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Effect of xanthan on the small-deformation rheology of crosslinked and uncrosslinked waxy maize starch

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Small-deformation oscillatory measurements have been used to characterise the effect of ordered xanthan (in 0.1 M KCl) on the rheological properties of gelatinised waxy maize starch (crosslinked and uncrosslinked). The uncrosslinked material shows a single DSC endotherm on heating, centred at ~70°C. The overall enthalpy change on gelatinisation of the crosslinked starch is the same (ΔH = 13.2 J/g), but occurs in two endothermic processes (centred at ~60 and ~74°C), tentatively attributed to thermal dissociation of, respectively, chemically modified and native granule structure. The thermal transitions for both samples are complete by 80°C, which was therefore chosen as the maximum temperature in the rheological investigations, to minimise loss of granule integrity and release of starch polysaccharides into the xanthan matrix.

Both samples, after gelatinisation in water, gave gel-like mechanical spectra at volume fractions below 20%, suggesting association between the swollen granules, in addition to the steric interactions which become dominant at higher concentrations. The magnitude of the increase in moduli observed on progressive addition of starch (1–5 wt %) to solutions of xanthan (0.25 or 0.50 wt %) is far too great to be explained by increased concentration of the xanthan phase on swelling of the starch granules. Comparison with the concentration-dependence of moduli for starch alone, however, suggests that xanthan acts by promoting association between the gelatinised granules, possibly by a depletion flocculation mechanism. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

It is well established that comparatively low concentrations of polysaccharides such as guar gum, locust bean gum (LBG), sodium carboxymethylcellulose (SCMC) and xanthan can cause large increases in the viscosity of starch, both during the gelatinisation process and on subsequent cooling (e.g. Howling, 1980; Christianson *et al.*, 1981; Sajjan & Rao, 1987). A detailed study (Alloncle *et al.*, 1989) of mixtures of cereal starch (wheat or maize) with galactomannans (guar gum or LBG) indicated that the observed enhancements in overall viscosity could be attributed to the increase in galactomannan concentration produced by swelling of the starch granules during gelatinisation. The purpose of the present investigation was to determine whether or not the effect of xanthan on starch rheology can be explained in the same way.

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Xanthan has a (1 → 4)-linked β-D-glucan (cellulose) backbone solubilised by attachment of charged trisaccharide sidechains [β-D-Man*p*-(1 → 4)-β-D-Glc*p*A-(1 → 2)-α-D-Man*p*-(1 →] at O(3) of alternate glucose residues, to give a pentasaccharide repeating sequence (Jansson *et al.*, 1975; Melton *et al.*, 1976), with non-stoichiometric substitution by acetate at O(6) of the inner mannose residues of the sidechains and by 4,6-linked pyruvate ketal on the terminal mannose residues. Unlike other polysaccharides used as food thickeners, including guar gum, LBG and SCMC, xanthan can exist in solution in a rigid, ordered, chain conformation. Formation and melting of the ordered structure occur as sharp, co-operative processes, with no detectable thermal hysteresis, and have been monitored by a wide range of physical techniques (see, for example, Morris *et al.*, 1977; Milas & Rinaudo, 1979; Norton *et al.*, 1984). As expected for a polyelectrolyte (Piculell & Nilsson, 1990), the conformational transitions are displaced to progressively higher temperature with increasing ionic

strength. It has been established by X-ray fibre diffraction analysis that the ordered structure is a 5-fold helix with regular packing of sidechains along the polymer backbone (Moorhouse *et al.*, 1977; Okuyama *et al.*, 1980), but whether the individual helices are single or double stranded remains a topic of heated debate (Mitchell, 1993).

In the sodium salt form, the flow properties of ordered xanthan are qualitatively similar to those of disordered polysaccharides interacting by physical entanglement, with viscosity levelling-out to a maximum Newtonian value (η_o) at low shear rates (Cuvelier & Launay, 1986). Addition of urea, however, causes a progressive reduction in η_o (Ross-Murphy *et al.*, 1983), indicating that entanglement is augmented by specific association between the ordered chains. The extent of association (as judged by the degree of departure from typical 'random coil' rheology) is enhanced by salt, with the order of effectiveness of common counterions being $Na^+ < K^+ < Ca^{2+}$. The levels of Ca^{2+} normally present in commercial samples, such as the material used in the present work, are sufficient to give characteristic 'weak gel' properties, which combine gel-like response to small deformations with the ability to flow freely under shear (Morris, 1991).

In the preceding paper (Abdulmola *et al.*, 1996) it was shown that the small-deformation rheology of starch–gelatin composites could be rationalised satisfactorily by application of the isostrain and isostress blending laws of Takayanagi *et al.* (1963). The initial aim of the present work was to apply the same approach to starches gelatinised in xanthan 'weak gel' networks. As before, waxy maize starch (crosslinked and uncrosslinked) was used to avoid complications from release of amylose into the polymer matrix, and the composites were characterised by low-amplitude oscillatory measurements. The central conclusion is that, in complete contrast to the starch–gelatin systems, the overall rheology of the starch–xanthan mixtures is dominated by the starch component, with the presence of xanthan appearing to promote association of the gelatinised granules.

MATERIALS AND METHODS

The starch samples were identical to those used in the studies of starch–gelatin composites reported in the preceding paper (Abdulmola *et al.*, 1996): phosphorus oxychloride crosslinked hydroxypropylated waxy maize starch (C* Cream 06716) and uncrosslinked waxy maize starch (SF 04202) from Cerestar. As before, these will be abbreviated to PCS (phosphate crosslinked starch) and WMS (waxy maize starch), respectively. Xanthan (Keltrol T) was a commercial sample from Kelco Inc., San Diego, USA (now a unit of the Monsanto Corporation). Potassium chloride was AnalaR grade from BDH. Distilled deionised water was used throughout.

Low amplitude oscillatory measurements (0.5% strain) of storage modulus (G'), loss modulus (G''), tan δ (G''/G') and complex dynamic viscosity $[\eta^* = (G'^2 + G''^2)^{\frac{1}{2}}/\omega$, where ω is frequency] were made on a sensitive prototype rheometer designed and constructed by one of us (R.K.R.), using the highly truncated cone-and-plate geometry described previously (Abdulmola *et al.*, 1996). Temperature was controlled by a circulating water bath and measured using a thermocouple attached to the stationary element. The periphery of the sample was coated with light silicone oil to prevent evaporation. Differential scanning calorimetry (DSC) studies of starch gelatinisation were made on a Setaram microcalorimeter. Baselines were interpolated from temperatures above and below the range of the gelatinisation process by a fourth-order polynomial function. Curve fitting was by least-squares analysis using a standard Microsoft Excel spreadsheet package (Version 5.0).

Composites were prepared at starch concentrations of 1, 2, 3, 4 and 5 wt % and xanthan concentrations of 0.25 and 0.50 wt %, with incorporation of 0.1 M KCl to stabilise the ordered conformation of the xanthan component. The individual constituents were prepared at twice the required concentration, mixed in equal proportions (w/w), and stirred for 15 min at 20°C. Xanthan was dispersed in 0.1 M KCl at room temperature, dissolved by mechanical stirring at 80°C, and cooled to 20°C before use. Starch slurries were prepared by mechanical stirring at room temperature.

The mixtures were loaded onto the rheometer at 20°C, held at 20°C for 10 min, heated to 80°C, held at 80°C for 30 min, and cooled again to 20°C. Mechanical spectra (frequency-dependence of G', G'' and η^*) were recorded at 20°C after completion of cooling. The heating and cooling stages were carried out at a fixed rate of 1°C/min, and the accompanying changes in rheology were monitored by measurements of G' at 10 rad s^{-1}. Xanthan solutions were characterised under the same time–temperature regime. For studies of starch in the absence of xanthan, the samples were loaded at 45°C and the heating step was started immediately, to minimise settling of ungelatinised granules onto the lower plate of the rheometer. Visual inspection of xanthan–starch mixtures showed that the 'weak gel' structure of xanthan at the concentrations used was sufficient to hold ungelatinised starch in suspension for several days.

The volume occupied by swollen starch granules after gelatinisation was estimated by weighing the sediment and supernatant from centrifugation (4000 g: 1 h; 25°C).

RESULTS

Calibration of xanthan rheology

Figure 1 shows the temperature-dependence of G', G'' and η^* for 0.5 wt % xanthan in 0.1 M KCl on heating and

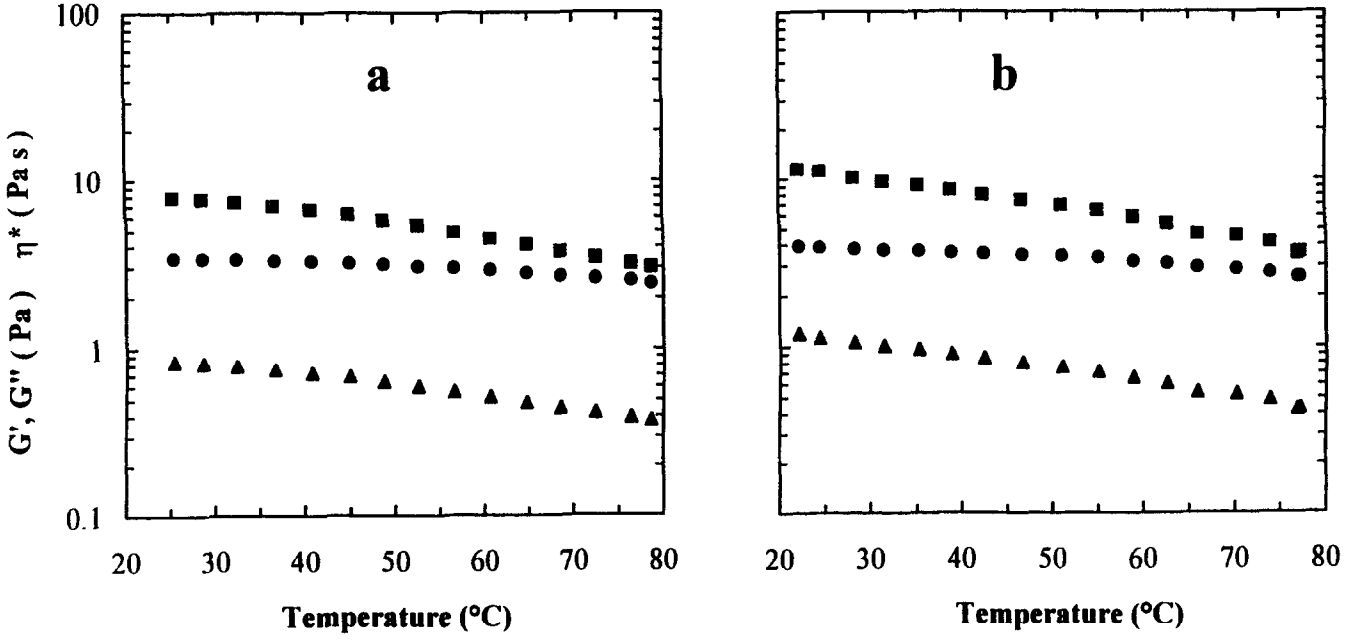

Fig. 1. Temperature-dependence of G' (■), G'' (●) and η^* (▲), measured at 10 rad s^{-1} and 0.5% strain, for xanthan (0.5 wt % in 0.1 M KCl) on (a) heating and (b) cooling at 1°C/min.

cooling (1°C/min) between 20 and 80°C. The traces are featureless, with no indication of the sharp changes that would be expected for a thermally induced conformational transition, confirming that, as anticipated from previous studies (e.g. Norton *et al.*, 1984), 0.1 M KCl is sufficient to stabilise the ordered structure of xanthan to the highest temperature used in investigation of the mixed systems (80°C). The mechanical spectrum obtained at 20°C (Fig. 2) is typical of a 'weak gel': elastic response (G') predominates over viscous flow (G'') throughout the accessible frequency range (ω = 0.1–100 rad s^{-1}), and log η^* decreases linearly with increasing log ω, but the frequency-dependence of G' and G'' is greater than for 'true' (self-supporting) gels, and the separation of the two moduli is smaller (tan $\delta \approx 0.5$, in comparison with < 0.1 for typical polysaccharide gels). As shown in Fig. 3, G', G'' and η^* remain essentially constant up to the highest amplitude of oscillation attainable on the instrument used (~25% strain), demonstrating that the strain used in characterisation of the mixed systems (0.5%) is well within the region of linear viscoelastic response for the xanthan 'weak gel' network.

Figure 4 shows the variation of G' (10 rad s^{-1}; 0.5% strain; 20°C) with concentration (c) for xanthan in 0.1 M KCl at polymer concentrations between 0.25 and 1.0 wt %, in direct comparison with the concentration-dependence of G', under the same conditions, for the gelatin sample used in the investigation of starch–gelatin composites reported in the preceding paper (Abdulmola *et al.*, 1996). The values for gelatin show the general form of concentration-dependence typical of conventional gel networks (Clark & Ross-Murphy, 1987), with a progressive increase in slope as the polymer concentration is lowered towards the minimum critical gelling concentration, c_o. The variation of log G' with log c for xanthan, by contrast, is linear ($r^2 = 0.995$), with a slope close to 2 (equation (1)).

$$\log G' = 2.258 \log c + 1.612 \quad (1)$$

where G' is expressed in units of Pa and c is in wt %. An approximate c^2 dependence of G' has been repor-

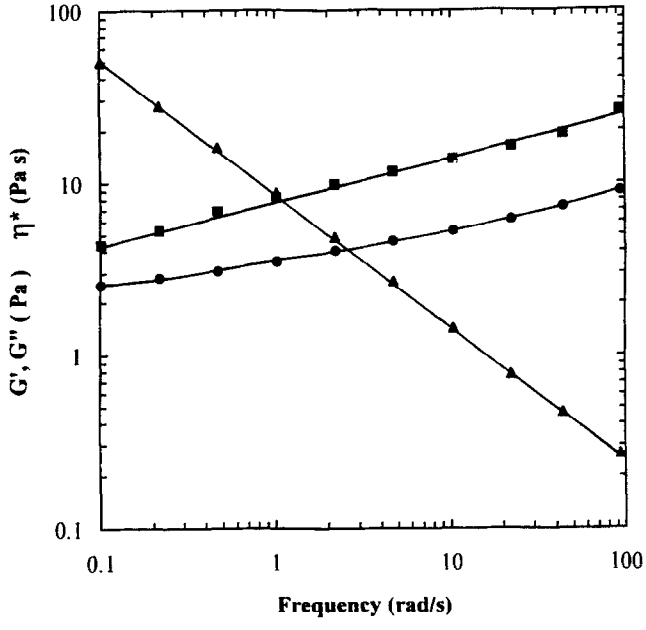

Fig. 2. Mechanical spectrum (0.5% strain) showing the frequency-dependence of G' (■), G'' (●) and η^* (▲) for xanthan (0.5 wt % in 0.1 M KCl) at 20°C.

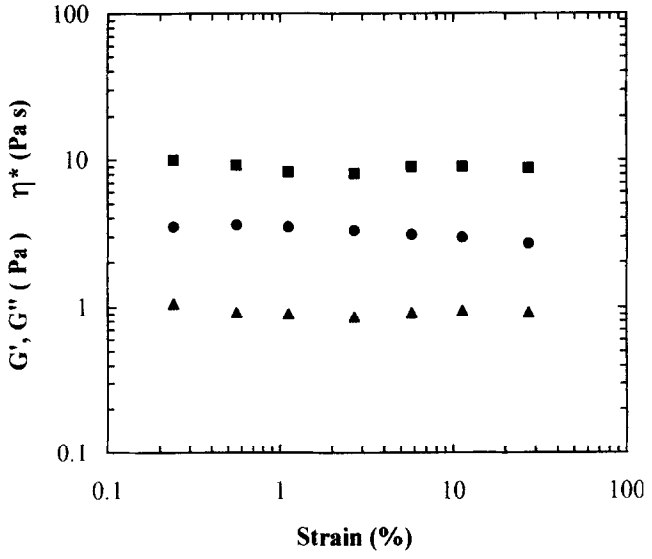

Fig. 3. Strain-dependence of G' (■), G'' (●) and η^* (▲), measured at 10 rad s^{-1}, for xanthan (0.5 wt % in 0.1 M KCl) at 20°C.

ted previously (Robinson *et al.*, 1991; Hember & Morris, 1995) for xanthan and for other conformationally ordered polysaccharides with 'weak gel' properties (welan and rhamsan).

Gelatinisation and swelling of starch samples

Figure 5 shows DSC traces obtained for 5 wt % PCS and WMS on heating at a low rate (0.1°C/min). The uncrosslinked sample (WMS) gives a single gelatinisation endotherm centred at ~70°C. The overall heat change for the crosslinked material (PCS) is approximately the same ($\Delta H \approx 13.2$ J/g for both samples), but occurs in two separate endothermic processes at lower and higher temperature than the single endotherm for WMS (at ~60 and ~74°C). As shown in Fig. 6, incorporation of xanthan at the highest concentration used in the mixed systems studied in the present work (0.5 wt %), or of gelatin at the highest concentration (1.5 wt %) used by Abdulmola *et al.* (1996), had no discernible effect on the DSC traces obtained for PCS. The position and intensity (ΔH) of the single endotherm observed for WMS were also unaffected by the presence of xanthan or gelatin. For both samples, the thermal changes associated with loss of conformational order within the granule are complete by 80°C (Fig. 5), which was therefore used as the gelatinisation temperature in the starch–xanthan investigations reported here, and for the starch–gelatin composites studied by Abdulmola *et al.* (1996).

The presence of two discrete peaks in the DSC scans for PCS was unexpected. Starches commonly show two endothermic processes in DSC when gelatinised under low-moisture conditions (e.g. Donovan, 1979), with the higher-temperature event corresponding to disordering of 'dry' crystalline structures. The two thermal transi-

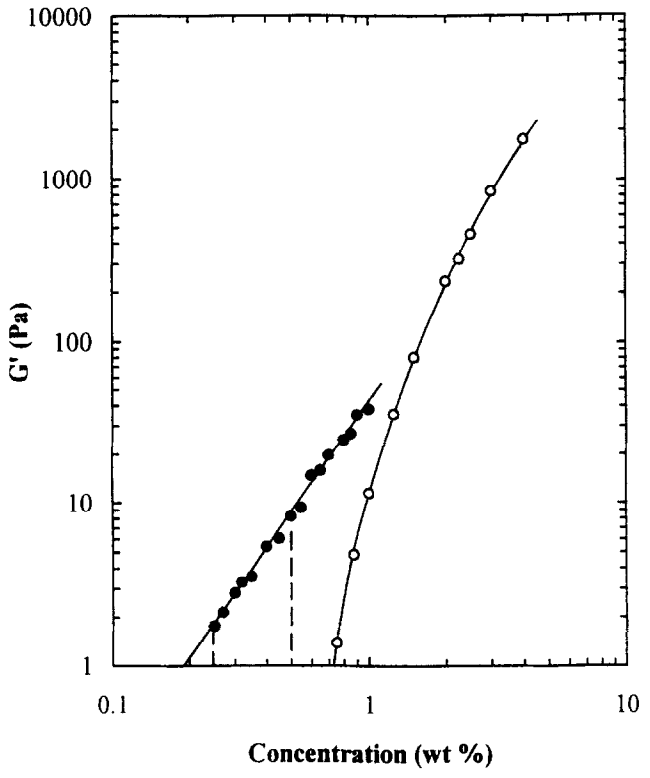

Fig. 4. Concentration-dependence of G' (10 rad s^{-1}; 0.5% strain; 20°C) for xanthan in 0.1 M KCl (●) and for gelatin at pH 7.0 in water (○). The vertical dashed lines show the xanthan concentrations used in the mixed systems (0.25 and 0.50 wt %).

tions observed for PCS, however, cannot be explained in the same way, since water was present in excess at the starch concentration used. As shown in Fig. 7, both peaks move to higher temperatures as the rate of heating is increased, but the first is displaced more than the second. Figure 8 shows the scan-rate dependence of T_{max}, the temperature at the peak maxima, for both transitions of PCS and for the single endotherm observed for WMS. T_{max} for WMS varies linearly with scan rate, and the slope is similar to those seen in previous studies of polysaccharide conformational transitions on the same instrument (e.g. Manning, 1992; Gidley *et al.*, 1992; Haque & Morris, 1993), indicating that the apparent increase in transition temperature with increasing scan rate is a simple 'overshoot' effect, reflecting the maximum rate at which heat can be transferred into the sample. The temperature-dependence of T_{max} for the second PCS peak is closely similar, and can therefore again be attributed to thermal lag. T_{max} for the first PCS peak, however, shows a much greater variation with scan rate, indicating that the underlying changes in granule structure are occurring on a slower timescale, comparable to the imposed rate of temperature change. A likely (though speculative) interpretation is that the low-temperature and high-temperature processes seen for PCS correspond to disordering of, respectively, substituted and unsub-

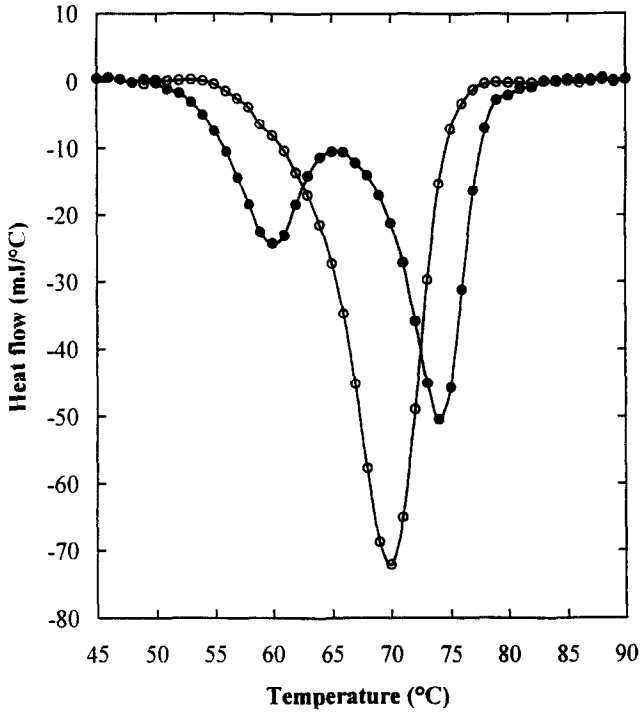

Fig. 5. DSC heating scans (0.1°C/min) for PCS (●) and WMS (○) at 5 wt % in 0.1 M KCl. Data points are shown at intervals of 1°C, but the traces were recorded at 30 points per °C, and are shown after subtraction of interpolated baselines.

stituted regions, and that disruption of the substituted (crosslinked) structures is a much slower process than for the uncrosslinked starting material.

In the investigation of starch–gelatin composites reported in the preceding paper (Abdulmola *et al.*, 1996), the phase volume of the gelatinised starch component (ϕ_Y) was determined by measurement of the

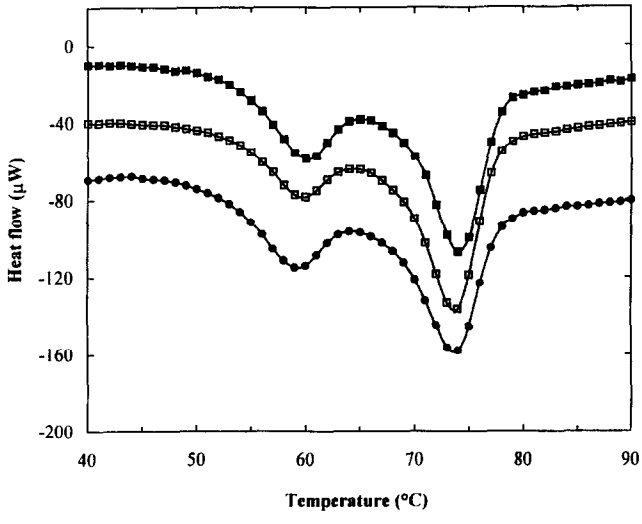

Fig. 6. DSC heating scans (0.1°C/min; uncorrected for baseline) for PCS (5 wt %), alone and in the presence of xanthan or gelatin: PCS alone in 0.1 M KCl (■); PCS + 0.5 wt % xanthan in 0.1 M KCl (□); PCS + 1.5 wt % gelatin in water at pH 7.0 (●). An arbitrary vertical displacement of the individual traces has been made to avoid overlap.

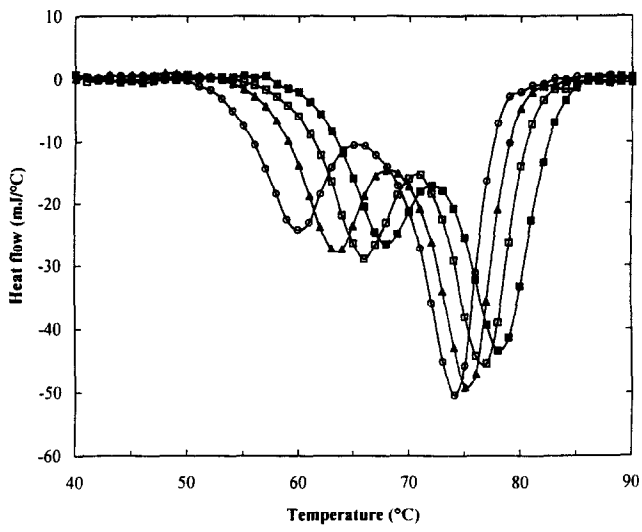

Fig. 7. DSC heating scans (after baseline subtraction) at 0.1 (○), 0.4 (▲), 0.7 (□) and 1.0 (■) °C/min for PCS (5 wt % in 0.1 M KCl).

increase in gelatin concentration due to swelling of the granules, and was found to vary linearly with starch concentration over the range used (1–5 wt %, as in the present work), giving swelling volumes (ml/g) of 9.0 for PCS and 9.65 for WMS. Essentially identical values of ϕ_Y were obtained by the simpler procedure of compar-

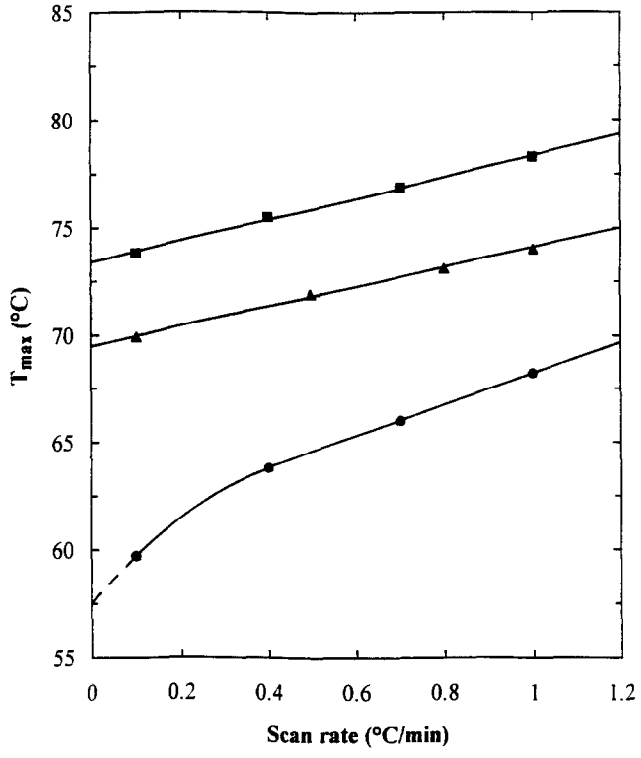

Fig. 8. > Scan-rate dependence of the temperature of maximum heat absorption (T_{max}) for the first (●) and second (■) endothermic processes observed in DSC heating scans of PCS (Fig. 6), and for the single endotherm observed for WMS (▲). Measurements were made using a starch concentration of 5 wt % in 0.1 M KCl.

ing the relative weights of sediment and supernatant from centrifugation. The centrifugation method was therefore used to screen for any changes in swelling volume in the presence of xanthan and KCl.

As shown in Fig. 9, the phase volumes obtained for PCS gelatinised in water were in good agreement with those derived from gelatin concentration. Incorporation of KCl (0.1 M) or xanthan (0.25 wt % in 0.1 M KCl) caused no significant or systematic change.

The swelling volumes reported by Abdulmola *et al.* (1996) were therefore used to derive the modulus of the xanthan phase (G'_X) as a continuous function of starch concentration in the composites studied here, by calculating the increase in xanthan concentration due to swelling of the granules, and then using equation (1) to obtain the corresponding modulus.

Rheology of swollen starches

The changes in G' and G'' observed on heating slurries of PCS and WMS through the temperature range of the gelatinisation process and on subsequent cooling are illustrated in Fig. 10 for a starch concentration of 10 wt %. The initial moduli of the ungelatinised samples are too low to be measured. The onset of the thermal transitions observed by DSC (Fig. 5) is accompanied by a massive increase in both moduli. G' and G'' for WMS (Fig. 10b) reach their maximum values at a temperature close to the mid-point of the DSC endotherm (i.e. at $T \approx T_{max}$) and then decrease again on further heating. The initial increase is obviously due to swelling of the granules; the subsequent decrease presumably reflects loss of mechanical strength as melting of internal order approaches completion. For PCS (Fig. 10a), the moduli reach their maximum values at a temperature close to T_{max} for the first endothermic process in DSC, and then remain essentially constant over the temperature range of the second endotherm, indicating that the chemical crosslinking in this material is sufficient to maintain structural rigidity after complete disordering of amylopectin.

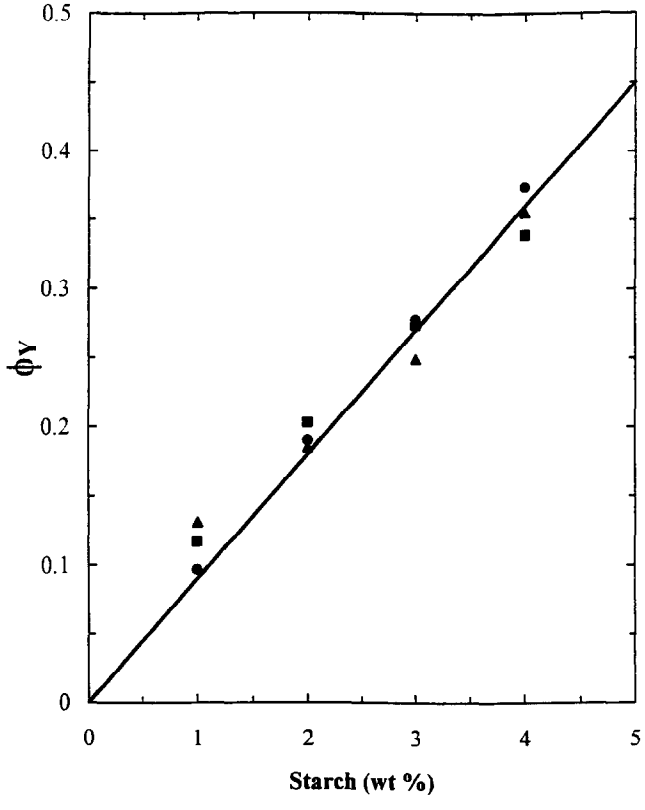

Fig. 9. Relationship between concentration and phase volume of gelatinised PCS, estimated by measurement of the relative weights of sediment and supernatant from sedimentation of PCS in water (●), in 0.1 M KCl (▲) and in 0.1 M KCl + 0.25 wt % xanthan (■).

On subsequent cooling from 80 to 20°C, the moduli of both samples remain virtually constant, strongly suggesting that the increases commonly observed for non-waxy starches (e.g. Hansen *et al.*, 1991) arise almost entirely from amylose released from the granules during gelatinisation. Figure 11 shows the mechanical spectra recorded for PCS and WMS on completion of cooling, at 20°C. Both are typical of a 'true' gel network but, at the concentration used for illustration (10 wt %), the moduli for WMS (Fig. 11b) are more than an order of magnitude lower than those for PCS (Fig. 11a), and the frequency-dependence of G'' is considerably greater, indicating a less extensively crosslinked network with a higher 'sol fraction' of material free to dissipate energy by movement through the solvent.

The same pattern of rheological response was observed at lower starch concentrations, with the sharp increases in G' and G'' on heating occurring at the same temperatures as in Fig. 10, and with virtually no change in moduli on cooling. As shown in Fig. 12a, the mechanical spectrum obtained for 2 wt % PCS after cooling to 20°C has obvious gel-like character (little frequency-dependence of G'; $G' \ll G''$), although the individual moduli are low and G'' increases steeply with frequency. By 3 wt % (Fig. 12b) the mechanical spectrum is typical of a gel network and, as shown in Fig. 12c, the moduli are independent of the amplitude of oscillation over three decades of strain (0.02–20%). WMS develops gel-like character at even lower concentration. The spectrum obtained at 1 wt % (Fig. 13a) is characteristic of a gelling system at the minimum critical degree of crosslinking required to form a continuous network (Durand *et al.*, 1987; Te Nijenhuis & Winter, 1989): the variation of log G' and log G'' with log ω remains linear over three decades of frequency, with a common slope of ~0.55. At 2 wt % (Fig. 13b) the spectrum is typical of a 'true' gel.

Figure 14 shows the variation of G' (10 rad s^{-1}; 0.5% strain) with starch concentration (c) for gelatinised PCS and WMS at 20°C. The curves cross at $c \approx 3$ wt %. For PCS, there is an approximately linear relationship between log G' and log c across the range of concentra-

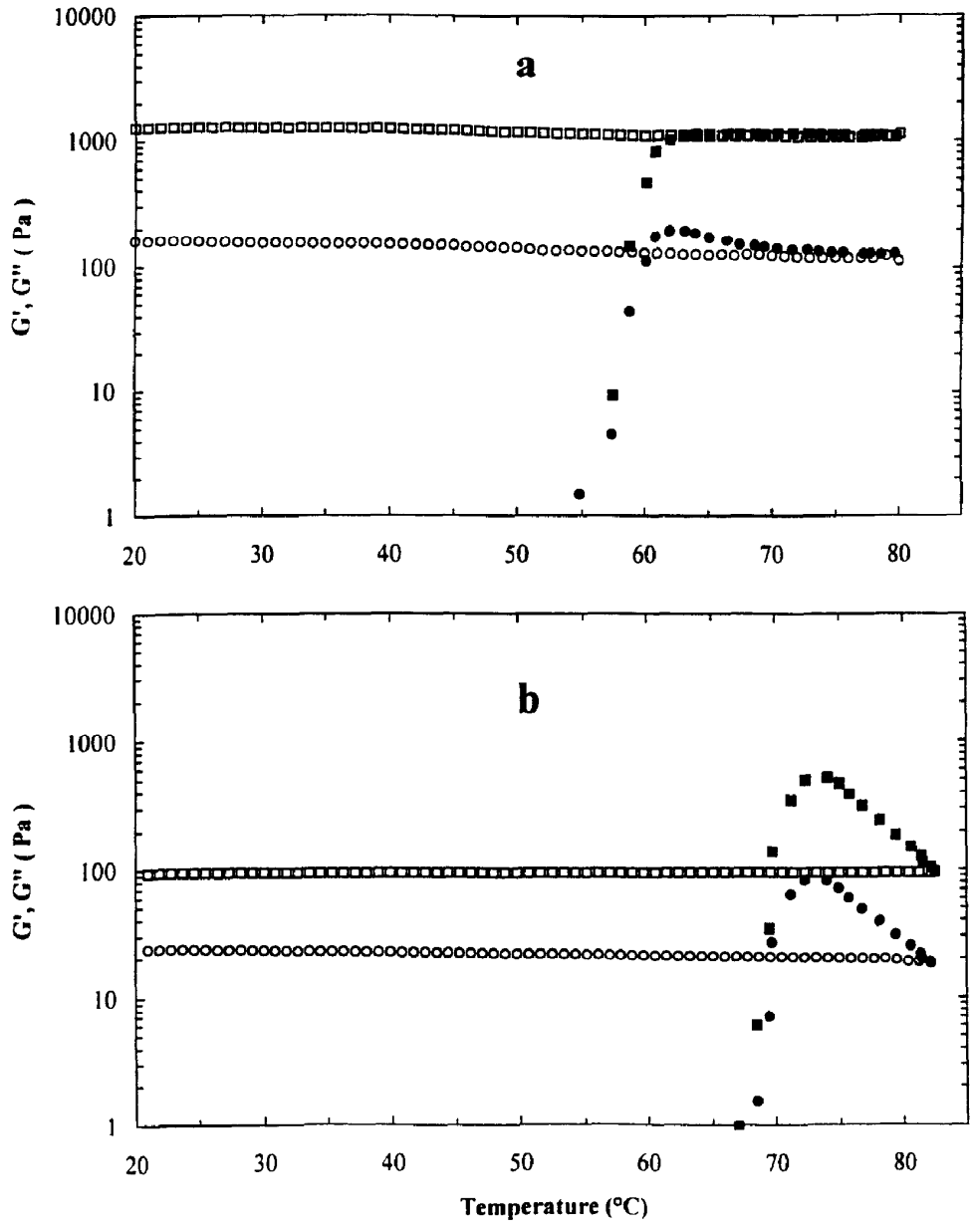

Fig. 10. Temperature-dependence of G' (squares) and G'' (circles), measured at 10 rad s^{-1} and 0.5% strain, for (a) PCS and (b) WMS (10 wt % in water) on heating (filled symbols) and cooling (open symbols) at 1°C/min.

tions studied (1–10 wt %). For WMS, where the networks formed at high concentrations are weaker, the range was extended to 25 wt %. The variation of log G' with log c is again approximately linear from 25 wt % to ~2 wt %, but with a steep increase in slope on further reduction in concentration to 1 wt % (which, as shown in Fig. 13a, is the critical concentration for network formation). The linear relationships between log G' and log c for PCS and WMS are given in equations (2) and (3), respectively.

$$\text{PCS}: \log G' = 4.15 \log c - 0.82 \quad (2)$$

$$\text{WMS}: \log G' = 1.15 \log c + 0.62 \quad (3)$$

where G' is expressed in units of Pa and c is in wt %.

For WMS, the slope of log G' vs log c is close to unity (with a 2-fold increase in concentration raising G' by a factor of ~2.2), consistent with the approximately linear relationship between modulus and concentration commonly reported for gelatinised starches (e.g. Ring, 1985; Steeneken, 1989). The variation of log G' with log c for PCS, however, is much steeper (i.e. the concentration-dependence of G' deviates strongly from linearity), with the slope of 4.15 corresponding to about an 18-fold increase in G' on doubling starch concentration.

Rheology of starch–xanthan composites

The changes in G' observed for the composite systems on heating and cooling between 20 and 80°C are illu-

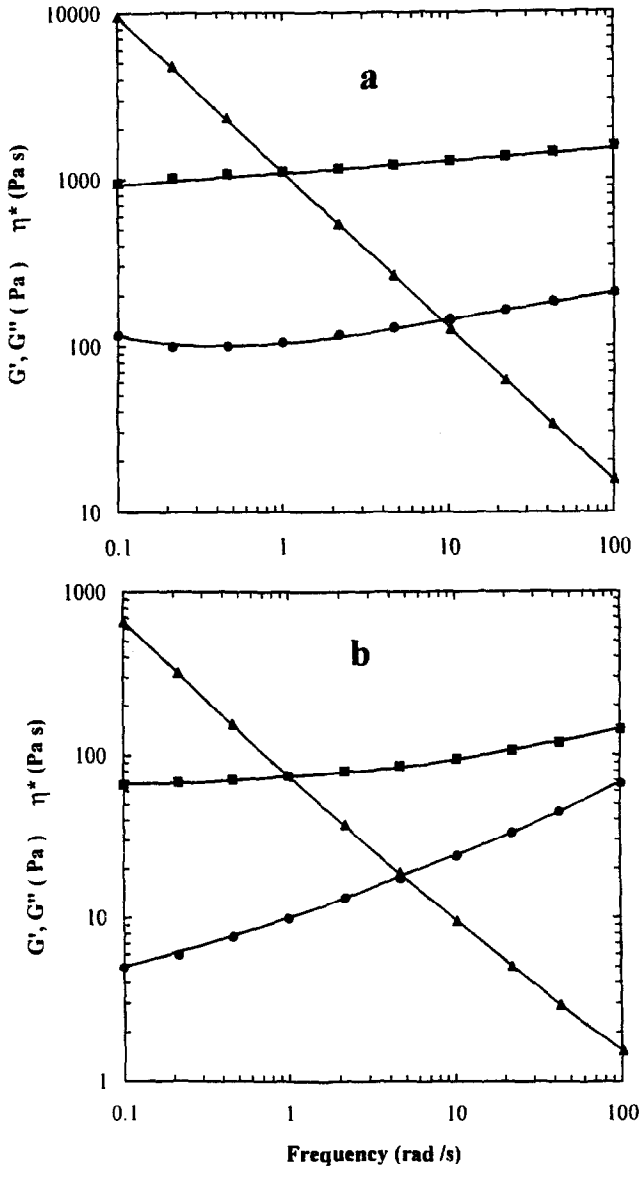

Fig. 11. Mechanical spectra (0.5% strain) showing the frequency-dependence of G' (■), G'' (●) and η^* (▲) for (a) PCS and (b) WMS (10 wt % in water) at 20°C, after completion of the heating and cooling cycle shown in Fig. 10.

strated in Fig. 15 for 4 wt % PCS in 0.5 wt % xanthan. The sharp increase in modulus attributable to swelling of the granules occurs over the same temperature range as in the absence of xanthan (Fig. 10a). The main difference is that G' increases significantly on cooling, reflecting the temperature-dependence observed for xanthan (Fig. 1), rather than remaining virtually constant, as was found for starch alone.

The final moduli of the starch–xanthan composites (G'_C), measured at 10 rad s^{-1} and 0.5% strain on completion of cooling to 20°C, are shown in Fig. 16 for, respectively, PCS and WMS, in comparison with the modulus of the xanthan component in the absence of starch (G'_O) and with the calculated moduli for the xanthan phase in the composite systems after swelling of

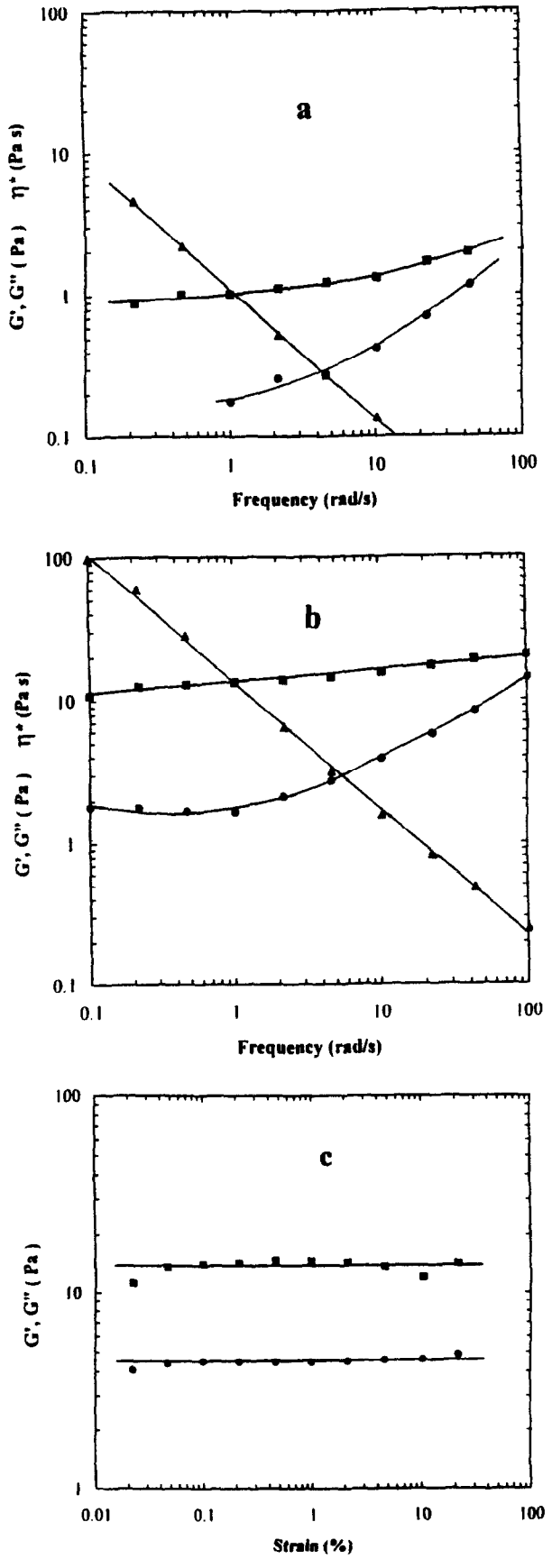

Fig. 12. Mechanical spectra (0.5% strain; 20°C) for gelatinised PCS at (a) 2 wt % and (b) 3 wt % in water: G' (■); G'' (●); η^* (▲). The strain-dependence of G' and G'' for the 3% sample is shown in (c).

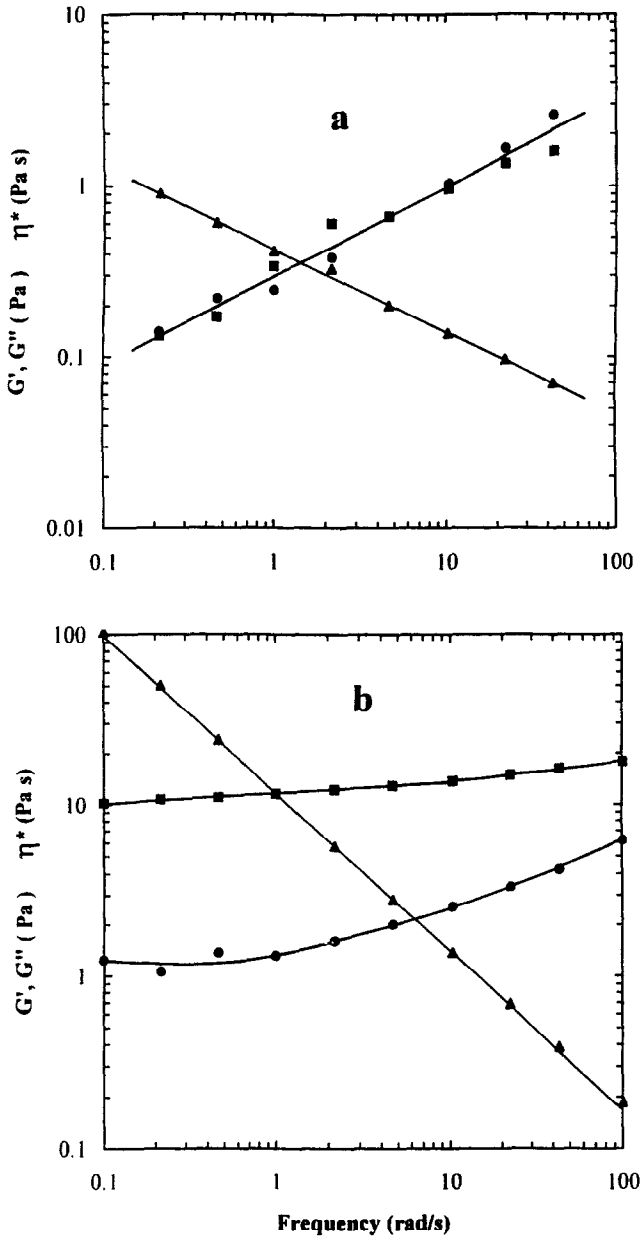

Fig. 13. Mechanical spectra (0.5% strain; 20°C) for gelatinised WMS at (a) 1 wt % and (b) 2 wt % in water; G' (■); G'' (●); η^* (▲).

the starch granules (G'_X). The numerical values of G'_C, G'_X and G'_O are listed, in logarithmic form, in Table 1.

As mentioned previously, our initial intention was to follow the procedure described in the preceding paper (Abdulmola *et al.*, 1996) and attempt to rationalise the increase in modulus due to the presence of starch by treating the gelatinised granules as a dispersed 'filler' (phase Y) in a continuous xanthan matrix (phase X) and applying the isostrain and isostress blending laws [equations (4) and (5), respectively] of Takayanagi *et al.* (1963).

$$G_C = G_X\phi_X + G_Y\phi_Y \text{ for } G_X > G_Y \quad (4)$$

$$1/G_C = \phi_X/G_X + \phi_Y/G_Y \text{ for } G_X < G_Y \quad (5)$$

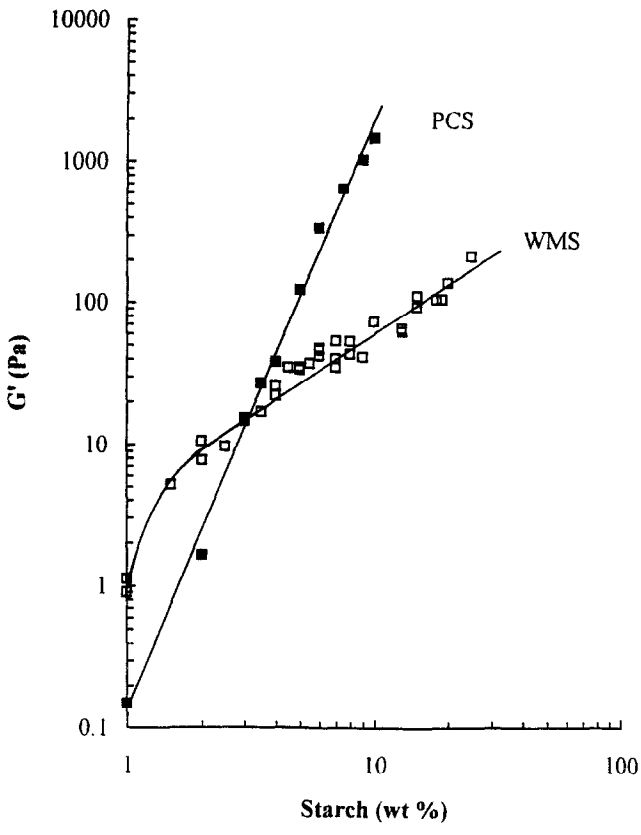

Fig. 14. Concentration-dependence of G' (10 rad s^{-1}; 0.5% strain; 20°C) for PCS (■) and WMS (□) gelatinised in water.

The phase volume of the starch component in the composite systems (ϕ_Y) is obtained by multiplying the starch concentration (wt %) by the swelling volume (ml/g) and dividing by 100 to convert from a percentage

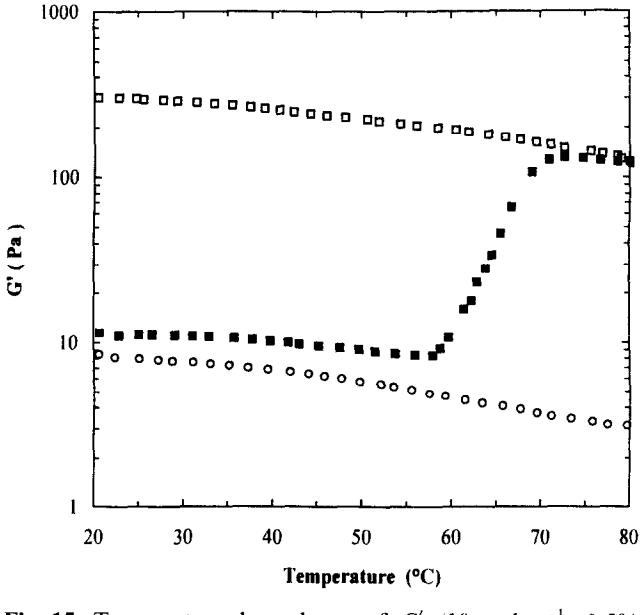

Fig. 15. Temperature-dependence of G' (10 rad s^{-1}; 0.5% strain) for PCS (4 wt % in 0.1 M KCl) on heating (■) and cooling (□) at 1°C/min in the presence of 0.5 wt % xanthan. The temperature-dependence of G' for 0.5 wt % xanthan alone is also shown (○).

Table 1. Phase volumes, polymer concentrations and moduli (G'/Pa) for starch-xanthan composites

	Starch (wt %)	ϕ_Y	ϕ_X	0.25 wt % xanthan			0.50 wt % xanthan			starch alone
				c_X	log G'_X	log G'_C	c_X	log G'_X	log G'_C	log G'
PCS	0	0.000	1.000	0.250	0.25	0.25	0.500	0.93	0.93	–
	1	0.090	0.910	0.275	0.35	0.81	0.549	1.03	1.51	−0.82
	2	0.180	0.820	0.305	0.45	1.17	0.610	1.13	1.88	0.21
	3	0.270	0.730	0.342	0.56	1.70	0.685	1.24	2.12	1.17
	4	0.360	0.640	0.391	0.69	2.01	0.781	1.37	2.48	1.58
	5	0.450	0.550	0.455	0.84	2.49	0.909	1.52	2.69	2.08
WMS	0	0.000	1.000	0.250	0.25	0.25	0.500	0.93	0.93	–
	1	0.097	0.903	0.277	0.35	0.81	0.554	1.03	1.30	0.00
	2	0.193	0.807	0.310	0.46	1.14	0.620	1.14	1.54	0.95
	3	0.290	0.710	0.352	0.59	1.32	0.704	1.27	1.55	1.17
	4	0.386	0.614	0.407	0.73	1.52	0.814	1.41	1.67	1.39
	5	0.483	0.517	0.484	0.90	1.67	0.967	1.58	1.73	1.53

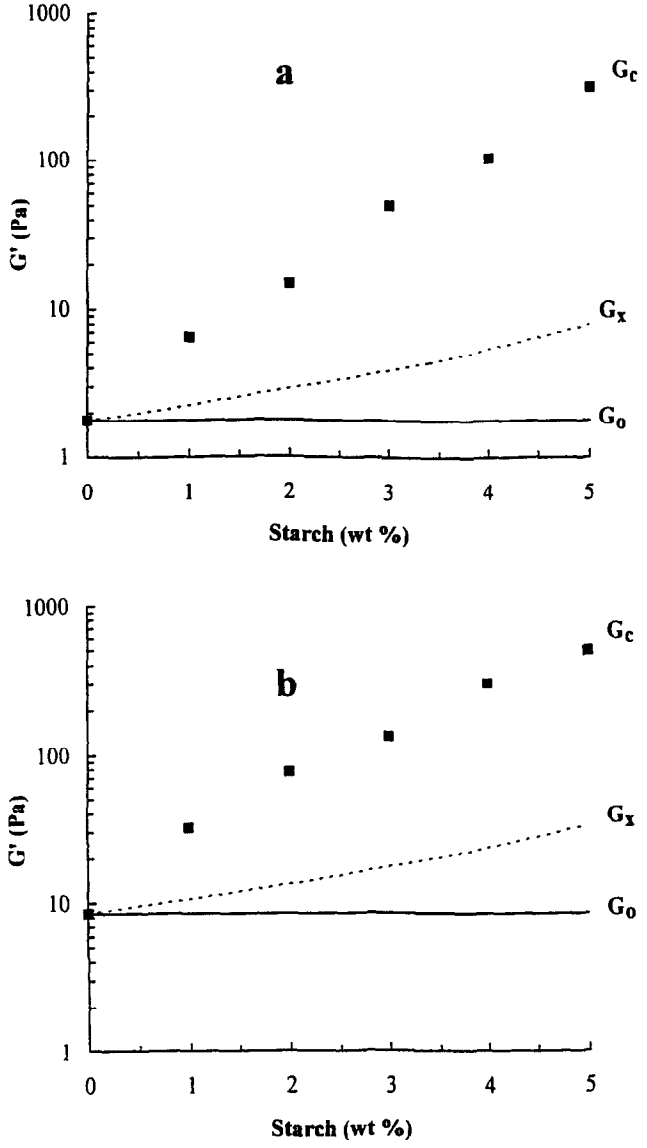

Fig. 16. Observed moduli (G'_C; ■) for PCS–xanthan composites containing (a) 0.25 and (b) 0.50 wt % xanthan, in comparison with the modulus for xanthan alone (G'_O; ——) and with calculated moduli for the xanthan phase in the mixed systems (G'_X; – –).

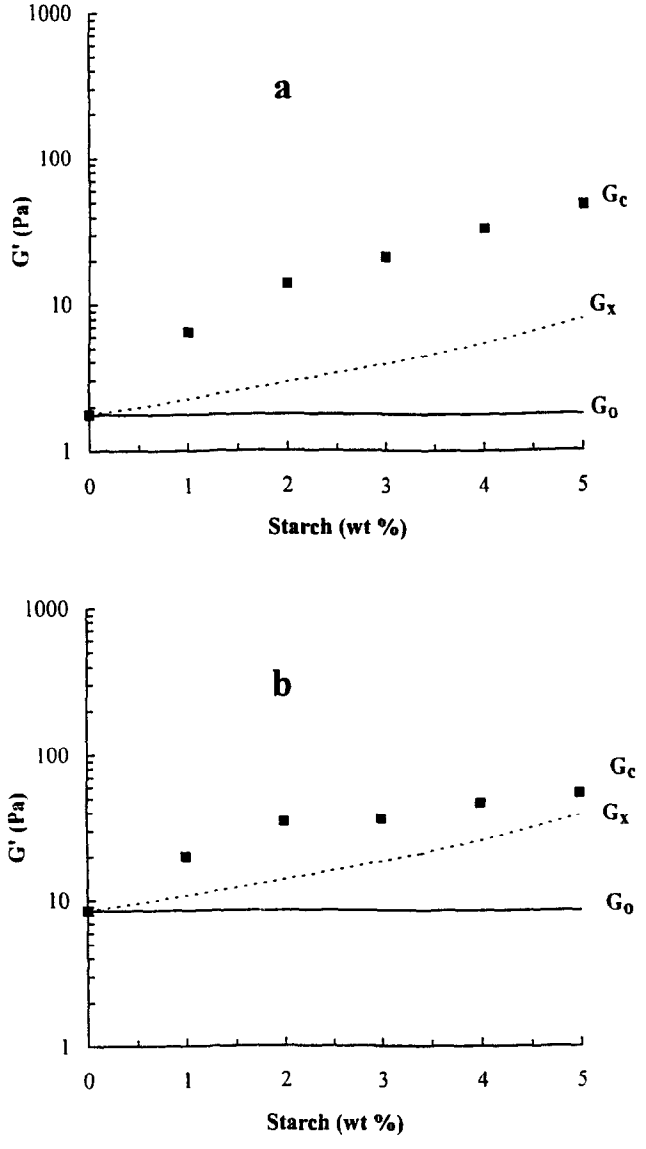

Fig. 17. Observed moduli (G'_C; ■) for WMS–xanthan composites containing (a) 0.25 and (b) 0.50 wt % xanthan, in comparison with the modulus for xanthan alone (G'_O; ——) and with calculated moduli for the xanthan phase in the mixed systems (G'_X; – –).

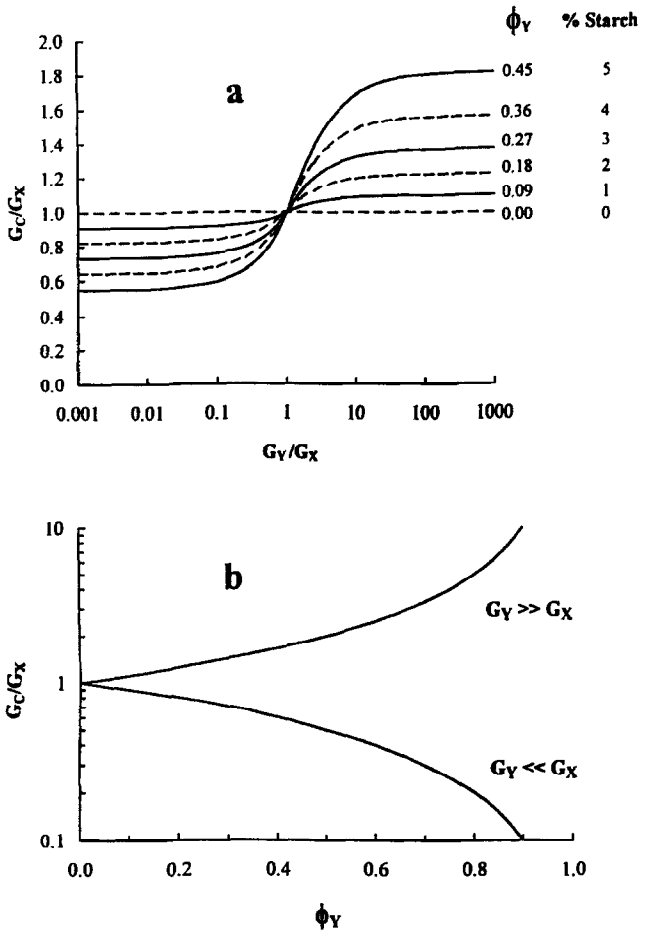

Fig. 18. Dependence of composite modulus (G_C) on the moduli of the continuous and discontinuous phases (G_X and G_Y, respectively) and their relative phase volumes (ϕ_X and ϕ_Y), as calculated by the polymer blending laws [equations (4) and (5)]. (a) Variation of G_C/G_X with relative 'hardness' of the filler phase (G_Y/G_X), illustrated for the starch phase volumes in the PCS composites studied. (b) Variation of G_C/G_X with phase volume (ϕ_Y) of infinitely 'hard' and infinitely 'soft' fillers.

figure to a volume fraction; ϕ_X is then obtained by difference ($\phi_X = 1 - \phi_Y$).

Figure 18a shows calculated values for the ratio of overall modulus (G_C) to that of the continuous phase (G_X) plotted against G_Y/G_X (the 'hardness' of the filler relative to that of the matrix), for values of ϕ_Y corresponding to the phase volumes of gelatinised PCS at the five concentrations used (1, 2, 3, 4 and 5 wt %). The curves intersect at $G_Y/G_X = 1$ (i.e. where the matrix and filler have the same modulus, giving $G_X = G_Y = G_C$, irrespective of relative phase volumes). The variation in composite modulus relative to that of the continuous phase occurs almost entirely between $G_Y/G_X = 0.1$ (where the filler is 10 times 'softer' than the matrix) and $G_Y/G_X = 10$ (where the hardness of the filler is 10 times that of the matrix), with further increase in hardness or softness having little effect. In the limiting cases of an infinitely soft or infinitely hard filler, the isostrain and isostress models reduce to:

$$G_C = G_X\phi_X = G_X(1 - \phi_Y) \qquad \text{for } G_X \gg G_Y \qquad (6)$$

and

$$1/G_C = \phi_X/G_X = (1 - \phi_Y)/G_X \text{ for } G_X \ll G_Y \qquad (7)$$

The resulting minimum and maximum values of G_C/G_X [given by, respectively, $(1 - \phi_Y)$ and $1/(1 - \phi_Y)$] are plotted against ϕ_Y (the phase volume of the dispersed filler) in Fig. 18b.

The phase volumes for gelatinised PCS and WMS at the highest concentration used are less than 0.5 (~0.450 for PCS and ~0.483 for WMS). Thus, in terms of blending law analysis with the assumption of a discontinuous starch phase, the maximum deviation of G'_C from G'_X should be less than a factor of 2 [as was found for the starch–gelatin composites studied by Abdulmola *et al.* (1996)]. In practice, however, the value of G'_C/G'_X obtained for 5 wt % PCS in 0.25 wt % xanthan (Fig. 16a) is ~45, and the corresponding values for virtually all the starch–xanthan composites studied are greater than 2 (Fig. 19).

Other theoretical analyses of the effect of hard filler particles on network rheology (see, for example, Nielsen, 1974) yield higher values of G'_C/G'_X and have been shown to give reasonable agreement with experimental results for model systems (e.g. Richardson *et al.*, 1981; Brownsey *et al.*, 1987; van Vliet, 1988). In all cases,

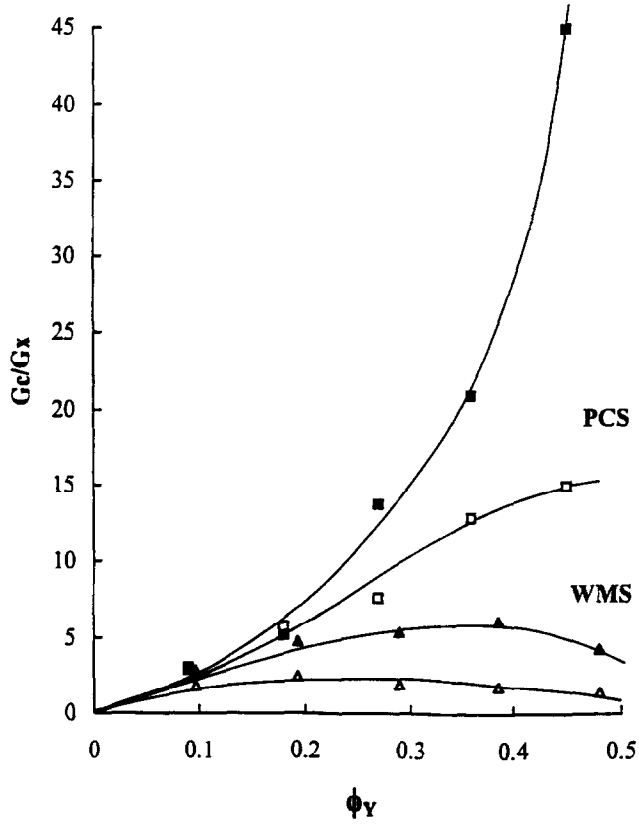

Fig. 19. Ratio of composite modulus (G'_C) to xanthan-phase modulus (G'_X) for starch–xanthan composites: PCS + 0.25 wt % xanthan (■); PCS + 0.50 wt % xanthan (□); WMS + 0.25 wt % xanthan (▲); WMS + 0.50 wt % xanthan (△); ϕ_Y denotes the phase volume of the starch component.

however, the calculated increase in G'_C/G'_X becomes progressively steeper as the phase volume of the filler particles is increased. The experimental values for PCS in 0.25 wt % xanthan follow this general pattern (Fig. 19), but when the xanthan concentration is raised to 0.5 wt % there is an obvious reduction in slope at high-phase volumes of PCS, and the values for WMS–xanthan composites pass through a shallow maximum at ~3–4 wt % starch, and then decrease. It seems clear, therefore, that the observed rheology of the starch–xanthan composites cannot be explained by regarding the starch component as an inert filler in a xanthan matrix.

A more rational picture emerges, however, if the behaviour of the composite systems is compared with that of gelatinised starch alone. As shown in Fig. 20, the separation between observed values of log G'_C for composites incorporating 0.5 or 0.25 wt % xanthan decreases progressively with increasing concentration of starch, and the individual curves show a progressive reduction in slope, which parallels the behaviour of the starch component alone but contrasts with the increase in slope shown in Figs 16 and 17 for the xanthan phase (giving rise to the maxima in G'_C/G'_X shown in Fig. 19). At high concentrations of starch, the moduli of the composites at both concentrations of xanthan appear to converge towards the values of G' derived by Abdulmola *et al.* (1996) for individual swollen granules (730 Pa for PCS; Fig. 20a: 55 Pa for WMS; Fig. 20b).

DISCUSSION

The gelatinisation conditions used in the present work, and in the investigation by Abdulmola *et al.* (1996) reported in the preceding paper, are unusually mild (heating to 80°C with negligible shear), and were chosen to maintain the integrity of the individual granules and to avoid complications from release of starch polysaccharides into the surrounding polymer matrix. Swelling of starch granules on heating occurs in two stages (Eliasson, 1986). The first is accompanied by a massive increase in G' and G'', and, as can be seen by comparison of the rheological changes shown in Fig. 10 with the DSC heating scans in Fig. 5, corresponds to the onset of thermal disruption of ordered structures within the granule. Release of polymeric material from the granules is largely confined to the second stage of the swelling, which typically begins at ~80°C. The swelling volumes reported by Eliasson (1986) for cereal starches on completion of the first swelling process were ~10 ml/g, in good agreement with the values obtained for PCS and WMS (9.0 and 9.65 ml/g, respectively).

Although the main aim of this investigation was to explore the rheology of starch–xanthan composites, the results obtained for starch alone show some unexpected and potentially informative features. First, the G' values for increasing concentrations of PCS and WMS (Fig. 14) display the 'cross-over' phenomenon commonly observed for starches of different swelling capacity (e.g. Steeneken, 1989; Evans & Lips,

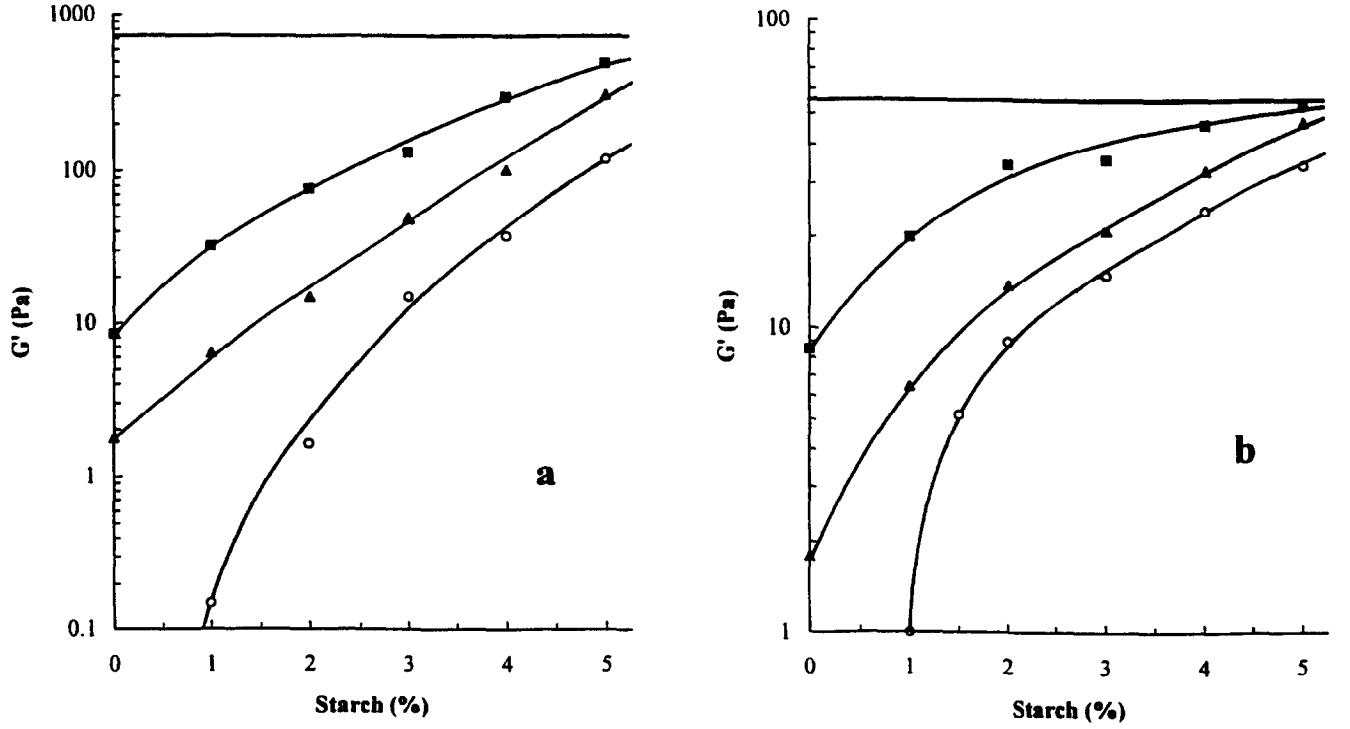

Fig. 20. Observed moduli for composites of (a) PCS and (b) WMS with 0.25 (▲) and 0.50 (■) wt % xanthan, in comparison with those for the same concentrations of starch alone (○). The horizontal lines show the moduli derived by Abdulmola *et al.* (1996) for individual swollen starch granules (730 Pa for PCS; 55 Pa for WMS).

1992). The normal interpretation is that, at low concentration, starches with a high swelling capacity occupy a greater volume and therefore generate greater modulus (and viscosity) whereas at higher concentrations, where full swelling cannot occur, the dominant effect is the greater rigidity of granules with a low swelling volume. However, there is little difference between the swelling volumes of PCS and WMS under the gelatinisation conditions used here, indicating that some other factor is involved in generating the observed cross-over.

More centrally, it is generally accepted that interactions between swollen starch granules become significant only when the system approaches close-packing (e.g. Evans & Haisman, 1979; Wong & Lelievre, 1981; Eliasson, 1986; Steeneken, 1989). Indeed Evans and Lips (1992) have recently modelled the rheology of gelatinised dispersions by classic (Hertzian) theory developed for (predominantly repulsive) interactions between elastic spheres and tested for dispersions of swollen Sephadex beadlets (Evans & Lips, 1990). As shown in Figs 12 and 13, however, both PCS and WMS have obvious gel-like rheology at concentrations as low as 2 wt %, where the degree of volume–occupancy by the swollen granules is less than 20%. It is difficult, therefore, to avoid the conclusion that there is some form of attractive interaction (i.e. association) between the granules which is capable of developing network structure at concentrations well below close-packing, a conclusion consistent with the 'stringy' character of starch pastes, which implies cohesive association. In simpler terms, the individual granules appear capable of interacting by sticking together as well as by cramming against one another. If this interpretation is correct, the higher values of G' for WMS in comparison with PCS at low concentrations of starch (Fig. 14) would correspond to greater 'stickiness' before chemical modification of the surface of the granule.

As shown in Fig. 20, xanthan appears to augment the properties of the starch component in the composite systems, rather than dominating the overall rheology, as found for gelatin (Abdulmola *et al.*, 1996). This cannot be due to differences in the strength of the two biopolymer matrices since, as shown in Fig. 4, 0.5 wt % xanthan (the higher of the two concentrations used here) has a larger value of G' than gelatin at the lowest concentration 0.88 wt %) used by Abdulmola *et al.* (1996). A possible explanation is that the adhesive interactions between gelatinised granules are enhanced by xanthan but not by gelatin.

As discussed previously, xanthan, under the ionic conditions used in the present work, exists in a rigid, ordered chain conformation throughout the temperature range studied, whereas gelatin, prior to the onset of gelation, has compact 'random-coil' geometry. Polymer chains can induce association (flocculation) of colloidal particles by two mechanisms, bridging and depletion (Walstra, 1993), both of which would be promoted by conformational rigidity. Bridging flocculation, as the name implies, involves chains adhering to the surface of individual particles and forming a link between them. The entropic barrier to association will clearly be much lower for a rigid chain than for a flexible coil. Depletion flocculation centres on the hydrodynamic volume swept out by the polymer chains, which again will be much greater for rigid molecules. As two particles approach each other (under random Brownian motion), a point will be reached at which surrounding polymer molecules, depending on their size, will be excluded from the intervening gap, creating a region of lower concentration. Partition into regions of high and low polymer concentration results in an overall loss of entropy, which can be offset by bringing the particles into closer contact (with consequent reduction in the volume of the excluded layer).

Either (or both) of these mechanisms would explain enhancement of starch rheology by the presence of xanthan, and at the moment we have no basis for distinguishing between them, although previous studies of the interaction of xanthan with latex particles (Takigami *et al.*, 1992) suggest that depletion flocculation is more likely at the polymer concentrations used in the present work (0.25 and 0.50 wt %). The central conclusion, however, is that rheological enhancement in starch–gelatin composites arises mainly from the increase in concentration of the gelatin matrix on swelling of the starch granules, which then remain as separate, dispersed particles, whereas the dominant effect in starch–xanthan systems is for the xanthan component to promote association of starch.

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