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Application of polymer blending laws to starch–gelatin composites

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The small-deformation rheology of a range of starch–gelatin composites has been studied, to test the applicability of the isostress and isostrain blending laws to biphasic biopolymer networks. Waxy maize starch (crosslinked and uncrosslinked) was used to minimise release of soluble material into the gelatin phase, and was gelatinised at 80°C. Phase volumes were determined by measurement of the increase in concentration of the gelatin phase due to swelling of the starch granules. The swelling volumes obtained for the crosslinked and uncrosslinked samples were 9.0 ml/g and 9.65 ml/g, respectively, and were independent of gelatin and starch concentration over the range used (0.88–1.50 wt % gelatin; 1–5 wt % starch). The gelatin-gelatinised starch composites and gelatin-phase samples isolated by centrifugation were gelled by quenching to 5°C and measured under a controlled time–temperature regime (150 min at 5°C; heated to 20°C at 0.25°/min). The value of the storage modulus (G') of the gelatinised starch granules, which is the only unknown parameter, was varied by a standard minimisation procedure to obtain the best least-squares fit between observed values of log G' for the composite gels and those calculated by the polymer blending laws. Good agreement between observed and calculated values was obtained using the isostress model when the trial value of the starch modulus was higher than that of the gelatin phase, and the isostrain model for the converse situation. The fitted moduli for the swollen granules (730 Pa and 55 Pa for the crosslinked and uncrosslinked samples, respectively) are close to those observed experimentally for the same starches gelatinised in water to a packing fraction of ~75%. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The central aim of this investigation was to provide a critical test of the isostress and isostrain blending laws developed initially for synthetic polymer composites (Takayanagi *et al.*, 1963) and subsequently extended to phase-separated biopolymer gels (Clark *et al.*, 1982, 1983; McEvoy *et al.*, 1985; Clark, 1987; Morris, 1991; Kasapis *et al.*, 1993a).

In outline, the procedure adopted was to gelatinise starch in a solution of gelatin, and obtain a clear sample of the gelatin phase by sedimentation of the swollen granules. The gelatin supernatant and the unseparated composite were then allowed to gel under identical time–temperature conditions, and characterised by small deformation oscillatory measurements of storage modulus (G'). The increase in gelatin concentration due to swelling of the starch during gelatinisation was determined from the concentration-dependence of G' for gelatin alone, thus yielding the phase volumes of the two components. Since the moduli of the composite and the gelatin phase are determined experimentally, the only unknown parameter is the modulus of the gelatinised starch granules. The value of this parameter was varied by a standard minimisation procedure to assess the quality of fit that could be achieved between experimental moduli for a range of starch–gelatin composites and values derived by application of the polymer blending laws.

To avoid complications from release of amylose into the gelatin phase, the starch used was from waxy maize. Most of the experiments were carried out using highly crosslinked starch to maintain the integrity of the granules after gelatinisation. Some comparative studies, however, were made with uncrosslinked waxy maize starch. In both cases the moduli of the composite gels

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could be matched with acceptable precision by the polymer blending laws, with the isostress model giving good agreement when the fitted modulus of the starch granules was higher than the known value of G' for the gelatin phase (strong 'filler' in a weak matrix) and the isostrain model matching the converse situation of a weak filler in a strong matrix. A preliminary account of some aspects of the work has been published elsewhere (Abdulmola *et al.*, 1996a).

MATERIALS AND METHODS

Phosphorus oxychloride crosslinked hydroxypropylated waxy maize starch (C* Cream 06716) and uncrosslinked waxy maize starch (SF 04202) were kindly supplied by Cerestar. For brevity, these samples will be denoted as, respectively, PCS (phosphate-crosslinked starch) and WMS (waxy maize starch). The gelatin used was an acid extract from pigskin, kindly supplied by Systems Bio-Industries. All solutions were made using distilled deionised water.

Slurries of ungelatinised starch and solutions of gelatin (pH adjusted to 7.0) were prepared at twice the required final concentrations and were mixed in equal amounts (w/w) at 45°C. The starch was gelatinised by holding the mixture for 45 min in a water bath at 80°C, with occasional gentle stirring (magnetic stirrer) to keep the granules in suspension. The samples were then split into two portions. One was centrifuged (4000 g) for 1 h at ~40°C to obtain a clear sample of the gelatin phase; the other was loaded onto an oscillatory rheometer at 45°C, quenched to 5°C, held for 150 min and heated at 0.25°C/min, with measurement of G' at 5, 10, 15 and 20°C. Gelatin supernatants from centrifugation, and standard gelatin solutions (pH 7.0) for calibration of the concentration-dependence of G', were measured under the same time–temperature regime. The concentration of gelatin in the supernatants was then obtained from the calibration curve and used to calculate the phase volumes of gelatin and starch.

Comparative estimates of phase volume were also obtained by direct measurement of the relative weights of sediment and supernatant from centrifugation, and by using optical rotation as an additional index of gelatin concentration in the supernatants. Optical rotation was measured at 365, 436, 546 and 578 nm on a Perkin–Elmer 241 polarimeter, using a 10 cm cell thermostatted at 40°C. Gelatin concentrations were determined by comparison with calibration curves at each wavelength.

Measurements of G' were made at 10 rad s^{-1} and 0.5% strain (within the linear viscoelastic region) using cone-and-plate geometry (50 mm diameter; 0.05 rad cone angle) on a sensitive prototype rheometer designed and constructed by one of us (R.K.R.). To circumvent problems of thermal expansion/contraction during heating and cooling, the cone was truncated over 45% of its diameter, giving a gap of 0.5 mm between the flat surfaces of the two elements, but keeping strain constant at a fixed, maximum, value across the outer portion (which constitutes 80% of the total area). The periphery of the sample was coated with light silicone oil to minimise evaporation of water. Temperature was controlled by a Haake circulating water bath and measured with a thermocouple attached to the stationary element.

Composites were prepared using starch concentrations of 1, 2, 3, 4 and 5 wt%. At 6 wt% or higher, it proved impossible to obtain a clear gelatin layer on centrifugation. Four gelatin concentrations were used in investigation of PCS: 0.88, 1.00, 1.25 and 1.50 wt%, giving a total of 20 composites. Studies of WMS were limited to a single gelatin concentration of 1.50 wt% (i.e. five composites).

The temperature used for gelatinisation was selected on the basis of differential scanning calorimetry (DSC) work reported in detail in the following paper (Abdulmola *et al.*, 1996b). The endothermic transitions of both PCS and WMS were complete by 80°C, which was therefore chosen as the best compromise between the conflicting requirements of ensuring full gelatinisation of the starch component while minimising thermal degradation of gelatin.

Curve fitting was by least-squares analysis using a standard Microsoft Excel spreadsheet package (Version 5.0).

RESULTS

Calibration of gelatin moduli

Figure 1 illustrates the changes in G' observed for gelatin alone on holding at 5°C after rapid cooling from the solution state, and on subsequent slow (0.25°C/min) heating. The gelation process (Fig. 1a) is comparatively rapid, and the holding period used in investigation of the composite gels (150 min) is sufficient to give essentially constant values of G' for the gelatin network.

The concentration-dependence of the final values of G' at the end of the holding period at 5°C is shown in Fig. 2. Similar calibration curves were obtained using the lower moduli recorded on heating to 10, 15 and 20°C (Fig. 1b). In each case, the variation of G' with gelatin concentration (c) could be fitted with reasonable precision to the general form of concentration-dependence anticipated from cascade theory (Clark & Ross-Murphy, 1985). A somewhat better standard of fit, however, was obtained using a fifth-order polynomial function (equation (1)).

$$\log G' = P(0) + P(1)/c + P(2)/c^2 + P(3)/c^3 + P(4)/c^4 + P(5)/c^5 \tag{1}$$

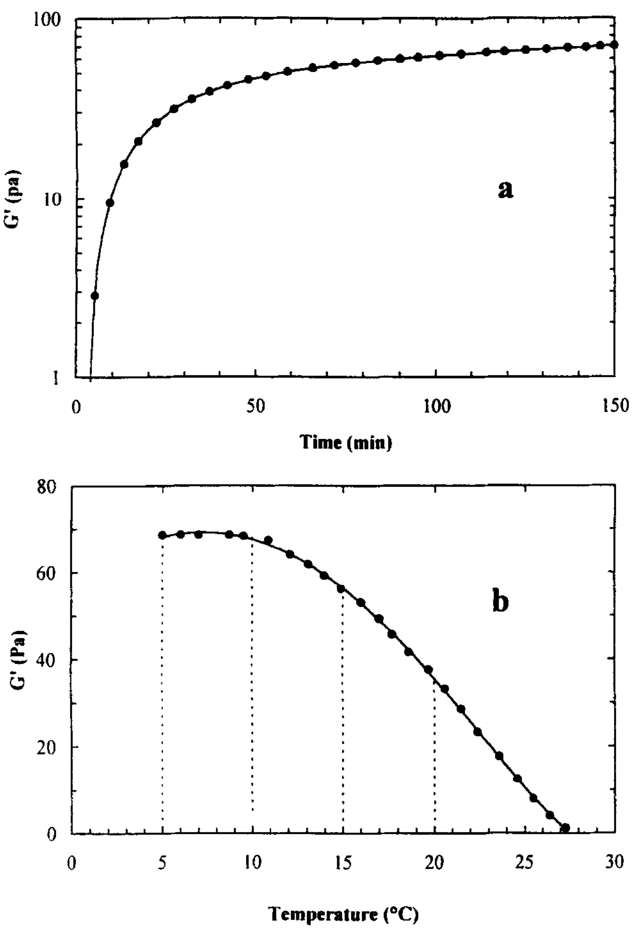

Fig. 1. Time–temperature dependence of G' (10 rad s^{-1}; 0.5% strain) for gelatin, illustrated for a concentration of 1.25 wt %. (a) Increase in modulus on gelation at 5°C after rapid quenching from 45°C. (b) Reduction in modulus on heating (0.25°C/min); vertical lines indicate the temperatures used for quantitative analysis.

It would, of course, be totally invalid to use an empirical function of this type for extrapolation. However, as shown later (in Table 2), the concentration of the gelatin phase in the composite gels did not exceed 2.9 wt %. The polynomial fitting procedure was therefore adopted as a precise method of obtaining gelatin concentration from measured values of G', by interpolation within the range used in construction of the calibration curves (0.80–4.00 wt %). The parameters of the polynomial equations obtained (with G' values in units of Pa and concentration in wt %) at 5, 10, 15 and 20°C are listed in Table 1.

Table 1. Parameters of polynomial fit to modulus-concentration data for gelatin

T(°C)	P(0)	P(1)	P(2)	P(3)	P(4)	P(5)
5	4.503	−4.056	−2.449	9.663	−8.881	2.639
10	4.776	−6.634	5.943	−2.837	−0.310	0.446
15	4.560	−5.973	5.356	−3.571	0.919	−0.002
0	4.551	−7.490	10.559	−11.797	6.882	−1.656

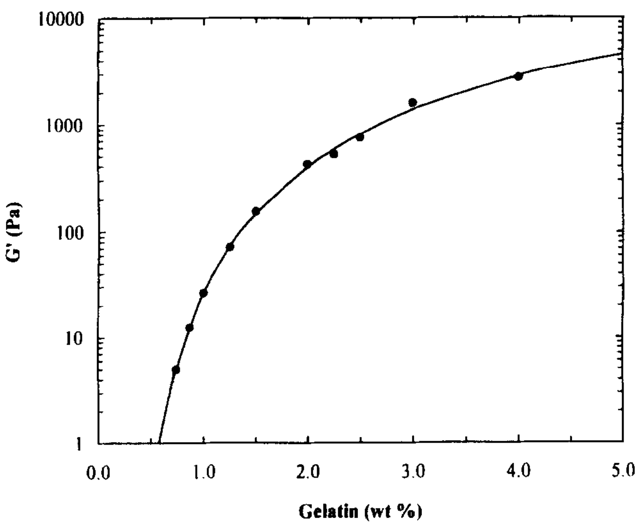

Fig. 2. Concentration-dependence of G' (10 rad s^{-1}; 0.5% strain) for gelatin after 150 min at 5°C.

Determination of phase volumes for gelatin–PCS composites

As illustrated in Fig. 3, increasing concentrations of PCS gave the expected progressive increase in G' for the gelatin supernatants from centrifugation, with the ratio of G' to G'_O (the modulus for the corresponding concentration of gelatin alone) showing no systematic dependence on the temperature at which the measurements were made. The gelatin concentrations obtained from G' values at 5, 10, 15 and 20°C were therefore averaged and, as illustrated in Fig. 4, were found to vary linearly with the concentration of gelatin present initially. It would therefore appear that the presence of gelatin, at the concentrations used (0.88–1.50 wt %), has no significant effect on the degree of swelling of PCS granules during gelatinisation. The mean value of the ratio of gelatin concentration in the supernatants relative to that in the initial solution was therefore calculated for each starch concentration, with the reciprocal giving a direct measure of the fraction of the total volume (phase volume, ϕ_X) occupied by the gelatin phase in the composite gels (since concentration is, of course, inversely proportional to volume for a fixed quantity of material).

The phase volume of the gelatinised starch granules was then obtained by difference ($\phi_Y = 1 - \phi_X$) and, as shown in Fig. 5a, was found to increase linearly ($r^2 = 0.99$) with increasing concentration of starch. Thus the volume occupied by the individual granules after gelatinisation appears to remain constant throughout the range of starch concentrations used (1–5 wt %). The plot of phase volume versus starch concentration (Fig. 5a) has a slope of 0.090 (i.e. with 1 g of PCS swelling to occupy a volume of 9 ml). A similar value (10.4 ml/g) has been reported previously for the equilibrium swelling volume of highly crosslinked waxy maize starch (Steeneken, 1989).

Table 2. Phase volume and concentration of gelatin in composites with PCS and WMS

	PCS						WMS		
Starch (wt %)	ϕ_Y	ϕ_X	Gelatin (wt %)				ϕ_Y	ϕ_X	Gelatin (wt %)
0	0.000	1.000	0.88	1.00	1.25	1.50	0.000	1.000	1.50
1	0.090	0.910	0.96	1.10	1.37	1.65	0.097	0.903	1.66
2	0.180	0.820	1.07	1.22	1.52	1.83	0.193	0.807	1.86
3	0.270	0.730	1.20	1.37	1.71	2.06	0.290	0.710	2.11
4	0.360	0.640	1.37	1.56	1.95	2.34	0.386	0.614	2.44
5	0.450	0.550	1.59	1.82	2.27	2.73	0.483	0.517	2.90

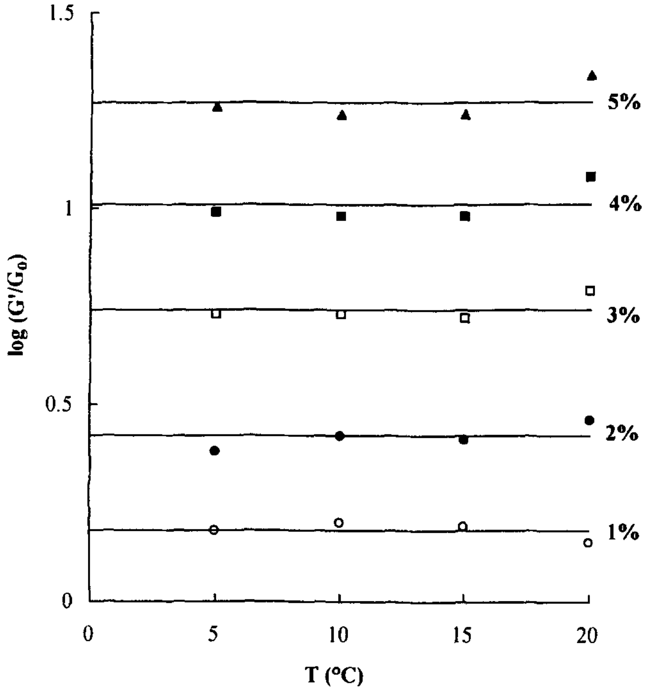

Fig. 3. G' for gelled supernatants from centrifugation of mixtures of gelatin (1.0 wt %) with 1 (○), 2 (●), 3 (□), 4 (■) and 5 (▲) wt % PCS after gelatinisation at 80°C. G'_O denotes the modulus for 1.0 wt % gelatin alone at each measuring temperature (T).

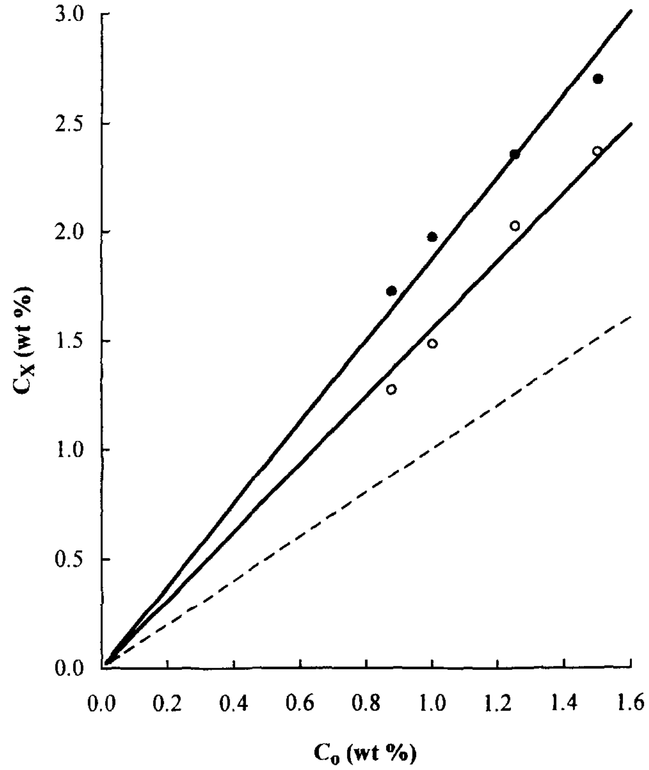

Fig. 4. Dependence of concentration (c_X) of the gelatin phase from composites with gelatinised PCS on the initial gelatin concentration (c_O) prior to gelatinisation, illustrated for PCS concentrations of 4 (○) and 5 (●) wt %. The dashed line corresponds to gelatin alone.

The plot of ϕ_Y vs PCS concentration obtained using optical rotation to measure the concentration of gelatin supernatants was also linear (Fig. 5b), but with a somewhat lower slope (0.084). The most likely explanation of the discrepancy is release of a small amount of soluble carbohydrate from the gelatinised starch granules into the surrounding gelatin solution. The optical rotation of α-D-glucans (starch polymers and oligomers) is positive, whereas that of gelatin is negative and of similar (slightly smaller) absolute magnitude (Kasapis *et al.*, 1993b). Since the concentrations of PCS used in the present work (1–5 wt %) are higher than the gelatin concentrations (0.88–1.5 wt %) by an average factor of ~2.5, the observed decrease of ~6.7% in calculated swelling volume (from 9.0 to 8.4 ml/g) could be explained by solubilisation of ~2.7% of PCS (6.7%/2.5), in good agreement with reported values (Steeneken, 1989) of ~2.6% for the solubility of highly crosslinked starches. At this level of solubility, however, the maximum concentration of starch carbohydrate released into the gelatin phase (~0.13 wt % from 5 wt % PCS) would be unlikely to have any significant effect on the rheology of the gelatin networks. The relationship between phase volume and starch concentration obtained from measurements of G' (Fig. 5a) was therefore used to derive precise values of ϕ_X, ϕ_Y and gelatin concentration (Table 2) for use in quantitative analysis of composite rheology.

As a further check on the relative proportions of the starch and gelatin phases, however, comparison was made of the weights of sediment and supernatant from centrifugation. As shown in Fig. 5c, the weight of the

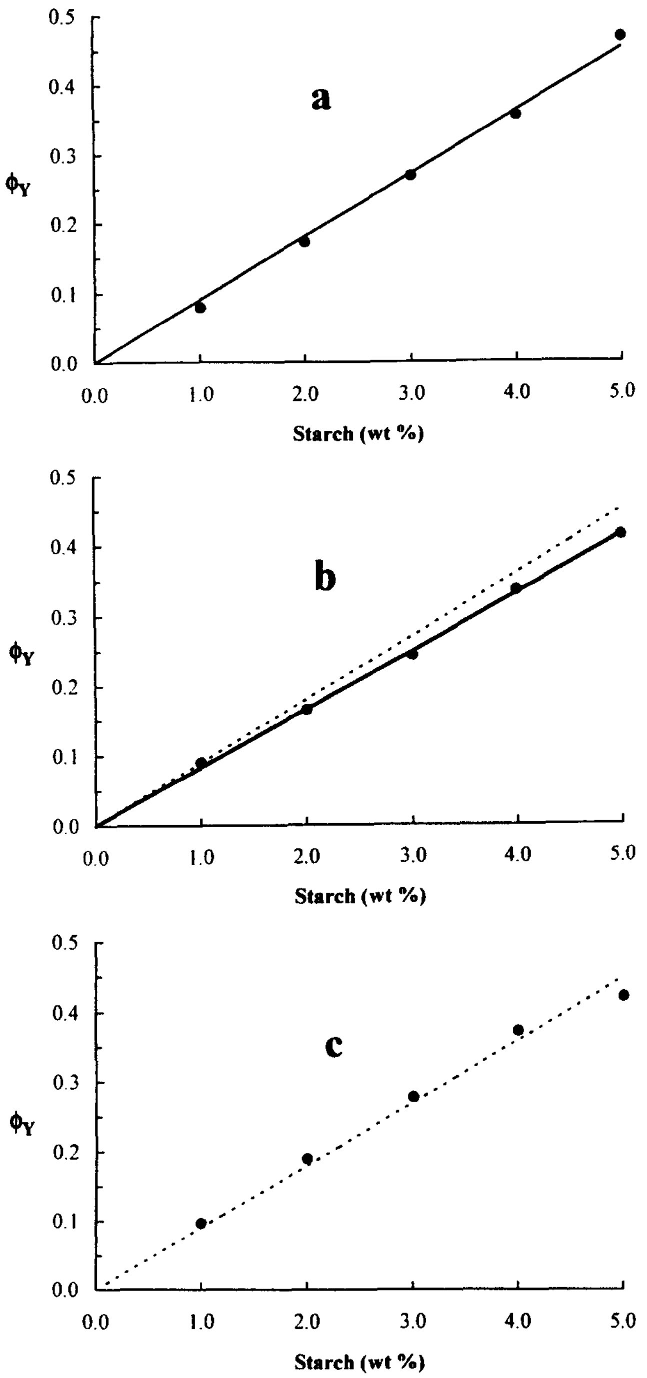

Fig. 5. Concentration-dependence of phase volume (ϕ_Y) for gelatinised PCS in composites with gelatin, as determined by (a) measurements of G' for the gelatin phase after gelation at 5°C, (b) optical rotation of the gelatin phase in the solution state at 40°C, and (c) relative weights of the sediment and supernatant from centrifugation. The dotted lines in (b) and (c) correspond to the fit obtained by linear regression analysis of the rheological data from (a).

sediment expressed as a fraction of the total weight of the system at each starch concentration used is in surprisingly close agreement with the volume fraction, ϕ_Y derived from measurements of G' for the gelled supernatant. This seems to imply that the gelatinised PCS granules are sufficiently deformable to give a close-packed sediment, with little, if any, void space available for occupancy by the solution phase.

Quantitative analysis of moduli for gelatin–PCS composites

Figure 6 shows the values of composite modulus (G'_C) from measurements at 10°C, expressed relative to the modulus for the corresponding concentration of gelatin alone (G'_O). Similar curves were obtained at the other measuring temperatures used (5, 15 and 20°C). In each case, G'_C/G'_O was found to increase systematically with increasing concentration of starch and with decreasing concentration of gelatin.

At first sight it might seem reasonable to assume that this behaviour is due to a progressive increase in the contribution of the PCS granules to the overall rheology of the composite gel as the ratio of starch to gelatin is raised. However, as illustrated in Fig. 7 for the gelatin concentration at which greatest enhancement in G' was observed (0.88 wt %), the main effect of the starch component is to raise the modulus of the gelatin phase (G'_X), with the direct contribution of the starch phase causing only a slight further increase in G' (by less than a factor of 2 at the highest starch concentration used). The deviation of G'_C from G'_X at higher gelatin concentrations (1.00, 1.25 and 1.50 wt %) was even smaller (Table 3).

The relationship between the moduli of the composite gels and those of the constituent phases was explored using the isostrain and isostress blending laws (equations (2) and (3), respectively).

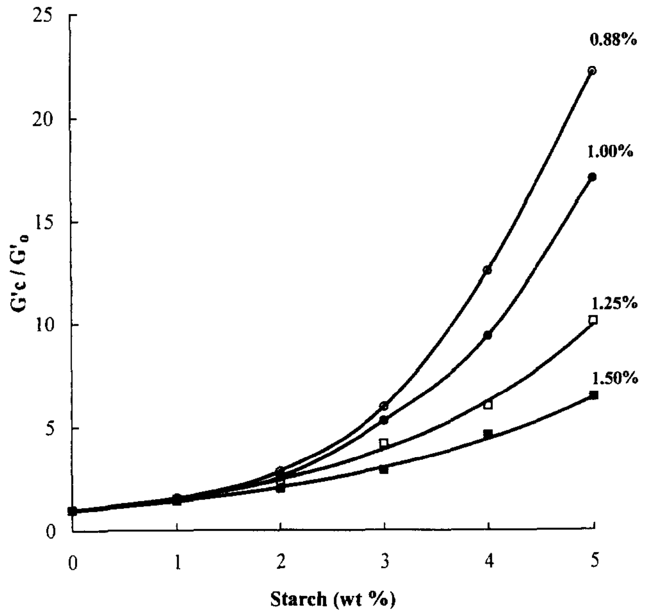

Fig. 6. Observed moduli (G'_C; 10°C) for composites of PCS gelatinised in 0.88 (○), 1.00 (●), 1.25 (□) and 1.50 (■) wt % gelatin, expressed relative to the corresponding modulus for gelatin alone (G'_O).

Table 3. Moduli (G'; 10 rad s^{-1}; 0.5% strain) for starch–gelatin composites

		Log(G'/Pa) at 5°C			Log(G'/Pa) at 10°C			Log(G'/Pa) at 15°C			Log(G'/Pa) at 20°C		
System	Starch (wt %)	Gelatin matrix	Composite (observed)	Composite (fitted)	Gelatin matrix	Composite (observed)	Composite (fitted)	Gelatin matrix	Composite (observed)	Composite (fitted)	Gelatin matrix	Composite (observed)	Composite (fitted)
PCS + 0.88% gelatin	0	1.08	—	—	1.06	—	—	0.96	—	—	0.68	—	—
	1	1.33	1.27	1.37	1.29	1.25	1.33	1.19	1.20	1.23	0.94	0.92	0.98
	2	1.56	1.53	1.64	1.52	1.51	1.60	1.43	1.43	1.51	1.20	1.17	1.29
	3	1.79	1.84	1.91	1.76	1.83	1.88	1.67	1.78	1.80	1.46	1.72	1.59
	4	2.01	2.18	2.18	1.99	2.16	2.16	1.92	2.08	2.08	1.72	1.95	1.90
	5	2.25	2.44	2.43	2.24	2.40	2.42	2.17	2.33	2.37	1.99	2.21	2.21
PCS + 1.00% gelatin	0	1.42	—	—	1.39	—	—	1.29	—	—	1.04	—	—
	1	1.62	1.59	1.66	1.58	1.59	1.62	1.49	1.46	1.53	1.27	1.20	1.31
	2	1.82	1.80	1.90	1.79	1.79	1.87	1.70	1.72	1.78	1.50	1.53	1.58
	3	2.02	2.12	2.13	2.00	2.10	2.11	1.92	2.02	2.04	1.73	1.87	1.85
	4	2.23	2.39	2.37	2.21	2.35	2.35	2.14	2.28	2.29	1.96	2.14	2.13
	5	2.45	2.65	2.59	2.44	2.61	2.58	2.38	2.54	2.53	2.20	2.41	2.39
PCS + 1.25%	0	1.86	—	—	1.84	—	—	1.75	—	—	1.55	—	—
	1	2.02	2.03	2.06	2.00	2.02	2.04	1.92	1.95	1.96	1.73	1.78	1.77
	2	2.19	2.22	2.25	2.17	2.20	2.24	2.10	2.12	2.17	1.92	1.97	1.99
	3	2.37	2.49	2.45	2.35	2.45	2.44	2.29	2.35	2.38	2.11	2.20	2.22
	4	2.56	2.65	2.64	2.55	2.61	2.64	2.48	2.51	2.59	2.31	2.40	2.44
	5	2.77	2.89	2.81	2.76	2.84	2.80	2.69	2.75	2.76	2.52	2.69	2.64
PCS + 1.50% gelatin	0	2.16	—	—	2.15	—	—	2.08	—	—	1.89	—	—
	1	2.31	2.33	2.34	2.30	2.31	2.33	2.23	2.24	2.26	2.05	2.11	2.08
	2	2.46	2.46	2.51	2.45	2.46	2.50	2.39	2.41	2.44	2.21	2.29	2.28
	3	2.63	2.65	2.68	2.62	2.61	2.67	2.56	2.49	2.62	2.38	2.38	2.47
	4	2.81	2.84	2.83	2.80	2.81	2.82	2.73	2.72	2.78	2.56	2.63	2.65
	5	3.01	3.01	2.95*	3.00	2.96	2.94*	2.92	2.87	2.89*	2.75	2.79	2.80
WMS + 1.50% gelatin	0	2.16	—	—	2.15	—	—	2.08	—	—	1.89	—	—
	1	2.32	2.35	2.29	2.31	2.33	2.27	2.24	2.24	2.21	2.06	2.06	2.04
	2	2.49	2.53	2.41	2.49	2.49	2.41	2.41	2.39	2.34	2.24	2.22	2.18
	3	2.67	2.62	2.54	2.67	2.56	2.54	2.59	2.49	2.47	2.42	2.36	2.31
	4	2.87	2.65	2.68	2.87	2.59	2.68	2.79	2.51	2.60	2.61	2.38	2.44
	5	3.09	2.77	2.82	3.09	2.70	2.82	3.00	2.63	2.73	2.82	2.53	2.57

*Isostrain model; all other values for PCS are fitted to isostress; all values for WMS are fitted to isostrain. Log G'_Y = 2.86 for PCS and 1.74 for WMS.

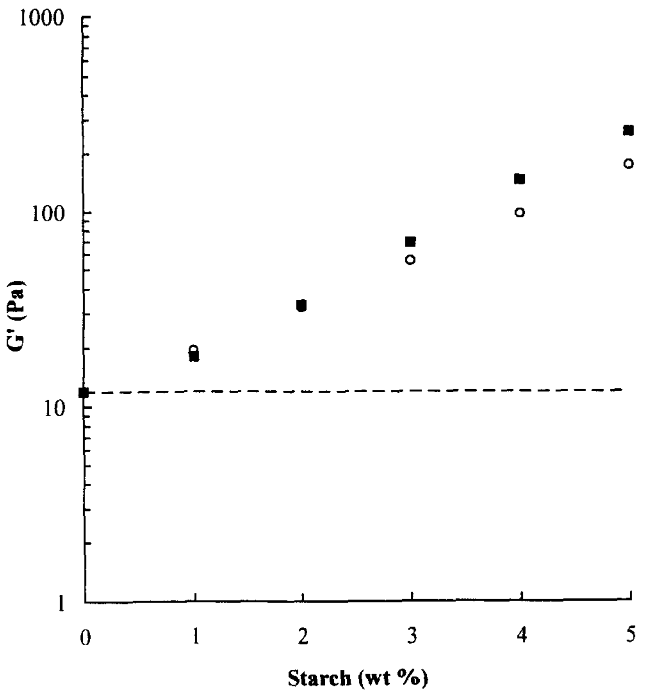

Fig. 7. Variation of composite modulus, G'_C (■) and gelatin-phase modulus, G'_X(○) with starch concentration for mixtures of PCS with 0.88 wt % gelatin. The dashed line shows the modulus (G'_O) of 0.88 wt % gelatin alone at the same temperature (10°C).

$$G'_C = \phi_X G'_X + \phi_Y G'_Y \tag{2}$$

$$1/G'_C = \phi_X/G'_X + \phi_Y/G'_Y \tag{3}$$

Strictly speaking, the isostrain model (equation (2)) sets an upper limit, or 'bound', on the possible range of moduli for the composite, with the isostress model (equation (3)) defining the minimum possible value (lower bound). However, for systems in which one component forms a continuous matrix with the other dispersed through it as a discontinuous 'filler', the modulus of the composite is expected to lie close to the upper bound if the matrix is more rigid (higher modulus) than the filler, and close to the lower bound if the filler is more rigid than the matrix (Clark, 1987). As a working assumption in fitting observed moduli for the starch–gelatin composites, the departures from strict compliance with the isostrain and isostress models were regarded as negligible, and equations (2) and (3) were used to derive calculated values of G'_C for quantitative comparison with experimental results.

As discussed previously, the only unknown parameter is the modulus of the starch phase, ϕ_Y, which was varied systematically to obtain the best least-squares fit between observed and calculated values of log G'_C. Since, as shown in Fig. 7 and Table 3, the moduli of the composite gels remain close to those of the gelatin phase at all concentrations of starch, it seems evident that the starch granules are present as dispersed particles in a gelatin matrix. Equation (2) was therefore used to generate calculated values of G'_C when the trial value of G'_Y was lower than the modulus of the gelatin phase (G'_X) and equation (3) was used for $G'_Y > G'_X$. The averaged values of phase volume (ϕ_X and ϕ_Y) and gelatin concentration (c) listed in Table 2 were used throughout, and G'_X was derived from c using the polynomial parameters (Table 1) for the appropriate temperature.

Since the degree of swelling of the starch granules is independent of gelatin concentration (Fig. 4) and starch concentration (Fig. 5), G'_Y was assumed to have a constant value at each measuring temperature for all 20 gelatin–PCS composites studied. Best agreement between observed and fitted values of log G'_C was obtained with log (G'_Y/Pa) = 2.97, 2.87, 2.74 and 2.86 at 5, 10, 15 and 20°C, respectively. Since these values are reasonably close, and show no obvious systematic dependence on temperature, a global fit was made for all composites at all measuring temperatures, yielding log G'_Y = 2.86 ($G'_Y \approx$ 730 Pa). The observed and calculated values of log G'_X are listed in Table 3, and the overall standard of agreement obtained is illustrated in Fig. 8.

As shown in Table 3, the best-fitting value of G'_Y for the galatinised PCS granules lies above the modulus derived for the surrounding gelatin matrix for all

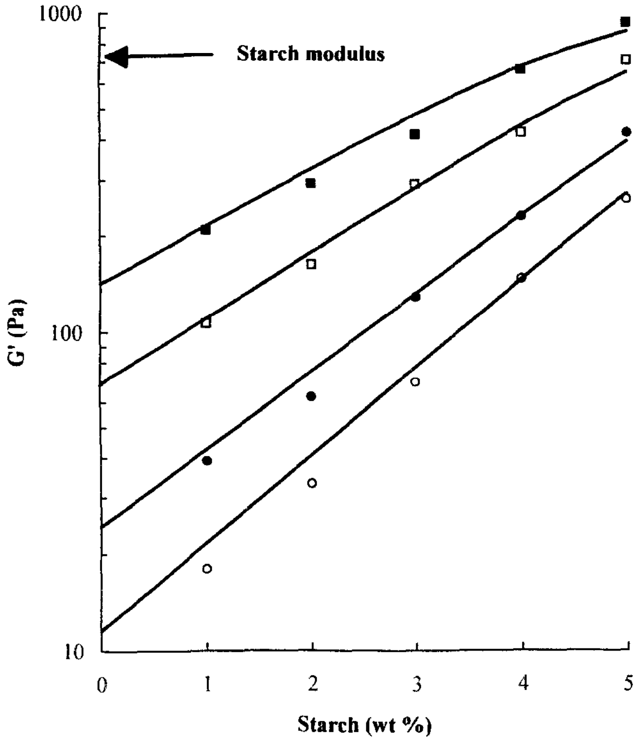

Fig. 8. Observed moduli (G'; 10°C) for composites of PCS with 0.88 (○), 1.00 (●), 1.25 (□) and 1.50 (■) wt % of gelatin, in comparison with calculated values (—) derived by application of the polymer blending laws. The best fitting value of G'_Y, the modulus of the gelatinised PCS granules, is indicated by the arrow on the vertical axis.

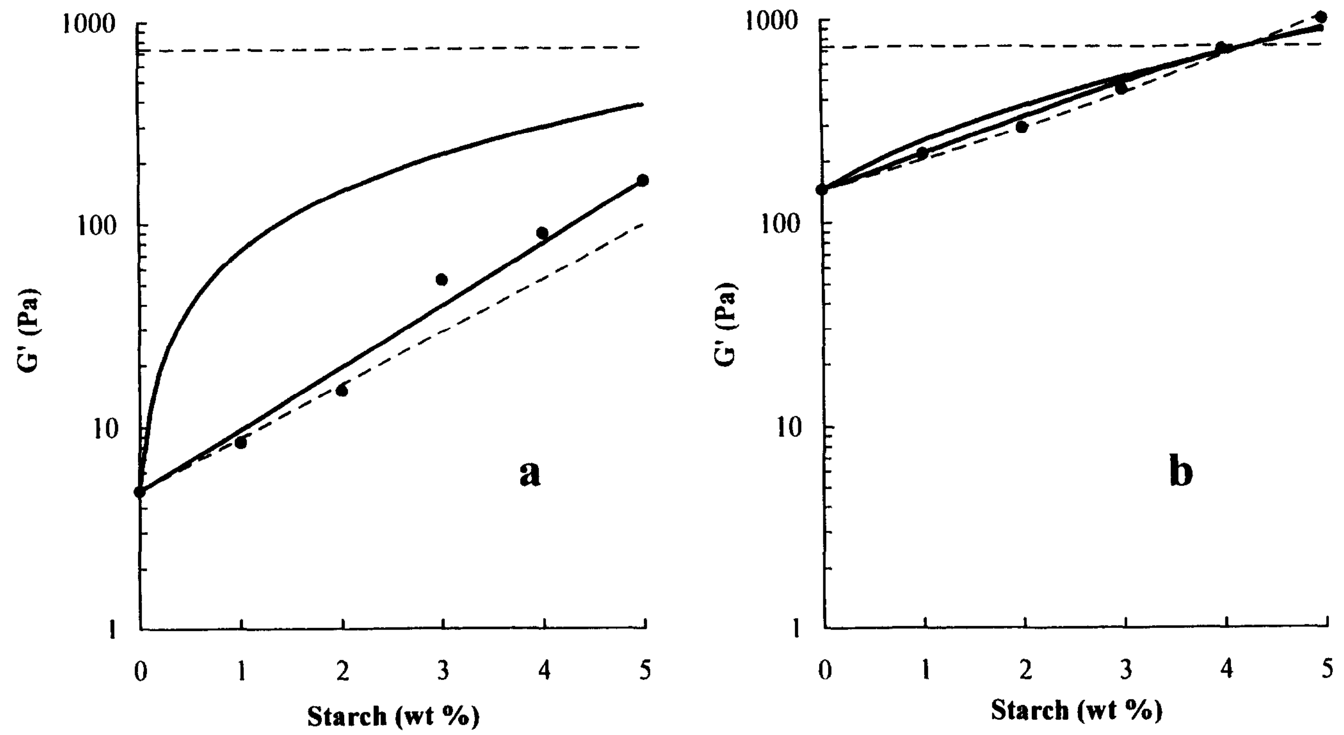

Fig. 9. Blending law analysis of observed moduli (●) for composites of gelatin with gelatinised PCS, illustrated for (a) 0.88 wt % gelatin at 20°C and (b) 1.5 wt % gelatin at 5°C. The horizontal and sloping dashed lines correspond to the individual moduli of, respectively, the starch and gelatin components, and the bold lines show the upper and lower bounds from equations (2) and (3).

systems studied, apart from the composite involving the highest concentration of both materials (1.5 wt % gelatin; 5 wt % PCS) at the three lowest measuring temperatures (5, 10 and 15°C). Thus virtually all measurements of G'_C were fitted to the isostress model (equation (3)); in the three exceptional cases where the isostrain model (equation (2)) was used, the amount by which the modulus of the gelatin phase exceeds the fitted value for PCS is small (i.e. $G'_X \approx G'_Y$), with both models therefore yielding virtually identical values of G'_C.

The way in which the relative values of G'_X and G'_Y affect the upper and lower bounds derived from equations (2) and (3), respectively, is illustrated in Fig. 9 for the lowest gelatin concentration (0.88 wt %) at the highest measuring temperature (20°C), the conditions that give the lowest values of G'_X and hence the greatest differences between G'_X and G'_Y, and for the highest concentration of gelatin (1.50 wt %) at the lowest measuring temperature (5°C), where the differences between G'_X and G'_Y are smallest. In the first case (Fig. 9a), where the fitted modulus for gelatinised PCS (G'_Y) is ~150 times greater than G'_O (the modulus for gelatin alone), the upper bound rises sharply above the lower bound as the concentration of the starch 'filler' is increased, reaching a maximum separation of almost an order of magnitude (upper bound values ~8 times higher than lower bound) at starch concentrations between ~1 and 2 wt %. At higher concentrations of starch the bounds converge again, as the modulus of the gelatin phase approaches that of the starch phase. At the opposite extreme (Fig. 9b), where $G'_Y/G'_O \approx 5$, the separation between the upper and lower bounds is much smaller (maximum ratio ~1.25), with the two curves meeting at a starch concentration of ~4 wt %, when the modulus of the gelatin matrix reaches that of the PCS filler.

The two main conclusions from Fig. 9 are (i) that the way in which the moduli of the constituent phases are combined to yield the overall modulus of the composite becomes progressively less important as their individual values converge, and (ii) that at low concentrations of gelatin, where the upper and lower bounds are widely separated (Fig. 9a), the isostress (lower bound) model gives a convincing fit to the experimental results.

Gelatin–WMS composites

The procedures described above for gelatin–PCS systems were also applied to a limited range of gelatin–WMS composites (1, 2, 3, 4 and 5 wt % WMS in 1.5 wt % gelatin). As shown in Fig. 10, the starch phase-volume (ϕ_Y), derived from measurements of G' for the gelatin phase at 5, 10, 15 and 20°C, again showed a linear dependence ($r^2 = 0.99$) on starch concentration, with no systematic dependence on measuring temperature. As would be anticipated from the absence of crosslinking, however, the swelling volume for WMS was somewhat higher than that obtained for PCS (9.65 ml/g in comparison with 9.0 ml/g for PCS). The

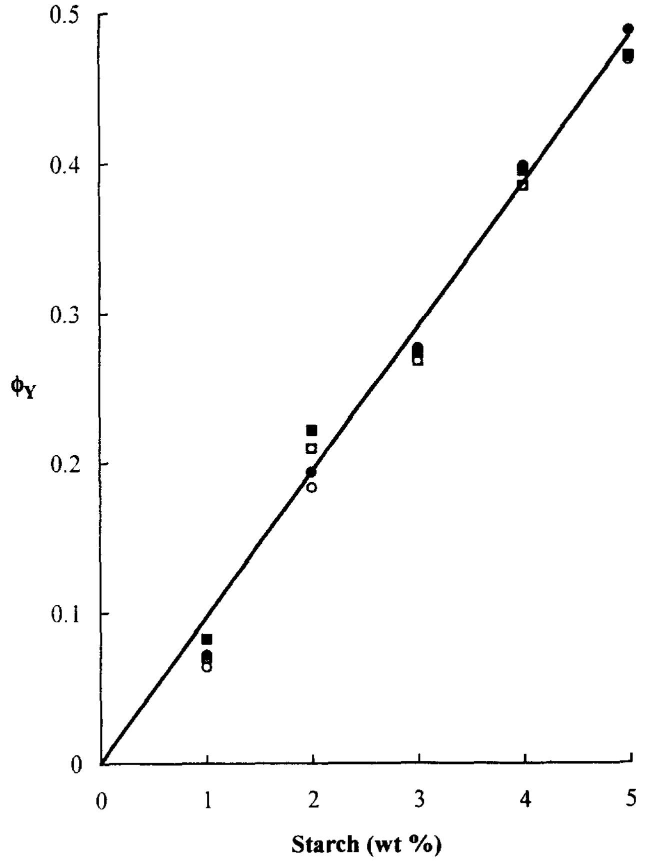

Fig. 10. Concentration-dependence of phase volume (ϕ_Y) for gelatinised WMS in composites with gelatin, determined from measurement of G′ for the gelatin phase at 5 (○), 10 (●), 15 (□) and 20 (■) °C.

corresponding values of phase volume (ϕ_X and ϕ_Y) and gelatin concentration in the final composites at each concentration of WMS are listed in Table 2.

The best-fitting value of log (G'_Y/Pa) obtained from least-squares minimisation of the difference between observed and calculated values of log G'_C at all starch concentrations and measuring temperatures used (Table 3) was 1.74 ($G'_Y \approx 55$ Pa, in comparison with ~730 Pa for PCS). Thus, as shown in Table 3, the modulus of the dispersed starch phase is now lower than that of the surrounding gelatin matrix at all concentrations of WMS used, and, as illustrated in Fig. 11 for the highest and lowest temperatures at which measurements were made (5 and 20°C), the experimental values of G'_C are in reasonable agreement with those calculated by the isostrain (upper bound) model (equation (2)).

DISCUSSION

In a number of recent investigations in this Laboratory, the isostrain and isostress models have been used to explore the rheological properties of phase-separated composites formed by binary mixtures of gelling biopolymers (Kasapis *et al.*, 1993a; Chronakis & Kasapis, 1993; Manoj *et al.*, 1996; Chronakis *et al.*, 1996). Two central problems in relating the properties of such composites to those of the individual polymers are (i) that the partition of solvent between the constituent phases cannot, at present, be determined directly and (ii) that the sequence (and rate) of network forma-

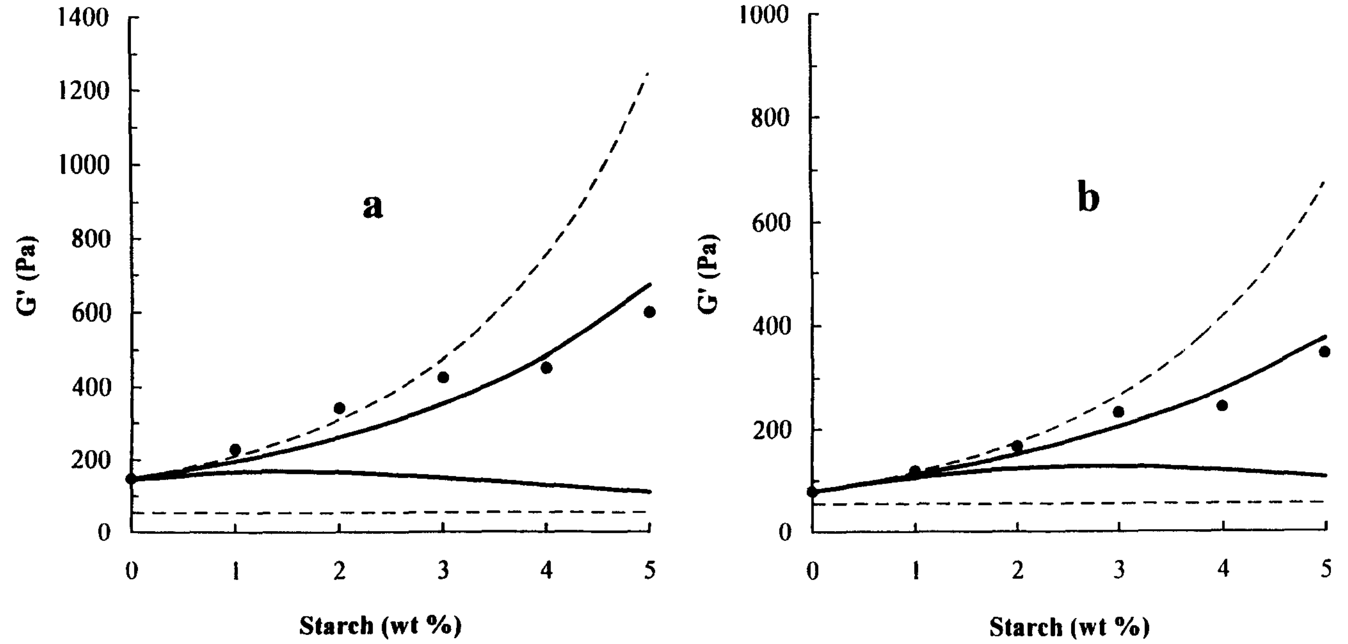

Fig. 11. Blending law analysis of observed moduli (●) at (a) 5°C and (b) 20°C for composites of 1.5 wt % gelatin with gelatinised WMS. The horizontal and sloping dashed lines correspond to the moduli of, respectively, the starch and gelatin components, and the bold lines show the upper and lower bounds from equations (2) and (3).

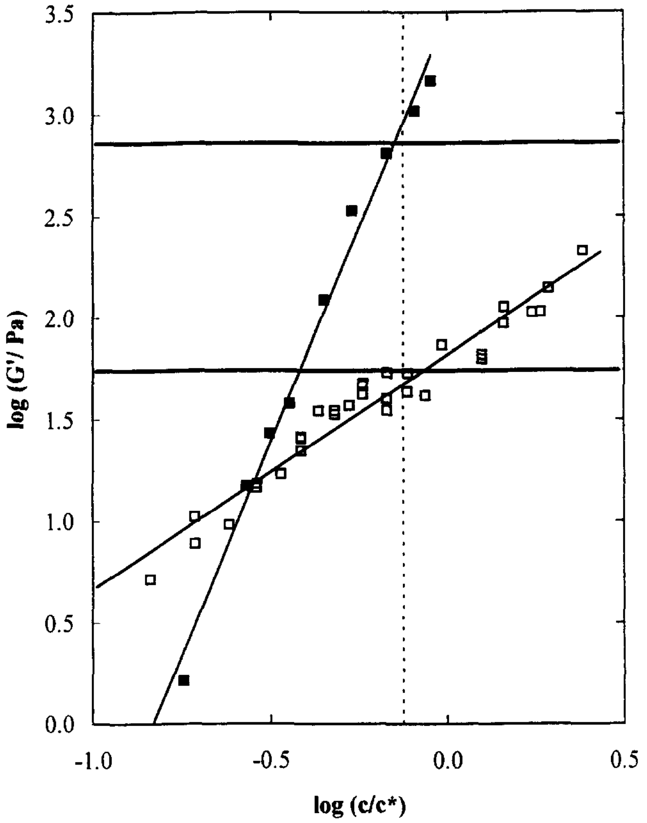

Fig. 12. Variation of G' (10 rad s^{-1}; 0.5% strain; 20°C; Abdulmola *et al.*, 1996b) with degree of space-occupancy (c/c^*) for gelatinised PCS (■) and WMS (□), in comparison with fitted moduli for individual swollen granules (horizontal lines) derived by blending-law analysis of starch–gelatin composites. The vertical dotted line corresponds to a packing fraction of 75% (i.e. c/c^* = 0.75).

tion may affect the rheology of the individual components. To avoid further complication in analysis of these complex systems, calculated moduli were derived using equation (2) when the modulus of the dispersed phase was lower than that of the surrounding continuous phase ($G'_Y < G'_X$) and equation (3) for $G'_Y > G'_X$, with no attempt to adopt more rigorous treatments (see, for example, Arridge, 1975). The results of the present investigation indicate that applying the isostrain and isostress models in this way does not introduce significant error.

The advantage of using starch–gelatin composites to test the validity of blending-law analysis is that the problems of unknown phase volumes and possible kinetic effects mentioned above are avoided. Phase volumes are defined with good precision (Figs 5 and 10), and the starch component is already swollen to its final volume prior to gelation of the gelation phase. However, although the standard of agreement between observed and calculated moduli (Figs 8 and 11; Table 3) is encouraging, it does depend on values of G'_Y (modulus of the starch granules) obtained by an iterative fit to the experimental moduli for the composites. The validity of the analysis therefore depends on whether or not these fitted values are physically realistic.

The following paper (Abdulmola *et al.*, 1996b) includes a systematic study of the concentration-dependence of G' for PCS and WMS gelatinised, in water, at the same temperature as used in the present work (80°C). The results obtained are shown in Fig. 12, in direct comparison with the fitted values of G'_X derived for the starch–gelatin composites (730 Pa for PCS and 55 Pa for WMS). To take account of the difference in degree of swelling of the two materials, the starch concentrations in Fig. 12 are scaled to the concentration at which the combined volume of the swollen granules would exactly equal the total volume of the system. This value is obtained by taking the reciprocal of the swelling volume (9.0 ml/g for PCS; 9.65 ml/g for WMS), and, by analogy with the onset of coil overlap in solutions of disordered polymers, is denoted as c^* (i.e. c^* = 11.1 wt% for PCS and 10.4 wt% for WMS). Encouragingly, the fitted moduli for both materials coincide with the experimental values at approximately the same degree of space-occupancy ($c/c^* \approx 0.75$). This implies that the overall modulus for suspensions of swollen starch granules becomes equal to that of the individual granules when the packing fraction reaches ~75%, which seems a realistic figure for close contact without serious distortion or compression.

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