Carbohydrate Polymers 17 (1992) 65–70

The effect of solvent partition on the mechanical properties of biphasic biopolymer gels: an approximate theoretical treatment

Edwin R. Morris

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

(Received 29 October 1990; accepted 9 November 1990)

The effect of solvent partition is considered for a biphasic mixed gel of two biopolymers (X and Y) which, at their nominal concentrations across the whole system, would have shear moduli of M_X and M_Y, with $M_Y = n^2M_X$. Using the simplifying assumptions that 1) each polymer is confined entirely to a single phase, 2) modulus is proportional to the square of polymer concentration and 3) the direct contribution of the polymer chains to phase volume (ϕ) is negligible, the moduli of the individual phases (G_X and G_Y) are calculated as a function of x, the proportion of solvent in phase X (with $\phi_X = x$ and $\phi_Y = 1 - x$). The isostrain and isostress blending laws for polymer composites are then used to calculate 'upper and lower bound' moduli (G_U and G_L), corresponding to a continuous network of, respectively, the stronger and weaker component, with the other phase dispersed within it:

$$G_U = G_X\phi_X + G_Y\phi_Y \qquad 1/G_L = \phi_X/G_X + \phi_Y/G_Y$$

The upper and lower bound curves (G_U versus x and G_L versus x) touch at a single 'critical point' where $G_X = G_Y = G_U = G_L = M_X(n + 1)^2$, with the two bounds passing through, respectively, minimum and maximum values. At the critical point, which occurs when $x = 1/(n + 1)$, the physical significance of the upper bound changes, with increasing x, from X continuous to Y continuous, with a corresponding change for the lower bound from Y continuous to X continuous. Practical application of this approach is suggested, with elimination of assumptions (2) and (3) by experimental measurements.

1 INTRODUCTION

In many applications, particularly in food systems, industrial polysaccharides are used in combination with other polymers, such as proteins. At low concentrations the two polymeric species may co-exist within a single aqueous phase, but at higher concentrations there is often spontaneous separation into two discrete phases, each containing the majority of one polymer and little of the other (see, for example, Tolstoguzov, 1986). In systems where both polymers can form a cross-linked network, the end result is a biphasic, composite gel (for a recent review of mixed polymer gels see Morris, 1990).

The mechanical properties of simple binary composites, such as filled rubbers and synthetic polymer blends, can be related to the corresponding properties of the individual components by 'blending laws' based on the relative proportions (phase volumes) of the two components and their spatial distribution (see, for example, Manson & Sperling, 1976). For example, if we consider a composite in which a weak material, X, is dispersed as discrete particles within a continuous matrix of a stronger material, Y, then the overall shear modulus (G) of the composite is related to the corresponding moduli of the component phases (G_X and G_Y) by

$$G = G_X\phi_X + G_Y\phi_v \qquad (1)$$

where ϕ_X and ϕ_Y denote the proportions of the total volume occupied by each component (with $\phi_X + \phi_Y = 1$). Similarly, if the weaker material forms the continuous

Carbohydrate Polymers 263-8223/92/$03.50

phase, with the stronger material dispersed through it, then the overall shear compliance ($J = 1/G$) can be obtained as the corresponding weighted-average of the individual compliances:

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

$$\text{i.e.}\quad 1/G = (\phi_X/G_X) + (\phi_Y/G_Y) \tag{2}$$

In the situation described by eqn (1), where the deformation of the weak 'filler' is dictated by the response of the surrounding stronger matrix, both components are deformed to the same extent (i.e. they are subjected to the same strain). In the converse situation, described by eqn (2), the strong filler is deformed less than the surrounding matrix, and the stress acting upon it is limited to the resistance of the matrix to the imposed deformation (i.e. both components experience the same stress). The two blending laws may therefore be denoted, respectively, as 'isostrain' and 'isostress' models.

Considerable progress has been made recently in applying the same approach to phase-separated biopolymer gels, notably by Dr A.H. Clark and his colleagues in Unilever Research (for a review see Clark, 1987), with eqns (1) and (2) being used to define, respectively, upper and lower bounds for the anticipated behaviour of biphasic gels. In contrast to the polymer composites discussed above, however, the phase volumes in such systems are not determined directly by the amount of each polymer present, but depend on the way in which the solvent is partitioned between the two phases.

To address this problem, Dr Clark has introduced a parameter, p, to characterise the relative solvent-avidity or 'water-holding capacity' of the two materials (effectively the ratio of solvent to polymer in one phase divided by the corresponding ratio in the other phase). This, however, is essentially an equilibrium treatment, and there is evidence from experimental studies of model systems that formation of one (or both) of the polymer networks may 'freeze' the system, and largely eliminate re-partition of solvent between the two phases (so that the final phase volumes may be under kinetic rather than equilibrium control). Thus, for example, in systems where, by appropriate changes in temperature, one component (X) may be induced to gel before the other (Clark *et al.*, 1982) the overall modulus may be close to that anticipated from the nominal concentration of X across the whole system, rather than the higher values predicted for the biphasic composite from eqn (1).

The purpose of the present study is to explore the effect of solvent partition on the mechanical properties of biphasic biopolymer gels, as calculated by the isostrain and isostress models, considering explicitly the entire range of phase volumes, $\phi_X = 0$ to 1.

2 DEFINITIONS AND ASSUMPTIONS

The starting point is to consider two gelling polymers X and Y at fixed concentrations, such that their shear moduli at these concentrations are M_X and M_Y respectively, with $M_X < M_Y$. The ratio of the two moduli, M_Y/M_X, is denoted as R and, for reasons that will become apparent later, it is convenient to define a further parameter, n, equal to the square-root of R. Thus

$$M_Y = RM_X = n^2M_X \tag{3}$$

We now consider a phase-separated system in which both polymers are present at the same nominal concentrations as in the individual systems discussed so far, and define x as the proportion of solvent in the phase where polymer X predominates. The shear moduli of the two phases are denoted by G_X and G_Y, and the values calculated for the resultant overall modulus of the composite by the isostrain (upper bound) and isostress (lower bound) analyses of eqns (1) and (2) are denoted by G_U and G_L, respectively.

To explore the way in which varying x alters the calculated values of G_X, G_Y, G_U and G_L, the following simplifying assumptions will be made.

(1) The two polymers are confined entirely to their respective phases; in real situations there will invariably be a low equilibrium concentration of each polymer in the phase where the other predominates (Tolstoguzov, 1986), but since the proportion is usually comparatively small the error introduced by this assumption is unlikely to be serious.

(2) The shear modulus for both polymers varies as the square of concentration; such behaviour is predicted theoretically for concentrations well above the minimum critical gelling concentration, c_o (Clark, 1987) and has been verified experimentally for many gelling systems, although much steeper concentration-dependences are predicted, and observed, at concentrations approaching c_o (for a recent review see Clark & Ross-Murphy, 1987). Thus, provided that the nominal concentrations defining M_X and M_Y are sufficiently high, this approximation should be reasonably valid.

(3) The volume of the polymer chains is negligible in comparison with the volume of the solvent. Thus the two phase volumes, ϕ_X and ϕ_Y, are both defined directly by the single variable x, with

$$\phi_X = x \qquad \text{and} \qquad \phi_Y = 1 - x \tag{4}$$

Except in extreme cases of unusually high concentrations of polymer in one or both of the phases, the error introduced by this assumption should again not be serious.

3 CALCULATION OF MODULI

The actual concentration of each polymer within the phase-separated system is higher than the overall nominal concentration by a factor of $1/\phi$, and so, on the assumption of a c^2 dependence, the modulus is raised by a factor of $1/\phi^2$. Thus

$$G_X = M_X/\phi_X^2 \quad \text{and} \quad G_Y = M_Y/\phi_Y^2 \tag{5}$$

It then follows directly from eqns (1) and (2) that:

$$G_U = M_X/\phi_X + M_Y/\phi_Y \tag{6}$$

$$\text{and} \quad 1/G_L = \phi_X^3/M_X + \phi_Y^3/M_Y \tag{7}$$

Setting M_Y to n^2M_X (eqn (3)) and ϕ_X and ϕ_Y to, respectively, x and $1 - x$ (eqn (4)) and rearranging terms then gives

$$G_U/M_X = 1/x + n^2/(1 - x) \tag{8}$$

$$\text{and} \quad G_L/M_X = n^2/[n^2x^3 + (1 - x)^3] \tag{9}$$

To simplify the presentation and discussion of results, the calculated moduli, G_U and G_L, are expressed as multiples of M_X (the modulus of the weaker component at its nominal concentration). The individual moduli of the two phases (eqn (5)) may be similarly scaled to M_X:

$$G_X/M_X = 1/x^2 \quad \text{and} \quad G_Y/M_X = n^2/(1 - x)^2 \tag{10}$$

As an illustrative example, the results obtained for a value of $n = 2$ ($M_Y = 4M_X$) are listed in Table 1 and presented in graphical form in Fig. 1. At low values of x the calculated values of G_X are very high, corresponding to extreme concentration of the polymer within a small phase volume, but with increasing x the calculated modulus decreases towards a final value of $G_X = M_X$ at $x = 1$ (since at this point, where all the solvent is in the X phase, the actual concentration of X is equal to its overall nominal concentration). Conversely, G_Y is very high at high values of x and decreases towards $G_Y = M_Y$ at $x = 0$ (where all the solvent is in the Y phase).

At one point in the continuum from $x = 0$ to $x = 1$ the two curves cross (i.e. $G_X = G_Y$), so that the rigidity of the phases is identical. The illustrative results plotted in Fig. 1 indicate that the isostrain and isostress curves both pass through this 'critical point', with G_U reaching a minimum value and G_L passing through a maximum. The purpose of the next section is to demonstrate analytically that this is indeed the case, and to define the values of x and G at the critical point (x_{crit} and G_{crit}, respectively).

Table 1. Variation of calculated moduli as a function of x, the fraction of solvent in phase X, illustrated for $n = 2$ ($M_Y = 4M_X$)

x	G_X/M_X	G_Y/M_X	G_U/M_X	G_L/M_X
0·00	∞	4·00	∞	4·00
0·05	400	4·43	24·2	4·66
0·10	100	4·94	14·4	5·46
0·15	44·4	5·54	11·4	6·38
0·20	25·0	6·25	10·0	7·35
0·25	16·0	7·11	9·33	8·26
0·30	11·1	8·16	9·05	8·87
0·35	8·16	9·47	9·01	8·97
0·40	6·25	11·1	9·17	8·47
0·45	4·94	13·2	9·48	7·53
0·50	4·00	16·0	10·0	6·40
0·55	3·31	19·8	10·7	5·29
0·60	2·78	25·0	11·7	4·31
0·65	2·37	32·7	13·0	3·51
0·70	2·04	44·4	14·7	2·86
0·75	1·78	64·0	17·3	2·35
0·80	1·56	100	21·2	1·94
0·85	1·38	178	27·8	1·62
0·90	1·23	400	41·1	1·37
0·95	1·11	1600	81·1	1·17
1·00	1·00	∞	∞	1·00

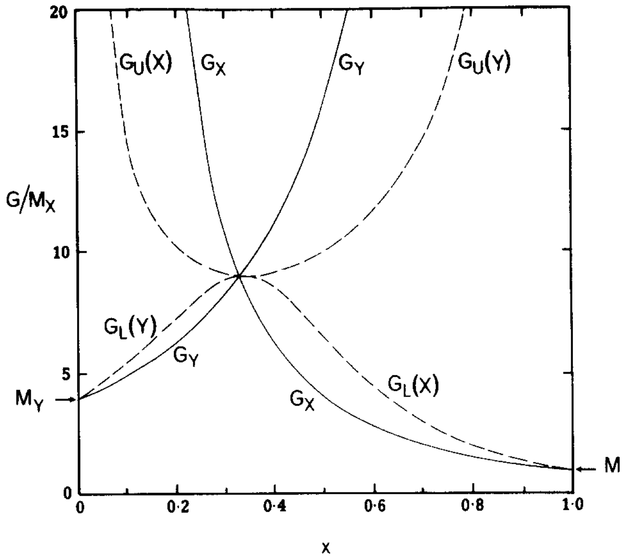

Fig. 1. Variation of calculated moduli as a function of x, the proportion of solvent in phase X, illustrated for $n = 2$ ($M_Y = 4M_X$). The solid lines show the moduli derived for the individual phases (G_X and G_Y). Broken lines show the values calculated for the resultant modulus of the composite gel by the isostrain and isostress blending laws (G_U and G_L, respectively). In both cases the continuous phase is indicated in brackets. All values are scaled to M_X, the modulus of polymer X alone at its nominal concentration across the whole system.

4 DETERMINATION OF 'CRITICAL POINT' PARAMETERS

Minimum value of G_u

Equation (8) defines the variation of G_U as a function of x for any specific fixed values of M_X and n. Expanding and collecting terms gives

$$G_U/M_X = [(n^2-1)x+1]/[x-x^2] \quad (11)$$

which is of the form

$$y = u(x)/v(x) \quad (12)$$

with $y = G_U/M_X$, $u = (n^2-1)x+1$ and $v = x-x^2$. The turning point of the curve (i.e. when $dy/dx = 0$) may, therefore, be defined by standard differentiation:

$$dy/dx = (v \cdot du/dx - u \cdot dv/dx)/v^2 = 0$$

i.e. $v \cdot du/dx = u \cdot dv/dx$ (13)

Thus $(x-x^2)(n^2-1) = (n^2x-x+1)(1-2x)$

Expanding and collecting terms gives

$$(n^2-1)x^2+2x-1 = 0 \quad (14)$$

Thus, by the standard solution for a quadratic equation

$$x = \{-2 \pm [4+4(n^2-1)]^{1/2}\}/\{2(n^2-1)\}$$

$$= (-1 \pm n)/(n^2-1)$$

Since, by definition, $n > 1$, only the positive value of the numerator is physically meaningful, giving

$$x = (n-1)/(n^2-1) = 1/(n+1) \quad (15)$$

Substituting $1/(n+1)$ for x in eqn (11) and simplifying gives

$$G_U/M_X = (n+1)^2 \quad (16)$$

Maximum value of G_L

Equation (9), which defines the variation of G_L with x, may be differentiated in the same way. Expanding the denominator and collecting terms gives

$$y = G_L/M_X = n^2/[(n^2-1)x^3+3x^2-3x+1]$$

$$-3x \quad = u/v$$

Since the numerator ($u = n^2$) is independent of x (i.e. $du/dx = 0$), eqn (13) in this case reduces to

$$u \cdot dv/dx = 0 = n^2[3(n^2-1)x^2+6x-3]$$

Dividing throughout by $3n^2$ gives

$$(n^2-1)x^2+2x-1 = 0$$

which is identical to eqn (14), again yielding $x = 1/(n+1)$ at the turning point of the curve. Substituting this value of x in eqn (9) and simplifying gives

$$G_L/M_X = (n+1)^2 \quad (17)$$

Intersection of G_X and G_Y

From eqn (10), $G_X = G_Y$ when

$$1/x^2 = n^2/(1-x)^2$$

i.e. when $(n^2-1)x^2+2x-1 = 0$

This is again identical to eqn (14), once more yielding $x = 1/(n+1)$ for the point of intersection of G_X versus x and G_Y versus x. Inserting this value in eqn (10) gives

$$G_X/M_X = G_Y/M_X = (n+1)^2 \quad (18)$$

Thus from all three analyses we have

$$x_{crit} = 1/(n+1) \quad (19)$$

and $G_{crit} = M_X(n+1)^2$ (20)

Some illustrative examples of the way in which these 'critical point' parameters vary with n (i.e. with the relative values of the moduli for the component polymers in isolation, at the same nominal concentrations as in the mixed system) are listed in Table 2. The critical point moves to progressively lower values of x as the disparity between M_X and M_Y increases. The case of $n = 2$ ($M_Y = 4M_X$) chosen for illustration (Fig. 1 and Table 1) yields a value of $G_{crit}/M_X = 9$, as shown in the figure. The maximum value of x_{crit} from this analysis is 0·5, corresponding to the limiting case of $M_Y = M_X$ ($n = 1$). Higher values would, of course, correspond to the converse situation of $M_Y < M_X$, with trivial inversion of nomenclature throughout.

5 DISCUSSION

With hindsight, it is perhaps intuitively obvious that under conditions of solvent-partition such that the moduli of the two component phases are identical, the isostrain and isostress blending laws should both yield this common value. It may be less obvious, however, that the common value should correspond to a minimum in isostrain ('upper bound') and a maximum in isostress ('lower bound') behaviour. Indeed the physical significance of the two bounds changes at the 'critical point'.

At values of $x < x_{crit}$, where $G_X > G_Y$ (Fig. 1), the upper bound (G_U) corresponds to a continuous

Table 2. Dependence of 'critical point' parameters on the relative moduli of the individual polymers at their overall nominal concentration

M_Y/M_X	n	x_{crit}	G_{crit}/M_X
100	10	0·091	121
49	7	0·125	64
25	5	0·167	36
16	4	0·200	25
9	3	0·250	16
4	2	0·333	9
1	1	0·500	4

network of polymer X with discrete 'gel islands' of phase Y dispersed within it. (Since $\phi_X < \phi_Y$ over this range of x values, however, a more realistic analogy might be with air cells in a meringue). Similarly, the lower-bound behaviour (G_L) would correspond to a continuous network of the predominant weaker phase (Y), with hard inclusions of the stronger, minor phase (analogous to frog-spawn!).

Above x_{crit}, however, where $G_Y > G_X$, the significance of the two blending laws swaps over, with the upper bound now corresponding to Y-continuous and the lower bound to X-continuous. Thus, if we could engineer conditions such that X remained the continuous phase throughout, the calculated modulus for the composite with increasing values of x would first descend along the upper bound, flatten out through x_{crit}, and then continue to decrease along the lower bound, reaching a final value of M_X at $x = 1$. Similarly, with Y continuous throughout, the modulus would start from a value of M_Y at $x = 0$, first ascend the lower bound, again flatten out around x_{crit}, and then increase steeply along the upper bound for higher values of x (due to increasing rigidity of the Y phase as a higher proportion of the solvent becomes associated with polymer X).

To illustrate the way in which this approach might be used experimentally, let us consider the mixed system analysed in Fig. 1 (with $M_Y = 4M_X$), and suppose that the observed modulus for the composite gel is $10M_X$. This value lies above the maximum of the lower bound curve, but corresponds to two points on the upper bound, one at $x = 0{\cdot}2$ with X as the continuous phase and the other at $x = 0{\cdot}5$, with Y continuous. Similarly, an observed modulus of $6M_X$ would lie below the minimum of the upper bound, but correspond to values of $x \approx 0{\cdot}13$ (Y-continuous) and $x \approx 0{\cdot}52$ (X-continuous) on the lower bound. In either case it might well be possible to determine experimentally which of the two possible interpretations reflects the actual state of dispersion of the component phases. For some systems the continuous phase may be identified by microscopy. In others, one of the constituent networks may be melted out at a lower temperature than the other; if this component forms the continuous phase the composite should collapse; if it forms the discontinuous phase the composite should become weaker but remain intact.

It should be emphasised however that, because of the approximations outlined in Section 3, the detailed quantitative treatment presented here is not intended for direct practical use, but simply to illustrate the general form of behaviour anticipated. Elimination of at least some of these approximations for specific mixed systems should, however, be comparatively straightforward, particularly if the analysis is implemented by computer.

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 the individual phases in a biphasic gel. In favourable cases, where phase separation occurs in the solution state prior to gelation (e.g. at high temperature for materials that gel on cooling), the individual phases may be separated by centrifugation and analysed by any appropriate, convenient method. The conformational changes leading to gel formation, however, are almost certain to alter the thermodynamic incompatability of the two polymers, and so change the way in which they, and the solvent, are partitioned between the phases. New techniques such as laser-Raman microscopy and scanning tunnelling microscopy (STM) may eventually allow direct experimental determination of phase composition. For the moment, however, there is no satisfactory 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.

In practical applications of the proposed approach, however, the other approximations introduced to simplify the present theoretical treatment can both be avoided. First, rather than assuming a c^2 dependence of G, the preferable procedure for real systems would be to determine the modulus for each component in isolation at several concentrations spanning a wide range, starting from the lowest nominal concentration to be used in the mixed systems and continuing to the highest concentration that is experimentally feasible. The modulus corresponding to the calculated concentration within the biphasic gel at each value of x could then be obtained by interpolation within the experimental range and, where necessary, by extrapolation to higher concentrations (where the assumption of a c^2 dependence is likely to be reasonably valid). Alternatively, and preferably, the experimental values could be fitted to the general form of concentration-dependence obtained from cascade theory (Clark, 1987) and the parameters of the fit used to obtain G at any concentration.

The direct contribution of the polymer chains to overall phase volume can also be determined experimentally for real systems. Calculation of the weight-fraction of each phase is clearly trivial (the weight of the polymer plus the weight of water, as determined by the relevant value of x, divided by the total weight of the system). Conversion to volume-fractions (ϕ) would then simply require density measurements for a few concentrations of each polymer.

In summary, the method outlined offers a systematic approach to interpretation of the overall mechanical properties of composite biopolymer gels in terms of the relative volumes of the constituent phases and their state of distribution. On the implicit assumption of rigorous applicability of the 'isostrain' and 'isostress' blending laws (eqns (1) and (2)), two discrete interpretations may be obtained for each mixed gel (one corresponding to X-continuous and the other to Y-continuous). Variation of the nominal concentrations of the two polymers (i.e. varying M_X and M_Y) would then yield a data set of calculated values for the moduli, volume fractions and state of dispersion of the individual phases, for critical evaluation.

An obvious first criterion would be internal consistency — do the calculated values vary in a systematic way with changes in polymer concentration? Another obvious consideration would be the likely physical reality of the calculated values; for example, an analysis yielding a continuous phase at very low phase volume might be viewed with suspicion. Wherever possible the results should, of course, also be compared with other experimental evidence, for example by comparison of calculated phase volumes and predicted continuity/discontinuity with indications from microscopy. The success or failure of such evaluations should give an indication of the usefulness, or otherwise, of the proposed approach and, more generally, provide a further test of the applicability of polymer blending laws to phase-separated biopolymer gels.

ACKNOWLEDGEMENT

The author is extremely grateful to Dr A.H. Clark for many constructive discussions, and for critical evaluation of this paper prior to submission.

REFERENCES

Clark, A.H. (1987). The application of network theory to food systems. In *Food Structure and Behaviour*, ed. J.M.V. Blanshard & P. Lillford. Academic Press, London, pp. 13-34.

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

Clark, A.H., Richardson, R.K., Robinson, G., Ross-Murphy, S.B. & Weaver, A.C. (1982). *Prog. Food Nutr. Sci.*, **6**, 149-60.

Manson, J.A. & Sperling, L.H. (1976). *Polymer Blends and Composites*. Heyden Press, London.

Morris, E.R. (1990). Mixed polymer gels. In *Food Gels*, ed. P. Harris. Elsevier, London, pp. 291-359.

Tolstoguzov, V.B. (1986). Functional properties of protein-polysaccharide mixtures. In *Functional Properties of Food Macromolecules*, ed. J.R. Mitchell & D.A. Ledward. Elsevier, London, pp. 385-415.