Large deformation and ultimate properties of biopolymer gels: 2. Mixed gel systems

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Biphasic, mixed gels of agarose and gelatin were prepared, and their mechanical behaviour in tensile tests was determined, up to failure, utilising four decades of (constant) strain rate. The behaviour of pure agarose and pure gelatin in such tests has been determined previously. Suitable 'blending-laws' relating the small deformation shear modulus of the composite to the moduli of the component phases have also been discussed elsewhere. This report extends the latter treatment to the more aggressive large deformation regime, deriving bounds for modulus and break stress which closely model observed behaviour.

(Keywords: gelatin; agarose; composite; biopolymer gel; tensile testing; failure envelope; ultimate properties; stress function; network; isostress; isostrain; matrix; filled systems)

INTRODUCTION

The mechanical properties of both agar and gelatin gels have been examined in considerable detail by ourselves and other workers[1]. Some aspects of this behaviour seem to be exhibited by gelling systems in general, and are attributable to the properties of a macromolecular network, rather than specific to the polymer of which it is composed. However, this work is concerned with how the material parameters of a composite system can be derived from those of the component phases. For the present purpose, it is sufficient to describe the mechanical response of the pure gels in a purely phenomenological fashion.

A mixed agar–gelatin gel displays a phase-separated microstructure, e.g. as roughly spherical inclusions of gelatin embedded in an agar matrix, or *vice versa*[1]. (In this sense, a 'phase' is to be considered as the gel component, consisting of biopolymer plus water. As will be seen, the manner in which the two polymers partition the available solvent is of particular relevance.) The various theoretical models which have been developed for this type of 'matrix-filler' combination have focussed mainly on small deformation, linear elastic behaviour[2–6]. Experimental work has largely been concerned with systems in which the moduli of the components differ by several orders of magnitude, e.g. fibre-reinforced resins or graphite-loaded rubbers. In the systems under discussion, the moduli of the two gel phases are of comparable magnitude. In addition, the failure properties depend rather markedly on the strain rate applied. Consequently, a novel theoretical framework has been developed, based on the original Takayanagi isostress and isostrain models[7,8], which bounds rather than defines the expected properties of the composite. Elements of the Takayanagi theory are fairly readily extended to the large deformation regime, details of the derivation being given in the Appendix. The picture which emerges is of a composite material whose properties are predominantly those of the supporting matrix, modified in a consistent manner by the presence of filler.

Optical and electron micrographs of the mixed gels bear a striking resemblance to those obtained for certain synthetic interpenetrating networks[9,10]. More importantly, a number of systems of practical importance, whose failure properties are of interest, might be regarded as gels containing a soft filler. Examples include latex systems, and the soil mechanics of some clay structures. There are also implications with respect to biological systems, proteins and polysaccharides being the major structural polymers in nature.

It is interesting to speculate on the possible extension of the range of experimental techniques, which must await the development of a more refined blending law. Easily broken materials might be rendered more tractable to experiment by the inclusion of a suitable filler of known properties. It is also worth noting that the partition of solvent by the two polymers can produce component gels of somewhat higher concentrations than can easily be achieved in isolation in the laboratory.

In what follows, the nominal stress (force per unit original cross-sectional area), strain and extension ratio are denoted by the symbols σ, ε and λ, respectively.

PROPERTIES OF SINGLE COMPONENT BIOPOLYMER GELS

The detailed behaviour of aqueous gels of agar or gelatin has been extensively discussed previously, and will be reviewed here only briefly (see previous paper).

The Young's modulus (or pseudo-equilibrium Young's modulus), E, is taken to be three times the shear modulus, G (i.e. deformation is assumed to occur at constant volume) and depends on concentration. The form of this dependence is of considerable interest in its own right, but for present purposes it suffices to state that when the polymer concentration is known, the modulus can be adequately determined (see e.g. ref. 11).

The response of stress to strain is non-linear, but does not greatly depend on strain rate over the range of conditions accessed. This profile could be fitted well by the phenomenological equation of Blatz, Sharda and Tschoegl (BST equation[12]), vis.

$$\sigma=\frac{2E}{3n}(\lambda^{n-1}-\lambda^{-(n+2)/2}) \qquad (1)$$

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The parameter n may be regarded as an empirical measure of deviations from 'ideal' behaviour ($n=2$ returns the well-known equation of rubber elasticity). Experiment has shown that n does not depend on agar or gelatin concentration, but takes different values for the two polymers ($n \simeq 3$ for gelatin, 4.2 for agar)—for details see ref. 13.

It is of relevance to understand how the properties of a gel are altered when solvent (water) is removed. This can be achieved experimentally by an air-drying technique, and it is found that a reduction in volume and increase in modulus occurs. Denoting initial and final states by i and f, an adequate empirical description is given by

$$\frac{G_i}{G_f}=\left(\frac{c_i}{c_f}\right)^q \tag{2}$$

Classical Flory–Rehner type swelling theory would give $q=2/3$ (e.g. ref. 14), but if completely labile crosslinks are assumed, G_f is given by the modulus–concentration relationships referred to above. The experimental value for gelatin ($q \approx 5/3$) lies somewhere between these two cases, although no corresponding data are available for agar. Removal of water did not change the shape of the stress response for gelatin (i.e. the BST exponent, n, was not altered).

While equation (1) is an adequate description of the stress profile, how far along this curve we can proceed before failure occurs depends on the strain rate employed. Plots of break stress against strain rate ($\log \sigma_B$ against $\dot{\varepsilon}$) display a shallow minimum, the break stress falling with decreasing strain rate, but rising again at the slowest rates. The characterization of this behaviour is detailed in a later section, but the salient trends are that the gelatin gels of different concentrations give parallel curves, the minimum occurring at the same strain rate, but the height of the minimum being a linear function of modulus.

Agarose gels display similar behaviour, but generally fail more readily than gelatin gels of comparable modulus (in particular, the minimum break stress is considerably smaller). Also, the minimum occurs at a lower strain rate.

EXPERIMENTAL

Preparation of samples

The gelatin was supplied by Croda as Croda boned (250 Bloom strength) gelatin (acid form). Concentration was in the range 5–25% by weight. For pure gelatin gels, samples were prepared by dispersing the gelatin into cold water and heating to 65°C until dissolved. Water lost by evaporation was replaced and the solution transferred to screw-top bottles, which were placed in water at approximately 60°C to allow deaeration to occur.

The agar was supplied by Lysander Foods, and was used at concentrations of 1% and 2% w/w. For the agar gels, the required amount of agar was dispersed in water and autoclaved to dissolve the agar. Mixed co-gels of agar and gelatin were prepared by cooling the above solution to 45°C and then dissolving the gelatin in the agar solution as above. In all cases, solutions were poured into a mould consisting of two polished glass plates separated by precision spacers, 1 cm for ring samples (see below).

Tensile specimen geometry

In previous work on filled gelatin gels[2], notched dumbbell specimens were used. For weaker gels, this geometry presents experimental problems.

Other specimen geometries have been studied by a number of groups; in particular Myers and Wenrick[15] have carried out a careful evaluation of dumbbell, ring and (hollow) oval specimens. In the latter cases, the specimen is hung over two polished dowel pins, one mounted on the transducer stage, and the other on the driven stage of the tensile testing instrument. At the maximum stresses reported here ($\approx 10^5$ Pa), the agreement between their results for ring and oval samples is excellent, and in succeeding sections, work on ring shaped specimens will be reported.

The rings themselves were cut from the cast gel sheet with two concentric cylinder knife edge cutters, to give a specimen with outer diameter 48.5 mm and inner diameter 37.0 mm (ratio $OD/ID=1.31$), using the knife edged dies and a hand press; the dowels were of stainless steel and were of diameter 12.5 mm. The Instron was a Model 1122 Universal Tester, the extension rates were 1–1000 mm/min and measurements were taken at room temperature, 22±0.5°C, in a temperature controlled room.

TREATMENT OF DATA

The tensile force in each leg of the ring is half the measured force, stress being obtained by division by the cross-sectional area. Strain was calculated on the basis that an increase in pin separation, x, results in an increase of total circumference of $2x$, the original circumference being calculated from the mean ring diameter. There is always a small 'tail' in the force–displacement curve while the ring straightens into a state of true simple tension. Data in this region were obtained from a backward extrapolation of the linear portion of the profile, which can usefully be accentuated by logarithmic plotting.

RESULTS AND DISCUSSION

When a body of composite material is deformed, any description of its mechanical response will require some assumptions to be made regarding the distribution of stress and strain by the component phases. Previous work on agar–gelatin systems[1] placed bounds on the modulus of the composite according to the isostress and isostrain limits of Takayanagi[8,9]. This approach is fairly readily extended to larger deformations. Details of the derivation are discussed fully in the Appendix, but for the moment attention is restricted to those predictions most easily comparable with experiment.

Modulus and shift parameter

In the limit of Hookean behaviour, the modulus bounds are given by

$$E_c=\phi_x E_x+\phi_y E_y \quad \text{(isostrain)} \tag{3}$$

and

$$\frac{1}{E_c}=\frac{\phi_x}{E_x}+\frac{\phi_y}{E_y} \quad \text{(isostress)} \tag{4}$$

where the ϕ_i are the volume fractions of components x and y, and the subscript c refers to the composite as a whole.

The generalization to large deformations, in terms of the BST function appropriate to each phase, predicts a series of parallel ($\log\sigma$ against $\log\varepsilon$) curves (cf. Appendix). These are linear up to 65% strain, with a slope of unity in the linear region. Two gels of different composition give stress curves which are superposable by a 'shift' through a distance $\log b$, where the parameter b is the ratio of the moduli of the two composites. Since the limiting slope is unity, this shift can be parallel to either axis, but shifts parallel to the abcissa were employed for compatibility with earlier work on glass-filled gelatin gels[2].

Two series of composite gels were tested, containing agarose at levels of 1% or 2% w/w and varying amounts of gelatin. If, for each series, the pure agar is chosen as reference state of modulus E_0, say, then it is convenient to express the composite modulus of the other systems in the series by the ratio E_c/E_0, and denote shift parameters relative to this state. In this way, the Young's modulus, shear modulus and shift parameter can conveniently be displayed as a single curve, and for a given composition, the three values should coincide.

Estimation of E *and* b

The modulus was calculated from the initial slope of the stress–strain curve, or from a non-linear least squares fit to equation (1). In most cases, agreement was better than ±5%.

For a given composition, the stress–strain profiles for a number of test replicates define a narrow envelope of curves. This is attributable to experimental scatter, no trend is observed with changing strain rate, and all replicates are considered to define the same curve. However, how far we can proceed along this curve before failure does depend on strain rate. The locus of failure values thus defines a segment of the stress–strain profiles known as the failure envelope[16] and is usually plotted as $\log \phi_B$ against $\log \varepsilon_B$. It was from the relative positions of the failure envelopes that the shift parameter, b, was obtained.

Partition of solvent

Calculation of the modulus bounds according to equations (6) and (7) requires a knowledge of the moduli of phases x and y, which in turn requires a knowledge of the polymer concentration in each of the two phases. Essentially, it is necessary to relate the nominal concentrations C_x^{nom}, C_y^{nom} (the weight per cents of agar and gelatin in solution prior to gelation), to the effective concentrations C_x^{eff}, C_y^{eff} in the resulting composite gel. Clark *et al.*[1] define a parameter p, a measure of the relative affinity of the two networks for solvent (water), and derive suitable expressions for the effective concentrations and volume fractions of the two phases.

Naively, it is possible to proceed by calculating the modulus of each phase based on its nominal polymer concentration. However, when solutions of agar and gelatin are cooled, the agarose gel sets at a higher temperature than gelatin. Thus, representing agar as phase y, it is expected that a gel forms at the nominal concentration C_y^{nom}, of modulus G_y^{nom}, say, which is then increased to C_{eff} (effective) by partition of water as the gelatin gels. We then generalize equation (2) to give

$$\frac{G_y^{\mathrm{nom}}}{G_y} = \left(\frac{C_y^{\mathrm{nom}}}{C_y^{\mathrm{eff}}}\right)^q \tag{5}$$

Predictions based on this treatment, for a value of $p=1$ and several values of q, are shown in *Figures 1* and *2* along with experimental moduli and shift parameters. The lower bound is relatively insensitive to the exact value of q, and is only shown once, for clarity. Appropriate choice of this parameter gives an upper bound which reproduced the minimum in the data, also reported by other workers[17,18]. The previous plot by Clark *et al.* corresponds to $q=0$.

Since the gels are phase-separated, partition of solvent must occur, but the assumption that p is independent of concentration is open to question. Clark *et al.* examined the sensitivity of the model to the value of p, and it is evident that any reasonable concentration dependence would not grossly affect their conclusions. Thermodynamically, p should be derivable from the Flory–Huggins interaction parameter χ[14]. Since data on 'deswollen' (air-dried) gelatin gels indicates some redistribution of crosslinks, q must be regarded as an additional

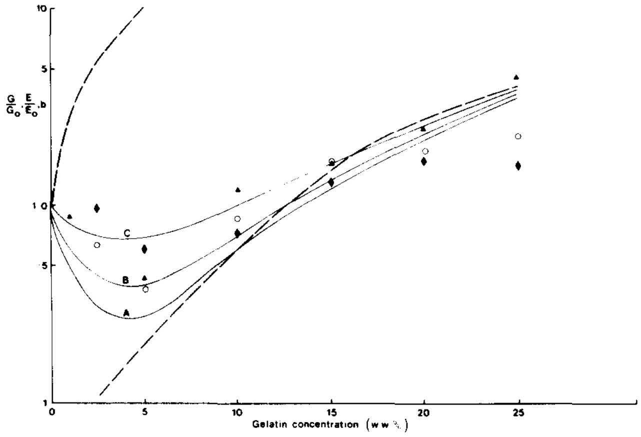

Figure 1 Shear modulus (▲), Young's modulus (○) and shift factor (◆) for the 1% agar gel series. Moduli are relative to the value for pure agar. Solid curves give the isostrain predictions for $p=1$ and $q=$ (A) 0, (B) 0.33 and (C) 0.67. Heavy curves give the isostrain (upper) and isostress (lower) predictions for a system with fully labile crosslinks

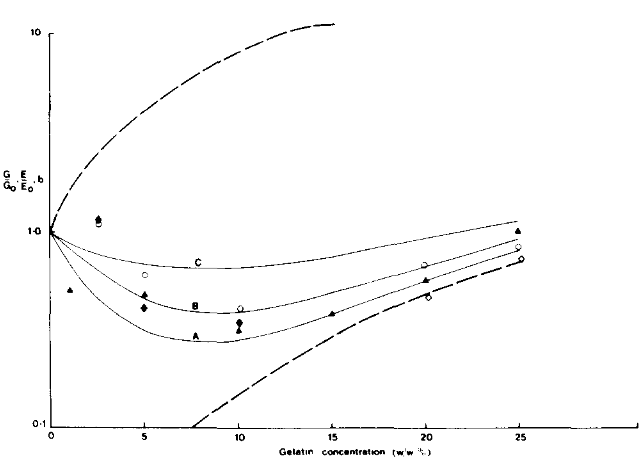

Figure 2 Shear modulus (▲), Young's modulus (○) and shift factor (◆) for the 2% agar gel series. Moduli are relative to the value for pure agar. Solid curves give the isostrain predictions for $p=1$ and $q=$ (A) 0, (B) 0.33 and (C) 0.67. Heavy curves give the isostrain (upper) and isostress (lower predictions for a system with fully labile crosslinks

parameter. An exact determination of either p or q would require additional experimentation, but the use of such parameters is not only reasonable, but necessary.

Ultimate properties

The theory was extended to encompass the expected behaviour of the break stress of the composite as a function of strain rate. This derivation is fully discussed in the Appendix, and is based on the assumption that failure of the composite occurs when the stress in the matrix phase is high enough to cause it to fail.

As composites are formed of increasing gelatin concentration, a phase-inversion takes place, a transition occurring from gelatin inclusions in an agar matrix to the inverse situation. The gelatin content at which this inversion occurs was estimated from the microscopy experiments reported by Clark *et al.* (2.5% for the 1% agar series, between 5 and 6% for the 2% series). Now, isostrain behaviour is expected when the higher modulus (agar) phase is the supporting phase, and isostress behaviour for the lower modulus gelatin matrix[8,9]. This transition is not evident from modulus data alone, since the predicted bounds tend to converge at higher gelatin content.

Break stress against strain rate curves for the 2% series are shown in *Figure 3* along with the curve for a 25% gelatin gel. The 'agar-like' to 'gelatin-like' transition is evident from the curve shapes.

The quantitative predictions of the model are most clearly demonstrated by calculating limits for the coordinates of the minima of these curves, $\dot{\varepsilon}_{\mathrm{min}}$, $\sigma_{\mathrm{B,min}}$. As mentioned above, and developed fully in the Appendix, the calculation of these limits assumes that failure occurs in the matrix phase. Consequently the details of the calculation depend on which component (agar or gelatin) constitutes the supporting phase. As the phase inversion is passed, a transition from isostrain to isostress behaviour is expected. Although no attempt has been made to model the details of the transition, the gross predictions of the model on either side of the (assumed) phase-inversion point (see above) have been presented in *Figures 4* and *5* for the 2% series, along with the experimental values. Similar results are obtained for the 1% series, except for an anomaly in the case of the $2\frac{1}{2}\%$ gelatin concentration, which is close to the phase inversion point. The values of the modulus for this gel put it closer to the isostrain ('agar-like') limit, but the failure properties would suggest isostress ('gelatin-like') behaviour.

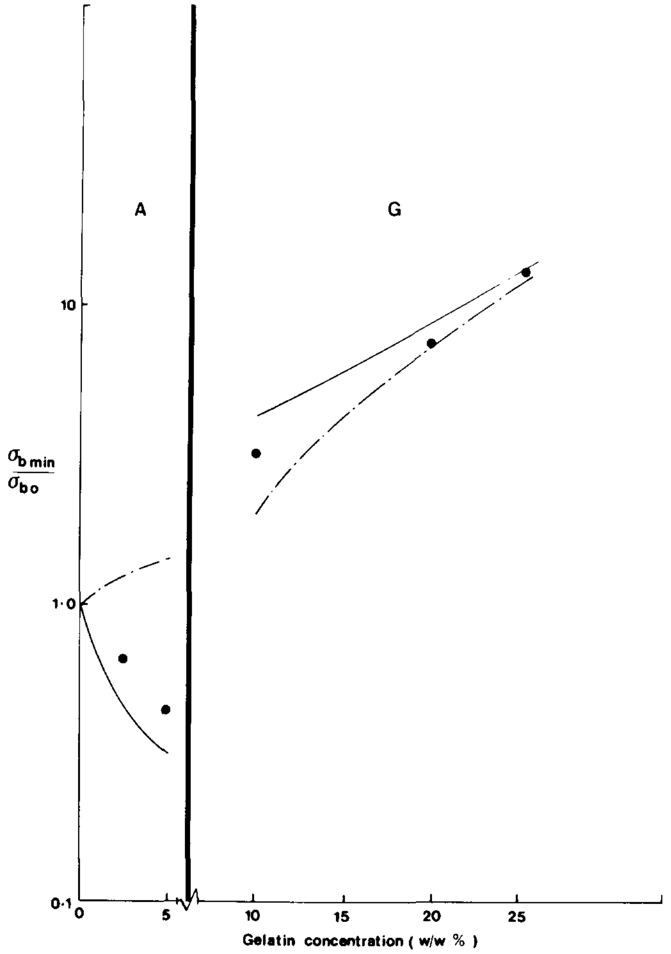

Figure 4 Isostrain (solid) and isostress (broken) predictions for the minimum break stress (relative to pure agar) for the 2% gel series (based on $p=1, q=0.33$). Solid circles denote experimental values. A, G, refer to agar and gelatin respectively as supporting phase.

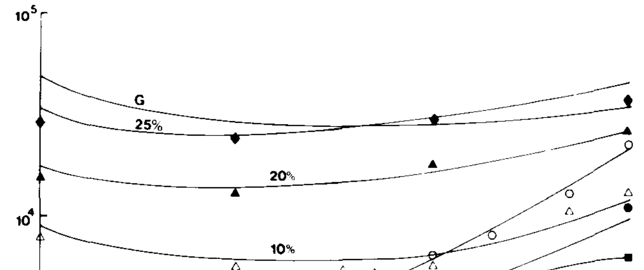

Figure 3 Break stress against strain rate for the 2% agar gel series. Numbers refer to gelatin concentration. Curve A is agar alone, and curve G that for 25% w/w gelatin alone

Of course, since failure is initiated by stress concentration at some microscopic defect (e.g. ref. 16), the inherent heterogeneity of these systems gives rise to considerable scatter in the data. Thus, some caution must be exercised when the analysis described above is carried out (see next section).

Statistical significance of failure data

The dependence of break stress on strain rate has been rationalized on theoretical grounds, but for the purposes of this report, a simple quadratic fitting procedure has been used, which makes predictive modelling simpler and renders statistical analysis more tractable.

Hayes[19] reports a numerical technique which fits the data set to polynomials of successively higher degree, applying a statistical test at each stage to ensure that any

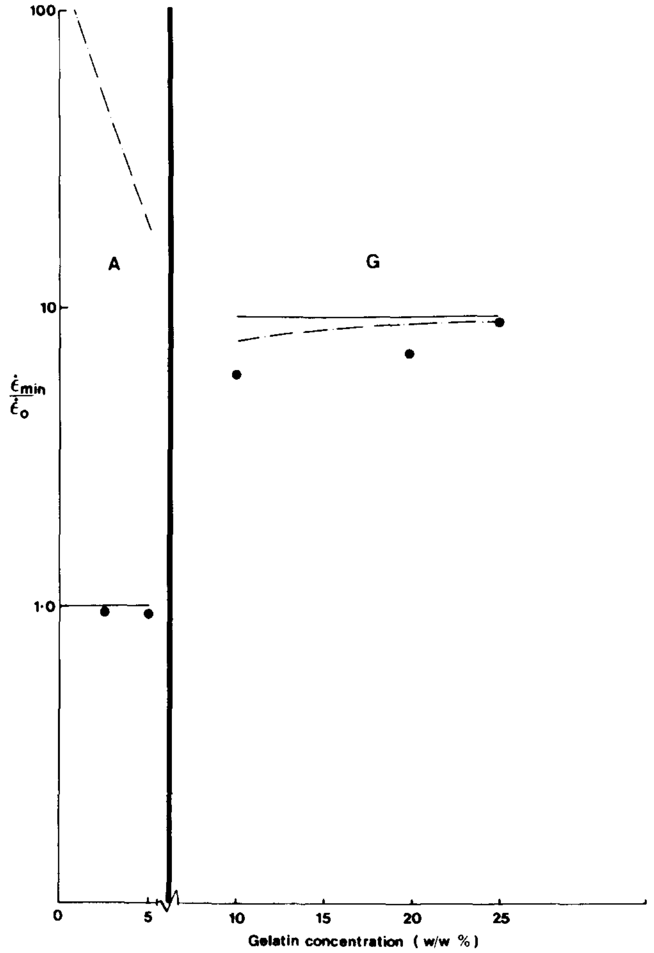

Figure 5 Isostrain (solid) and isostress (broken) predictions for the strain rate at which minimum break stress occurs (relative to pure agar) for the 2% gel series (based on $p=1$, $q=0.33$). Solid circles denote experimental values. A, G, refer to agar and gelatin respectively as supporting phase

improvement is significant. Application to the break stress/strain rate curves confirms that a quadratic fit is more significant than a linear fit, which is in turn more significant than taking the mean of the break stress values (*Tables 1* and 2). This confirms the dependence on strain rate, and shows that the observed curvature is not an artefact due to data scatter. (The solid curves in *Figure 3* are the 'best fit' quadratic plots).

Table 1 Statistical analysis of break stress vs. strain rate data

Gelatin concentration (w/w %)	No. of points	Hypothesis A	Hypothesis B
Gelatin			
5	10	90	75
10	17	95	50
15	14	99.5	95
20	12	75	99
25	13	95	99.9
Air-dried gelatin			
12.5	15	90	50
16.8	8	50	90
19.5	7	75	75
21.5	9	90	90

Hypothesis A – Linear regression is more significant than mean value
Hypothesis B – –Quadratic regression is more significant than linear regression
Entries in the table give the probability that the hypothesis is true (expressed as a percentage)

Table 2 Statistical analysis of break stress vs. strain rate data

Gelatin concentration (w/w %)	No. of points	Hypothesis A	Hypothesis B
1% Agar series			
0	9	99.5	75
2.5	10	97.5	50
5	15	99.9	90
10	16	less than 50	73
15	14	99.5	90
20	15	97.5	less than 50
25	14	99	50
2% Agar series			
0	14	99	50
2.5	15	99.9	50
5	15	99.9	50
10	11	95	90
20	16	99.9	90
25	14	97.5	75

Hypothesis A – Linear regression is more significant than mean value
Hypothesis B – Quadratic regression is more significant than linear regression
Entries in table give the probability that the hypothesis is true (expressed as a percentage)

The quadratic coefficients, and the derived co-ordinates of the minimum $[\dot{\varepsilon}_{min}, \sigma_{min}]$, being functions of a random variable, are themselves random variables, and amenable to the hypothesis testing of statistical analysis. (Note that care must be taken as to the proper estimate of variance to use for each parameter (see, e.g. ref. 20).) In general, σ_{min} is a well-defined parameter. The minima, however, are shallow, and two calculated values of $\dot{\varepsilon}_{min}$ are not significantly different if the best estimates are closer than, say, half a decade on the strain rate axis. Our conclusions are summarized below.

For all systems, the data can be fitted by an equation of the form:

$$\log\sigma_B = a(\log\dot{\varepsilon})^2 + b\log\dot{\varepsilon} + c \tag{6}$$

For a series of concentrations of a given polymer, only coefficient c varies significantly, in a manner which leads to the result

$$\sigma_{B,min} = AE + B \quad (A, B \text{ constants, but different for agar, gelatin}) \tag{7}$$

For single component gels, $\dot{\varepsilon}_{min}$ for agar ($1.18\times10^{-3}\ s^{-1}$) is significantly different from the value for gelatin ($1.16\times10^{-2}\ s^{-1}$) (>70% significance).

Composites in which agarose is the matrix phase cannot be distinguished from agarose itself on statistical grounds. Nonetheless, the isostress model predicts values of $\dot{\varepsilon}_{min}$ which differ from the value for a pure agarose gel by several orders of magnitude. Thus, while the expected isostrain behaviour cannot be confirmed statistically, the isostress prediction must be discounted as a possibility.

For 'gelatin-like' systems, isostress behaviour is anticipated, but the predicted variation in ε_{min} is too small to allow statistically significant resolution. When $\sigma_{B,min}$ is considered, all curves are significantly different from their neighbours. Overall we conclude that the numerical values are inconsistent with isostrain behaviour.

SUMMARY AND CONCLUSIONS

The Takayanagi model has been extended to encompass large deformation and failure properties, in a manner which places bounds on the mechanical behaviour of a phase-separated composite system in the presence of a solvent component, if the properties of the component phases are known. For a mixed biopolymer gel, these component properties can be deduced from the composition via a solvent affinity parameter p, and a 'deswelling parameter', q, which could, in principle, be determined experimentally (e.g. by performing a series of osmotic measurements and modulus determinations on single component gels). Observations on the behaviour of deswollen gels (see ref. 13) makes this approach seem eminently reasonable.

Many of the rationalizations employed depend on being able to relate modulus to concentration in an adequate fashion. Work on this problem has been extensively discussed previously (e.g. ref. 11), and not only does the relationship developed fit data well, but has the same functional form for all biopolymer gels studied (including globular proteins).

The microscopy evidence for phase-inversion leads to the expectation of a transition from isostrain to isostress behaviour. This is seen in the behaviour of the ultimate properties, if not from the modulus dependence, and validated by statistical analysis.

Thus, the model can place definite limits on the behaviour of a composite, phase-separated gel, provided the properties of the component polymers are known. Although the built-in assumptions are not unreasonable, it may at worst be regarded as an empirical parameterization with predictive properties that are encouragingly successful. More optimistically, it provides a framework for the development of more refined treatments, utilizing the ideas of solvent partition between component phases, realistic 'blending-laws', and the extension of current models beyond the regime of linear behaviour.

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APPENDIX

Derivation of theoretical expressions

Initially it is assumed that phases x and y behave in the composite as they do in isolation (viz. equation (1)). Previous use of this equation invoked incompressibility, which automatically ensures that the volume fractions of the two components remain constant at all deformations.

The isostrain case

Consider a thin horizontal section through the composite material (*Figure 6a*). It is readily shown that[21] the areas of the two phases (*Figure 6b*) are given by

$$A_x = \phi_x A \qquad A_y = \phi_y A \tag{A1}$$

If we assume that each component experiences the same strain (and hence the same strain rate) then (*Figure 6c*)

$$\sigma_c = F_c/A = (F_x + F_y)/A \tag{A2}$$

and substituting from (A1) and employing the BST equation gives

$$\sigma_c = \phi_x \sigma_x \neq \phi_y \sigma_y = \phi_x E_x f_x(\lambda_c) + \phi_y E_y f_y(\lambda_c) \tag{A3}$$

where, e.g.

$$\sigma_x = F_x/A_x = E_x f_x(\lambda_c) = (2E_x/3n_x)(\lambda^{n_x - 1} - \lambda^{-(n_x + 2)/2})$$

The upper bound on the modulus (equation (3)) is readily obtained in the Hookean limit.

The isostress case

Focussing attention on a thin vertical section through the composite (*Figure 7*) it is readily shown (e.g. ref. 21) that the initial 'lengths' of phases x and y are given by

$$l_{x_0} = \phi_x l_0 \qquad l_{y_0} = \phi_y l_0 \tag{A4}$$

If each phase experiences the same stress, the deformation in each phase is such that

$$\Delta l = \Delta l_x + \Delta l_y$$

leading to

$$\varepsilon_c = \phi_x \varepsilon_x + \phi_y \varepsilon_y \tag{A5}$$

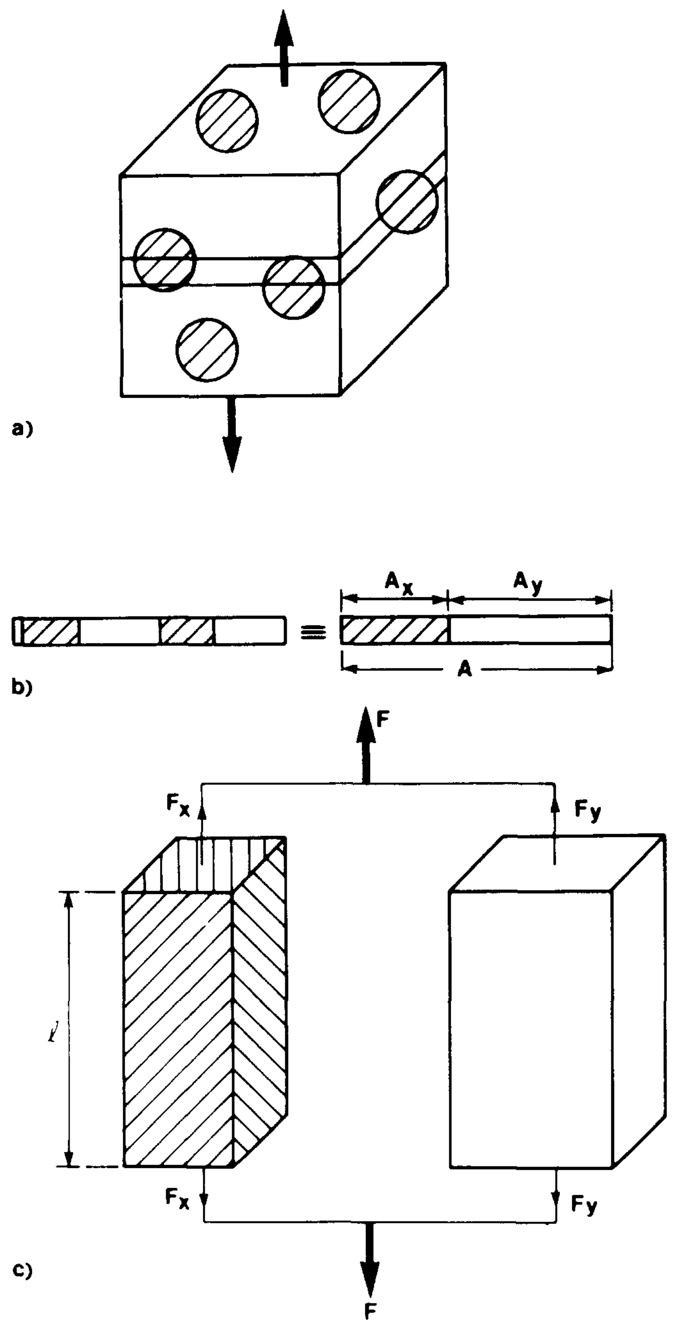

Figure 6 Schematic diagram of the isostrain model

Similar expressions are derived for $\lambda_c,\dot{\varepsilon}_c$. The stress is given by

$$\sigma_c = E_x f_x(\lambda_x) = E_y f_y(\lambda_y)$$

leading to the expression

$$\lambda_c = \phi_x f_x^{-1}(\sigma_c/E_x) + \phi_y f_y^{-1}(\sigma_c/E_y) \qquad \text{(A6)}$$

This latter equation cannot be readily simplified analytically, but can easily be computed for predictive modelling. Again, the limiting case of small deformation returns the (lower) bound in the modulus.

The stress–strain profiles predicted by (A5), (A6) were calculated using appropriate values for volume fraction and modulus, doubly logarithmically. It was found that all plots, including that for pure agar (the single BST

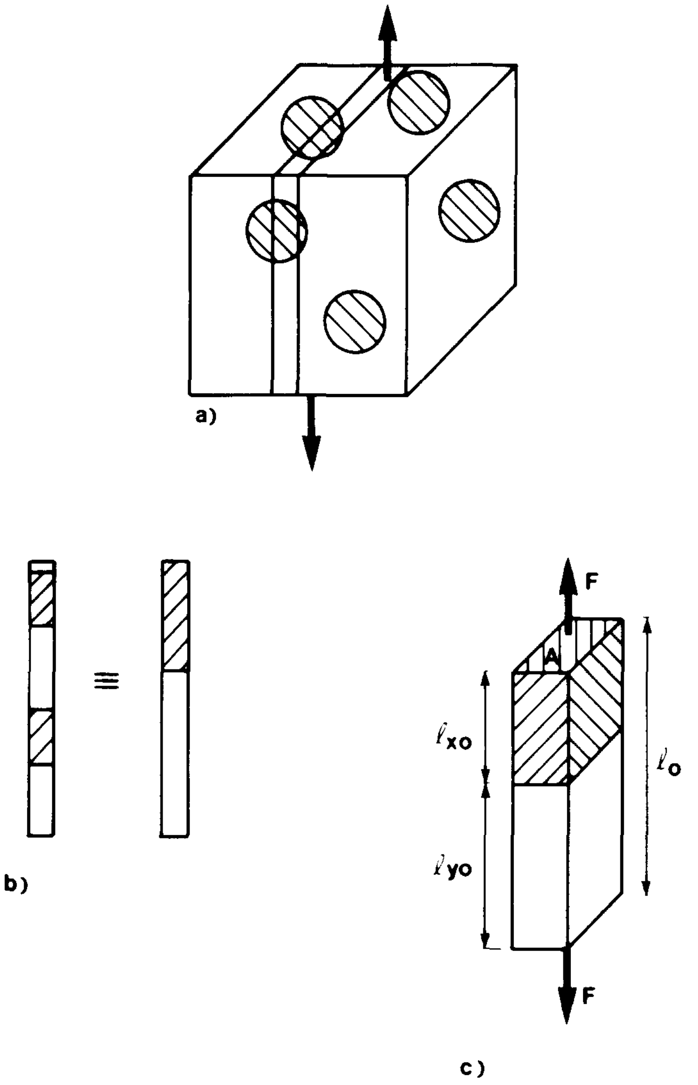

Figure 7 Schematic diagram of the isostress model

equation[1]) were linear up to roughly 65% strain, showing an upward curve thereafter. The degree of curvature was markedly different for different composites at higher strains, but indistinguishable from experimental scatter up to about 200%. No test specimens attain as much as 120% before breaking. Thus, within the limits of experimental resolution and accessibility,

$$f_x \sim f_y \sim f$$

$$\log\sigma_c = \log(f(\lambda_c)) + \log E_c \simeq \log\varepsilon_c + \log E_c, \varepsilon_c < 0.65 \qquad \text{(A7)}$$

It is the form of equation (A7) which allows the use of the so-called stress concentration parameter b introduced in ref. 2. If any such systems could attain higher strains without breaking, a more complex treatment would be required (see e.g. ref. 22).

If we now assume that failure occurs when the matrix phase (phase x, say) breaks, we have (cf. equation (6)).

$$\log\sigma_{B,x} = a(\log(\dot{\varepsilon}_x))^2 + b\log\dot{\varepsilon}_x + c \qquad \text{(A8)}$$

Since $\varepsilon = \dfrac{\sigma_c}{E_c} = \dfrac{\sigma_x}{E_x}$ for the isostrain case

$$\log \sigma_{\mathrm{B,c}} = a(\log \dot{\varepsilon})^2 + b \log \dot{\varepsilon} + c + \log(E_c/E_x) \qquad \text{(A9)}$$

which is the curve for the matrix shifted vertically by an amount $\log(E_c/E_x)$.

For the isostress case, $\sigma_c = E_c\varepsilon_c = E_x\varepsilon_x$ and it is easily shown that

$$\begin{aligned} \log \sigma_{\mathrm{B,c}} = {} & a(\log \dot{\varepsilon}_c + \log(E_c/E_x))^2 \\ & + b(\log \dot{\varepsilon}_c + \log E_c/E_x)) + c \end{aligned} \qquad \text{(A10)}$$

i.e. the curve for the matrix shifted horizontally by an amoung $\log(E_c/E_x)$.

This analysis has assumed Hookean behaviour (valid up to ≈65% strain), but since the curves are characterized by the position of the minimum, which, experimentally, lies within the linear range, the general conclusions are valid. The more severe assumption is that failure only occurs in the matrix, which implies that if the stress is high enough to cause failure within a filler 'particle', the growing crack cannot cross the matrix-filler 'interface'. A close examination of the microstructure of such a mixed gel[1] shows that such an 'interface' is rather poorly defined. Nonetheless, this model does predict the observed behaviour rather successfully, and must be regarded as a suitable starting point for future refinements.