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Phase equilibria and gelation in gelatin/maltodextrin systems — Part IV: composition-dependence of mixed-gel moduli

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The storage moduli (G') of phase-separated co-gels formed by quench-cooling mixed solutions of gelatin and potato maltodextrin (Paselli SA-2 and SA-6) have been related quantitatively to the experimentally-determined concentration-dependence of G' for the constituent polymers. Distribution of water between the phases was examined explicitly by using polymer blending laws to derive calculated moduli for gelatin-continuous and maltodextrin-continuous networks over the entire range of solvent partition. Allowance was made for the direct contribution of polymer chains, and for density differences between the phases, in calculating relative phase-volumes. The effect of gel formation prior to phase-separation was calculated using classical theory for network de-swelling. Good agreement with observed moduli for more than 30 gelatin/maltodextrin combinations was achieved using a single adjustable parameter, p (the ratio of solvent to polymer in the gelatin phase divided by the same ratio for the maltodextrin phase), with an optimum value of $p \approx 1{\cdot}8$ for both SA-6 and SA-2.

1 INTRODUCTION

The first three papers of this series (Kasapis *et al.*, 1993*a, b, c*) reported, respectively, the effect of temperature and concentration on the rate of gelation of potato maltodextrins (Paselli SA-2 and SA-6) and the concentration-dependence of gel modulus; the incompatability effects observed for mixed solutions of SA-2 or SA-6 with gelatin at 45°C; and the formation of biphasic gels when hot solutions of maltodextrin and gelatin were quenched to 5°C. The present paper describes the quantitative analysis of mixed-gel moduli in relation to those obtained for the constituent polymers in isolation.

After gelation, phase-separated networks may be regarded as biphasic polymer composites. The mechanical properties of such composites can be estimated by the isostrain and isostress 'blending laws' (see, for example, Takayanagi *et al.*, 1963; Manson & Sperling, 1976). According to this model, when the supporting phase is stronger than the discontinuous phase the strain is uniform throughout the material, i.e. both phases are deformed by the same amount (isostrain conditions). The shear modulus of the composite is then given by the simple additive formula:

$$G_C = \phi_X G_X + \phi_Y G_Y \tag{1}$$

where G_C is the shear modulus of the composite, G_X and G_Y are the moduli of the constituent phases (X and Y) and ϕ_X and ϕ_Y are their respective phase volumes (with $\phi_X + \phi_Y = 1$). The above equation indicates that the overall strength of the network is proportional to the

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phase-volume of the more rigid (continuous) phase. In the converse situation, where the dispersed 'filler' is stronger than the continuous matrix, increasing amounts of the weaker supporting phase will increase the degree of deformation produced by a given stress. As a result, the compliance ($J = 1/G$) is proportional to the phase-volume of the more deformable continuous phase:

$$J_C = \phi_X J_X + \phi_Y J_Y$$

i.e.

$$1/G_C = \phi_X/G_X + \phi_Y/G_Y \qquad (2)$$

Both phases are now subjected to the same stress (isostress conditions) but the extent of deformation is less for the stronger beads of the discontinuous phase.

The overall strength of the composite is obviously higher when the stronger component forms the continuous network. Thus eqn (1) refers to an upper limit (or bound) for the composite modulus whereas eqn (2) describes a lower limit appropriate to a weaker continuous phase. When the distribution of the two phases does not comply with either of the idealised extremes (isostrain or isostress conditions), the usefulness of the model lies in defining an area of modulus versus composition in which experimental results should be confined if the rigidity of the material is determined by simple phase separation.

In contrast to the polymer composites for which the blending laws were first developed, the phase volumes (ϕ_X and ϕ_Y) in aqueous binary gels are not determined solely by the amount of each polymer present, but depend also on their solvent-avidity or 'water-holding capacity'. The partition of solvent between the two phases may be characterised (Clark, 1987) by the ratio of solvent to polymer in one phase divided by the corresponding ratio in the other phase:

$$p = (w_X/x)/(w_Y/y) \qquad (3)$$

Therefore, in a system where the weights (x and y) of the two polymers and of the water ($w = w_X + w_Y$) are known, the 'p-factor' defines the phase volumes and hence the effective concentration of each polymer within its own phase.

The above analysis was first applied to composite aqueous gels by Clark *et al.* (1982, 1983). Experimental moduli were recorded for a series of mixed gels (usually holding the overall concentration of one component constant and varying the other) and trial values of p were used to generate calculated upper and lower bound curves until a convincing fit was obtained. In the present work a rather different procedure has been used (Morris, 1992), with explicit consideration of all possible distributions of solvent between the component phases for each mixed-gel sample.

2 EXPERIMENTAL DETERMINATION OF GEL MODULI

The materials used were identical to those in the preceding papers (Kasapis *et al.*, 1993*a*, *b*, *c*): potato maltodextrins Paselli SA-2 and SA-6 from Avebe and second-extract limed-ossein gelatin (LO-2) from Sanofi. Mixed systems were prepared by combining appropriate amounts of individual stock solutions held at 80°C. Samples were then quenched on the platen of a Bohlin VOR rheometer pre-set at a measuring temperature of 5°C. Small-deformation oscillatory measurements were performed using parallel-plate geometry (15 mm radius; 1 mm separation) at 1% strain and a frequency of 1 Hz. Values of rigidity modulus (G') for quantitative analysis were taken after 25 ks (about 7 h).

Experimental measurements at fixed gelatin concentrations and varying maltodextrin content were made on three different series of mixed gels: 2% LO-2 + SA-6; 5% LO-2 + SA-6 and 4% LO-2 + SA-2. The results are listed in Table 1. Corresponding values of G' measured under identical experimental conditions for a range of concentrations of the three individual polymers (SA-2, SA-6 and LO-2) are shown in Table 2.

Table 1. Variation of G' (Pa) with maltodextrin concentration (c; % w/w) in mixed gels with LO-2 set at 5°C for 25 ks (about 7 h)

2% LO-2 + SA-6		5% LO-2 + SA-6		4% LO-2 + SA-2	
c	log *G′*	*c*	log *G′*	*c*	log *G′*
0·0	2·72	0·0	3·63	0·0	3·45
2·5	2·65	2·5	3·61	2·0	3·43
5·0	2·81	5·0	3·57	4·0	3·50
7·5	2·62	7·5	3·44	6·0	3·56
10·0	2·58	10·0	3·41	8·0	3·59
12·5	2·68	12·5	3·47	10·0	3·78
15·0	3·05	15·0	3·40	12·0	3·97
17·5	3·09	17·5	3·81	14·0	4·11
20·0	3·35	20·0	4·02	16·0	4·20
22·5	3·67	22·5	4·34	20·0	4·23
25·0	3·78	25·0	4·41	22·0	4·34
27·5	4·06			24·0	4·40
30·0	4·40				

Table 2. Variation of G' (Pa) with concentration (c; % w/w) for gelatin and maltodextrin gels set at 5°C for 25 ks

LO-2		SA-6		SA-2	
c	log *G′*	*c*	log *G′*	*c*	log *G′*
1·0	1·20	10·0	0·39	12·0	1·93
2·0	2·72	12·5	0·70	14·0	2·89
4·0	3·45	17·5	2·18	18·0	3·81
5·0	3·63	20·0	2·80	22·0	4·24
10·0	4·06	25·0	3·45	26·0	4·39
15·0	4·48	30·0	4·25	30·0	4·45
20·0	4·60	35·0	4·63		
24·0	4·67	40·0	5·18		

3 SOLVENT-PARTITION IN BIPHASIC GELS

Figure 1 shows the results of a simple analysis (Morris, 1992) of the effect of solvent partition in a phase-separated mixed gel comprising two polymers, X and Y, which at their nominal concentrations across the whole system would have moduli M_X and M_Y, respectively. Upper and lower bound moduli (G_U and G_L) were calculated using the following assumptions.

1. The two polymers are confined entirely to their respective phases.
2. The modulus of both polymers is proportional to the square of concentration (as found experimentally for many gelling systems at concentrations well above the minimum critical gelling concentration c_o).
3. The volume of the polymer chains is negligible in comparison with the volume of the solvent.

As the fraction of solvent in the polymer-X phase (S_X) increases from 0 to 1, the calculated values of G_X decrease whereas those of G_Y increase. A point is reached where the solvent partition between the phases is such that the two curves cross (i.e. $G_X = G_Y$). At the same time the upper (X-continuous) bound descends from the top-left of the diagram (Fig. 1), with the lower (Y-continuous) bound rising from bottom-left, meeting at the same 'critical point'. Beyond this point the physical significance of the bounds swaps over, with the upper bound now corresponding to a Y-continuous system and the lower bound to X-continuous. If the identity of the continuous phase is known, from investigations such as those described in the preceding paper (Kasapis *et al.*, 1993*c*), it should then be possible to determine the precise value of S_X (and hence of *p*) required to give perfect agreement with the observed modulus for a specific binary gel.

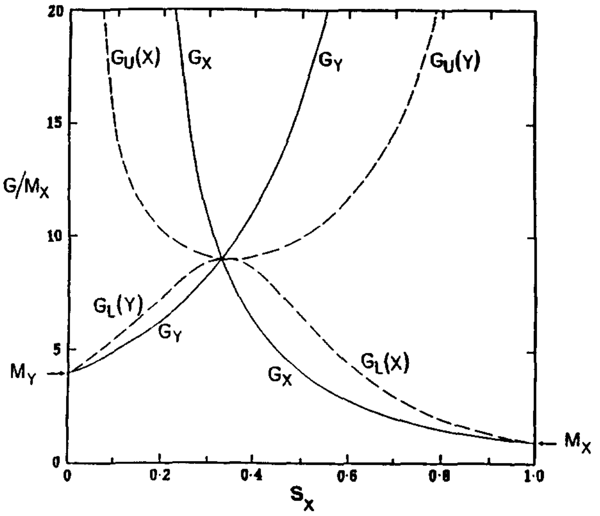

Fig. 1. Calculated effect of solvent-partition in biphasic gels, assuming complete de-mixing, c^2-dependence of moduli, and negligible contribution of polymer chains to phase-volume (Morris, 1992). G_X and G_Y are the moduli of the individual phases, varying with S_X, the fraction of solvent in the polymer-X phase, and converging at $S_X = 1$ and $S_X = 0$ to the moduli (M_X and M_Y) of X and Y at their nominal concentration across the whole system. G_U and G_L are upper and lower bound moduli for the composite gel from isostrain and isostress blending laws, with the continuous phase indicated in parentheses.

The calculated bounds shown in Fig. 1 depend solely on the starting values of M_X and M_Y, which in turn would be directly dependent on the total concentration of the two polymers. Because of the simplifying assumptions made in their derivation, however, the equations used by Morris (1992) to obtain G_U and G_L from M_X, M_Y and S_X cannot be applied directly to real systems. The first assumption, that each polymer is confined entirely to a single phase, presents the most serious problem, since at the moment there is no satisfactory way of determining the composition of individual phases in a biphasic gel. New techniques such as picolitre-scale sampling with subsequent analysis by capillary electrophoresis (Ewing *et al.*, 1989) may eventually allow direct experimental determination of phase composition. At present, however, there is no practical alternative to the working assumption that the errors introduced by ignoring 'cross-contamination' between the phases are not large enough to seriously compromise the analysis. The other approximations of an assumed c^2 dependence of modulus and neglect of the volume occupied by the polymer chains can, however, be readily eliminated by experiment, as described below.

4 POLYMER CONTRIBUTION TO PHASE VOLUME

In previous investigations of biopolymer mixed gels (e.g. Clark *et al.*, 1982, 1983) the polymer concentrations used have been sufficiently low that the approximation of equating phase-volume to the volume of water in each phase does not introduce a significant error (unless one of the phases becomes grossly more concentrated than the other). In some of the systems studied in the present work, however, the polymers constitute about a third of the total sample, so that their direct contribution to phase volume can no longer be ignored.

The total weight of water in the system (w) can, of course, be calculated by subtracting the combined weights of the two polymers from the total weight. For each value of S_X in the bounds calculations, the weight of water in phases X and Y is then simply:

$$w_X = S_X w \qquad \text{and} \qquad w_Y = (1 - S_X)\, w \tag{4}$$

The total weights of the phases are obtained by adding in the weight of the appropriate polymer:

$$W_X = x + w_X \qquad \text{and} \qquad W_Y = y + w_Y \tag{5}$$

with the effective concentrations (% w/w) of polymers X and Y in their respective phases being given by:

$$c_X = 100x/W_X \quad \text{and} \quad c_Y = 100y/W_Y \tag{6}$$

To a good first approximation the total weights of the two phases define the phase volumes (ϕ_X and ϕ_Y in eqns (1) and (2)). To obtain true phase volumes, however, the relative weights must be adjusted for density differences between the phases.

Since the correction is a minor one, the concentration-dependence of gel density for the three polymers (SA-2, SA-6 and LO-2) was calibrated by the rather crude (but rapid) procedure of filling a pre-weighed measuring cylinder with the appropriate solution, allowing the gel to form, reading off its volume, and determining its relative density from the ratio of the weight of the gel to the weight of the same volume of water. The results obtained for a few concentrations of each polymer are shown in Fig. 2. To within the precision of the measurements, the values for all three systems lie on a single straight line, yielding the following relationship between polymer concentration (c) and relative density (D) for each phase.

$$D_X = 1{\cdot}0 + Rc_X \quad \text{and} \quad D_Y = 1{\cdot}0 + Rc_Y \tag{7}$$

with the slope of the line in Fig. 2 giving a numerical value of $R = 0{\cdot}0034$. The volumes of the phases can then be calculated from their total weights and individual densities:

$$V_X = W_X/D_X \quad \text{and} \quad V_Y = W_Y/D_Y \tag{8}$$

Finally, the relative phase volume in the composite gel are given by:

$$\phi_X = V_X/(V_X + V_Y) \quad \text{and} \quad \phi_Y = V_Y/(V_X + V_Y) \tag{9}$$

5 MODULI OF CONSTITUENT PHASES

Having derived phase volumes (ϕ_X and ϕ_Y) for each value of S_X by the procedure detailed above (eqns (4)–(9)), the remaining parameters required in order to obtain calculated moduli for the binary gels (eqns (1) and (2)) are the moduli (G_X and G_Y) generated by the constituent polymers at the effective concentrations (c_X and c_Y) within their respective phases (eqn (6)). These can be obtained from direct measurement of the concentration-dependence of modulus for the individual gelling systems.

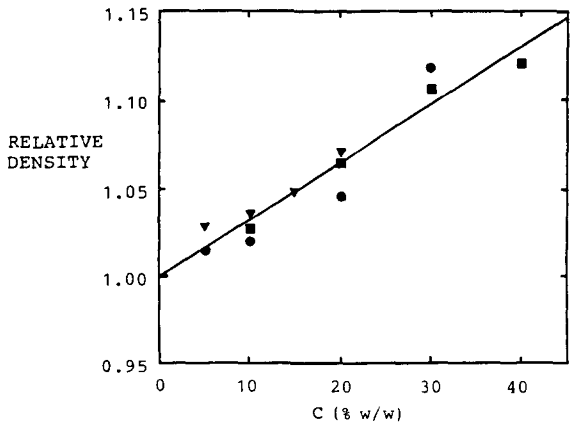

Fig. 2. Concentration-dependence of gel density for LO-2 (▼), SA-6 (■) and SA-2 (●).

Concentration-dependence of gel moduli

The first paper of this series (Kasapis *et al.*, 1993*a*) demonstrated that the variation of G' with concentration (Table 2) for SA-2 and LO-2 could be fitted, with good precision, to the general form anticipated from cascade theory (Clark, 1987). The concentration-dependence of modulus for SA-6 was quite different in form, giving a linear plot of log G' versus log c throughout the entire range of concentrations at which measurements could be made.

In the present work the slope and intercept of the linear plot for SA-6 and the parameters of the cascade fit (functionality, equilibrium constant and 'front factor') for SA-2 and LO-2 have been used to calculate the values of G' corresponding to the concentrations (c_X and c_Y) of polymer within the individual phases for each value of S_X.

Network de-swelling

The modulus-concentration relationships discussed above apply to systems in which the polymer concentration remains unchanged after gel formation. If, however, a network is formed at one concentration and is then taken to a different concentration by introduction or removal of solvent (swelling or de-swelling), the final modulus will be the same as that of a gel formed directly at the same concentration only if the crosslinks are sufficiently labile to re-adjust to a new equilibrium condition. If the crosslinks are effectively permanent, then the initial and final moduli (G_i and G_f) are related to the initial and final concentrations (c_i and c_f) by:

$$G_i/G_f = (c_i/c_f)^q \tag{10}$$

Classical network-swelling theory (Flory, 1953) yields a value of $q = 2/3$, giving a very much smaller difference in modulus than in gels formed directly at c_i and c_f.

The relevance of this behaviour to the analysis of mixed-gel moduli is that unless the system has already separated into discrete phases in the sol state, the first component to gel will do so at its original, nominal concentration across the whole system. Subsequent gelation of the second component within the pores of the existing gel will then create a separate (discontinuous) phase, making a portion of the solvent unavailable to the polymer in the originai (continuous) network. This removal of solvent can be regarded as 'de-swelling' of the continuous network, raising its modulus, but to a value substantially lower than it would have attained if phase-separation to the same phase volumes had occurred prior to gelation.

In several previous studies of mixed gel systems where the concentration of the faster-gelling species was held constant, with a systematic increase in the concentration of the second, slower-gelling component, the modulus of the resulting gels remained close to that of the faster-gelling polymer at its nominal concentration, or indeed fell below it, rising to higher values only after phase inversion to a continuous network of the second component at very high concentration (see for example McEvoy *et al.*, 1985; Clark, 1987). Application of the concept of network de-swelling to these systems gave reasonable agreement with experimental results. Qualitatively, the slight reductions in overall modulus induced by gelation of the second component as a discontinuous, included phase can be explained by the reduction in phase volume of the original network (from an initial value of 1 when it occupied the entire system) outweighing the associated slight increase in its modulus (and the modulus contribution of the discontinuous phase).

The results obtained in the present work, holding gelatin concentration constant and increasing maltodextrin concentration, show (Table 1) a similar pattern of initial slight decrease (or little change), presaging the need to consider network de-swelling in their interpretation.

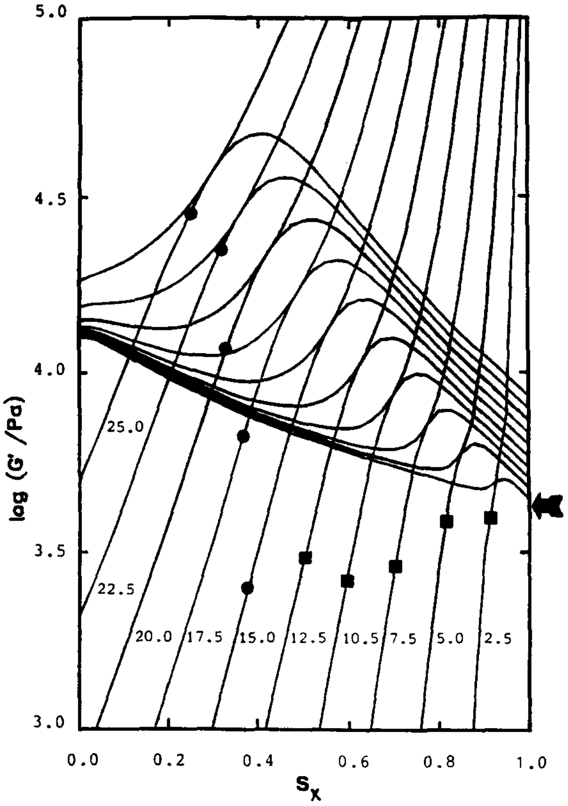

Fig. 3. Calculated bounds for mixed gels of 5% (w/w) LO-2 with the concentrations (% w/w) of SA-6 shown to the right of the individual traces. Experimental values are plotted on the maltodextrin-continuous bound for physically-realistic (●) and physically-unrealistic (■) situations. The experimental modulus for 5% LO-2 in isolation is shown by the arrow on the right-hand axis.

6 QUANTITATIVE ANALYSIS OF MIXED-GEL MODULI

In the following treatment of gelatin/maltodextrin gels, gelatin is regarded as polymer X throughout, so that the parameter S_X refers to the fraction of solvent in the gelatin phase. Curves analogous to those in Fig. 1, showing the variation of upper and lower bounds as a function of solvent partition, were calculated for each of the combinations of gelatin and maltodextrin concentration investigated experimentally (Table 1), using a PASCAL program to implement the algorithms developed above. Calculations were made either on the assumption that both components were restricted to their individual phases at the time of gelation, or on the assumption that one or other gelled first at its nominal concentration across the entire system, with subsequent de-swelling to its final phase volume.

Figure 3 shows the family of bounds obtained for 5% (w/w) LO-2 in combination with SA-6 (2·5 to 25·0% (w/w)), assuming that both polymers gel at their final concentration in their respective phases. Since the concentration-dependence of modulus for both components is rather different from the c^2 dependence used in the calculations by Morris (1992), the detailed form of the bounds is also different from that in Fig. 1, but the general pattern of the upper and lower bounds touching at a single critical point remains. The curves corresponding to a maltodextrin-continuous network (running from bottom-left to top-right of the diagram), however, pass through the critical point with little inflection, whereas those for gelatin-continuous systems show a very pronounced 'kink', in some cases passing through maximum and minimum values on either side of the critical point.

From the gel-time evidence presented in the preceding paper (Kasapis *et al.*, 1993*c*)), phase inversion from a gelatin-continuous to a maltodextrin-continuous network at this concentration of LO-2 occurs at an SA-6 concentration of about 15% (w/w). When the experimental moduli obtained for the composite gels at and beyond the point of phase inversion (15–25% (w/w) SA-6) are plotted (Fig. 3) on the calculated bound for a maltodextrin-continuous network, the points show a gratifyingly smooth progression to lower solvent fraction in the gelatin phase (i.e. lower S_X) with an increasing content of maltodextrin. At lower concentrations of SA-6 (2·5–12·5% (w/w)), where a continuous gelatin phase is anticipated, however, the experimental values all lie completely below the calculated bound for a gelatin-continuous network, again indicating the need to invoke initial gelation within a single phase, with subsequent de-swelling. For illustrative purposes, the experimental moduli for these systems are included in the diagram, plotted on the (physically-unrealistic) maltodextrin-continuous bound. Their departure from the previous smooth progression at higher concentrations of SA-6 is clear.

Similar behaviour was observed (Fig. 4) with SA-2 as the maltodextrin component, in combination with 4% (w/w) LO-2. Phase-inversion in this system occurs (Kasapis *et al.*, 1993*c*) at an SA-2 concentration of about 10% (w/w). The values of S_X giving exact agreement between observed and calculated moduli for the maltodextrin-continuous gels (10–24% (w/w) SA-2) again show a progressive decrease with increasing concentration of maltodextrin. At lower concentrations (2–8% (w/w) SA-2), where gelatin forms the continuous matrix, the experimental moduli either fall below the gelatin-continuous bound (at 2% SA-2) or agree with calculated moduli only at unrealistically high values of S_X (within the range 0·95–0·98, which would imply that virtually all the water is in the gelatin phase, leaving the maltodextrin essentially anhydrous).

To explore the validity of the concept of equilibrium control of solvent partition in these systems, the analysis was modified slightly to display the calculated bounds as a function of the 'solvent-avidity' parameter, p, rather than of solvent fraction, S_X. The modification is trivial since, from eqns (3) and (4), the two parameters are directly related by the total amounts (x and y) of each polymer present.

$$p = (S_X/x)/([1 - S_X]/y) \tag{11}$$

When the data already presented in Fig. 3 are re-plotted in this way (Fig. 5), it is obvious that the experimental results for the maltodextrin-continuous networks can be matched, with very acceptable precision, by a single value of $p \approx 1{\cdot}8$ ($\log p \approx 0{\cdot}26$). A similar standard of agreement, with the same value of p, was observed for maltodextrin-continuous networks of SA-6 when a lower concentration of LO-2 (2% (w/w)) was used.

Gratifyingly (and perhaps surprisingly), when the analysis is applied to the results obtained (Fig. 4) for co-gels of LO-2 (4% (w/w)) in combination with a different maltodextrin (SA-2), the same value of p again gives excellent agreement between observed and calculated moduli for maltodextrin-continuous networks

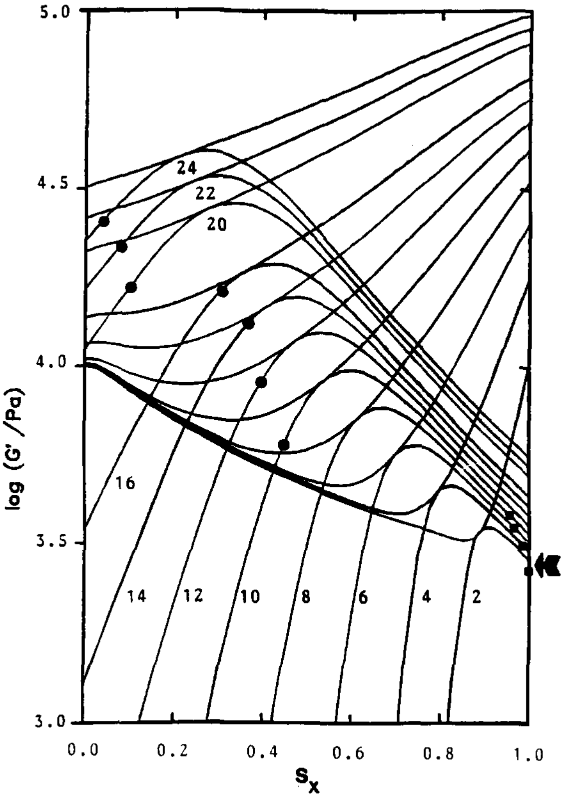

Fig. 4. Calculated bounds for mixed gels of 4% (w/w) LO-2 with the concentrations (% w/w) of SA-2 shown beside the individual traces. Experimental moduli for gelatin-continuous (■) and maltodextrin-continuous (●) networks are plotted on the appropriate bounds. The experimental modulus for 4% LO-2 in isolation is shown by the arrow on the right-hand axis.

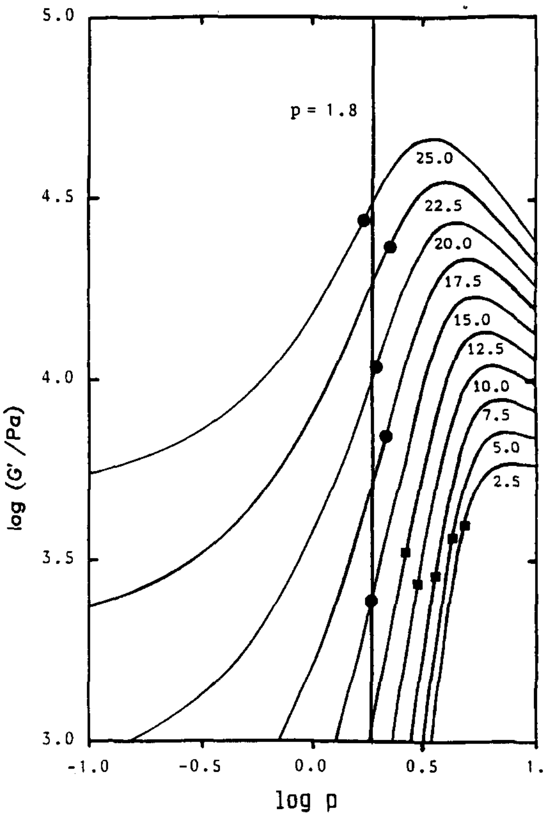

Fig. 5. Calculated lower bounds for 5% (w/w) LO-2 with SA-6 at the concentrations (% w/w) shown, plotted as a function of the solvent-avidity parameter, p. Symbols as in Fig. 3.

(Fig. 6). The agreement extends from the point of phase inversion at about 10% (w/w) SA-2 to a maltodextrin concentration of 16% (w/w), but at higher concentrations (20, 22 and 24% (w/w) SA-2) the experimental moduli fall below the calculated values. A possible explanation of this behaviour is that at very high concentrations, in the presence of an incompatible species (gelatin), the rate of SA-2 gelation (Kasapis *et al.*, 1993*a*) is faster than that of phase separation, so that the network forms at the original, nominal concentration, with again subsequent de-swelling on gelation of the gelatin component.

As the final stage of the analysis, the quantitative validity of this interpretation, and of the analogous interpretation of the low experimental moduli for gelatin-continuous networks, was assessed by deriving the expected moduli for initial gelation and subsequent de-swelling of either component. Since the (kinetically-controlled) sequence of gel formation should not affect the thermodynamics of the interaction between the two polymers, p was held constant at the value of 1·8 derived from analysis of the SA-6 continuous gels (and of the SA-2 continuous gels at intermediate concentrations of maltodextrin). The swelling factor, q, was held constant at the theoretical value for a permanent network (so that the only adjustable parameter of the fit is the solvent-avidity factor, p).

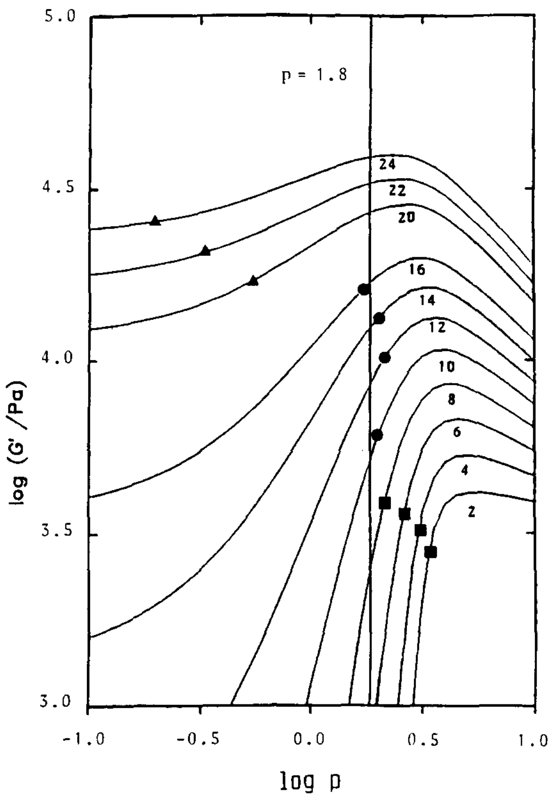

Fig. 6. Calculated lower bounds as a function of p, for 4% (w/w) LO-2 with SA-2 at the concentrations (% w/w) shown. The symbols show experimental moduli, plotted in physically meaningful positions for intermediate concentrations of SA-2 (●) and in analogous but physically unrealistic positions for higher (▲) and lower (■) concentrations.

The overall standard of agreement achieved between experimental and calculated moduli for the three series of mixed gels is shown in Figs 7–9. For SA-6 in the presence of 2% (w/w) LO-2 (Fig. 7) the fit is excellent, with little more than random experimental scatter of the observed values around the fitted curve. At 5% (w/w) LO-2 (Fig. 8) the overall agreement is again very acceptable, particularly at high concentrations of SA-6, although there is perhaps a slight systematic tendency to overestimation of moduli at intermediate concentrations. Finally, an almost perfect fit was obtained for SA-2 in the presence of 4% (w/w) LO-2 (Fig. 9), on the assumption of rapid formation and subsequent de-swelling of the maltodextrin network at very high concentrations of SA-2.

7 DISCUSSION

This study is the first practical application of the approach suggested by Morris (1992) for explicit analy-

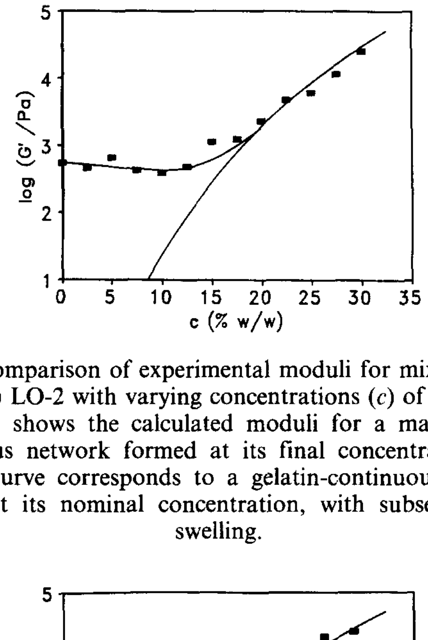

Fig. 7. Comparison of experimental moduli for mixed gels of 2% (w/w) LO-2 with varying concentrations (c) of SA-6. The steep line shows the calculated moduli for a maltodextrin-continuous network formed at its final concentration. The shallow curve corresponds to a gelatin-continuous network formed at its nominal concentration, with subsequent de-swelling.

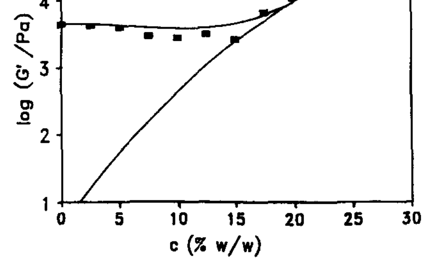

Fig. 8. Experimental and calculated moduli for 5% LO-2 with varying concentrations (c) of SA-6. The lines have the same significance as in Fig. 7.

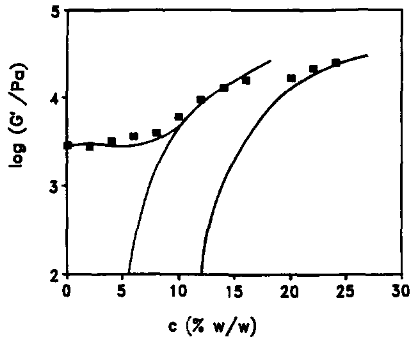

Fig. 9. Experimental and calculated moduli for 4% LO-2 with varying concentrations (c) of SA-2. The two lines at lower values of c have the same significance as in Figs 7 and 8. The line at high concentrations corresponds to maltodextrin-continuous networks formed at their nominal concentration, with subsequent de-swelling.

sis of water partition in phase-separated biopolymer gels. The central finding, that experimental results for a very wide range of compositions, and for two different maltodextrins, could be rationalised by a fixed value of a single parameter, p, was neither anticipated nor assumed, but emerged directly from the analysis.

The 'p-factor' was first introduced (Clark, 1987) as an entirely empirical way of describing the distribution of water between polymer phases. However, recent modelling of phase diagrams for gelatin-amylopectin-water (Durrani *et al.*, 1993), using the Flory-Huggins theory for ternary systems, has allowed p to be predicted in terms of gelatin–water, amylopectin–water and gelatin–amylopectin χ-values. A similar treatment (A.H. Clark, unpublished) of the SA-6/LO-2 phase diagram reported by Kasapis *et al.* (1993*b*) shows that, taking $\chi = 0{\cdot}46$ for gelatin and $\chi = 0{\cdot}55$ for starch, p would be expected to vary with polymer concentration within the range $p = 1{\cdot}3$ to $p = 2{\cdot}2$. Similar values are anticipated for gelatin in aqueous mixtures with other starch-based polymers, including SA-2.

The value of $p \approx 1{\cdot}8$ obtained from the present work lies almost exactly in the centre of the calculated range. The results, however, show no convincing indication of any systematic variation of p with polymer concentration (Figs 4 and 6). It is possible that this reflects some fundamental difference between phase-separated gels and the biphasic solutions analysed theoretically (such as the formation of a continuous network preventing the system reaching thermodynamic equilibrium), but it is more likely to come from experimental scatter and/or from the currently unavoidable, but physically unrealistic, assumption of complete de-mixing of the two polymers.

Direct determination of phase-composition is an obvious major target for future research on biopolymer co-gels. Another is to extend the approaches developed for small-deformation moduli into the more difficult area of predicting failure properties at large deformation. For the moment, the coincidence of drastic changes in composition-dependence of mixed-gel moduli (Figs 3 and 5) with evidence of phase-inversion from gel-time measurements, melting behaviour and microscopy (Kasapis *et al.*, 1993*c*), and the broad agreement between estimates of solvent-partition from solution χ-values and from analysis of gel moduli, are extremely encouraging.

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