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Dilute and semi-dilute solution properties of (1 → 3), (1 → 4)-β-D-glucan, the endosperm cell wall polysaccharide of oats (*Avena sativa* L.)

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Abstract

This paper describes the solution rheology of a high MW β-D-glucan, $[\eta] = 9.3 \pm 0.5$ dl/g, extracted and purified from oat bran. The semi-dilute solution behaviour, when characterised by steady and dynamic shear rheometry, was found to exhibit properties consistent with those of an entangled polysaccharide system. The steady shear data for the concentration (C) region from 0.2 to 2% (w/w) oat β-D-glucan solutions were fitted to the Cross equation over a wider range, in terms of the $C[\eta]$, than investigated previously. For the higher concentration samples, $>\sim 2.7\%$, there was less indication of a zero-shear rate Newtonian plateau. Data for the calculated zero-shear rate viscosity for the latter systems did not fall on the well-known master curve. Instead they showed a systematic deviation, and followed a yield stress modified Cross equation of Rayment and co-workers indicating behaviour more consistent with that of a filled or disperse system, than of an entangled polymer solution.

Keywords: Oat β-glucan; Semi-dilute solution; Viscosity; Oscillatory shear rheometry

1. Introduction

The major component of the endosperm cell walls of the oat grain or caryopsis (*Avena sativa* L.) is a (1 → 3), (1 → 4)-β-D-glucan, known as oat β-glucan. Traditionally oats are used for feed and also milled for human food, such as oatmeal for porridge and ready-to-eat breakfast cereals.

The early interest in oat β-glucan arose from knowledge of its highly viscous properties and therefore potential commercial value as a thickening agent in food formulations and other industrial applications (Wood, 1984). This interest has been stimulated further by the results of numerous animal and human studies showing that oat bran and oat products have beneficial effects in lowering fasting plasma cholesterol levels (Anderson & Bridges, 1993; Braaten et al., 1994b). A reduction in the fasting concentration of plasma cholesterol is considered to reduce the risk of coronary heart disease (CHD). However, not all studies have demonstrated a cholesterol-lowering effect in response to an oat rich diet, a reflection in part of the differences in concentration and physico-chemical properties of β-glucan in different oat products. Nevertheless, on the basis of a review of clinical data (Anon, 1997), the Food and Drug Administration (FDA) of the USA allowed a health claim that the inclusion of oat products in the daily diet may reduce the risk of CHD, based on the capacity of the β-glucan to lower plasma cholesterol levels in human subjects. Oat β-D-glucan also has potential therapeutic value in the treatment of diabetes mellitus, since it is known to reduce postprandial glycaemia and insulinaemia (Braaten et al., 1994a; Wood et al., 1994a). The detailed mechanism(s) by which oat β-D-glucan elicits these metabolic improvements is still uncertain, but its capacity to hydrate and generate viscosity in the stomach and small intestine is undoubtedly an important factor. (Ellis, Rayment, & Wang, 1996; Wood et al., 1994a).

Purified β-glucan extracted from oats is a linear polysaccharide, containing about 70% of 4-O- and 30% of 3-O-linked β-D-glucopyranosyl units. The (1 → 3) linkages occur singly, whereas the (1 → 4) linkages occur in groups of two or three (Parrish, Perlin, & Reese, 1960; Wood, Weisz, Fedec, & Burrows, 1989;

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Wood, Weisz, & Blackwell, 1994b). The overall structure is thus mainly β-(1 → 3)-linked cellotriosyl and cellotetraosyl units. The presence of the (1 → 3) linkages in the oat β-D-glucan is responsible for the solubility in water compared to related (1 → 4) β-D-linked polymers, such as cellulose and mannans, which are also more ordered, fibrous and water insoluble.

Despite the industrial interest in the food manufacturing and brewing sectors, and the medical implications of cereal β-glucan consumption outlined above, there had been few detailed macromolecular (Vårum and Smidsrφd, 1988; Vårum, Smidsrφd, & Brant 1992) and rheological studies of the solution properties until recently. Earlier steady-shear viscosity measurements showed that oat gum solutions exhibited non-Newtonian, shear-thinning behaviour (Wood, 1984). More recently, Bohm and Kulicke (1999a,b), Doublier and Wood (1995), Gomez, Navarro, Manazarea, Horta, and Carbonell (1996, 1997b), Gomez, Navarro, Garnier, Horta, and Carbonell (1997a), reported the flow and viscoelastic properties of oat and barley β-glucan solutions. The cereal β-glucans appear to be, on average at least, structurally identical except for differences in the relative amounts of the β-(1 → 3)-linked cellotriosyl and cellotetraosyl units (Wood, Weisz & Blackwell, 1991). The aim of the present work was to carry out a more detailed investigation of the dilute and semi-dilute solution properties of the β-glucan derived from oat bran and used in previous clinical trials (Braaten et al., 1994a; Wood et al., 1994a). Both steady shear and dynamic experiments were performed. Molecular dispersion of oat gum in an aqueous solution is difficult to achieve because of the problem of β-glucan aggregation (Wang, Wood, Cui, & Ross-Murphy, 2001). Accordingly, a study of the effect of hydration time and heating regimes on the rheology of oat gum was included.

2. Materials and methods

2.1. Preparation and purification of samples from oat bran

Oat gum was prepared in the POS Pilot Plant, Saskatoon, SK, as previously described (Wood et al., 1989). Briefly, this method involved using sodium carbonate at pH 10 at about 45 °C to extract oat β-glucan from oat bran (cv. Hinoat). The soluble fraction was adjusted to pH 4.5, the precipitated protein removed, and the β-glucan precipitated with isopropanol. Analysis of the β-glucan content of this isolate was carried out by the method of McCleary and Glennie-Holmes (1985) using the Megazyme test kit (Megazyme International Ireland, Bray, Co. Wicklow, Ireland) and found to be about 80/100 g on a dry weight basis. Small amounts of starch, pentosans and protein were also present (Doublier & Wood, 1995). The moisture content of the β-glucan samples was determined by force-air oven drying for 16 h at 104 °C using AACC method 44-15A (American Association of Cereal Chemists, 1983). Further purification was carried out as described by Wood et al. (1991) using ammonium sulphate precipitation, but disappointingly only increased purity to 86/100 g β-glucan. For comparison purposes all polymer concentrations quoted, for both oat gum and the purified sample, are based on a β-glucan (% w/w) basis.

2.2. Physical methods

2.2.1. Intrinsic viscosity measurement

The oat gum (80% β-glucan) and the more purified (86%) oat β-glucan sample solutions were both prepared by dispersing in deionized water for 1 h at 80 °C and then mixing overnight using a magnetic stirrer at room temperature. The solutions were filtered (0.45 μm, *Acrodisc* PF Syringe Filter, Pall Corporation, Ann Arbor, MI, USA) to remove any insoluble particulate matter. The intrinsic viscosities of the oat gum and the purified oat β-glucan were determined by dilute solution viscometry using a Cannon Ubbelohde Dilution B glass viscometer (size 50, 0.8–0.4 cSt; Glass Artefact Viscometers, Braintree, Essex, UK) suspended in a constant temperature water bath at 25 ± 0.05 °C. Viscosity measurements (duplicates) were made on oat β-glucan concentrations ranging from 0.033 to 0.10% (w/w). Here relative viscosity, η_r, fell in the range $1.2 < \eta_r < 2.0$, so that the viscosity is essentially Newtonian. Intrinsic viscosity $[\eta]$ was calculated by using the following relationship:

$$[\eta] = \lim_{c\to 0}(\eta_{\mathrm{sp}}/C) = \lim_{c\to 0}(\ln\,\eta_r/C) \tag{1}$$

where C is concentration of polymer, η_r is relative viscosity and η_{sp} is specific viscosity, defined as $\eta_r - 1$. Huggins–Kramer plots of η_{sp}/C and $\ln(\eta_r)/C$ versus C were then used to estimate the intrinsic viscosity $[\eta]$ by extrapolation to zero concentration.

2.2.2. Steady shear and dynamic measurements

The steady shear and dynamic frequency sweep experiments on oat gum solutions were performed on a Rheometric Scientific Fluids Spectrometer (RFS-II, Rheometric Scientific Ltd, Piscataway, NJ, USA.) with cone and plate geometry (diameter 25 mm, cone angle 0.02 radians).

For both steady and dynamic shear measurements, the oat gum samples (β-glucan concentration range 0.45–1.8% (w/w)) were dispersed by stirring in deionized water, using the following times and temperatures: (1) stirred at 80 °C for 1 h and then at room temperature for 24 h (i.e. normal conditions of hydration); (2) stirred at 90 °C for 1 h and then at room temperature for 48 h; (3) stirred at 100 °C for 1 h and then at room temperature for 64 h. These conditions were selected in order to monitor the effects on the degree of hydration of the samples. Sodium azide (0.01% (w/w)) was added to all the solutions to prevent microbial growth.

The behaviour of solutions of oat gum prepared under normal conditions of hydration (i.e. stirred at 80 °C for 1 h and then at room temperature for 24 h) was investigated using a broader β-glucan concentration range, from 0.18 to 3.6% (w/w).

All these rheological measurements were performed in duplicate with the RFS-II at a temperature of 25 °C. For steady shear measurements, the shear rate range was 0.1–1000 s^{-1}. For dynamic experiments initial strain sweep measurement were carried out by measuring complex shear modulus (G^*) over a range of strains from 0.1 to 100%, in 5% increments, at frequencies of 1 or 10 rad/s. From this, a strain was selected to be within the linear viscoelastic range, and frequency sweep experiments were performed using this pre-determined linear strain, over a radial frequency (ω) range from 0.1 to 100 rad/s to measure the frequency (ω) dependent storage (G') and loss moduli (G'').

3. Results

3.1. Intrinsic viscosity of oat β-glucan

The intrinsic viscosity of the oat gum sample was found to be ~9.3 ± 0.5 dl/g, which is in agreement with the result 9.6 dl/g reported by Doublier and Wood (1995). The intrinsic viscosity of the more purified oat β-glucan sample was also measured and found to be 7.5 ± 0.3 dl/g.

3.2. Steady shear viscosity of oat gum

In Fig. 1, oat gum solutions in the concentration range 0.27–1.8% (w/w), show the typical shear-thinning behaviour of semi-flexible polysaccharides. Such systems in semi-dilute solution are typically regarded as entanglement networks (Bohm & Kulicke, 1999a; Doublier & Wood, 1995; Ross-Murphy, 1994). For steady shear measurements at lower concentrations (0.18–0.27% (w/w)) the viscosity-shear rate profile was essentially Newtonian, whereas it became more shear-rate dependent at higher concentrations. All data were fitted to the Cross-equation (Cross, 1965), given below as Eq. (2), perhaps the best empirical model for describing shear-thinning (or pseudoplastic) behaviour of semi-dilute polysaccharide solutions, using Fig.P software (Biosoft, Cambridge, UK).

$$\eta = \eta_\infty + [\eta_{0x} - \eta_\infty]/[1 + (a\dot{\gamma})^p] \tag{2}$$

Here η_{0x} and η_∞ are limiting (Cross) viscosities, at zero and infinite shear rate, a and $\dot{\gamma}$ are a relaxation time and shear rate, respectively, and p is an exponent. It is clear from Fig. 1 that in the initial semi-dilute region (i.e. $C \approx 0.45–1.8\%, C[\eta] \approx 4–16$), the oat gum data fit the Cross model extremely well.

However, the behaviour of the 2.7 and 3.6% oat gum solutions was rather different from the rheological profiles observed for the lower concentrations of oat gum (Fig. 1). Thus, the data seemed to show an upward deviation, with enhanced shear sensitivity at lower shear rates rather than the normal Newtonian plateau observed for the lower

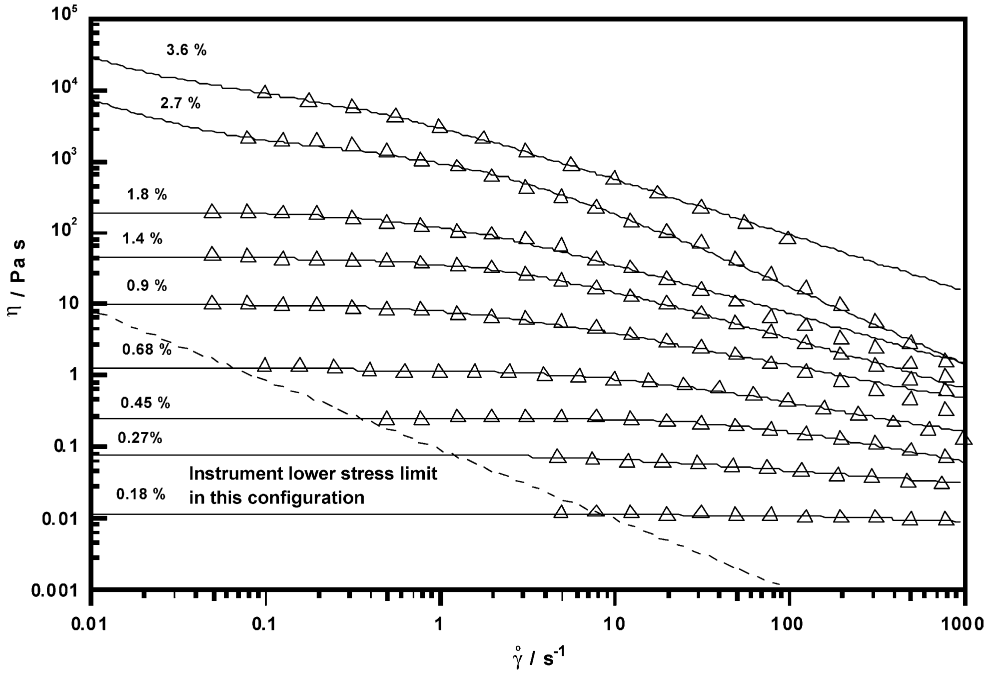

Fig. 1. Log η versus log shear rate for different concentrations of oat gum solution, (expressed as β-glucan % (w/w)): triangles. Solid lines represent the appropriate least squares fitted Cross equation. Dashed line shows the lowest specified measurable stress for this (50 mm cone and plate) geometry taken from the RFS-II manual (Rheometric Scientific, Piscataway, NJ, USA).

concentrations. Not surprisingly, when the Cross model was applied, a poor fit was obtained. These results are similar to those obtained in our earlier rheological studies of mixtures of guar galactomannan and insoluble particulate inclusions or ‘fillers’ (Rayment, Ross-Murphy, & Ellis, 1995, 1998, 2000). Here the viscosity became more shear rate dependent at low shear rates as the volume fractions of these fillers in the polymer solution increased. There was also evidence of an apparent yield stress associated with particulate inclusions and this was also observed with the higher oat gum concentrations. As in our previous experiments, this type of rheological behaviour can be more easily described with a yield stress modified Cross equation as follows:

$$\eta = \eta_\infty + [\eta_{0x} - \eta_\infty]/[1 + (a\dot{\gamma})^p] + (\tau_x/\dot{\gamma}) \qquad (3)$$

Here, compared to Eq. (2), τ_x is the so-called apparent yield stress (Rayment et al., 1995). In subsequent fits the Cross high shear rate viscosity η_∞ parameter was fixed at 5×10^{-3} Pa, (although setting it to be 0 made no difference except to values of a at the lowest concentrations). In other words, Eq. (2) has three and Eq. (3) has four independent parameters. Table 1 gives the shear rate viscosity data for β-glucan solutions fitted to the Cross Eq. (2) and, for the highest concentration samples, to the yield modified Cross model (3). The values calculated for the apparent yield stress parameter (τ_x) were significant only for samples when the concentration was above 2.7% (w/w). As can be seen from this table, values of all the parameters generally varied in the expected way with increasing concentration. On the few occasions where this is not the case, the standard error of the particular parameter was higher.

3.3. Steady shear viscosity of oat gum under different hydration conditions

As mentioned above, to establish if it is possible to increase the amount of dissolved oat gum above that achieved by the standard procedure (80 °C, 1 h), other protocols were employed. In these, the hydration process was carried out either by stirring the solutions at 90 °C for 1 h and then at room temperature for 48 h or at 100 °C for 1 h followed by 64 h at room temperature. Steady shear viscosity measurements were recorded for each of these differently prepared solutions and zero-shear viscosity was estimated from Eq. (2). These results were then compared to the standard method of hydration (see Table 2), showing that, from 0.45–1.8% (w/w) zero-shear viscosity decreased with an increase in temperature of dissolution. These reductions in viscosity suggest that the sample has undergone depolymerisation during heat treatment, disruption of polymer aggregates, or possibly both effects (Picout, Ross-Murphy, Errington, & Harding, 2001; Picout, Ross-Murphy, Jumel, & Harding, 2002).

3.4. Concentration and zero-shear viscosity

The concentration dependence of zero-shear specific viscosity ($\eta_{sp,0}$) can be presented, as seen in Fig. 2, as a double logarithmic plot of $\eta_{sp,0}$ against the coil overlap parameter, $C[\eta]$. This standard procedure follows the approach of Morris, Cutler, Ross-Murphy, Rees, and Price (1981) and many others including Bohm and Kulicke (1999a), Doublier and Wood (1995) and Wang, Ellis, Ross-Murphy and Burchard (1997). Here data for the dilute range were obtained by capillary viscometer and for the semi-dilute range ($>0.18\%$ (w/w)) using the RFSII.

As shown in many previous publications (see, for example, Lapasin & Pricl, 1995), two distinct linear regimes of slope can be identified from this plot. In the first regime, which corresponds mostly to the dilute solution regime (i.e. $C^* \approx 1/[\eta]$), the slope is about 1.1, whereas the second, semi-dilute solution regime, has a slope of ≈4.4. Both values are similar to those reported by other workers for oat β-glucan and barley β-glucan (Bohm & Kulicke, 1999a; Doublier & Wood, 1995) and similar polysaccharides such as guar galactomannan (Robinson, Ross-Murphy, & Morris, 1982).

Kulicke and Keniewske (1984) established a useful empirical model for describing the zero-shear rate specific viscosity dependence on concentration, viz.

$$\eta_{sp,0} = C[\eta] + a(C[\eta])^2 + b(C[\eta])^n \qquad (4)$$

where a, b and n are parameters. This model fits reasonably well to the oat gum data. However, after this fitting, the first

Table 1
Shear rate viscosity data for different concentrations (C) of oat gum (expressed as β-glucan % (w/w)) fitted to the Cross Eq. (2) and yield stress modified Cross Eq. (3)

C, % (w/w)	Eq. (2) (η_0) (Pa s)	Eq. (2) (a)	Eq. (2) (p)	Eq. (3) (η_0) (Pa s)	Eq. (3) (a)	Eq. (3) (τ_x)	Eq. (3) (p)
3.6	12800	7.32	0.72	8500	3.5 ± 0.2	190 ± 15	0.73
2.7	1990	0.94	1.00	1480	0.7 ± 0.4	60 ± 60	1.00
1.8	190	0.80	0.75	180	1.2 ± 0.3	0.7 ± 0.6	0.64
1.4	44	0.61	0.60	N/A	N/A	N/A	N/A
0.9	9.60	0.43	0.52	N/A	N/A	N/A	N/A
0.68	1.20	0.10	0.40	N/A	N/A	N/A	N/A
0.27	0.08	0.05	0.27	N/A	N/A	N/A	N/A
0.18	0.01	0.02	0.17	N/A	N/A	N/A	N/A

± values represent standard errors (SE) from non-linear fitting.

Table 2
Zero-shear viscosities of oat gum samples, expressed in terms of β-glucan concentration, following different hydration treatments

Concentration, % (w/w)	η_0 (Pa s) (80 °C for 1 h; room temperature: 24 h)	η_0 (Pa s) (90 °C for 1 h; room temperature: 48 h)	η_0 (Pa s) (100 °C for 1 h; room temperature: 64 h)
1.8	198	110	71
1.6	43	39	29
0.9	11.0	5.1	4.8
0.45	0.42	0.25	0.22

parameter, *a*, was found to be very small. Accordingly, by eliminating *a*, a still simpler model can be introduced as follows:

$$\eta_{sp,0} = C[\eta] + b'(C[\eta])^{n'} \tag{5}$$

Here b' and n' are the new parameters. (We note this model now has one *less* parameter than that of two intersecting straight lines). Fig. 2 shows the experimental data obtained in the current study and also data reported by Doublier and Wood (1995). Both sets of data fit very well. Overall, the behaviour of the β-glucan solutions seems to be consistent with that of many other random coil polysaccharides, except at the highest polymer concentrations. An explanation of this apparent anomalous behaviour is given in Section 4.

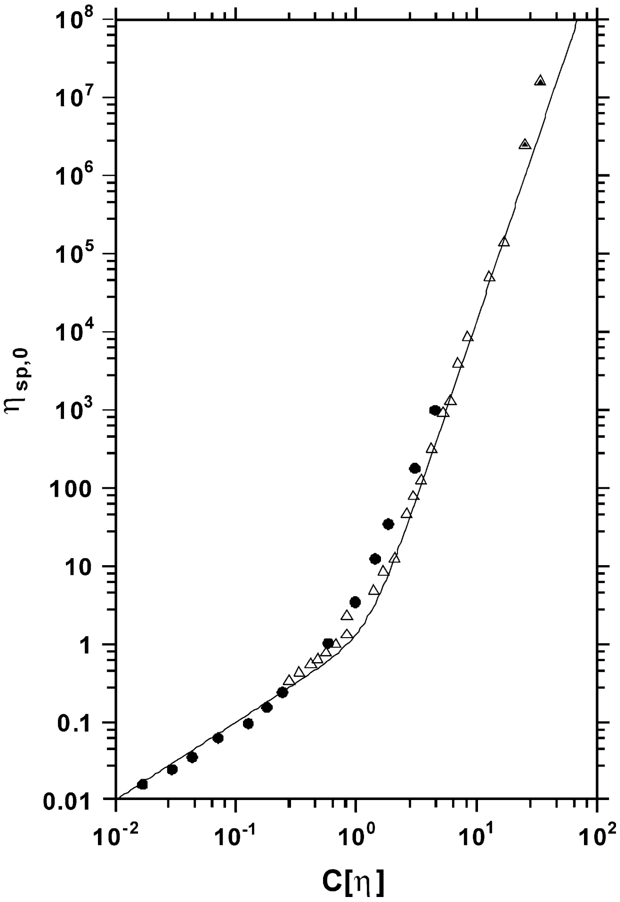

Fig. 2. Log $\eta_{sp,0}$ versus log $C[\eta]$ for oat β-glucan. Filled circles: data of Doublier and Wood (1995); triangles: present work, fitted using appropriate Cross equations. Solid line represents our modified Kulicke–Keniewske equation (Eq. (5)). The two upper triangles (part solid) were fitted to the yield stress modified Cross equation, Eq. (3), all others using Eq. (2).

3.5. Dynamic measurements

In strain sweep experiments, the G^* values were reasonably independent of strain for 1.8, 0.9 and 0.45% (w/w) oat gum solutions from 0.25 to 25%, so 25% strain was used in the frequency sweep experiments described below.

Fig. 3 shows the storage modulus G' and loss modulus G'' for solutions of 1.8, 0.9 and 0.45% (w/w) of oat gum plotted against frequency ω. As the frequency increased, the storage modulus G' increased faster than the loss modulus G'' and the solution property changed from a liquid-like to a more solid-like behaviour ($G' > G''$) (Ferry, 1980; Ross-Murphy, 1994). There was a cross-over between G' and G'' at 2.8 and 22.5 rad/s for 1.8 and 0.9% oat gum solutions, respectively. No cross-over point was found for the 0.45% oat gum solution over the experimental range, i.e. G'' was always $> G'$.

4. Discussion

4.1. Dilute solutions

The β-glucan samples tested in this study were from the same pilot plant extraction as the β-glucan used by Doublier and Wood (1995). It is not surprising, therefore, that the intrinsic viscosity of both samples (80% of oat β-glucan) were found to be about the same, i.e. 9.3 dl/g in this work, 9.6 dl/g in

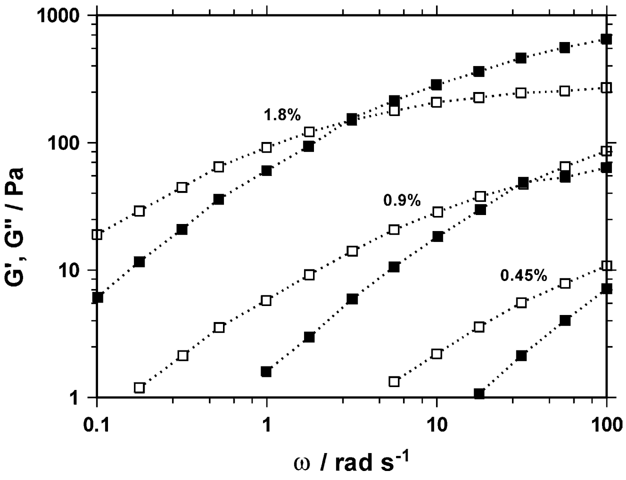

Fig. 3. Log G' ■ and log G'' □ versus log ω for different concentrations of oat β-glucan solutions, as indicated. Dotted lines are a guide to the eye.

the earlier work. Gomez et al. (1997b) reported a significantly lower value of 5.2 dl/g for barley β-glucan, which is similar to more recent values (Bohm & Kulicke, 1999a).

4.2. Semi-dilute solutions

Rheological data for semi-dilute solutions of oat and barley β-glucan have been reported (Doublier & Wood, 1995; Gomez et al., 1996). The work of Doublier and Wood covers some of the same ground as this paper, although the measurements were more limited.

The results of our own rheological studies of oat β-glucan solution appear to be straightforward, in that oat gum behaves like any other polysaccharide entangled system, such as guar galactomannan, at least up to 1.8% (w/w). However, at higher concentrations, the data appear to show a change in behaviour. These solutions appear to show an upward trend at the low shear rates, indicating that the system is more rate-dependent, and there is evidence of an apparent yield stress. The same type of 'power-law' behaviour has been reported in previous studies of guar galactomannan and insoluble particulates (filler), such as starch granules and microcrystalline cellulose (Rayment et al., 1995, 1998, 2000). A possible interpretation of the results in the present study is that the β-glucan solutions contain insoluble particulates, which could be impurities in the original β-glucan sample (e.g. protein, starch) and/or aggregates of β-glucan. The contribution of the filler to the rheology would likely only become noticeable at the higher β-glucan concentrations. Both starch and protein impurities could contribute to the filler effect. The amount of β-glucan aggregates detected at low concentrations under the conditions of size exclusion chromatography is low, but these will be more favoured at higher concentrations (Vårum et al., 1992; Wang, Wood, & Cui, 2002).

In mixtures of proteins and polysaccharides, there is a tendency to phase separate. Doublier and Wood (1995) suggested that the protein might form essentially insoluble aggregates due to these effects. We consider this a less likely explanation for the observed behaviour. Attempts were made in this study to improve the solubility of β-glucan by using higher temperatures and longer hydration times to encourage dissolution of possible aggregates. In most cases the solutions were, if not totally transparent, at least only very slightly turbid. The results presented in Table 2 clearly show that the zero-shear viscosity, estimated from the Cross equation, decreased under conditions selected to improve solubility of β-glucan, i.e. higher temperatures and longer hydration times. The reduction in viscosity can be attributed to polymer degradation, due to cleavage of glycosidic bonds, and/or disruption of supramolecular aggregates. Recently, Wang et al. (2001) distinguished between these two processes by determining intrinsic viscosity using water–cadoxen mixtures as solvents for dispersing polysaccharides. High temperature and pressure (autoclaving at 121 °C for 15 min) depolymerised the β-glucan, but microwave heating at 100 °C for up to 1 h did not.

Bohm and Kulicke (1999a,b) published rheological studies of barley β-glucan in concentrated solution (from 2 to 10% (w/w)). Their studies showed a transition from typical solution behaviour to gel-like properties over a period of several hours. Compared to oat β-glucan, the intrinsic viscosity and, presumably, the molecular weight of barley β-glucan are significantly lower and thus the zero-shear viscosity of barley β-glucan solution is also lower than that of oat β-glucan solution at the same concentration. In particular, the zero-shear viscosity of 6 and 10% (w/w) of barley β-glucan solutions corresponds to that for ~2% (w/w) oat β-glucan solution. Making higher concentrations was extremely difficult as we mention above. It may be that, like amylose systems (Clark, Gidley, Richardson, & Ross-Murphy, 1989; Gidley, 1989), lower MW samples undergo substantial aggregation and gelation, whereas this is not so favoured, either thermodynamically or kinetically, at higher molecular weight.

As noted earlier, Fig. 2 shows that the concentration dependence of $\eta_{sp,0}$ for these oat β-glucan solutions at concentrations $<\sim 1.8\%$ (w/w) is compatible with data seen in studies of many other polysaccharide solutions. However, the anomalous behaviour at the highest β-glucan concentrations can only be explained if the β-glucan solution contains particles possibly from β-glucan aggregation. It also appears, from this plot, that the effect of concentration (volume packing) on the viscosity of the β-glucan, and the transition between dilute and semi-dilute, is more continuous than some have previously recognised. This is borne out by the excellent fit of the data to the modified non-linear Kulicke–Keniewske (KK) model.

Models that show two (or even three) discontinuous changes of slope in the log η_{sp} (or more formally $\eta_{sp,0}$ to indicate that this is a zero-shear rate value) versus log $C[\eta]$ are quite soundly based theoretically. However, they neglect the nature of the biopolymer solutions (or mixtures) and the effects of finite chain length and molecular weight distribution (almost all theoretical approaches are for very long, monodisperse, flexible chains, where asymptotic behaviour will be seen). While for pragmatic reasons it may be attractive to continue representing the data in this form, statistically it can scarcely ever be justified, since models, such as the modified KK equation described above fit the data just as well (if not even better) and with fewer parameters. The rationale for pursuing the discontinuous models lies in the attraction of identifying clear 'critical concentrations' at the various discontinuities. In fact, these are by their nature, rather artificial, and it is more appropriate to regard the change in rate of increase as occurring over perhaps a range of $\sim 2-4\times$ in concentration (or $C[\eta]$) terms.

The dynamic mechanical results seem to be largely consistent with much of the data published in the literature for the rheology of polysaccharide solutions

(Lapasin & Pricl, 1995). Nevertheless, results at higher frequencies partly contradict the data published by Doublier and Wood (1995), who reported mechanical spectra with rather different shaped profiles and cross-over frequencies for the same type of β-glucan at similar polymer concentrations.

5. Conclusions

Results from both dilute and semi-dilute solutions confirm earlier conclusions by Wood and Doublier that the response of the oat gum β-glucan solutions are of the entangled network form, with a zero-shear viscosity plateau and with the usual form of the $\eta_{sp,0}$ versus $C[\eta]$ behaviour. The only exception to this is at the highest polymer concentrations, where anomalous behaviour occurs and, following Rayment and co-workers, we attribute this to the presence of insoluble filler material. Despite this, the form of the $\eta_{sp,0}$ versus $C[\eta]$ curve allows us to employ a modified version of the Kulicke–Keniewske model, which suggests there is continuous curvature in the intermediate region between dilute and semi-dilute regions. This indeed is to be expected from both polydispersity and finite chain length effects.

Perhaps the one major disappointment was that, despite much effort, we were unable to prepare a high purity sample. Even after extensive preparative and separation work, the purity of the sample did not exceed 86%. This means that dilute solution work and the macromolecular interpretation thereof was not attempted. We still surmise, following our own recent work on (1 → 4) polysaccharides (Picout et al., 2001, 2002; Picout & Ross-Murphy, 2002), that the persistence length in water will be similar to, but slightly below that of the cellulose backbone, say ~3–4 nm, because of the influence of the irregular (1 → 3) linkage pattern. To establish this unequivocally requires both a higher purity sample, and appropriate solubilisation approaches (Picout et al., 2001, 2002; Wang et al., 2001, 2002) to avoid the micellar structure observed by others (Vårum et al., 1992)

The differences observed in zero-shear specific viscosity with different heat treatments indicate that the details of dispersion methods applied may also affect subsequent rheological measurements quite profoundly. This includes cross-over values of G' and G'', and indeed possible gelation or gelation rate, which is more likely with lower MW than the oat β-glucan sample used here (Bohme & Kulicke 1999b; Doublier & Wood, 1995). These possibilities are under investigation.

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