

# Polysaccharide substitutes for gluten in non-wheat bread

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

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

(Received 30 June 1992; revised version received 6 May 1994; accepted 13 May 1994)

Breads with a specific volume up to, and beyond, that of conventional wheat bread can be made with rice flour (which does not contain gluten) by incorporation of hydroxypropylmethylcellulose (HPMC) and ispaghula husk (isabgol) from *Plantago ovata* Forsk. Isabgol disperses to a fibrillar 'weak gel' network stable over the temperature range of proving (fermentation with yeast) and initial heating in the baking oven. Weakening of the isabgol network at higher temperature is accompanied by thermal gelation of HPMC, so that the overall network strength (storage modulus,  $G'$ ) remains virtually constant, and the gas-cell structure developed during proving is retained. Gelation of HPMC (and of methylcellulose) involves two distinct processes which we suggest correspond to partial dissociation and subsequent aggregation of cellulosic 'bundles' present in the solution state at low temperature, a mechanism directly analogous to the thermal gelation of globular proteins.

## INTRODUCTION

It is well established that the gluten fraction of wheat flour has a crucial role in stabilising the gas-cell structure in bread, although its precise mode of action is not yet fully understood in molecular detail (Blanshard *et al.*, 1986). The aim of the present work was to explore the feasibility of producing acceptable bread from rice flour, which does not contain gluten, by using polysaccharides as gluten substitutes.

We have obtained very encouraging results from the combined use of two materials that seem to confer stability over different, complementary, ranges of temperature: a hydrophobic cellulose derivative (hydroxypropylmethylcellulose) and ispaghula husk. The present paper was prepared as a preliminary overview for presentation at the conference *Frontiers in Carbohydrate Research 3* held in April 1992. Since then, the following specific aspects of the work have been reported in greater detail: the structures and processes involved in thermogelation of methylcellulose (Haque & Morris, 1993), the effect of hydroxypropyl substituents (Haque *et al.*, 1993a), the solution rheology of ispaghula seed husk (Haque *et al.*, 1993b), and the effectiveness of ispaghula and hydroxypropylmethylcellulose when used together in bread-making (Haque & Morris, 1994).

## MATERIALS AND METHODS

Ispaghula seed husk was from Weikfield International, Nagar Road, Pune 411014, India, and was obtained through the UK distributors, P.S. Sahney & Co., London, UK. Dispersions were prepared in hot ( $\sim 95^\circ\text{C}$ ) deionised water by manual stirring, and were homogenised using a Silverson high-shear blender. 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.

A sample of wheat gluten ('Abravit') was kindly supplied by ABR Food Ltd, Northants, UK, and was dispersed in deionised water by mechanical stirring at ambient temperature.

The cellulose derivatives studied (Table 1) were from the Methocel range produced by the Dow Chemical Company. Solutions were prepared by the following method. Approximately one-third of the total volume of water needed was heated to  $\sim 95^\circ\text{C}$ , 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  $\sim 95^\circ\text{C}$ , shaken vigorously to disrupt the gel, and degassed under reduced pressure in a vacuum

\*To whom correspondence should be addressed.

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 in this Department by one of us (RKR). 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). Measurements of light transmission were made at 460 nm and 1 cm pathlength using a Unicam SP 1800 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded at 200 MHz on a Bruker AM200 spectrometer, using solutions prepared in  $\text{D}_2\text{O}$  rather than in water.

Breadmaking trials were carried out on a domestic scale (350 g portions in standard baking tins), following normal procedures for home baking. A full account of the formulations and conditions used has been presented elsewhere (Haque & Morris, 1994). Loaf volume was determined by displacement of mustard seed, and expressed as reciprocal density (ml/g).

## HYDROPHOBIC CELLULOSE DERIVATIVES

Chemical derivatisation can solubilise cellulose by disrupting intermolecular association within the native fibrils. Introduction of methyl groups (Grover, 1986) confers solubility in water when, on average, about 1.4 of the 3 available hydroxyl groups on each sugar ring are converted to  $\text{OCH}_3$  (i.e. at a 'degree of substitution',  $\text{DS} \approx 1.4$ ). The derivatives become soluble in organic solvents, and lose their solubility in water, at  $\text{DS} \approx 2.6$ . The range of substitution allowed in methylcellulose for food use lies towards the bottom end of this 'solubility window' (between  $\text{DS} \approx 1.64$  and  $\approx 1.92$ ).

In contrast to underivatised polysaccharides where temperature-dependent gels invariably form on cooling and melt on heating, these materials have the unusual property of forming gels at high temperature and reverting to solutions on re-cooling. The gelation

temperature can be raised, and the gel properties modified, by including a limited amount of a larger and more polar substituent, the hydroxypropyl group.

The samples studied in the present work were commercial materials A4M, E4M, F4M and K4M from the Dow Chemical Company. In each case, '4M' denotes a solution viscosity of 4 Pa s measured under standard conditions in a capillary viscometer. The initial letter 'A' denotes methylcellulose; 'E', 'F' and 'K' correspond to hydroxypropylmethyl derivatives with different levels of incorporation of the two substituents within the ranges shown in Table 1.

Methylcellulose derivatives have an established history of use in baking (Grover, 1986). From practical experience, the manufacturers recommend K4M as the most suitable material for breadmaking, and we have followed this advice in our own trials. Measurements of the temperature course of gel formation, however, revealed an unexpected complexity of behaviour, which can best be understood by considering first the simpler A4M system.

## Formation and dissociation of methylcellulose gels

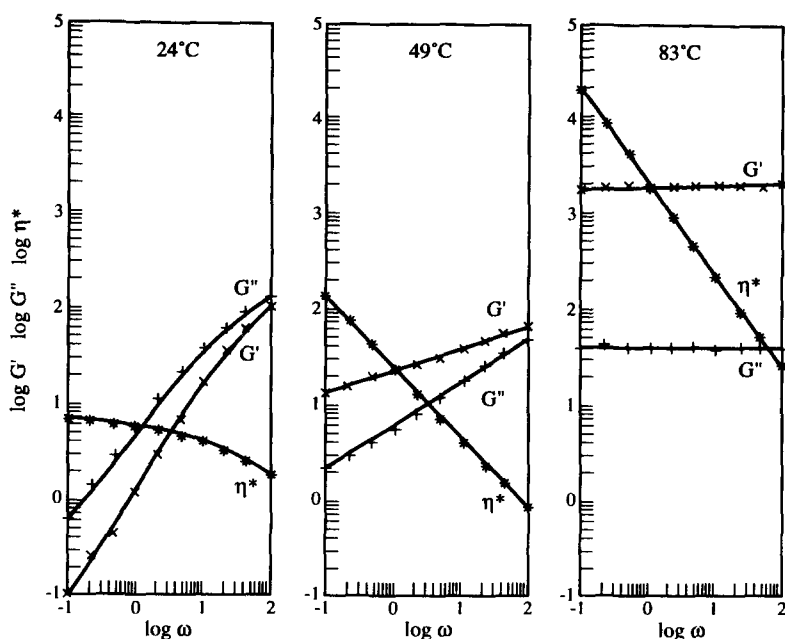
Figure 1 shows typical mechanical spectra (frequency-dependence of  $G'$ ,  $G''$  and  $\eta^*$ ) for A4M (2%) at temperatures spanning the range of the sol-gel transition. At low temperature ( $24^\circ\text{C}$ ) the behaviour is similar to that observed for entangled networks of underivatised 'random coil' polysaccharides. At low frequency,  $G''$  (characterising viscous flow) is substantially higher than  $G'$  (characterising elastic response). Both moduli increase steeply with increasing frequency, and  $G'$  approaches  $G''$  (reflecting the increasing difficulty of disentanglement within the period of oscillation). At high temperature ( $83^\circ\text{C}$ ) the spectrum is typical of a strong gel (Clark & Ross-Murphy, 1987), with elastic response ( $G'$ ) dominating and little frequency-dependence in either modulus.

The temperature-course of gelation, however, is less straightforward. As illustrated in Fig. 2, there are two distinct 'waves' of structure-formation on heating, with two corresponding processes, offset to lower temperature, in dissociation of the gel network on cooling. Both

**Table 1. Composition\* and enthalpy values for cellulose derivatives**

Material	$\Delta H$ (J/g)	Average number of substituents per residue	
		Methoxyl	Hydroxypropyl
A4M	15.9	1.6–1.9	0
E4M	14.5	1.8–2.0	0.20–0.31
F4M	15.0	1.7–1.9	0.10–0.20
K4M	4.2	1.1–1.6	0.10–0.30

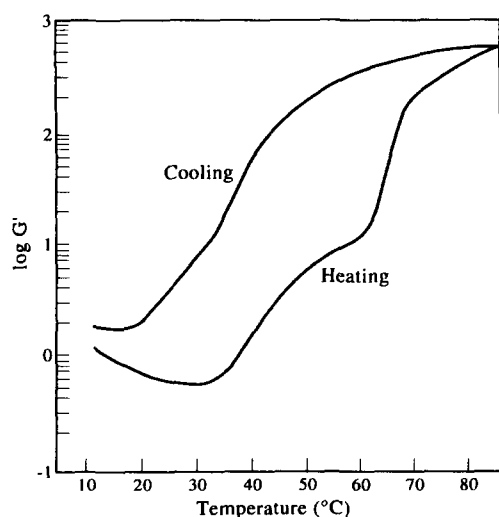
\*Composition ranges by courtesy of The Dow Chemical Company.



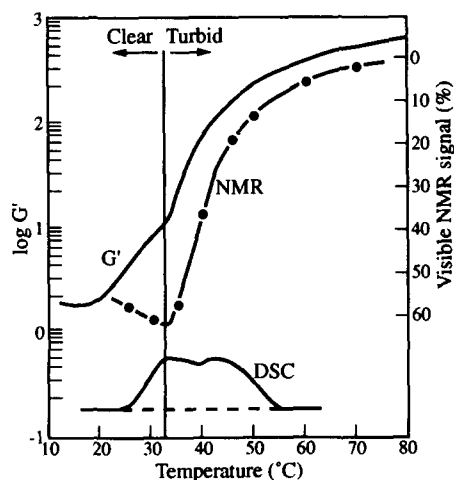
**Fig. 1.** Mechanical spectra for methylcellulose (2% A4M), showing the variation of  $G'$  (Pa),  $G''$  (Pa) and  $\eta^*$  (Pa s) with frequency,  $\omega$  ( $\text{rad s}^{-1}$ ), in the solution state at low temperature (24°C), as a gel at high temperature (83°C), and at a temperature (49°C) towards completion of the first process shown in the heating scan in Fig. 2, but before the onset of the second wave of structure formation.

are accompanied (Fig. 3) by enthalpy changes in DSC. The transition from one process to the other corresponds to the maximum in detectable high-resolution  $^1\text{H}$  NMR signal (i.e. to maximum mobility of the polysaccharide chains) and to the loss of obvious turbidity on cooling. Instrumental measurements of turbidity (Fig. 4) also show maximum transmission of light at this point, with a substantial reduction at both higher and lower temperature. Optical rotation measurements (Fig. 4) show clear evidence of a conformational transition accompanying the changes in transmission over the lower temperature range.

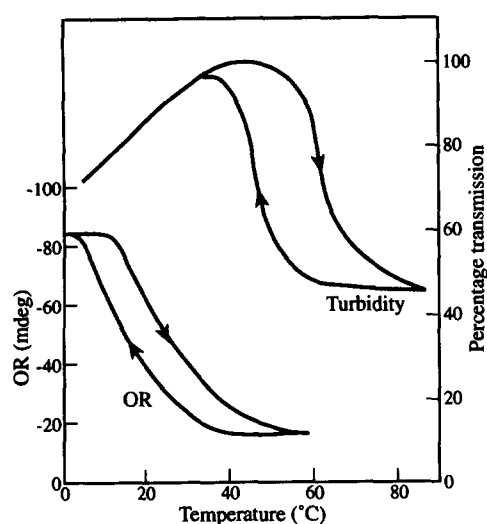
The obvious interpretation of this behaviour is that there are structures present in solutions of methylcellulose at low temperature which melt out during the initial stages of heating and, in doing so, allow the development of a different structure at higher temperature. A direct analogy would be the thermal gelation of globular proteins (Clark & Ross-Murphy, 1987) where unfolding of the native globule is a necessary precursor to network formation by intermolecular association of exposed hydrophobic regions from the protein core.



**Fig. 2.** Changes in rigidity modulus ( $G'/\text{Pa}$ ) for methylcellulose (2% A4M) on heating and cooling at a fixed rate of  $1^\circ\text{C min}^{-1}$ .



**Fig. 3.** Loss of methylcellulose gel structure on cooling, as monitored by loss of rigidity ( $G'$ ; Fig. 2), enthalpy changes in DSC and the percentage of the  $^1\text{H}$  NMR signal detectable in high-resolution spectra at 200 MHz.

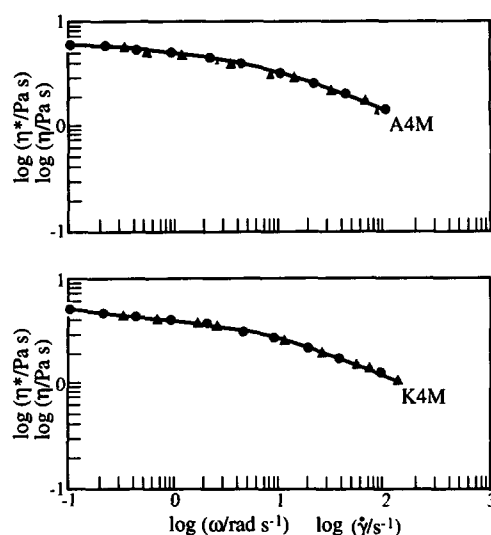


**Fig. 4.** Changes in conformation and turbidity of methylcellulose (0.25% A4M) on heating and cooling, as monitored, respectively, by optical rotation (10 cm pathlength; 365 nm) and percentage transmission (1 cm pathlength; 460 nm).

The absolute intensity of  $^1\text{H}$  NMR (calibrated against a standard solution of dextran) gives direct evidence of conformational rigidity in solution. The resonances from the methyl substituents are superimposed on those of the non-anomeric protons of the polysaccharide, but both can be quantified together (by integration over the approximate range 3.0–4.2 ppm). At high temperature (Fig. 3) the detectable signal is almost entirely suppressed, as in other polysaccharide gels. The maximum intensity in the sol state, however, is about 60% of that anticipated for the fully visible signal (the precise value is dependent on the exact proportion of methyl substituents, but using the DS range shown for A4M in Table 1, and allowing for experimental error in integration, it can be bracketed at around  $58 \pm 6\%$ ). It would therefore appear that at least one-third of the polymer remains conformationally immobile at low temperature.

The shear-rate dependence of solution viscosity (Fig. 5) also provides some indirect support for this proposal. Steady shear viscosity ( $\eta$ ) and dynamic viscosity ( $\eta^*$ ) superimpose closely at equivalent numerical values of shear rate ( $\dot{\gamma}/\text{s}^{-1}$ ) and frequency ( $\omega/\text{s}^{-1}$ ), indicating (Clark & Ross-Murphy, 1987) that, as in solutions of disordered coils, there are no specific interactions between the individual species. The overall form of shear-thinning is also, superficially, similar to that observed for disordered polysaccharides (Morris, 1990). Quantitative analysis, however, reveals that the curvature is quite different and, in particular, the terminal slope of  $\log \eta$  vs  $\log \dot{\gamma}$  is substantially lower than usual ( $-0.56$  rather than  $-0.76$ ), consistent with an appreciable departure from 'random coil' geometry.

We have no direct evidence of the nature of the ordered structure in solution. A likely possibility,



**Fig. 5.** Shear-rate dependence of  $\eta$  (▲) and frequency-dependence of  $\eta^*$  (●) for methylcellulose (A4M) and hydroxypropylmethylcellulose (K4M) in 2% solution at 25°C.

however, is that during chemical derivatisation small regions of native cellulose structure remain intact, linking several chains together into bundles, with long regions of heavy substitution interspersed with shorter stretches of low (or zero) substitution along each bundle. The methyl groups in regions of dense substitution would then have natural partners for hydrophobic clustering, again directly analogous to the interior of globular proteins.

In the initial stages of heating, we envisage partial dissociation of these clusters, corresponding to the increase in detectable NMR (Fig. 3), the decrease in turbidity (Fig. 4), the reduction in  $G'$  (Fig. 2) and much of the conformational change detected by optical rotation (Fig. 4). On further heating, we envisage separation of the component strands at the ends of the bundles, with a consequent massive increase in hydrodynamic volume, leading to the first increase in  $G'$ . The analogy here is with the swelling of starch granules during gelatinisation, to form a viscoelastic paste. In partial support of this interpretation, the mechanical spectra obtained towards the end of the first process (49°C; Fig. 1) show a significant frequency-dependence of both moduli, and reduction in  $G'$  with increasing amplitude of oscillation (showing structural breakdown) begins at far lower strain ( $\sim 2\%$ ) than in normal gels, consistent with weak, topological interactions of the type proposed. The second increase in  $G'$  (Fig. 2) can then be attributed to hydrophobic association of strands radiating from different bundles, to give the final, stable network (83°C; Fig. 1). Involvement of residual cellulosic structure in network crosslinking would offer a direct explanation of why methylcelluloses prepared under homogeneous conditions (with, therefore, a more

even distribution of substituents) do not gel (Takahashi *et al.*, 1987).

Although still highly speculative, the proposed model is consistent with the established properties of other gelling biopolymers. In particular, the thermal hysteresis in optical rotation (Fig. 4) is very similar to that observed for underivatised polysaccharides such as agarose and kappa carrageenan, where conformational ordering on cooling is accompanied by aggregation of the ordered structures, with melting of the aggregates then occurring over a higher temperature range (Rees *et al.*, 1982). Dissociation of the postulated cellulosic 'bundles' would similarly be expected to occur at higher temperatures than those at which the bundles will form again on cooling.

By extension of this argument, dissociation of the gel network on cooling may reflect the relative stabilities of molecular association within and between the bundles. Adoption of the proposed fibrillar structure might be expected to maximise favourable enthalpic interactions, but cause a severe loss of entropy. Conversely, the entropy of a gel network structure would be higher, but the degree of ordered packing would be decreased. Conversion from the fibrillar structure at low temperature to the network structure at high temperature, with the converse change on cooling, would then be an expected consequence of the increasing importance of entropy with increasing temperature (as in the formation and melting of other polysaccharide gels).

In the above discussion we have made no explicit reference to the role of water. It is, however, implicit in the concept of methyl substituents providing a drive to chain-chain association. Where our present model departs from previous interpretations (Sarkar, 1979; Rees, 1972) is in suggesting that, at low temperature, the methyl groups are shielded from the aqueous environment by mutual association within fibrillar bundles, rather than by 'cages' of structured water (Rees, 1972). Our intention at this stage, however, is not to suggest a definitive interpretation, but to draw attention to some aspects of the gelation process that do not appear to have been reported previously, in the hope of stimulating further studies (and discussion) of this intriguing system.

### Hydroxypropylmethylcellulose

The behaviour of K4M is broadly similar to that of A4M but with, of course, substantial quantitative differences. There is again clear evidence (Fig. 6) of two separate processes over different ranges of temperature. The initial increase in  $G'$  is once more preceded and accompanied by a large change in optical rotation (diagnostic of a change in chain conformation), with a further increase at higher temperature accompanied by loss of mobility (NMR) and by enthalpy changes in DSC (endothermic on heating; exothermic on cooling, as in A4M). The enthalpy changes are, however, much

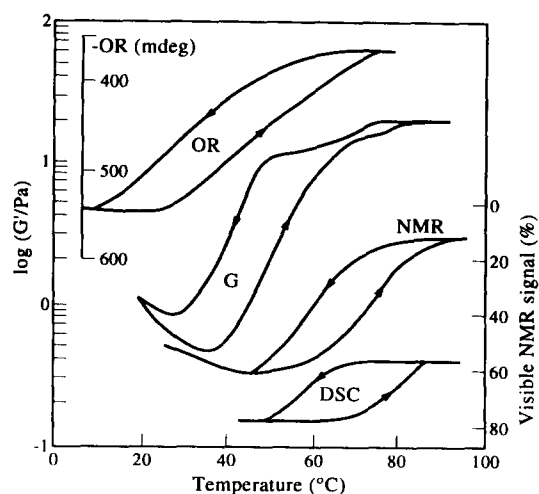


Fig. 6. Conformational and rheological changes for hydroxypropylmethylcellulose (1% K4M) on heating and cooling, as monitored by optical rotation (365 nm; 10 cm cell), rigidity modulus ( $G'$ ), percentage of visible  $^1\text{H}$  NMR signal, and heat changes in DSC (shown as integrals of the endotherm observed on heating and exotherm obtained on cooling).

smaller ( $\Delta H \sim 4.2$  J/g in comparison with  $\sim 16$  J/g for A4M), and the accompanying increase in  $G'$  is also much smaller, giving substantially lower moduli for the final gels at equivalent concentrations of polymer.

Comparative studies with E4M and F4M gave  $\Delta H$  values close to that for A4M, indicating that the heat changes are directly related to the methoxyl content, since the DS ranges for all three are similar (Table 1) and higher than for K4M. The magnitude of the second increase in  $G'$  and the strength of the final network were also higher for E4M and F4M than for K4M (again consistent with their higher methoxyl content) but still much lower than for comparable concentrations of A4M, showing the antagonistic effect of the more polar hydroxypropyl substituents on hydrophobic association. The temperature course of gelation in all three hydroxypropyl derivatives was also displaced to higher temperature than in A4M, again consistent with a reduction in hydrophobicity.

As in A4M, the maximum intensity of visible NMR signal (Fig. 6) for K4M was about 60% of the value expected for totally mobile, disordered chains, and the terminal slope of  $\log \eta$  vs  $\log \dot{\gamma}$  (and of  $\log \eta^*$  vs  $\log \omega$ ; Fig. 5) was substantially lower than the value of  $-0.76$  characteristic of entangled coils (Morris, 1990). The evidence of ordered 'bundles' in solution therefore extends to hydroxypropyl derivatives.

A phenomenon common to all three samples containing hydroxypropyl substituents (E4M, F4M and K4M), but not observed when only methoxyl groups were present (A4M), is a sharp drop in  $G''$  on heating (Fig. 7), coincident with the sudden onset of extreme turbidity (as detected visually) and immediately preceding the second 'wave' of increase in  $G'$ . As the concen-

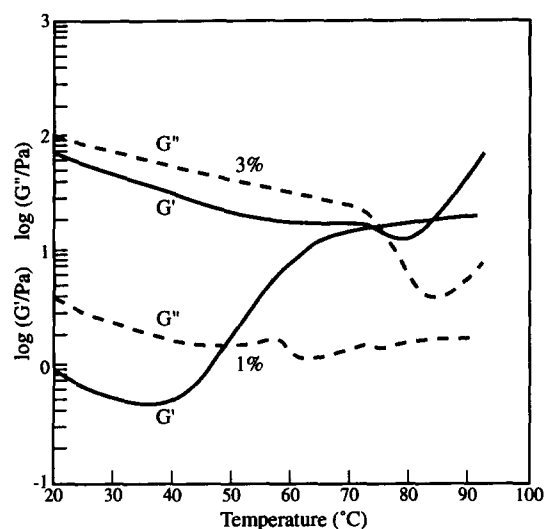


Fig. 7. Changes in  $G'$  and  $G''$  (Pa) on heating at a fixed rate of  $1^\circ\text{C min}^{-1}$ , for hydroxypropylmethylcellulose (K4M) at concentrations of 1 and 3%.

tration of polymer is increased, this process is displaced to progressively higher temperature, and becomes accompanied by a small dip in  $G'$  prior to the rapid increase associated with formation of the final gel network. The first increase in  $G'$  also becomes less evident at higher concentrations. One strange consequence of these changes is that, at temperatures below the second, major increase in  $G'$ , the rigidity of concentrated samples may drop below those of much more dilute preparations. This behaviour is illustrated in Fig. 7 for K4M at concentrations of 1 and 3%.

In terms of our tentative model for gelation of methylcellulose, the reduction in the initial increase in  $G'$  at higher concentrations may be due to a restriction in the degree of 'swelling' of individual cellulosic bundles due to the physical proximity of others competing for the same space. A possible interpretation of the sharp decrease in  $G''$  and the accompanying dip in  $G'$ , is that the relatively hydrophilic hydroxypropyl substituents favour the initial formation of small micellar clusters in the early stages of hydrophobic association of the individual 'denatured' bundles. These proposals are, however, entirely speculative and require substantial further investigation.

### ISPAGHULA HUSK (ISABGOL)

Ispaghula husk, obtained by milling the seeds of *Plantago ovata* Forsk, has been used traditionally as a laxative and for alleviation of specific bowel disorders (Leeds, 1985), particularly in the Indian subcontinent where it is known as 'isabgol' (the name which, for brevity, we will now adopt). It has a high content of polysaccharide, whose primary structure is not yet fully elucidated. The essential features have, however, been

established (Kennedy *et al.*, 1979; Sandhu *et al.*, 1981). The polymer backbone consists of  $\beta$ -D-xylose, linked both (1  $\rightarrow$  3) and (1  $\rightarrow$  4), with single-sugar sidechains of  $\beta$ -D-xylose and  $\alpha$ -L-arabinose and disaccharide sidechains of  $\alpha$ -D-GalA-(1  $\rightarrow$  2)- $\alpha$ -L-Rha.

Isabgol does not completely dissolve in water, but swells to a mucilaginous dispersion with the general appearance of wallpaper paste. Figure 8 shows the mechanical spectrum and shear-rate dependence of viscosity for a 2% dispersion. Although the dispersion flows, the mechanical spectrum is similar to that of a gel ( $G' > G''$  with little frequency-dependence) and the dynamic viscosity ( $\eta^*$ ) from small-deformation oscillatory measurements is substantially higher than the steady-shear viscosity ( $\eta$ ) measured under rotation. These are the characteristic properties of a 'weak gel' network (Clark & Ross-Murphy, 1987).

Examination of isabgol dispersions by phase-contrast microscopy, using toluidine blue to stain for polysaccharide, gave clear evidence of the likely origin of this behaviour. The micrographs showed a matrix of fibrillar strands, with a range of lengths extending to 20–30  $\mu\text{m}$ . A common feature of polysaccharides with 'weak gel' properties (Morris, 1991) is that they exist in solution as rigid, ordered structures that form tenuous associations to give a continuous, but readily broken, network. It seems reasonable to assume that the analogous rheological properties of isabgol arise in exactly the same way, but with structural rigidity at a supra-molecular, rather than a molecular level.

Formation of a fibrillar network has been reported previously (Sandhu *et al.*, 1981) in studies of the polysaccharide component of isabgol, but on the length-scale of electron microscopy rather than light microscopy. In a brief examination, we extracted the polysaccharide in alkali (at a concentration of  $\sim 1.2$  mg/ml in 2.5 M NaOH at  $25^\circ\text{C}$ ) and obtained, after neutralisation, a stable solution with the shear-thinning behaviour characteristic of disordered coils.

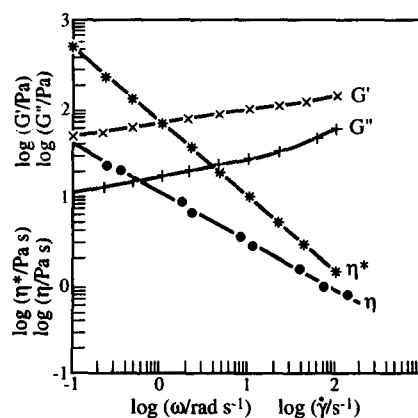


Fig. 8 Frequency ( $\omega$ ) dependence of  $G'$ ,  $G''$  and  $\eta^*$  and shear-rate ( $\dot{\gamma}$ ) dependence of viscosity ( $\eta$ ) for a 2% dispersion of isabgol.

On dialysis to remove the salt produced by neutralisation of the alkali, however, the solution formed a gel within the dialysis bag. The network showed obvious syneresis, and continued to contract on storage to about 30% of its original volume; substantial further contraction was observed after freezing and thawing. It seems likely that this behaviour corresponds to progressive aggregation of the fine fibrillar network described previously (Sandhu *et al.*, 1981) towards the much larger assemblies seen in dispersions of native isabgol.

On heating, the isabgol networks become progressively weaker (Fig. 9), particularly at high temperatures where hydroxypropylmethylcelluloses show their main increase in rigidity. In mixed solutions of isabgol and K4M, at appropriate concentrations of both, the two effects cancel out, to give an essentially constant value of  $G'$  above about 50°C. We believe that this behaviour is central to the effectiveness of the two materials when used in combination in breadmaking. Perhaps fortuitously, the temperature-dependence of  $G'$  for gluten is almost identical in form to that shown in Fig. 9 for the isabgol-K4M mixed system.

## BREADMAKING

Our baking trials so far have been carried out on a small scale, using the techniques and equipment of a domestic kitchen rather than those of a commercial bakery. The effects that we have observed, however, are so large that there seems little doubt of their validity.

Figure 10 shows the results obtained in a preliminary evaluation following a standard recipe for wheat bread. The degree of aeration of the final products is characterised by the specific volume of the loaves (measured by a displacement method). The control was a batch

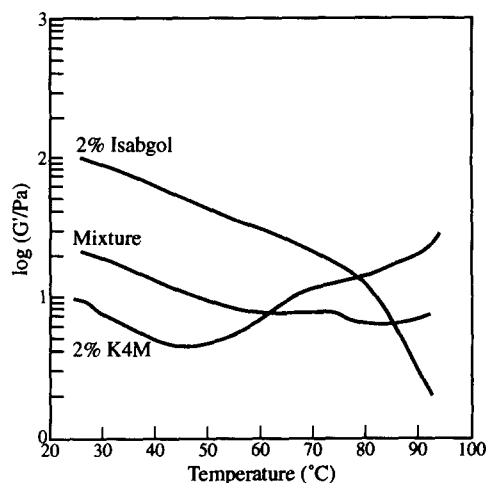


Fig. 9. Changes in rigidity modulus ( $G'$ ) on heating ( $1^{\circ}\text{C min}^{-1}$ ) for a 2% dispersion of isabgol, a 2% solution of hydroxypropylmethylcellulose (K4M), and a mixed solution containing 1% of each.

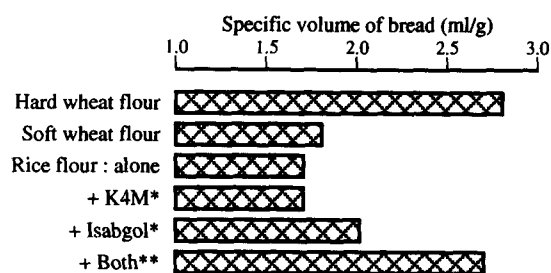


Fig. 10. Loaf volumes for bread prepared from wheat flours, and from rice flour, alone or with incorporation of K4M and isabgol (\*2% replacement level), or together (\*\*2% K4M + 1% isabgol).

produced using a hard-wheat flour recommended for breadmaking. The specific volume of 2.8 ml/g is somewhat lower than in normal commercial bread, but is perfectly acceptable.

The first comparison was with a soft-wheat flour of the type normally used in cakes, which gave, as expected, a much lower specific volume. The specific volume obtained with rice flour was lower still. Incorporation of K4M alone (replacing 2% of the rice flour) gave no detectable improvement. The same level of replacement with isabgol gave a slightly higher specific volume, but the degree of aeration was still far from satisfactory. When the two materials were used together (at replacement levels of 2 and 1%, respectively), however, the loaf volume was close to that of the hard-wheat control.

Substantial further improvement was achieved by varying parameters such as moisture content and proving temperature (i.e. the temperature used in fermentation with yeast) to identify conditions appropriate to the rice-based system rather than to wheat bread. Figure 11

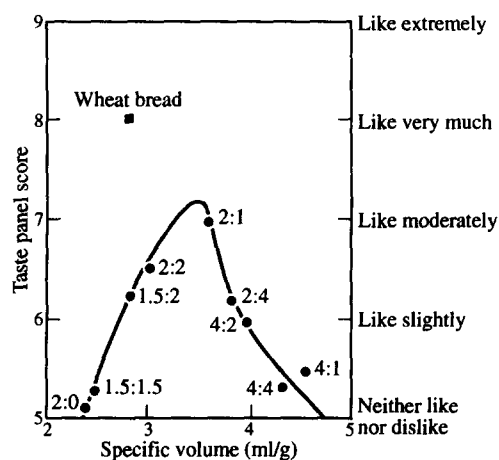


Fig. 11. Taste-panel scores (●) for rice breads over a range of specific volumes. The two numbers beside each point denote, respectively, the amounts of hydroxypropylmethylcellulose (K4M) and isabgol used, expressed as percentage replacement of rice flour. The verbal descriptors corresponding to the numerical scores from the panel are shown on the right-hand axis. The score assigned to wheat bread is shown for direct comparison (■).

shows specific volumes for some representative samples incorporating isabgol and K4M at various levels of replacement of the rice flour, together with results from a taste-panel evaluation using a hedonic scale from 1 ('dislike extremely') to 9 ('like extremely').

The specific volumes obtained were in some cases over 4.5 ml/g, in comparison with 3.8 ml/g for typical commercial bread. The maximum hedonic rating on the 9-point scale was ~ 7.0, against 8.0 for wheat bread. The comparison may not, however, be a fair one since, at least in Britain, our expectations of the characteristics of bread are based entirely on experience of products made from wheat flour. The rice bread that we have produced would certainly not be confused with wheat bread. There are, for example, obvious differences in colour (rice bread is whiter) and taste (with the characteristic rice taste carrying through to the final product). It would be more realistic to regard rice bread as a different, complementary product (in the same way as rye bread is sold in North America).

These issues are, however, subsidiary to the central problem of achieving a satisfactory degree of aeration in the absence of gluten. The obvious effectiveness of the isabgol-K4M system appears to arise from the isabgol network stabilising gas-cells as they are formed during proving and preventing them collapsing during the initial stages of heating in the baking oven, with the cellulosic matrix taking over at higher temperature.

## ACKNOWLEDGEMENTS

We thank Dr M. J. Gidley and Mr D. Caswell (Unilever Research) for NMR measurements, Dr I. C. M. Dea

and Mrs K. Groves (Leatherhead Food Research Association) for microscopy, Dr N. Sarkar and Dr P. Smith (Dow Chemical Company) for helpful discussions and The British Council for the award of a Study Fellowship to Mr A. Haque.

## REFERENCES

- Blanshard, J.M.V., Frazier, P.J. & Galliard, T. (1986). *Chemistry and Physics of Baking*. Special Publication No. 56, Royal Society of Chemistry, London.
- Clark, A.H. & Ross-Murphy, S.B. (1987). *Adv. Polym. Sci.*, **83**, 57–192.
- Grover, J.A. (1986). In *Food Hydrocolloids*, Vol. 3, ed. M. Glicksman. CRC Press, Boca Raton, FL, pp. 121–54.
- Haque, A. & Morris, E.R. (1993). *Carbohydr. Polym.*, **22**, 161–73.
- Haque, A. & Morris, E.R. (1994). *Food Res. Int.*, **27**, 379–93.
- Haque, A., Richardson, R.K., Morris, E.R. & Dea, I.C.M. (1993b). *Carbohydr. Polym.*, **22**, 223–32.
- Haque, A., Richardson, R.K., Morris, E.R., Gidley, M.J. & Caswell, D.C. (1993a). *Carbohydr. Polym.*, **22**, 175–86.
- Kennedy, J.F., Sandhu, J.S. & Southgate, D.A.T. (1979). *Carbohydr. Res.*, **75**, 265–74.
- Leeds, A.R. (1985). *Dietary Fibre Perspectives*. John Libbey, London.
- Morris, E.R. (1990). *Carbohydr. Polym.*, **13**, 85–96.
- Morris, E.R. (1991). *Int. Food Ingredients*, **1**, 32–7.
- Rees, D.A. (1972). *Chem. Ind. London*, 630–6.
- 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.
- Sandhu, J.S., Hudson, G.J. & Kennedy, J.F. (1981). *Carbohydr. Res.*, **93**, 247–59.
- Sarkar, N. (1979). *J. Appl. Polym. Sci.*, **24**, 1073–87.
- Takahashi, S.-I., Fujimoto, T., Miyamoto, T. & Inagaki, H. (1987). *J. Polym. Sci. A*, **25**, 987–94.