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.

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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