Carbohydrate Polymers **22** (1993) 223–232

Xanthan-like 'weak gel' rheology from dispersions of ispaghula seed husk

Anwarul Haque, Robert K. Richardson, Edwin R. Morris*

Department of Food Research & Technology, Cranfield University, Silsoe College, Silsoe, Bedford, UK MK45 4DT

&

Iain C. M. Dea

Leatherhead Food Research Association, Randalls Road, Leatherhead, Surrey, UK KT22 7RY

(Received 26 June 1993; accepted 12 July 1993)

Dispersions of isabgol, the milled seed husk from *Plantago ovata* Forsk (alternatively known as ispaghula), show 'weak-gel' properties broadly similar to those of xanthan and related polysaccharides with rigid, ordered structures in solution. The origin of this behaviour is attributed to tenuous association of fibrillar assemblies visualised by light microscopy. The network structure is retained to $\sim$80°C, but decreases steeply at higher temperatures. The melting process is accompanied by a sharp change in optical rotation of the extracted polysaccharide component of isabgol. An earlier change in optical rotation at lower temperature is tentatively attributed to conformational rearrangement of xylan chains within an ordered, intermolecular structure. Aqueous solutions of the extracted polysaccharide form gels which gradually contract on prolonged storage, consistent with progressive re-formation of the fibrillar structure seen for intact isabgol. Loss of gel-like character in isabgol dispersions occurs over the same temperature range as thermogelation of hydroxypropylmethylcellulose, suggesting opportunities for combined use of the two materials as a substitute (or supplement) for gluten in baked products.

INTRODUCTION

The genus *Plantago* comprises about 200 species of herbs or shrubs widely distributed in the temperate regions of the world (Glicksman, 1969). The outer skin (or husk) of the seeds yields a viscous polysaccharide mucilage on extraction with boiling water. The dried extract from *P. psyllium* and related species is available commercially as 'psyllium seed gum'. Material of similar, but not identical, composition from *P. ovata* Forsk (or *P. ispaghula* Roxb.) is known as ispaghula (sometimes also referred to as 'blond' psyllium, because of its light colour).

Ispaghula husk has a long history of medicinal use, particularly in the Indian sub-continent, where it is known as 'isabgol' (the name which, for brevity, will now be adopted to refer specifically to the milled seed husk of *P. ovata* Forsk). Its main application is as a laxative, and for alleviation of large-bowel disorders such as diverticular disease (see, for example, Leeds, 1985).

Isabgol contains $\sim$15% of non-polysaccharide material (Kennedy *et al.*, 1979). The remaining 85% appears to consist of a single polysaccharide, comprising D-xylose ($\sim$62%), L-arabinose ($\sim$20%), L-rhamnose ($\sim$9%) and D-galacturonic acid ($\sim$9%). The sugars present, and their approximate proportions, were first determined by Laidlaw and Percival (1949, 1950). Although the full primary structure has yet to be elucidated, the principal features have been established (Kennedy *et al.*, 1979; Sandhu *et al.*, 1981). The polysaccharide has a linear backbone of β-D-xylose residues in the pyranose ring form, with single-sugar sidechains of α-L-arabinose (furanose ring form) and β-D-xylose (pyranose ring form) and disaccharide sidechains with terminal α-D-galacturonic acid linked to O-2 of α-L-rhamose. All three types of sidechain may be attached to either O-2 or O-3 of xylose in the polymer backbone.

---

*To whom correspondence should be addressed.

Carbohydrate Polymers 0144-8617/94/$07.00

The backbone has both (1 → 3) and (1 → 4) linkages, but their sequence, and the distribution of sidechains, have not yet been determined.

It has recently been reported (Haque *et al.*, 1993) that mixtures of isabgol and hydroxypropylmethylcellulose (HPMC) are an effective substitute for wheat gluten in bread-making, with the two materials stabilising gas cells over different, complementary ranges of temperature. We now give a fuller description of the rheological, structural and conformational properties of isabgol, and compare the temperature dependence of rheology for gluten and for mixtures of isabgol with HPMC.

MATERIALS AND METHODS

The isabgol sample used was from Weikfield International, Nagar Road, Pune 411014, India, and was obtained through the UK distributors P. S. Sahney & Co. Ltd, 5 Acton Vale Industrial Park, The Vale, Cowley Road, London, W3. A sample of wheat gluten ('Abravit') was kindly supplied by ABR Food Ltd, Hunters Road, Weldon Industrial Estate, Corby, Northants, UK NN17 1JR. The HPMC sample was Methocel K4M from Dow, and was identical to the material used by Haque *et al.* (1993) for production of gluten-free bread. The extent of substitution in this specific batch (number of substituents per sugar ring) is 1·40 for methyl and 0·22 for hydroxypropyl (pers. comm., 1992, Dr N. Sarkar, The Dow Chemical Company, Inc.).

The polysaccharide fraction of isabgol was extracted by dispersing the milled husk (2·5 g) in 2·5 M NaOH (500 ml), soaking for 30 min at ambient temperature, and removing the insoluble non-carbohydrate fraction by filtration. The filtrate was then neutralised with HCl, dialysed exhaustively against deionised water to remove the salt formed on neutralisation, and freeze-dried.

Isabgol dispersions were prepared in hot (~95°C) deionised water by manual stirring, and homogenised using a Silverson high-shear blender. Gluten was dispersed in deionised water by mechanical stirring at ambient temperature. Methocel solutions were prepared by the following method. Approximately one-third of the total volume of water needed was heated to almost boiling (~95°C), and the polysaccharide was dispersed in it, by vigorous manual stirring, to give a thick, homogeneous paste. The remainder of the water was then added at ambient temperature, and stirring was continued until a clear solution was obtained (typically 30 min). The sample was then heated again to ~95°C, shaken vigorously to disrupt the gel, and degassed under reduced pressure in a vacuum desiccator. The heating, shaking, and evacuation steps were repeated until no further bubbles of gas were released under suction.

Rheological measurements under low-amplitude oscillatory shear were made using cone-and-plate geometry (50 mm radius; 0·02 rad cone angle) on a sensitive prototype rheometer designed and constructed by one of the authors (R.K.R.). Temperature was controlled using a programmable circulating water bath and monitored by a thermocouple attached to the stationary element. The exposed periphery of the sample was coated with light silicone oil to minimise loss of water at high temperature. Steady-shear viscosity was measured on a Sangamo Viscoelastic Analyser, using a 50 mm, 2 degree cone-and-plate configuration.

Differential scanning calorimetry (DSC) measurements were made using a Setaram microcalorimeter. Sample and reference pans were balanced to within 0·5 mg. Optical rotation was measured at 365 nm on a Perkin-Elmer 241 polarimeter, using a jacketed cell of pathlength 10 cm. Temperature was controlled by a circulating water bath and measured using a thermocouple in the neck of the cell (but out of the light path). Readings were taken after thermal equilibration at each temperature (typically 5 min). Samples for light microscopy were exposed directly to a 0·1% aqueous solution of toluidine blue, which stains polysaccharides pink/lilac, and were examined on an Olympus BHS microscope, using transmitted bright-field illumination.

RHEOLOGY OF ISABGOL DISPERSIONS

Isabgol does not completely dissolve in water, but swells to a mucilaginous dispersion with the general appearance of wallpaper paste. Figure 1 shows the mechanical spectrum (frequency dependence of G', G'' and η^*) obtained for a 1% (w/v) dispersion at 25°C. The spectrum is typically gel-like, with elastic response (storage modulus, G') exceeding viscous flow (loss modulus, G'') throughout the accessible range of frequency (ω). The complex dynamic viscosity (η^*) shows no indication of levelling out to a constant 'Newtonian' value at low frequency; instead, $\log \eta^*$ decreases linearly with increasing $\log \omega$, with a slope of −0·84, substantially steeper than the maximum value of −0·76 observed (Morris, 1990) for disordered polysaccharides interacting by topological entanglement. Similar behaviour is well documented for xanthan and related materials, which generate 'weak-gel' networks by tenuous association of rigid, ordered molecular structures in solution (Ross-Murphy *et al.*, 1983; Morris, 1991; Robinson *et al.*, 1991).

Increasing the concentration (c) of isabgol by a factor of 2 (to 2% (w/v); Fig. 2) gives about an eight-fold increase in G' (from ~6·5 to ~50 Pa s at 0·1 rad s^{-1}), so that the modulus is approximately proportional to c^3 within this range of concentration (which spans the values relevant to the baking trials reported by Haque

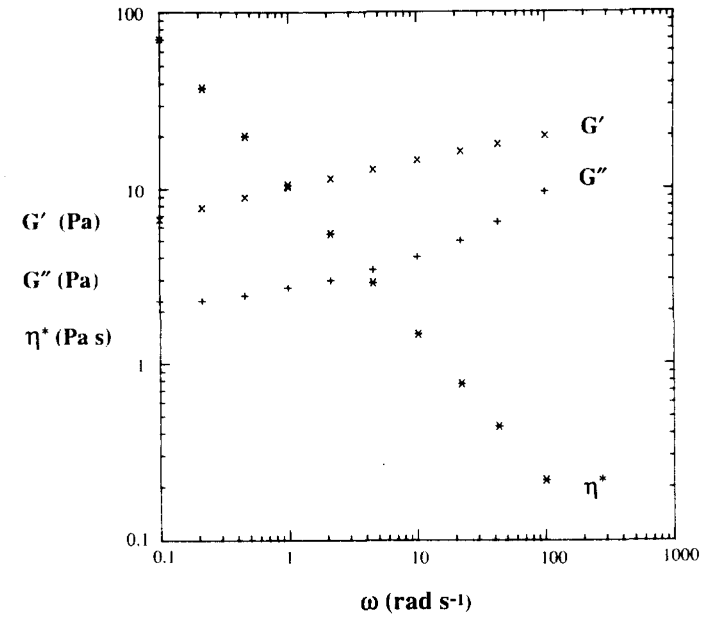

Fig. 1. Mechanical spectrum (25°C; 2% strain) for 1% (w/v) isabgol, showing the variation of G' (×), G'' (+) and η^* (*) with frequency (ω).

et al. (1993)). Steady shear viscosity (η) from rotational measurements on the same sample is appreciably lower (Fig. 2) than η^* from small-deformation oscillatory measurements (2% strain) at equivalent values of frequency (ω) and shear rate ($\dot{\gamma}$). This is again a characteristic feature of 'weak gels' (Clark & Ross-Murphy, 1987), where molecular associations survive low-amplitude oscillation but are broken down under steady shear, and contrasts with the behaviour of entangled coils, which show close 'Cox–Merz' superposition (Cox & Merz, 1958) of $\eta^*(\omega)$ and $\eta(\dot{\gamma})$.

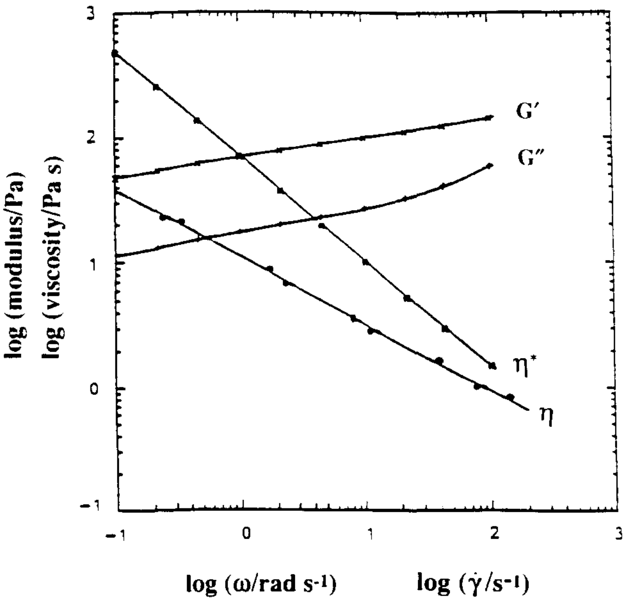

Fig. 2. Frequency (ω) dependence of G', G'' and η^*, and shear rate ($\dot{\gamma}$) dependence of steady shear viscosity (η) for 2% (w/v) isabgol at 25°C.

As shown in Fig. 3, G', G'' and η^* remain independent of amplitude of oscillation up to the highest values at which reliable measurements could be made (10% strain). Thus, the amplitude used throughout the investigations reported below (2% strain) is well within the 'linear region' of mechanical response, where the weak-gel network is not disrupted by the strains imposed in making the measurements.

TEMPERATURE DEPENDENCY OF RHEOLOGY

Figures 4 and 5 show the temperature dependent changes in G', G'' and $\tan\delta$ observed for isabgol dispersions at, respectively, 1 and 2% (w/v). At both concentrations, the values recorded at equivalent temperatures on heating and cooling ($1\,\mathrm{deg\,min^{-1}}$) superimpose closely (i.e. there is no significant thermal hysteresis in the temperature-course of rheological change).

The most notable feature is a sharp decrease in both moduli above ~80°C, with an associated increase in $\tan\delta$ (G''/G'). Such behaviour is characteristic of gel melting, but at the highest temperature at which measurements could be made (~93°C) the moduli are still descending steeply, indicating that the melting process has not reached completion. This conclusion is reinforced by the high-temperature mechanical spectrum presented in Fig. 6, which shows clear indications of residual gel-like character ($G' > G''$ at low frequency, with little frequency-dependence in either modulus).

The changes in rheology at lower temperature (Figs 4 and 5) are more gradual, but there is evidence of an initial decrease in moduli, with associated increase in $\tan\delta$, followed by a 'plateau' of reduced temperature

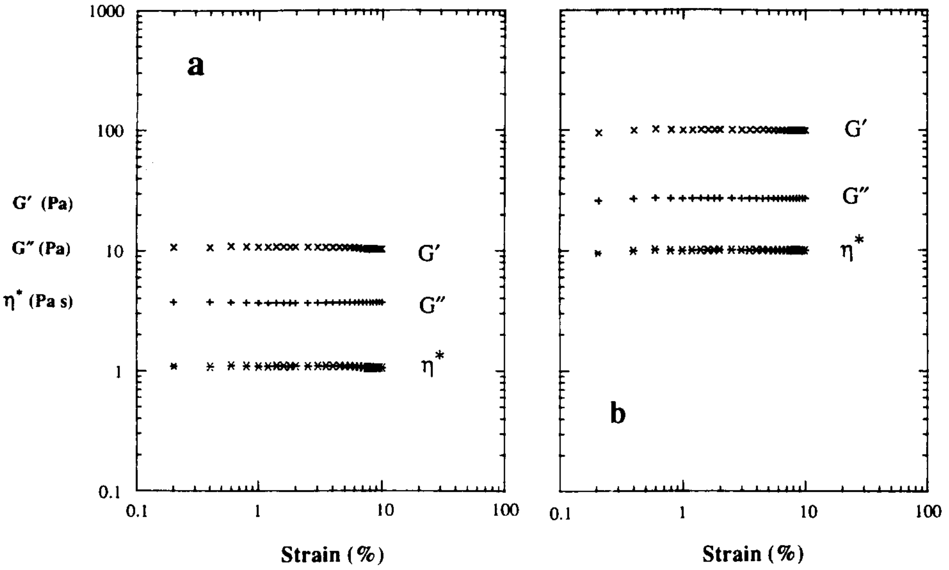

Fig. 3. Strain dependence (10 rad s^{-1}; 25°C) of G' (×), G'' (+) and η^* (∗) for isabgol dispersions at (a) 1% (w/v) and (b) 2% (w/v).

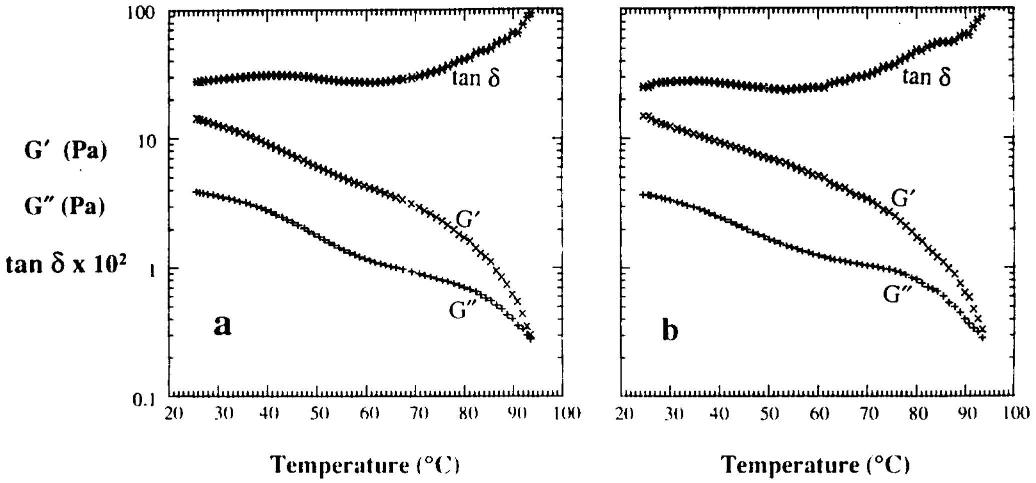

Fig. 4. Temperature dependence of G' (×), G'' (+) and tan δ (∗) for 1% (w/v) isabgol on (a) heating and (b) cooling at 1 deg min^{-1}. Measurements were made at 10 rad s^{-1} and 2% strain.

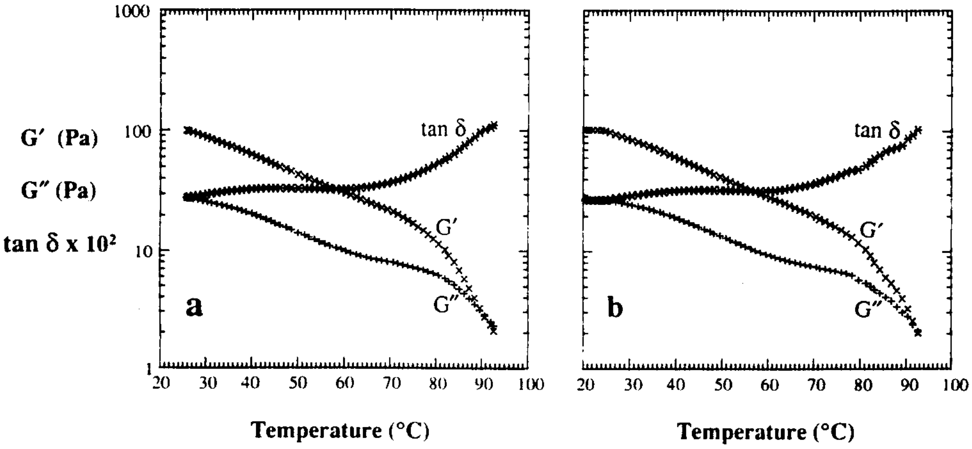

Fig. 5. Temperature dependence of G' (×), G'' (+) and tan δ (∗) for 2% (w/v) isabgol on (a) heating and (b) cooling. Conditions as in Fig. 4.

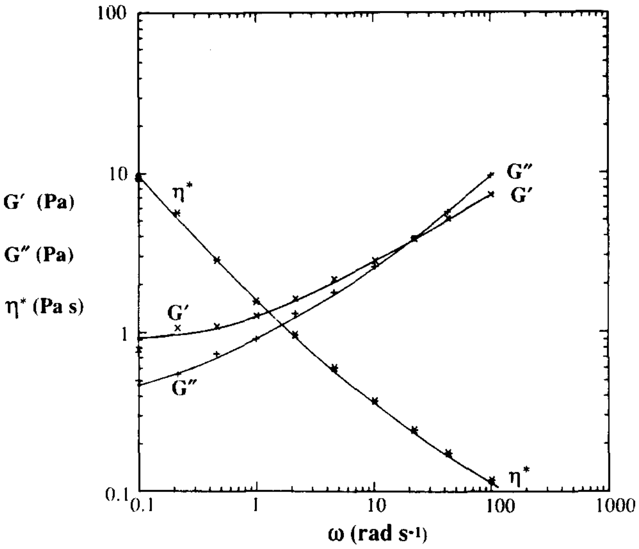

Fig. 6. Frequency dependence (2% strain) of G' (×), G'' (+) and η^* (*) for 2% (w/v) isabgol at 91°C.

dependence before the onset of the final melting process. As reported below, a similar pattern of change is observed in optical rotation of the polysaccharide component of isabgol.

LIGHT MICROSCOPY

Figure 7(a) shows an illustrative micrograph for isabgol powder strained with toluidine blue. Large fragments of plant cell wall material with sizes in the range 1–2 mm are clearly visible. On hydration in the stain, these swelled rapidly and the outlines of the cells became indistinct.

After dispersion to the 'weak-gel' state, isabgol gave micrographs showing a matrix of fibrillar strands with a range of lengths extending to 20–30 μm (Fig. 7(b)). The whole matrix stained red/lilac with toluidine blue, as expected for material composed predominantly of polysaccharide.

NETWORK PROPERTIES OF ISABGOL POLYSACCHARIDE

As shown in Fig. 8, freshly prepared solutions of the polysaccharide component of isabgol (1% (w/v) in deionised water) gave flow properties broadly similar to those of disordered coils, with a Newtonian plateau in $\log \eta$ versus $\log \dot{\gamma}$ at low shear-rate. In successive scans between low and high values of $\dot{\gamma}$ (over a period of ~30 min), however, the measured viscosity showed a progressive shift to higher values at equivalent shear rates.

At longer times, solutions of the extracted polysaccharide formed cohesive gels. These showed obvious syneresis, and continued to contract on storage over long periods (to about 30% of their original volume after three months). Substantial (approximately two-fold) further contraction was observed on freezing and thawing. Gradual formation of intermolecular junctions, accelerated by freeze–thaw cycling, is well documented for a number of other plant polysaccharides, particularly the galactomannans (e.g. Dea *et al.*, 1977, 1986).

It was observed, however, that the high-salt solutions formed by neutralisation of the alkaline extract remained stable on prolonged storage, with no evidence of gelation or precipitation. Since high ionic strength would normally be expected to promote association of charged polysaccharide chains by screening electrostatic repulsion, this behaviour is probably a 'salting in' effect, arising from non-specific (lyotropic) modification of the solvent quality of water by the high concentration of salt (2·5 M).

POLARIMETRY AND DSC

Figure 9 shows the temperature dependence of optical rotation (365 nm; 10 cm pathlength) for a dilute solution of the extracted polysaccharide (0·1% (w/v) in deionised water). The values recorded on heating and on cooling superimpose closely, and show two regions of steep descent at low and high temperature, with an intermediate region (from ~45 to ~65°C) in which there is little change in optical activity. The overall temperature-course is broadly similar to the changes in $\tan\delta$ observed (Figs 4 and 5) on heating and cooling dispersions of intact isabgol.

DSC measurements showed no discernible enthalpic transitions for isabgol dispersions (2% (w/v)) throughout the temperature-range of rheological and chiroptical change. Similar featureless traces were obtained for moderately concentrated (2% (w/v)) solutions of the extracted polysaccharide.

BEHAVIOUR OF ISABGOL IN COMBINATION WITH HPMC

Figure 10 shows the mechanical spectrum (25°C) obtained for a 1% (w/v) dispersion of isabgol in the presence of 1% (w/v) HPMC. The 'weak-gel' properties of isabgol ($G' > G''$) are clearly evident at low frequency, but are progressively obscured at higher frequencies by the contribution to overall rheological response from entanglement-coupling of HPMC (Haque *et al.*, 1993).

The rheological changes observed on heating (Fig. 11(a)) are fully reversible on cooling (Fig. 11(b)), but with the thermal hysteresis anticipated from the thermogelation behaviour of HPMC alone.

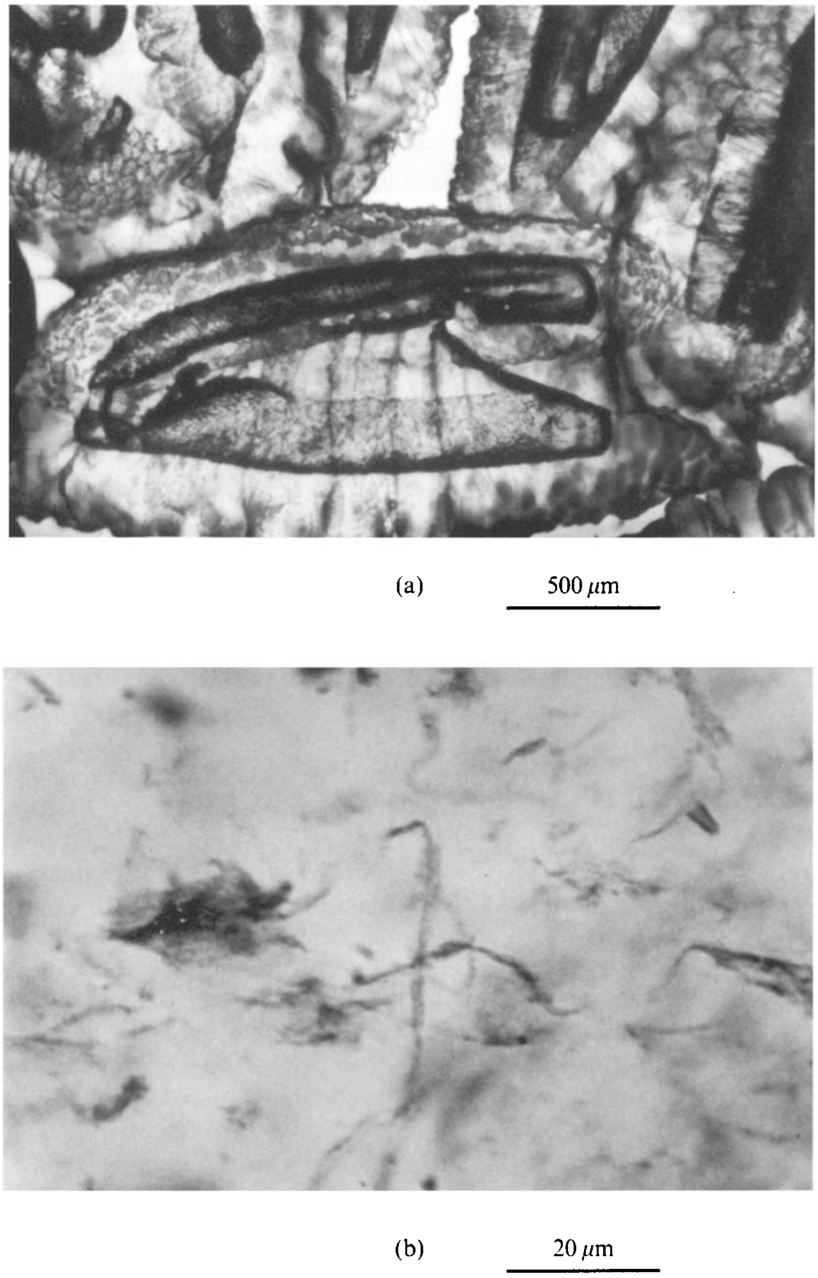

Fig. 7. Light micrographs for isabgol, stained with toluidine blue, (a) in powder form, and (b) in the 'weak-gel' state.

Figure 12 presents a direct comparison of the changes in solid-like response (G'; 10 rad s^{-1}) on heating for 2% (w/v) isabgol, 2% (w/v) HPMC, and a 50/50 mixture of the two (i.e. with both materials present at 1% (w/v), as in Figs 10 and 11). The onset of the steep decline in G' for isabgol occurs at about the same temperature (80°C) as the onset of the second, major 'wave' of increase in G' for HPMC. In the mixed system, the two effects cancel out, with the first, smaller, increase in G' for HPMC similarly balancing the progressive weakening of the isabgol network over the same temperature-range, to give an essentially constant value of G' above about 50°C.

COMPARISON WITH GLUTEN

Figure 13 shows the mechanical spectrum obtained for a 2% (w/v) dispersion of wheat gluten at 33°C (chosen as representative of the proving temperatures typically used in bread-making). The spectrum has obvious gel-like character, with $G' > G''$, little frequency dependence in either modulus, and $\log \eta^*$ decreasing linearly with increasing $\log \omega$. The gel-like character persists on heating (Fig. 14), with G' remaining higher than G'' throughout the accessible temperature range. The ratio of the two moduli ($\tan \delta = G''/G'$) remains constant up to ~55°C, although the individual values both decrease. At higher

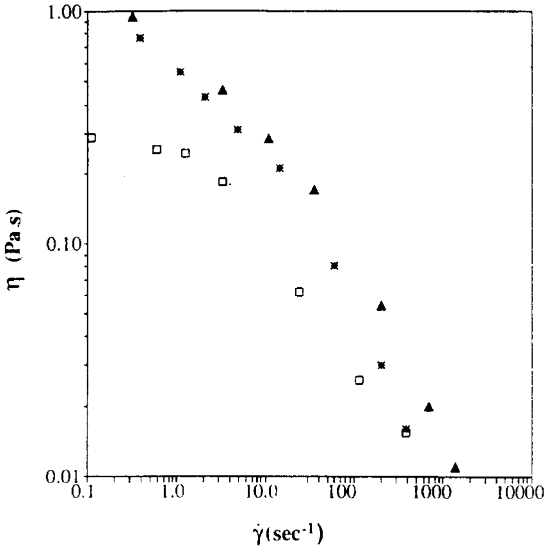

Fig. 8. Measured viscosities for a freshly prepared solution of isabgol polysaccharide (1% (w/v); 25°C) as the applied shear rate ($\dot{\gamma}$) was increased (□), decreased (*), and again increased (▲) over a period of ~30 min.

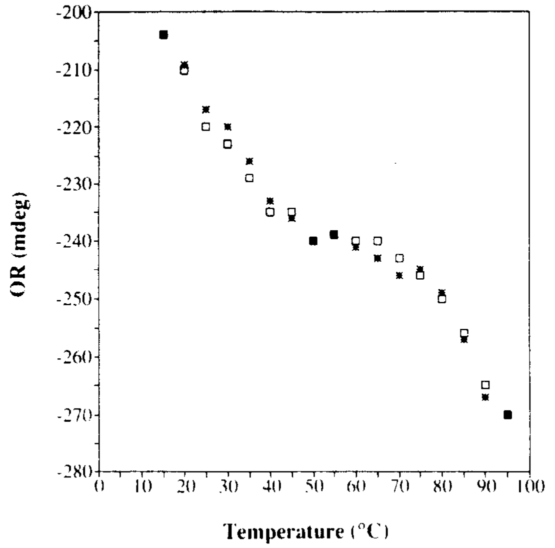

Fig. 9. Temperature dependence of optical rotation (365 nm; 10 cm pathlength) for isabgol polysaccharide (0·1% (w/v)) on heating (□) and cooling (*).

temperatures the proportion of solid-like response increases (i.e. tan δ decreases), mainly due to a continued reduction in G'', with G' remaining essentially constant to ~90°C. Indeed, the temperature dependence of G' for gluten is closely similar in form (Fig. 14) to that observed for the mixed system of isabgol and HPMC shown in Fig. 12, although the absolute values are appreciably higher.

DISCUSSION

Previous studies of the rheology of isabgol (Baveja & Gupta, 1968*a*, *b*, 1969) and psyllium seed gum (Mattha, 1977*a*, *b*) have been confined to measurements of viscosity under steady shear. Observations of particle-suspending behaviour (Baveja & Gupta, 1968*b*) and of hysteresis between apparent viscosities recorded on increasing and decreasing the applied shear rate (Baveja & Gupta, 1968*a*, 1969) are, however, entirely consistent with the evidence reported here, from low-amplitude oscillatory measurements, that dispersions of isabgol have gel-like properties.

Formation of conventional polysaccharide gels by association of disordered coils into ordered 'junction zones' (Rees *et al.*, 1982) involves substantial loss of entropy and will therefore occur only if the enthalpic advantage is correspondingly large (i.e. if the non-cova-

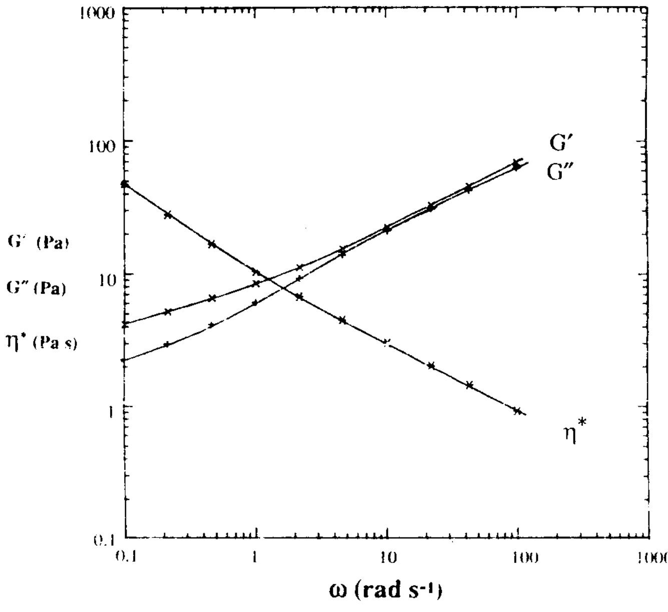

Fig. 10. Frequency dependence of G' (×), G'' (+) and η^* (*) for 1% (w/v) isabgol in combination with 1% (w/v) HPMC, measured at 25°C and 2% strain.

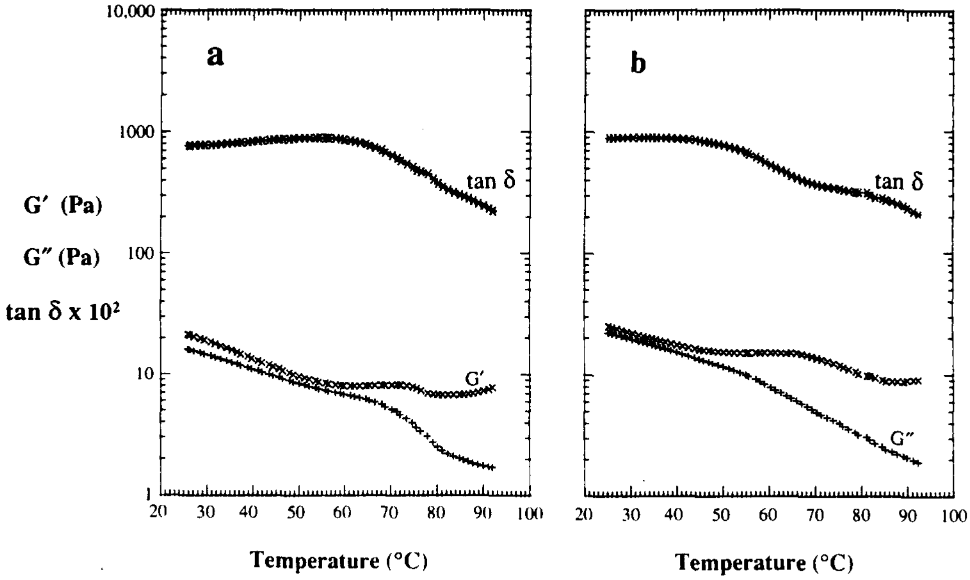

Fig. 11. Temperature dependence of G' (×), G'' (+) and tan δ (*) for 1% (w/v) isabgol in combination with 1% (w/v) HPMC on (a) heating and (b) cooling at 1 deg min^{-1}. Measurements were made at 10 rad s^{-1} and 2% strain.

lent bonding within the intermolecular junctions is strong). Rupture of the resulting networks therefore requires appreciable force. If, however, the polysaccharide chains are already ordered, their association into intermolecular junctions involves little loss of entropy, and will therefore occur even if the bonding is weak (Flory, 1956), giving tenuous networks that break at low stress. This is the situation in 'weak gels' (Morris, 1991).

There is abundant evidence that, except at high temperature and low ionic strength, xanthan exists in solution in a rigid, ordered chain conformation (see, for example, Norton *et al.*, 1984). Association of the ordered chains into a weak, but continuous, network is promoted by salt, with divalent cations (Ca^{2+}) proving particularly effective (Ross-Murphy *et al.*, 1983). Conformational order in solution has also been demonstrated for other bacterial polysaccharides with 'weak-gel' properties, such as the commercial 'biogums' welan and rhamsan (Robinson *et al.*, 1991) and the exopolysaccharides from certain *Arthrobacter* species (Darke *et al.*, 1978).

It therefore seems reasonable to assume that the analogous 'weak-gel' properties of isabgol (Fig. 2) arise in exactly the same way, but with tenuous interactions now occurring between the fibrillar supramolecular assemblies visualised by light microscopy (Fig. 7(b)) rather than at the molecular level.

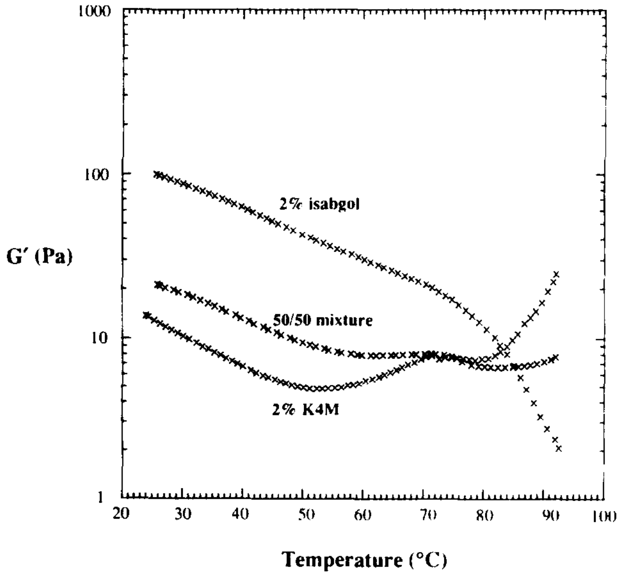

Fig. 12. Variation of G' (10 rad s^{-1}; 2% strain) on heating (1 deg min^{-1}) for 2% (w/v) isabgol, 2% (w/v) HPMC (K4M), and a 50/50 mixture of the two samples.

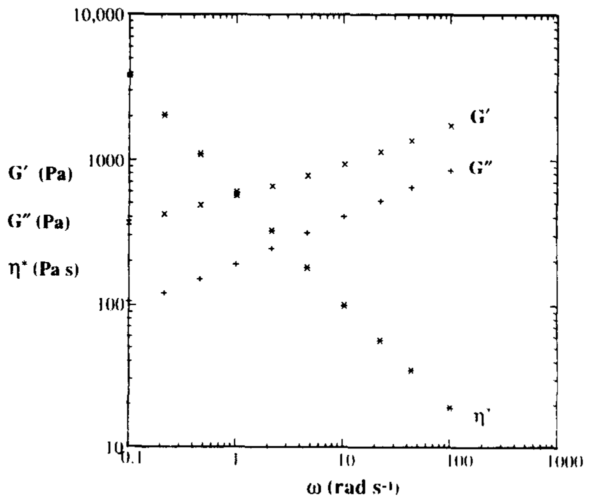

Fig. 13. Frequency dependence of G' (×), G'' (+) and η^* (*) for a 2% (w/v) dispersion of wheat gluten, measured at 33°C and 2% strain.

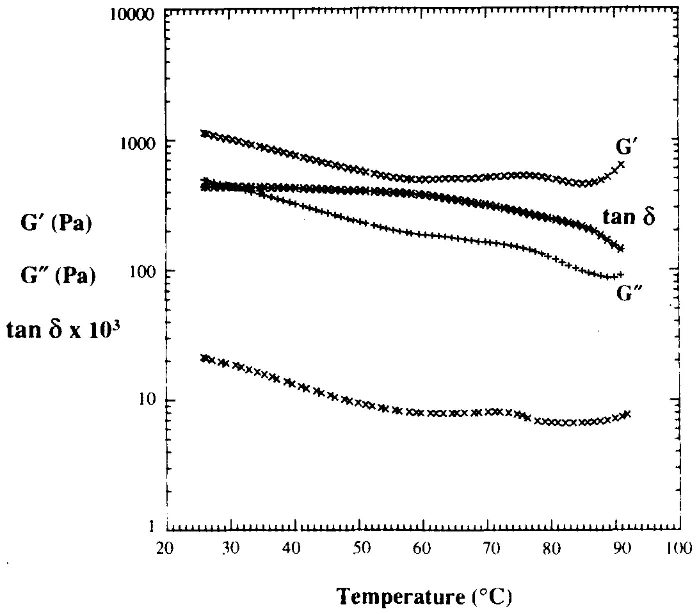

Fig. 14. Variation of G' (×), G'' (+) and tan δ (*) for 2% (w/v) wheat gluten on heating at 1 deg min^{-1}. Measurements were made at 10 rad s^{-1} and 2% strain. The temperature dependence of G' for 1% (w/v) isabgol + 1% (w/v) HPMC (Fig. 12) is included for direct comparison (bottom trace).

Fibrillar strands have been observed previously in studies of the polysaccharide component of isabgol (Sandhu *et al.*, 1981), but on the length-scale of electron microscopy. Gradual association of these strands towards the much larger assemblies present in dispersions of intact isabgol might explain the progressive contraction of network structure observed for isabgol polysaccharide in salt-free conditions.

In the absence of a full description of the primary structure of the polysaccharide, the nature of the intermolecular associations leading to formation of fibrils must remain speculative. Some general conclusions can, however, be drawn. First, ordered packing demands a regular pattern of inter-residue linkage along the polymer chain. Extended regions of consecutive (1 → 3) linkages can probably be dismissed: (1 → 3)-β-D-xylan adopts a co-axial triple helix structure (Atkins & Parker, 1969) closely similar to that of curdlan and related (1 → 3)-β-D-glucans (Deslandes *et al.*, 1980), and the characteristic diffractions of this structure are absent from X-ray patterns for isabgol powder or oriented fibres (Sandhu *et al.*, 1981). Remaining possibilities would include a regular repeating sequence of linkage type, such as the alternating arrangement of (1 → 3) and (1 → 4) linkages found in agars (Araki & Arai, 1967) and carrageenans (Anderson *et al.*, 1973), or distribution of the (1 → 3) linkages in such a way as to leave extended blocks of (1 → 4)-β-D-xylan, as suggested by Sandhu *et al.* (1981).

The latter proposal is an attractive one, and is consistent with the known properties of β-(1 → 4)-xylans. Because of the absence of the hydroxymethyl group at C-6, the xylan chain has considerably greater conformational freedom than cellulose, and packs in the solid state as a twisted three-fold ribbon (Settineri & Marchessault, 1965), not in the extended two-fold structure characteristic of cellulosic materials. The packing arrangement incorporates columns of bound water, which can be displaced to accommodate monosaccharide sidechains at C-2 and/or C-3 of the xylan backbone, without otherwise affecting the lattice structure (Fowle *et al.*, 1970; Nieduszynski & Marchessault, 1972). Such behaviour would, of course, explain the ability of the highly branched isabgol polysaccharide to form condensed fibres.

Fibrillar assembly, with associated development of network properties, is clearly a slow, time dependent process, as demonstrated by the sequential flow curves shown in Fig. 8, and by the formation and progressive contraction of a cohesive gel structure at longer times. It also appears to be concentration dependent, since dilute solutions of the extracted polysaccharide show the electrochemical and electroviscous properties expected of a normal polyelectrolyte (Bandyopadhyay, 1960, 1961), with no evidence of complications from progressive aggregation over the timescale of the measurements. The close agreement between optical rotation values recorded at the beginning and end of a lengthy heating and cooling cycle (Fig. 9) also argues against any significant aggregation at the low concentration used (0·1% (w/v)).

Changes in optical rotation over the same temperature range as the first sharp decrease shown in Fig. 9 have been reported previously for arabinoxylan preparations from sugar cane (Dea *et al.*, 1973), and attributed to conversion from an ordered structure to a disordered coil. The same interpretation cannot be applied to the isabgol system, since it is the second sharp reduction in optical rotation at higher temperature that corresponds (Figs 4 and 5) to the rheological changes that would be expected to accompany loss of conformational order.

One possible explanation is that the transition at lower temperature corresponds to a change in ordered structure, such as conversion from three-fold chain geometry to the two-fold cellulose-like conformation, which is sterically and energetically feasible (Rees & Skerrett, 1968) and is indeed adopted by acetylated xylan in the solid state (Gabbay *et al.*, 1972). A transition of this type, between two structures of comparable enthalpy, would explain the absence of any detectable thermal changes in DSC over the same temperature range. The absence of detectable DSC peaks accompanying the second change in optical rotation and the associated loss of network structure has a more trivial explanation; these processes occur at and beyond the upper temperature limit of the calorimeter.

It must be again emphasised that the above discussion of the possible molecular origin of isabgol fibrils is highly speculative. What does, however, seem clear is that they are directly responsible for the 'weak-gel' properties of isabgol, and that these properties could be of considerable practical value in areas beyond the established, traditional use as 'soluble dietary fibre'.

One patented application (Kobayashi & Kanamori, 1984) is for improvement of dough rheology, particularly in products such as noodles and pasta where good cohesion on stretching is required. The evidence presented here, that isobgol dispersions retain a gel-like character up to the temperatures required for thermogelation of hydrophobic cellulose derivatives (Fig. 12) or globular proteins, points to potential new applications in structuring baked products from flours deficient in gluten.

ACKNOWLEDGEMENTS

We thank Mrs K. Groves for microscopy, Mr H. McEvoy for expert advice and practical assistance, and The British Council for the award of a Study Fellowship to one of us (A. H.).

REFERENCES

Anderson, N.S., Dolan, T.C.S. & Rees, D.A. (1973). *J. Chem. Soc. Trans. Perkin I*, 2173–6.

Araki, C. & Arai, K. (1967). *Bull. Chem. Soc. Japan*, **40**, 1452–6.

Atkins, E.D.T. & Parker, K.D. (1969). *J. Polym. Sci. C*, **28**, 69–81.

Bandyopadhyay, P.C. (1960). *J. Sci. Industr. Res.*, **19B**, 378–81.

Bandyopadhyay, P.C. (1961). *J. Sci. Industr. Res.*, **20B**, 101–4.

Baveja, S.K. & Gupta, B.M. (1968*a*). *Indian J. Pharmacy*, **30**, 187–91.

Baveja, S.K. & Gupta, B.M. (1968*b*). *Indian J. Pharmacy*, **30**, 247–51.

Baveja, S.K. & Gupta, B.M. (1969). *Indian J. Pharmacy*, **31**, 69–71.

Clark, A.H. & Ross-Murphy, S.B. (1987). *Advan. Polym. Sci.*, **83**, 57–192.

Cox, W.P. & Merz, E.H. (1958). *J. Polym. Sci.*, **28**, 619–22.

Darke, A., Morris, E.R., Rees, D.A. & Welsh, E.J. (1978). *Carbohydr. Res.*, **66**, 133–44.

Dea, I.C.M., Rees, D.A., Beveridge, R.J. & Richards, G.N. (1973). *Carbohydr. Res.*, **29**, 363–72.

Dea, I.C.M., Morris, E.R., Rees, D.A., Welsh, E.J., Barnes, H. A. & Price, J. (1977). *Carbohydr. Res.*, **57**, 249–72.

Dea, I.C.M., Clark, A.H. & McCleary, B.V. (1986). *Food Hydrocolloids*, **1**, 129–40.

Deslandes, Y., Marchessault, R.H. & Sarko, A. (1980). *Macromolecules*, **13**, 1466–71.

Flory, P.J. (1956). *Proc. Roy Soc. A*, **234**, 50–73.

Fowle, L.G., Juritz, J.F.W. & Stephen, A.M. (1970). *S. Afr. Med.*, **44**, 152.

Gabbay, S.M., Sundararajan, P.R. & Marchessault, R.H. (1972). *Biopolymers*, **11**, 79–94.

Glicksman, M. (1969). *Gum Technology in the Food Industry*. Academic Press, New York.

Haque, A., Morris, E.R. & Richardson, R.K. (1993). In *Frontiers in Carbohydrate Research 3*, eds. T. Eads, R.P. Millane, J.N. BeMiller & R. Chandrasekaran. Elsevier, New York, in press.

Kennedy, J.F., Sandhu, J.S. & Southgate, D.A.T. (1979). *Carbohydr. Res.*, **75**, 265–74.

Kobayashi, H. & Kanamori, T. (1984). Japanese Patent 88039/84.

Laidlaw, R.A. & Percival, E.G.V. (1949). *J. Chem. Soc.*, 1600–7.

Laidlaw, R.A. & Percival, E.G.V. (1950). *J. Chem. Soc.*, 528–34.

Leeds, A.R. (1985). *Dietary Fibre Perspectives*. John Libbey, London.

Mattha, A.G. (1977*a*). *Pharm. Acta Helv.*, **52**, 210–13.

Mattha, A.G. (1977*b*). *Pharm. Acta Helv.*, **52**, 214–17.

Morris, E.R. (1990). *Carbohydr. Polym.*, **13**, 85–96.

Morris, E.R. (1991). *Int. Food Ingredients*, **1**, 32–7.

Nieduszynski, I.A. & Marchessault, R.H. (1972). *Biopolymers*, **11**, 1335–44.

Norton, I.T., Goodall, D.M., Frangou, S.A., Morris, E.R. & Rees, D.A. (1984). *J. Mol. Biol.*, **175**, 371–94.

Rees, D.A. & Skerrett, R.J. (1968). *Carbohydr. Res.*, **7**, 334–48.

Rees, D.A., Morris, E.R., Thom, D. & Madden, J.K. (1982). In *The Polysaccharides, Vol. 1*, ed. G.O. Aspinall. Academic Press, New York, pp. 195–290.

Robinson, G., Manning, C.E. & Morris, E.R. (1991). In *Food Polymers, Gels and Colloids*, ed. E. Dickinson. Special Publication No. 82, Royal Society of Chemistry, Cambridge, UK, pp. 22–33.

Ross-Murphy, S.B., Morris, V.J. & Morris, E.R. (1983). *Faraday Symp. Chem. Soc.*, **18**, 115–29.

Sandhu, J.S., Hudson, G.J. & Kennedy, J.F. (1981). *Carbohydr. Res.*, **93**, 247–59.

Settineri, W.J. & Marchessault, R.H. (1965). *J. Polym. Sci. C*, **11**, 253–64.