0.94%. The exponents in the more concentrated regime were approximately half that in the less concentrated regime. Replotting comparable literature data (Takada et al., 1998) from a study of borate cross-linked PVA (not shown) revealed that this trend was clearly not restricted to the current study. The scaling exponent of 3.1 for below the critical concentration compares well with that of 2.6 reported for guar gum-borate (Pezron et al., 1990) although considerably lower than that determined (4.7) for PVA-borate (Cheng & Rodriguez, 1981). It is essentially identical to the value of 3.11 reported by Gao et al. (2008) in their study of borate cross-linked KGM. The viscosity increase upon increasing polymer concentration can be interpreted using Eq. (4), derived from transient network theory:

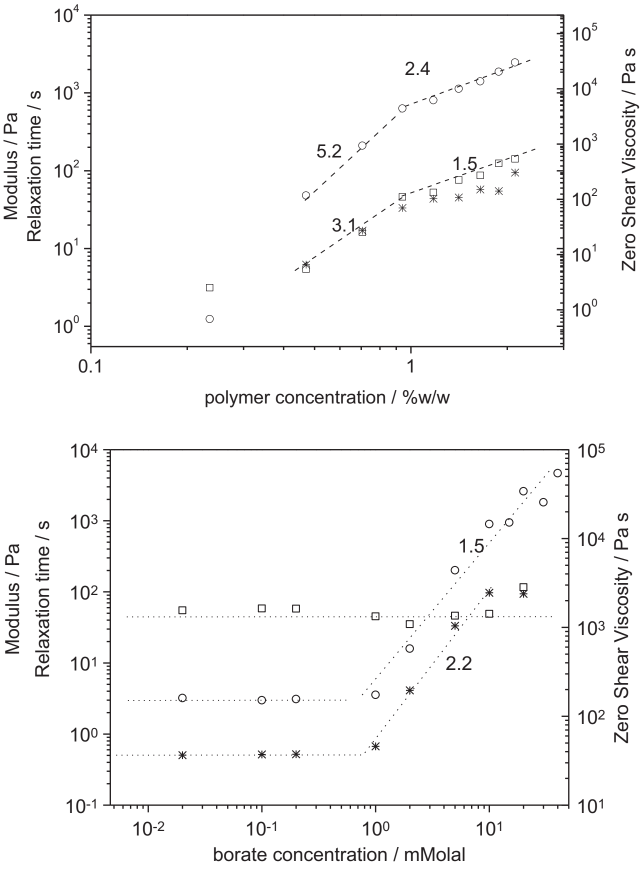

Fig. 8. The dependence of the plateau moduli (□) and relaxation time (*) at $G'G''_{\mathrm{crossover}}$ and the zero shear viscosity (○) on the polymer concentration of a KGM solution cross-linked with 5 mMolal borate (top) and on the borate concentration of a cross-linked KGM, 0.94% (bottom).

$$\eta_0 \sim G'_p \tau \tag{4}$$

Thus increase in the plateau modulus indicates that viscosity increase can in part be attributed to increased connectivity of the system, whilst a comparable trend in the relaxation time suggests a further contribution to viscosity from retarded network dynamics.

3.4. Comparison of scaling exponents with those predicted from associating polymer models

One of the key features characterising the rheology of associating polymer solutions is a concentration regime in which the zero shear viscosity exhibits a very high dependence upon the polymer concentration. Thus power law exponents of 9.0 (Abdala, 2002) and 7.9 (English, Gulati, Jenkins, & Khan, 1997) have been reported for hydrophobically modified alkali-soluble emulsion (HASE) polymers. In the Rubinstein and Semenov (2001) 'sticky reptation' model which predicts scaling of the order $\eta_0 \sim c^{8.5}$ this is attributed to the conversion of intra-molecular bonds to inter-molecular ones. A similar phenomenon in un-entangled polymer solutions, 'sticky Rouse' (Rubinstein & Semenov, 2001), predicts $\eta_0 \sim c^{5.9}$. In both the entangled and un-entangled case increasing the polymer concentration beyond a critical point gives a new regime characterised by mostly inter-molecular bonds and thus having a lower concentration dependence: $\eta_0 \sim c^{3.75}$ for the entangled case and $\eta_0 \sim c^{1.1}$ for the un-entangled. The concentration dependence of the zero shear viscosity of borate cross-linked KGM, Fig. 8 at least qualitatively agrees with the Rubinstein and Semenov approach. The recorded exponents of 5.2 and 2.4 clearly agree more closely with the un-entangled 'sticky Rouse' model.

3.5. Scaling of zero shear viscosity, plateau moduli and relaxation times with cross-linker concentration

Fig. 8 also illustrates the scaling of the zero shear viscosity, plateau modulus and relaxation time with the borate concentration at a fixed polymer concentration, 0.94%. At low cross-linker concentrations ($\leq$0.5 mM) η_0, $\tau_{\text{crossover}}$ and $G'_{p\,\text{crossover}}$ are initially independent of [borate]. In a second regime the [borate] dependence of $\tau_{\text{crossover}}$ and η_0, may be described by a power law whilst $G'_{p\,\text{crossover}}$ remains essentially independent of cross-linker concentration. Insensitivity of G' in the high-frequency regime to borate concentration has been reported previously (Ratcliffe et al., 2004). Thus the increase in viscosity with increased borate concentration can largely be attributed to retarded network dynamics, with minimal increase in connectivity. A linear relationship was noted between G'_p and the borate ion concentration (up to approximately 12 mM) for a PVA-borax system (Schultz & Myers, 1969). In the dilute regime one might have expected to witness an initial viscosity below that of the un-cross-linked polymer as a consequence of the contraction of polymer molecules due to intramolecular cross-links. Such a phenomenon has been noted for certain associative polymers (Regalado, Selb, & Candau, 1999) but was not apparent within the borate and polymer concentration range studied here. The borate independent regime is considered to represent the system of polymer with insufficient cross-links to achieve an elastically active network. The termination of this regime at approximately 0.4 mM borate agrees well with values reported for guar gum of 0.2–1.0 mM (Pezron et al., 1990).

4. Conclusions

This study comprised characterisation of a commercial konjac glucomannan sample with respect to its dynamic rheological behaviour, and the influence of borate addition. Native polymer solutions demonstrated evidence of specific segment–segment interactions, typified by non-equivalence of the dynamic and shear viscosities when overlaid according to the Cox-Merz procedure. The failure of a single element Maxwell model to predict the frequency dependence of the storage and loss moduli was attributed to a complex relaxation process; in part this reflected sample polydispersity. The enhancement of zero shear viscosity with increasing KGM concentration was resolved into components expressing connectivity ($G'_{p\,\text{crossover}}$) and network dynamics (τ). Thus it was demonstrable that the viscosity increase arose from both retardation of network dynamics, and increased connectivity. The exponents describing the scaling of the plateau moduli, relaxation time and viscosity were found to be comparable to those reported for guar gum (Wientjes et al., 2000).

Having thoroughly characterised the KGM samples, oscillatory shear measurements were undertaken in order to probe the microstructure of networks formed upon cross-linking KGM with borate ions. The cross-linking reaction was apparently instantaneous and the resultant physical 'gels', whilst elastic at short times, flowed at long times. As a consequence of these properties loading samples of the cross-linked material onto conventional parallel plate, cone and plate or couette geometries was inherently difficult. Considerable improvements were achieved by an in situ cross-linking procedure in which the cross-linking agent – the monoborate anion – was gradually liberated from boric acid by reaction with a sparingly soluble base, magnesium oxide. A number of drawbacks became apparent during the routine use of this procedure, however and efforts were made to develop an improved technique. The outcome was the use of a four-bladed vane geometry, firstly in a dual role as a paddle mixer (mixing cross-linker solution into KGM solutions) and measuring geometry, and finally just in the latter role. In this case the vane was inserted into pre-'gelled' KGM which relaxed around the geometry.

Small strain oscillation measurements were made within the LVR for systems comprising (i) varying concentrations of KGM (0.47–2.35%) cross-linked by a fixed amount (5 mM) of borate and (ii) a fixed KGM concentration (0.94%) cross-linked by varying borate concentrations (0.02–40 mM). The resultant frequency sweeps were characterised at all polymer and cross-linker concentrations by the retention of a low frequency terminal regime. Thus the cross-links did not resemble permanent cross-links but were able to uncouple at long times, i.e. could be described as transient. An apparent truncation of the terminal regime for certain samples was attributed to retardation of the dynamics such that part of the terminal regime was shifted to experimentally inaccessibly low frequencies.

For all but the most highly cross-linked samples the frequency sweep still exhibited a crossover point demarcating the transition from a regime dominated by elastic behaviour (at short times) to one dominated by viscous behaviour (at long times). As a rule with increased concentration of polymer or cross-linker this crossover shifted to lower frequencies. Presumably in highly cross-linked samples the frequency shift was sufficiently large to place the crossover outside the experimental window. Frequency sweeps of samples with high borate or polymer concentrations were typified by pronounced maxima and minima of the loss modulus. The minima coincided with a region in which the storage modulus reached a maximum value, whilst the maxima corresponded to the steep decline in the storage modulus with decreasing frequency. The crossover point, and loss modulus maxima and minima turned out to be useful points at which to determine the plateau moduli and relaxation time. Observation of high frequency maxima in the loss moduli was unexpected. In light of comparison to the Leibler et al. (1991) model and because of their enhancement with increased polymer concentrations these may relate to specific segment–segment interactions.

The relaxation spectra of the borate cross-linked KGM networks were complex, and unlike that of the native polysaccharide could not be readily superimposed by a time concentration superposition procedure. Calculation of reduced moduli by subtraction of the moduli of the parent polymer from those of the cross-linked network facilitated isolation of relaxation spectra of the borate cross-links (Kesavan & Prud'homme, 1992). The reduced moduli concurred reasonably with those predicted from a single element Maxwell model.

In a manner analogous to that employed for native KGM solutions the viscosity of the cross-linked material was resolved into components representing connectivity (G'_p) and network dynamics (τ). For both the plateau moduli and relaxation times dependence on the polymer and borate concentrations could be described by one or more power law regimes. Such behaviour is characteristic of associating polymer solutions, and to an extent the borate cross-linked system can be considered using models developed with such polymers in mind. These models offer an explanation of the scaling regimes observed and hence may assist in understanding the stress relaxation process. The observed onset of unusual scaling behaviour at high borate levels may be associated with the increasing influence of the polyelectrolyte effect.

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References

Abdala, A. A. (2002) Solution rheology and microstructure of associative polymers. PhD Thesis. U.S.A.: North Carolina State University.

Carnali, J. O. (1992). Gelation in physically associating biopolymer system. *Rheologica Acta*, *31*, 399–412.

Cescutti, P., Campa, C., Delben, F., & Rizzo, R. (2002). Structure of the oligomers obtained by enzymatic hydrolysis of the glucomannan produced by the plant *Amorphophallus konjac*. *Carbohydrate Research*, *337*, 2505–2511.

Cheng, A. T. Y., & Rodriguez, F. (1981). Mechanical properties of borate crosslinked poly(vinyl alcohol) gels. *Journal of Applied Polymer Science*, *26*, 3895–3908.

Colby, R. H., Rubinstein, M., & Daoud, M. (1994). Hydrodynamics of polymer solutions via two parameter scaling. *Journal De Physique II*, *4*, 1299–1310.

Cox, W. P., & Merz, E. H. (1958). Correlation of dynamic and steady flow viscosities. *Journal of Polymer Science*, *28*, 619–622.

Dave, V., Sheth, M., McCarthy, S. P., Ratto, J. A., & Kaplan, D. L. (1998). Liquid crystalline, rheological and thermal properties of konjac glucomannan. *Polymer*, *39*, 1139–1148.

Dea, I. C. M., Morris, E. R., Rees, D. A., Welsh, E. J., Barnes, H. A., & Price, J. (1977). Associations of like and unlike polysaccharides: Mechanism and specificity in galactomannans, interacting bacterial polysaccharides, and related systems. *Carbohydrate Research*, *57*, 249–272.

Deuel, H., Neukom, H., & Weber, F. (1948). Reaction of boric acid with polysaccharides. *Nature*, *161*, 96–97.

Doi, M. (1981). Explanation for the 3.4 power law of viscosity of polymeric liquids on the basis of the tube model. *Journal of Polymer Science: Polymer Letters Edition*, *19*, 265–273.

Doi, M. (1983). Explanation for the 3.4 power law of viscosity of polymeric liquids on the basis of the tube model. *Journal of Polymer Science: Polymer Physics Edition*, *21*, 667–684.

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

Doi, M., Graessley, W. W., Helfand, E., & Pearson, D. S. (1987). Dynamics of polymers in polydisperse melts. *Macromolecules*, *20*, 1900–1906.

English, R. J., Gulati, H. S., Jenkins, R. D., & Khan, S. A. (1997). Solution rheology of a hydrophobically modified alkali-soluble associative polymer. *Journal of Rheology*, *41*, 427–444.

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

Free, D. L. (1976). U.S. Patent No. 3,974,077. Virginia: U.S. Patent and Trademark Office.

Gao, S., Guo, J., & Nishinari, K. (2008). Thermoreversible konjac glucomannan gel crosslinked by bora. *Carbohydrate Polymers*, *72*, 315–325.

Gittings, M. R., Cipelletti, L., Trappe, V., Weitz, D. A., In, M., & Lal, J. (2001). The effect of solvent and ions on the structure and rheological properties of guar solution. *Journal of Physical Chemistry A*, *105*, 9310–9315.

Graessley, W. W. (1980). Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular-weight and solvent power. *Polymer*, *21*, 258–262.

Graessley, W. W. (1982). Entangled linear, branched and network polymer systems–molecular theories. *Advances in Polymer Science*, *47*, 67–117.

Grisel, M., & Muller, G. (1996). Rheological properties of schizophyllan in presence of borate ions. *Progress in Colloid and Polymer Science*, *102*, 32–37.

Harris, P. C. (1993). Chemistry and rheology of borate-crosslinked fluids at temperatures to 300 °F. *Journal of Petroleum Technology, March*, 264–269.

Inoue, T., & Osaki, K. (1993). Rheological properties of poly(vinyl alcohol)/sodium borate aqueous solutions. *Rheologica Acta*, *32*, 550–555.

Jacon, S. A., Rao, M. A., Cooley, H. J., & Walter, R. H. (1993). The isolation and characterisation of a water extract of konjac flour gum. *Carbohydrate Polymers*, *20*, 35–41.

Kato, K., & Matsuda, K. (1973). Isolation of oligosaccharides corresponding to the branching-point of konjac mannan. *Agricultural and Biological Chemistry*, *37*, 2045–2051.

Katsuraya, K., Okuyama, K., Hatanaka, K., Oshima, R., Sato, T., & Matsuzaki, K. (2003). Constitution of konjac glucomannan: Chemical analysis and ^{13}C NMR spectroscopy. *Carbohydrate Polymers*, *53*, 183–189.

Kesavan, S., & Prud'homme, R. K. (1992). Rheology of guar and HPG cross-linked by borate. *Macromolecules*, *25*, 2026–2032.

Kurokawa, H., Shibayama, M., Ishimaru, T., Nomura, S., & Wu, W. (1992). Phase behaviour and sol–gel transition of poly(vinylalcohol) borate complex in aqueous solution. *Polymer*, *33*, 2182–2188.

Leibler, L., Rubinstein, M., & Colby, R. H. (1991). Dynamics of reversible network. *Macromolecules*, *24*, 4701–4707.

Maeda, M., Shimahara, H., & Sugiyama, N. (1980). Detailed examination of the branched structure of konjac glucomannan. *Agricultural and Biological Chemistry*, *44*, 245–252.

Maekaji, K. (1978). Determination of acidic component of konjac mannan. *Agricultural and Biological Chemistry*, *42*, 177–178.

Maerker, J. M., & Sinton, S. W. (1986). Rheology resulting from shear-induced structure in associating polymer solutions. *Journal of Rheology*, *30*, 77–99.

Milner, S. T., & McLeish, T. C. B. (1997). Parameter-free theory for stress relaxation in star polymer melts. *Macromolecules*, *30*, 2159–2166.

Murakami, I., Fujino, Y., Ishikawa, R., & Ochiai, H. (1980). Temperature dependence of the viscosity of aqueous poly(vinyl alcohol)-borax solutions. *Journal of Polymer Science: Polymer Physics Edition*, *18*, 2149–2153.

Murakami, R., & Motozato, Y. (1992). Viscosity of aqueous glucomannan–borate complex solutions. *Polymer*, *33*, 1108–1109.

Nickerson, R. F. (1971). Thickening of poly(vinyl alcohol) by borate. *Journal of Applied Polymer Science*, *15*, 111–116.

Nishinari, K., Williams, P. A., & Phillips, G. O. (1992). Review of the physico–chemical characteristics and properties of konjac mannan. *Food Hydrocolloids*, *6*, 199–222.

Ochiai, H., Fujino, Y., Tadokoro, Y., & Murakami, I. (1982). Polyelectrolyte behavior of poly(vinyl alcohol) in aqueous borax solutions. *Polymer Journal*, *14*, 423–426.

Ochiai, H., Kurita, Y., & Murakami, I. (1984). Viscosity behavior of the polyelectrolyte poly(vinyl alcohol) having some intrachain crosslinks. *Die Makromolekulare Chemie*, *185*, 167–172.

Pezron, E., Ricard, A., & Leibler, L. (1990). Rheology of galactomannan-borax gels. *Journal of Polymer Science, Part B*, *28*, 2445–2461.

Power, D. J., Rodd, A. B., Paterson, L., & Boger, D. V. (1998). Gel transition studies on nonideal polymer networks using small amplitude oscillatory rheometry. *Journal of Rheology*, *42*, 1021–1037.

Prud'homme, R. K., Constein, V., & Knoll, S. (1989). The effects of shear history on the rheology of hydroxypropyl guar gels. In J. E. Glass (Ed.), *Polymers in aqueous media, performance through association*. Washington, DC: American Chemical Society.

Ratcliffe, I., Williams, P. A., English, R. J., & Meadows, J. (2004). Small deformation measurements of transient gels using vane rheometry. In P. A. Williams, & G. O. Phillips (Eds.), *Gums and stabilisers for the food industry 12* (pp. 360–367). Cambridge: The Royal Society of Chemistry.

Ratcliffe, I., Williams, P. A., Viebke, C., & Meadows, J. (2005). Physicochemical characterization of konjac glucomannan. *Biomacromolecules*, *6*(4), 1977–1986.

Regalado, E. J., Selb, J., & Candau, F. (1999). Viscoelastic behaviour of semidilute solutions of multisticker polymer chains. *Macromolecules*, *32*, 8580–8588.

Richardson, R. K., & Ross-Murphy, S. B. (1987). Non-linear viscoelasticity of polysaccharide solutions. 1. Guar galactomannan solutions. *International Journal of Biological Macromolecules*, *9*, 250–256.

Robb, I. D., & Smeulders, J. B. A. F. (1997). The rheological properties of weak gels of poly(vinyl alcohol) and sodium borate. *Polymer*, *38*, 2165–2169.

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.

Rubinstein, M., & Semenov, A. N. (2001). Dynamics of entangled solutions of associating polymers. *Macromolecules*, *34*, 1058–1068.

Saffour, Z., Viallier, P., & Dupuis, D. (2006). Rheology of gel-like materials in textile printing. *Rheologica Acta*, *45*, 479–485.

Savins, J. G. (1968). Shear thickening phenomena in poly(vinyl) alcohol–borate complexes. *Rheologica Acta*, *7*, 87–93.

Schultz, R. K., & Myers, R. R. (1969). The chemorheology of poly(vinyl alcohol)–borate gels. *Macromolecules*, *2*, 281–285.

Shimahara, H., Suzuki, H., Sugiyama, N., & Nisizawa, K. (1975). Isolation and characterization of oligosaccharides from an enzymic hydrolysate of konjac glucomannan. *Agricultural and Biological Chemistry*, *39*, 293–299.

Smith, F., & Srivastava, H. C. (1959). Constitutional studies on the glucomannan of konjak flour. *Journal of the American Chemical Society*, *81*, 1715–1718.

Takada, A., & Nemoto, N. (1997). Dynamics of associating polymers in solution: Dynamic light scattering and dynamic viscoelasticity of poly(vinyl alcohol) in aqueous borax solutions. *Progress in Colloid and Polymer Science.*, *106*, 183–187.

Takada, A., Nishimura, M., Koike, A., & Nemoto, N. (1998). Dynamic light scattering and dynamic viscoelasticity of poly(vinylalcohol) in aqueous borax solutions. 4. Further investigation on polymer concentration and molecular weight dependencies. *Macromolecules*, *31*, 436–443.

van Ruymbeke, E., Liu, C.-Y., & Bailly, C. (2007). Quantitative tube model predictions for the linear viscoelasticity of linear polymers. *Rheology Reviews*, 53–134.

Wall, F. T., & Flory, P. J. (1951). Statistical thermodynamics of rubber elasticity. *Journal of Chemical Physics*, *19*, 1435–1439.

Wientjes, R. H. W., Duits, M. H. G., Jongschaap, R. J. J., & Mellema, J. (2000). Linear rheology of guar gum solutions. *Macromolecules*, *33*, 9564–9605.

Williams, M. A. K., Foster, T. J., Martin, D. R., Norton, I. T., Yoshimura, M., & Nishinari, K. (2000). A molecular description of the gelation measurement of konjac mannan. *Biomacromolecules*, *1*, 440–450.

Wise, E. T. (1995). Quantitative evaluation of a smart gel: The PVA/borate system and its response to cis-diols (Ph.D thesis). University of Pittsburgh, U.S.A.

Yang, X. H., & Zhu, W. L. (2006). Note. Modelling the rheological properties of the solution of konjac glucomannan and milk powder. *Food Science and Technology International*, *12*(2), 127–132.

Yang, X. H., & Zhu, W. L. (2010). Expanded discrete relaxation model for konjac glucomannan hydrocolloid. *International Journal of Polymeric Materials*, *59*, 161–172.

Yang, X. H., Zhu, W. L., & Yan, J. F. (2006). A time-temperature rheological study of konjac glucomannan hydrocolloid. *Journal of Biomaterials Science: Polymer Edition*, *17*, 53–59.

Yin, W., Zhang, H., Huang, L., & Nishinari, K. (2008). Effects of the lyotropic series salts on the gelation of konjac glucomannan in aqueous solutions. *Carbohydrate Polymers*, *74*, 68–78.
Yoshimura, M., & Nishinari, K. (1999). Dynamic viscoelastic study on the gelation of konjac glucomannan with different molecular weights. *Food Hydrocolloids*, *13*, 227–233.
Zhang, H., Yoshimura, M., Nishinari, K., Williams, M. A. K., Foster, T. J., & Norton, I. T. (2001). Gelation behaviour of konjac glucomannan with different molecular weights. *Biopolymers*, *59*, 38–50.
Zittle, C. A. (1951). Reaction of borate with substances of biological interest. *Advances in Enzymology*, *12*, 493–527.