Heterogeneous Polymer–Polymer Composites.   I. Theory of Viscoelastic Properties and Equivalent Mechanical Models

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Synopsis

The representation and interpretation of dynamic mechanical properties of heterogeneous polymer–polymer composites are discussed in terms of equivalent mechanical models and the viscoelastic form of the well-known Kerner equation.   Model parameters calculated from dispersed phase volume fraction and matrix Poisson's ratio (using the Kerner equation) are in fairly good agreement with experimental values for systems comprising soft inclusions in a hard matrix.   The effects of partial phase inversion on dynamic properties are discussed in terms of an extension of the Kerner equation. Model calculations indicate that the in-phase component of the complex modulus depends primarily on dispersed phase volume concentration, while the out-of-phase component depends on both the concentration and the morphology of the dispersed phase.   Although substantial information about the microstructure of polymer–polymer composites can in principle be deduced from dynamic measurements, quantitative correlation between dynamic properties and use properties such as impact strength (which may have a quite different dependence on structural parameters) is probably fortuitous.

INTRODUCTION

Dynamic mechanical properties have been extensively used for the characterization of heterogeneous polymer systems such as semicrystalline polymers, block and graft copolymers, and blends of incompatible polymers (Bohn[1] and Ferry[2] give many examples).   In these systems, each type of region experiences its own transitions; changes in composition and morphology are reflected in isochronal viscoelastic properties by changes in the breadth, location, and intensity of the observed transitions.   Thus, in the case of impact polystyrene, the intensity of the characteristic dispersed phase transition has been correlated[3,4] with dispersed-phase morphology— and hence indirectly with the efficiency of impact reinforcement by addition of rubber.   The effects of changes in composition and phase structure on the dynamic Young's modulus of polymer–polymer composites are explored in this paper in terms of a modified form of the well-known Kerner equation.[5]   Although model calculations have recently been published[6] which indicate that the bounds predicted by one of the published theories for the viscoelastic properties of heterogeneous media are qualitatively in

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agreement with observed behavior, direct comparisons of experimental data with theory have generally been restricted to a consideration of the composition dependence of the elastic shear modulus, or of the in-phase component of the dynamic shear modulus, at a single temperature (see, for example, refs. 3 and 7). A phenomenological representation of the dynamic Young's modulus in terms of one or the other of two simple mechanical models has been used by several authors.[8-16]

THEORETICAL

Elastic Modulus

The calculation of the elastic properties of multiphase media from the properties of the constituent phases is a very old problem; Hashin[17] and Nielsen[20] have given extensive reviews. More recently, the analogous viscoelastic calculation has been undertaken.[21-23] Exact upper- and lower-bound expressions for the elastic moduli have been derived[17-19]; similar bounds can also be written for viscoelastic moduli using the correspondence principle. (The correspondence principle states that expressions for the complex moduli of composites may be obtained by replacement of phase elastic moduli by phase complex moduli in exact expressions for the corresponding elastic moduli.) The bounds are reasonably close when the phase moduli are not greatly different. However, shear moduli of the constituent phases of polymer–polymer composites may differ by two or more orders of magnitude; in such cases, approximate but single-valued expressions are more useful for comparison with experiment.

In 1956, Kerner[5] presented expressions for the gross bulk and shear moduli of a multicomponent suspension. For two components, Kerner's result for shear modulus may be written in the form

$$\frac{G}{G_m} = \frac{(1 - v)G_m + (\alpha + v)G_i}{(1 + \alpha v)G_m + \alpha(1 - v)G_i} \qquad (1)$$

where G is elastic shear modulus, v is the volume concentration of inclusions, subscript m denotes a matrix property, subscript i denotes an inclusion property, and α is a function of ν_m, the Poisson ratio of the matrix:

$$\alpha = 2(4 - 5\,\nu_m)/(7 - 5\,\nu_m). \qquad (2)$$

The result stated in eq. (1) has appeared several times in the literature. It has been obtained by a somewhat different approach by Uemara and Takayanagi[24] who cite similar results of Okano.[25] For inclusions stiffer than the matrix, Kerner's results are formally identical to the lower-bound expressions derived by Hashin and Shtrikman.[19] Halpin and Tsai[26,27] write eq. (1) in a somewhat different form, which more clearly displays the concentration dependence of the composite modulus and which is useful for extension to nonspherical inclusions. The present form is more convenient for manipulations involving complex moduli.

Dynamic Modulus

Based on a composite sphere model, Christensen[21] has derived an approximate expression for complex shear modulus:

$$G^*/G_m^* = 1 + \gamma_{1G}v/(\gamma_{2G} + \gamma_{3G}v) \tag{3a}$$

where

$$\gamma_{1G} = 15(1 - \nu_m)(G_i^*/G_m^* - 1) \tag{3b}$$

$$\gamma_{2G} = (7 - 5\nu_m) + 2(4 - 5\nu_m)G_i^*/G_m^* \tag{3c}$$

$$\gamma_{3G} = -2(4 - 5\nu_m)(G_i^*/G_m^* - 1) \tag{3d}$$

and $G^* = G' + iG''$ is the dynamic shear modulus. The viscoelastic Poisson's ratio—in general a complex function of frequency— is assumed to be a real constant. Substitution of the γ_{iG} into eq. (3a) with subsequent rearrangement of terms leads to

$$\frac{G^*}{G_m^*} = \frac{(1 - v)G_m^* + (\alpha + v)G_i^*}{(1 + \alpha v)G_m^* + \alpha(1 - v)G_i^*}. \tag{4}$$

Equation (4) has the same form as eq. (1), except that dynamic shear moduli replace elastic shear moduli. The result stated in eq. (4) was previously obtained by Uemara and Takayanagi[24] by application of the correspondence principle to their form of eq. (1), with the implicit assumption that Poisson's ratio is a real constant.

An expression for the dynamic Young's modulus E^* can readily be obtained by recalling that

$$E^* = 2(1 + \nu^*)G^* \tag{5}$$

where $\nu^* = \nu' + i\nu''$ is the viscoelastic Poisson's ratio. If it is assumed that $\nu^* = \nu' = \nu$, where ν is elastic Poisson ratio, then substitution of eq. (4) into eq. (5) yields

$$\frac{E^*}{E_m^*} = \gamma \frac{(1 - v)E_m^* + \beta(\alpha + v)E_i^*}{(1 + \alpha v)E_m^* + \alpha\beta (1 - v)E_i^*} \tag{6a}$$

where

$$\beta = (1 + \nu_m)/(1 + \nu_i) \tag{6b}$$

$$\gamma = (1 + \nu)/(1 + \nu_m). \tag{6c}$$

Explicit expressions for E', E'', and the loss tangent, $\tan \delta = E''/E'$, are given in Appendix I.

Mechanical Models

Takayanagi and co-workers[15] and a number of other authors[8–10,16] have reported considerable success in representing the viscoelastic properties of a variety of heterogeneous materials in terms of simple mechanical models

comprising elements (assumed to have the viscoelastic properties of the constituent phases of the composite medium) connected partly in series and partly in parallel. Two such models are illustrated in Figure 1.

In essence, these models represent attempts to construct average response curves intermediate between the bounds given by simple series and parallel rules of mixing. The parameters λ and φ can be interpreted as representing the extent of series and parallel character of the observed behavior. Thus, the larger φ, is the more closely the models approach a
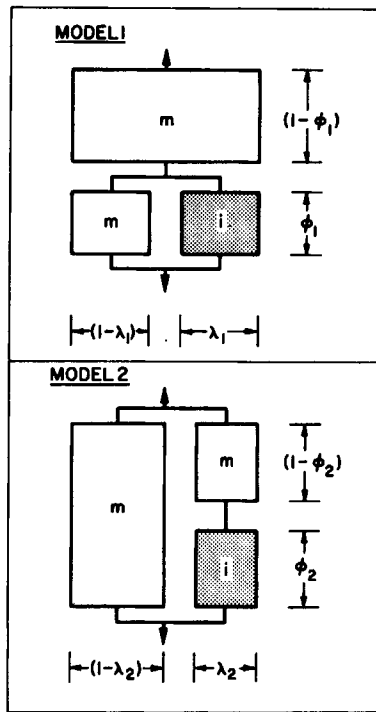

Fig. 1. Equivalent mechanical models for the representation of dynamic mechanical properties of two-phase systems. Regions m are assumed to have the properties of the continuous phase; regions i, those of the dispersed phase.

simple parallel connection; similarly, the larger λ is, the more closely the models approach a simple series connection. With appropriate choice of parameters, these models are equivalent to each other and also to eq. (4). However, in general, $\lambda_1 \neq \lambda_2$ and $\varphi_1 \neq \varphi_2$ for a given response.

Under the assumption that $\nu^* = \nu' = \nu$, the dynamic shear modulus for model 1 of Figure 1 is

$$G^* = \left[\frac{\varphi_1}{\lambda_1 G_i^* + (1 - \lambda_1)G_m^*} + \frac{(1 - \varphi_1)}{G_m^*} \right]^{-1} \tag{7}$$

where $\lambda_1 \varphi_1 = v$. Equation (7) reduces to eq. (4) provided that the parameters φ_1 and λ_1 are given by:

$$\varphi_1 = v\,(1 + \alpha)/(\alpha + v) \tag{8}$$

$$\lambda_1 = (\alpha + v)/(1 + \alpha) \tag{9}$$

where α is defined by eq. (2).

Similarly for model 2, the dynamic shear modulus is given by

$$G^* = \lambda_2 \left[\frac{\varphi_2}{G_i{}^*} + \frac{(1 - \varphi_2)}{G_m{}^*} \right]^{-1} + (1 - \lambda_2)G_m{}^* \tag{10}$$

where $\lambda_2 \varphi_2 = v$. Equation (10) reduces to eq. (4) provided that the parameters φ_2 and λ_2 are given by

$$\varphi_2 = (1 + \alpha v)/(1 + \alpha) \tag{11}$$

$$\lambda_2 = v(1 + \alpha)/(1 + \alpha v). \tag{12}$$

Equations (10) and (7) are also equivalent; thus, for a given response, φ_1 and λ_1 are related to φ_2 and λ_2 by

$$\lambda_1 = 1 + v - \varphi_2 \tag{13}$$

$$\lambda_1 \varphi_1 = \lambda_2 \varphi_2 = v. \tag{14}$$

Models 1 and 2 have generally been applied[8–16] to dynamic Young's modulus data; for this purpose, expressions identical in form to eqs. (7) and (10) have been used with G^*, $G_m{}^*$, and $G_i{}^*$ replaced by E^*, $E_m{}^*$, and $E_i{}^*$, respectively. These expressions are correct provided that $\nu = \nu_m = \nu_i$; under this condition, the expressions for E^* analogous to eqs. (7) and (10) are entirely equivalent to eq. (6), and eqs. (8) and (9) and (11) to (14) are still applicable. Takayanagi et al.[14] have given expressions similar to eqs. (8) and (9) for the special case $\nu = \nu_m = \nu_i = 0.5$.

RESULTS AND DISCUSSION

Comparison with Experimental Data

Uemara and Takayanagi[24] have used an approximate form of eq. (6), obtained by assuming that $\nu = \nu_m = \nu_i = 0.5$, to represent dynamic Young's modulus data on a styrene–acrylonitrile copolymer interpolymerized with polybutadiene particles. At $v = 0.2$, excellent agreement between theory and experiment was found. At larger volume fractions of rubber—the range studied was $0.2 < v < 0.5$—there was some discrepancy between theory and experiment; part of this discrepancy may be attributed to the fact that the volume fraction of rubber and the volume fraction of dispersed phase were assumed to be equal. As the model calculations presented later illustrate, calculated values of E^* are very sensitive to the volume fraction and morphology of the dispersed phase. Thus, the theoretical calculation should ideally be based either on independent information regarding the
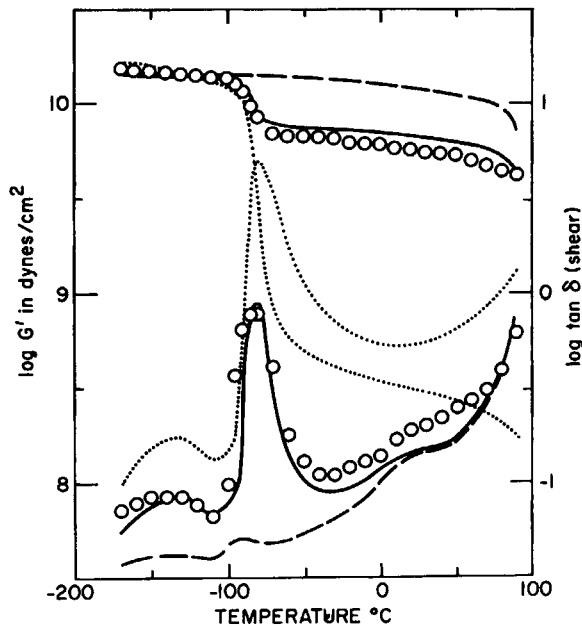
Fig. 2. In-phase component of dynamic shear modulus and loss tangent vs. temperature for an impact polystyrene and its separated phases (from ref. 7). Dotted line, insoluble gel; dashed line, soluble part; circles, data on composite; solid line, calculated from eq. (4) assuming $\nu_m = 0.35$.

morphology of the composite or on dynamic data obtained on the isolated phases of the composite. Although the latter alternative may be questioned on the grounds that the properties of a phase isolated from a composite may not be representative of the properties of that phase within the composite, a rather good representation of composite behavior is obtained by application of eq. (4) to such data. Thus, we have analyzed dynamic shear modulus data obtained by Cigna[7] on an impact polystyrene and its constituent phases, isolated by solvent extraction, in terms of eq. (4); the results are presented in Figure 2. Although the calculated values of G' are somewhat high (and the corresponding values of the loss tangent, somewhat low) in the temperature range between the glass transition regions characteristic of the component polymers, the location and magnitude of the loss tangent maximum corresponding to the dispersed phase are correctly predicted. The shape of the modulus–temperature curve is given with substantial accuracy.

Another comparison of experiment with theory is realized by comparing published values of the equivalent mechanical model parameters φ and λ with values calculated from v and ν_m, using the equations given previously. We have analyzed two sets of data in this way. Takayanagi et al.[12,14] have represented dynamic Young's modulus data on several rubber-modified polystyrene and styrene–acrylonitrile copolymers in terms of model 1,

TABLE I
Calculated and Empirical Values of Model Parameters

v	λ_1	φ_1	λ_2	φ_2	$\nu_m{}^a$
0.36^b	0.6	0.6	0.473^d	0.761^d	0.48
0.23^b	0.6	0.38	0.365^d	0.63^d	0.285
0.44^b	0.775	0.568	0.662^d	0.665^d	−0.957
0.49^b	0.7	0.7	0.62^d	0.79^d	0.54
0.3^c	0.633^e	0.474^e	0.45	0.667	0.30
0.5^c	0.694^e	0.720^e	0.62	0.806	0.52
0.7^c	0.905^e	0.774^e	0.88	0.795	8.9

ᵃ Calculated from λ; and φ_1, or λ_2 and φ_2, and v using eqs. (2) and (8) or (2) and (11).
ᵇ Data of Takayanagi et al.[12,14]
ᶜ Data of Matsuo et al.[110]
ᵈ Calculated from λ_1 and φ_1 using eqs. (13) and (14).
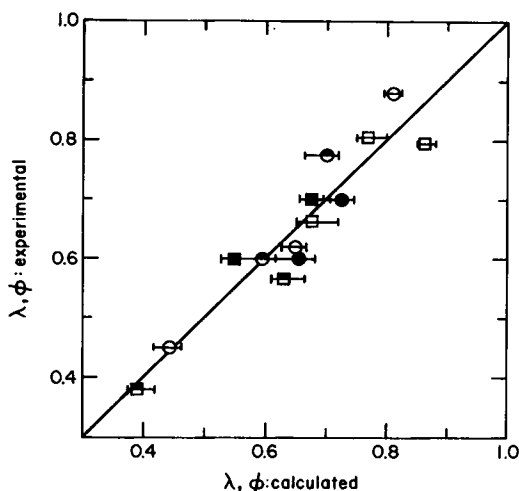ᵉ Calculated from λ_2 and φ_2 using eqs. (13) and (14).

Fig. 3. Comparison of experimental model parameters with values calculated from eqs. (2), (8), (9), (11), and (12), as appropriate, with $\nu_m = 0.35$. Error bars indicate effect of allowing ν_m to vary between 0.2 and 0.5. Open symbols, data of ref. 10; filled symbols, data of ref. 12; half-filled symbols, data of ref. 14. In each case, circle = λ; square = φ.

using the parameters given in Table I. Matsuo et al.[10] represented similar data on a two-phase polyacrylate–poly(urethane urea) system in terms of model 2; these parameters are also given in Table I. Based on the assumption the $\nu_m = 0.35$ in each case, we have calculated values of φ and λ; the results are summarized graphically in Figure 3. Limits on the calculated values of φ and λ obtained by assuming $0.2 \leq \nu_m \leq 0.5$ are indicated by error bars. For the most part, there appears to be good agreement between calculated and empirical values.

Since models 1 and 2 have been shown to be equivalent, Table I includes not only the published experimental values of λ and φ for the model origi-

nally used, but also calculated values of λ and φ for the alternate model. We conclude that the interpretation of these parameters in terms of series and parallel character of response is dubious at best since the qualitative interpretation of relative character can be reversed by an essentially trivial change in the model used.

A more sensitive comparison of the mechanical model representation with the theoretical result involves the calculation of ν_m from the empirical values of φ and λ. Results of this calculation are summarized in Table I. The agreement between calculated and expected values of ν_m is not very good; two of the values obtained are totally unreasonable. However, the calculated values of ν_m are very sensitive to changes in φ and λ, whereas the calculated values of E^* are not very sensitive to changes in ν_m, as will be demonstrated subsequently. Thus, the calculated value of ν_m depends strongly on the way in which the curve fitting is performed. Generally, the procedure involves comparison of calculated curves of E' and E'' with experimental data; the values of φ and λ are adjusted to achieve as close a match as possible to E' and E'' simultaneously. In applying the theoretical result to data on systems containing a dispersed rubber phase, it is found that the loss tangent curve is reasonably accurately reproduced, while the calculated values of E' are invariably too high. It is concluded that a representation in terms of eq. (6) is essentially equivalent to the published representation in terms of model 1 or model 2 for all but two of the materials discussed. The exceptions can probably be attributed to partial phase inversion; this is almost certainly the case for the $v = 0.7$ data of Matsuo et al., and may also apply to the data of Takayanagi et al. at $v = 0.44$. In both cases, the value of v was determined by overall composition rather than by an independent analysis of relative phase volumes.

All of the systems discussed so far are of the general type soft inclusions/ hard matrix. For the inverse case—hard inclusions/soft matrix—the present representation apparently fails. For example, shear modulus data of Schwarzl et al.[29] on a series of polyurethane–sodium chloride composites are reported to be well represented by a theory due to van der Poel.[30] Although the correctness of both the theoretical calculation of shear modulus and the approximations made in comparing the theory with experimental data have been questioned,[22] the fact remains that a substantially greater dependence of shear modulus on filler concentration is observed than can be accounted for in terms of eq. (4). Similarly, data of Kraus et al.[16] on a polystyrene-reinforced styrene–butadiene copolymer could not be adequately represented by model 1 with parameters calculated from eqs. (8) and (9) with $\nu_m = 0.5$.

On the basis of these comparisons with experimental data, eq. (4), or equivalently eq. (6), represents dynamic data on a variety of systems of the type soft inclusions/hard matrix reasonably well. Although the representation is somewhat in error when examined in detail, the general features and trends indicated by the experimental data are correctly reproduced. Systems of the type hard inclusions/soft matrix apparently cannot be repre-

sented very well in these terms. In the remainder of this section, some possible origins of the observed discrepancies between theory and experiment will be explored.

Among the assumptions made in the derivation of eq. (4) are these: (1) interactions between particles can be ignored; (2) Poisson's ratio is a real constant; (3) there is perfect adhesion between matrix and inclusions; and (4) the size and spatial distributions of the inclusions are random. The first of these assumptions restricts applicability of the calculation to small concentrations—strictly speaking, no more than a few per cent. Nielsen,[31,32] and Lewis and Nielsen[33] have considered modifications to eq. (1) which introduce corrections for maximum packing fraction of filler and deviation of particle shape from sphericity. These corrections are particularly important for particles stiffer than the matrix and allow a good fit to data on such composites to be obtained; they will be further considered in a subsequent paper.[34]

The assumption that Poisson's ratio is a real constant is, of course, incorrect for real viscoelastic materials; however, the out-of-phase component of ν^* (= $\nu' + i\nu''$) is rather small. On the basis of some measurements reported by Theocaris,[35] ν'' if of the order $-0.1\ \nu G''/G' \leqslant \nu'' \leqslant -0.01\ \nu G''/G'$, where ν is the elastic value of Poisson's ratio. We have performed model calculations based on eq. (4) and the data presented in Figure 3, assuming Poisson's ratio to be complex and assuming ν'' to lie within the above specified range. The changes observed in the calculated values of G', G'', and the loss tangent were entirely negligible.

The assumption of perfect adhesion at the matrix–inclusion interfaces is an important one; the effect of imperfect adhesion in the *elastic* case has been studied by Sato and Furukawa.[36,20] As expected, the nature of the interfacial bond has a profound influence on the elastic modulus, especially for the hard filler/soft matrix case. For no adhesion, the properties approach those of a foam. In the case of a soft filler/hard matrix system, the principle effect should be in the out-of-phase component of the dynamic modulus. However, for application of the theory to rubber-modified plastics, in which there is usually substantial chemical grafting between the phases, the possibility that poor interfacial adhesion will affect the small-strain dynamic properties is remote.

Finally, it is almost invariably assumed in the application of expressions such as eq. (4) that the effective properties of the constituent phases of the composite may be replaced by their properties in bulk. This assumption will clearly be invalid if the inclusions are under a hydrostatic tension or compression (perhaps induced by differential thermal expansion)[37,38] sufficient to alter their mechanical response. Generally, it is also assumed that the structure of the composite is simple, so that the properties of the individual phases can be taken to be the bulk properties of the pure polymeric constituents and the phase volumes can be calculated from the overall composition. This assumption is clearly incorrect for any multicomponent system in which a partial phase inversion takes place. High-impact poly-

styrene, which is well known to have a complicated phase structure in which a part of the polystyrene is occluded in the dispersed rubbery phase, is a familiar example. The effect of changes in phase morphology and the dependence of the complex modulus on v and v_m are discussed in the next section.

Model Calculations

In order to illustrate the functional dependence of eqs. (4) and (6) on v, v_m, and effective phase properties, model calculations have been performed using isochronal Young's modulus data obtained at 110 Hz on poly(methyl methacrylate) and on a crosslinked acrylic rubber prepared by copolymerization of butyl acrylate with 1,3-butylene dimethacrylate in a mole ratio of 95:5. Experimental methods and polymerization conditions are described elsewhere.[34] Although the calculations are based on a particular pair of polymers, the conclusions reached are more dependent on the functional form of the equations than on the specific properties of these polymers. Similar behavior should be expected for other pairs of materials which have widely separated glass transitions.

Inclusions of the two types schematically illustrated in Figure 4 are considered: simple inclusions of one polymer in the other, and composite
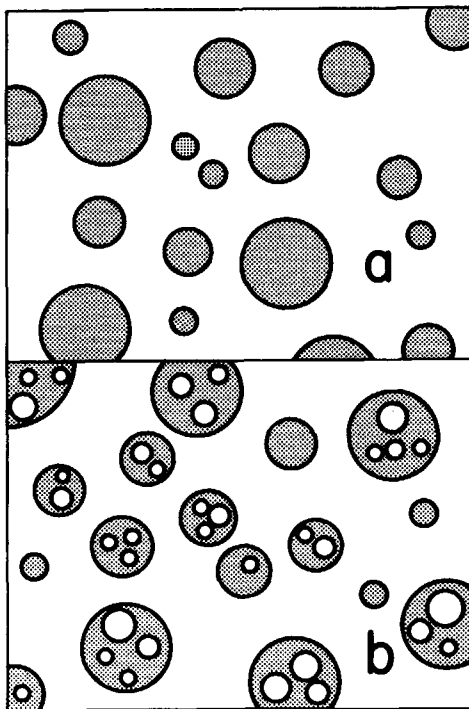

Fig. 4. Schematic sketch of particulate composites with simple inclusions (a) and composite inclusions (b).

inclusions in which part of the polymer forming the continuous phase is occluded by the polymer forming the dispersed phase. In the latter case, the calculation is performed in two stages. The properties of the inclusions are calculated using eq. (6) by assuming simple inclusion geometry; the values so obtained are then used in conjunction with eq. (6) to compute the properties of the composite. Similar calculations, based on the upper- and lower-bound expressions given by Hashin[28] for the shear modulus of an assemblage of composite spheres, have recently appeared for the glassy matrix–simple rubbery inclusion and glassy matrix–composite rubbery inclusion cases. Although the same general trends are observed, the spread between the bounds precludes a quantitative comparison with experimental data and makes difficult an assessment of the relative importance of, for example, changes in dispersed phase volume fraction on the one hand versus changes in morphology on the other.

Simple Inclusions

Dependence of E^* on v and Phase Morphology. Figures 5 and 6 present E^* data on the model rubber and glass used for the present calculations. Calculated curves for the two simple inclusion cases—glass phase continuous and rubber phase continuous—at several values of v are included in these figures. The calculation has been performed using eq. (6) under the assumption that $\gamma = 1$ and approximating Poisson's ratio for each material as 0.35 at temperatures below and as 0.5 at temperatures above the loss tangent maximum corresponding to the glass transition.

As expected, the calculated values of E' tend to lie closest to the curve describing the continuous phase, even at unrealistically high values of dispersed phase volume fraction. An isothermal section through this plot at some intermediate temperature, say 50°C, would generate the familiar Kerner equation plot of modulus versus composition as given, for example, by Nielsen.[20] The temperature dependence of E' in the region between the two transition regions parallels that of the material forming the continuous phase.

Hashin[22] has pointed out that the loss tangent predicted by the composite sphere model is identical to that of the matrix for porous materials (foams) as well as for a material comprising a very rigid filler in a soft matrix. This is essentially the behavior observed in Figure 6, except that a highly concentration-dependent loss maximum corresponding to the dispersed phase appears.

The locations of the loss tangent maxima on the temperature scale are seen to be somewhat shifted toward lower temperatures for the continuous hard phase case, and to higher temperatures for the continuous soft phase case. The effect is much more pronounced for the dispersed phase maxima than for the continuous phase maxima. A detailed examination of the calculation reveals that both the location and the magnitude of the dispersed phase loss maxima depend strongly on the ratio E_m'/E_i'; thus, the dispersed phase loss maximum for a composite containing inclusions of higher rubbery
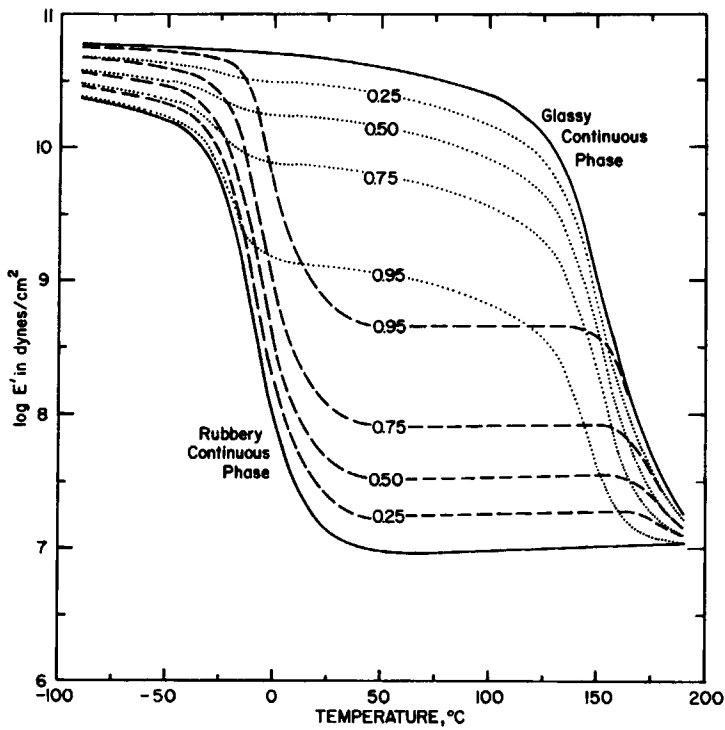
Fig. 5. In-phase component of dynamic Young's modulus vs. temperature. Upper solid curve, poly(methyl methacrylate); lower solid curve, poly(butyl acrylate-co-1,3-butylene dimethacrylate); dotted curve, calculated from eq. (6) assuming simple rubbery inclusions in a glassy matrix; dashed curve, calculated from eq. (6) assuming simple glassy inclusions in a rubber matrix. Calculated curves are labeled with the assumed values of dispersed-phase concentration.
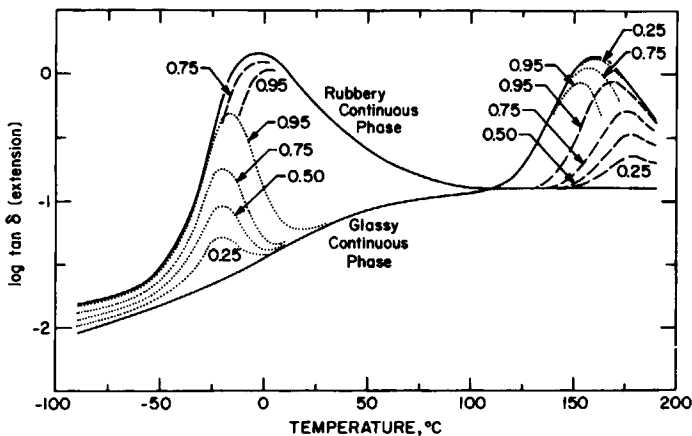

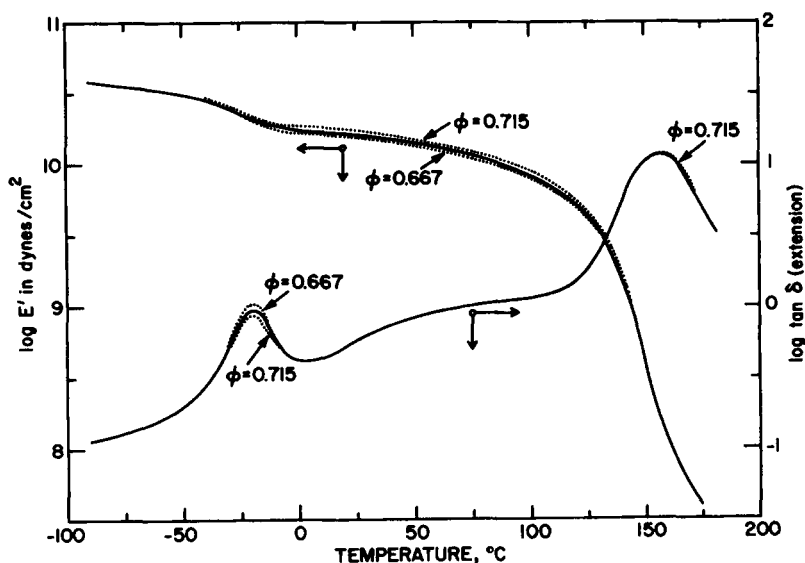Fig. 6. Loss tangent vs. temperature. Key as for Fig. 5.

Fig. 7. Effect of changes in ν_m on calculated values of E' and tan δ for simple rubbery inclusions in a glassy matrix; $v = 0.5$. Solid curve, $\nu_m = 0.35$; others as labeled.

modulus is somewhat higher at a given value of v, while the location of the maximum is shifted slightly to higher temperatures.

Qualitatively, the loss tangent curves of the composites are identical to those of the corresponding continuous phase with a small additive contribution attributable to the dispersed phase. The apparent contribution of the *dispersed* phase to the composite loss tangent, especially on a logarithmic scale, depends on the value of the *continuous*-phase loss tangent. Thus, in Figure 6, for the continuous glass phase case, the apparent dispersed-phase loss maxima would be much smaller if the transition temperature of the dispersed-phase polymer were, say, 50°C higher. In fact, the *absolute* contribution of the dispersed phase to the loss tangent would also be smaller, since the magnitude of the dipersed-phase contribution is a function of the difference between the dispersed-phase and continuous-phase loss tangents. Explicit expressions for the loss tangent are given in Appendix I.

Dependence of E^* on ν_m. To perform the calculations described, it is necessary to assume values for ν_m and to evaluate the importance of ν_m to the results obtained. Model calculations assuming $0.2 \leq \nu_m \lesssim 0.5$ have been performed. The results generally indicate only a slight dependence on ν_m.

One example is presented in Figure 7 for the case $v = 0.5$, $\beta = \gamma = 1$, with the hard phase assumed to be continuous. This calculation is equivalent to one based on model 1 of Figure 1 with the parameters φ_1 and λ_1 assuming values $0.715 \geq \varphi_1 \geq 0.667$ and $0.700 \leq \lambda_1 \leq 0.750$. The changes in E' and the loss tangent wrought by this variation are seen to be rather small. Model calculations involving deviations of β from unity have also been performed; calculated values of modulus and loss tangent are relatively

insensitive to changes in β.   In terms of eq. (4) or (6), the specific value chosen for ν_m is seen to be of minor importance.   The mechanical models of Figure 1 are found to be a reasonable approximation to eq. (6) for model parameters corresponding to physically reasonable values of Poisson's ratio.

Composite Inclusions

Since the location and magnitude of the dispersed phase maximum depend strongly on phase volume and on the ratio E_m'/E_i', it is to be expected that the behavior of a material containing composite inclusions will differ sub-stantially from that of a material containing simple inclusions.   Two sets of calculations have been performed: in the first, overall composition is held constant while phase volume and hence morphology are varied; in the second, the phase volume is held constant while overall composition and hence, again, morphology are varied.

Constant Composition.   Figures 8 and 9 present results obtained assum-ing constant composition but variable phase volume.   The figures are largely self-explanatory.   It will be noted that, in each case, the dispersed-phase loss tangent maximum is highly phase-volume dependent.   The continuous-phase loss tangent maximum is less phase-volume dependent, but displays a substantial broadening which resolves into a double maxi-
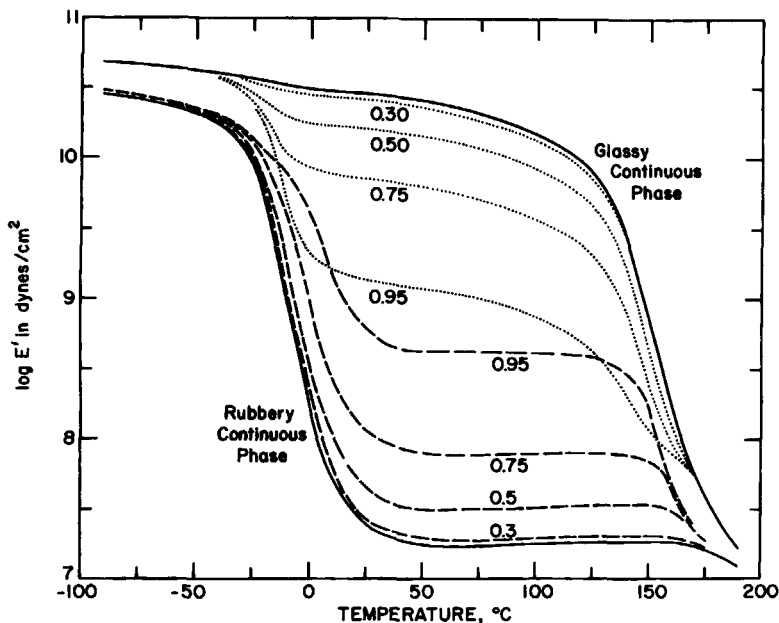

Fig. 8. Dependence of E' on dispersed-phase volume fraction and morphology assum-ing composite inclusions and constant overall composition.   Upper curves, glassy con-tinuous phase, total rubber content = 25 vol-%; lower curves, rubber continuous phase, total glass content = 25 vol-%; solid curves, simple inclusions; broken curves, composite inclusions.   Labels indicate dispersed-phase volume fraction.

mum at sufficiently high phase volumes. Although the calculations have been carried to unrealistically high values of phase volume, the broadening indicated at lower phase volumes is clearly an early manifestation of the double maximum observed at higher phase volumes. These effects are attributable to the individual contributions of the continuous-phase polymer present (1) in the continuous phase and (2) as subinclusions in the dispersed-phase regions. The morphology-dependent temperature separation of loss tangent maxima previously observed for simple inclusions naturally gives rise to the broadened maxima observed for the composite inclusions.
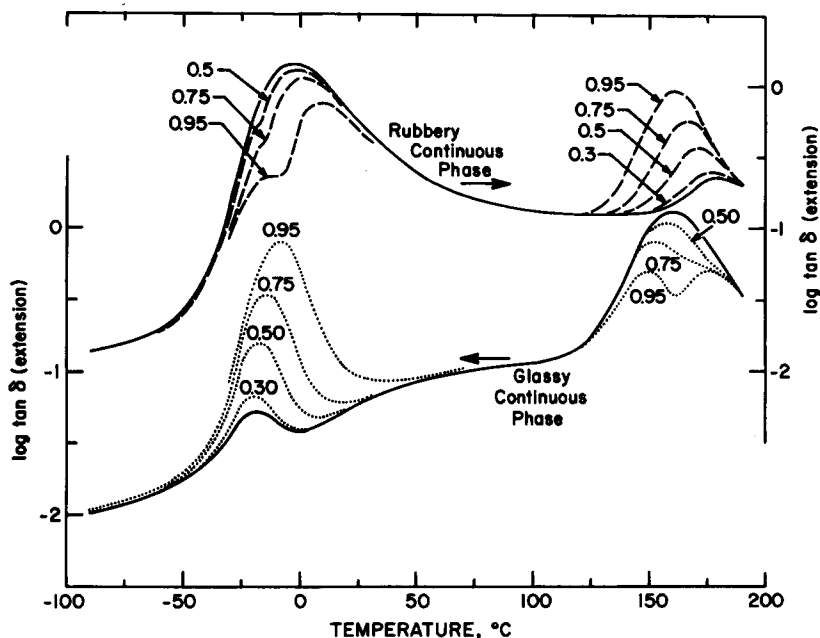

Fig. 9. Dependence of tan δ on dispersed-phase volume fraction and morphology as suming composite inclusions and constant overall composition. Key as for Fig. 8.

The level of the in-phase component of E^* is seen to be highly phase-volume dependent; it is again observed that the temperature dependence of E' away from the dispersed-phase transition region is dominated by the temperature dependence of the continuous phase.

Constant Phase Volume. Figures 10 and 11 present results obtained assuming constant phase volume but variable composition. The level of E' in the region between the transition regions characteristic of the constituent phases is insensitive to changes in overall composition, provided that the dispersed-phase volume fraction remains constant. This is not particularly surprising, but simply arises from the fact that there is always a large difference between the values of E' for the continuous phase and the
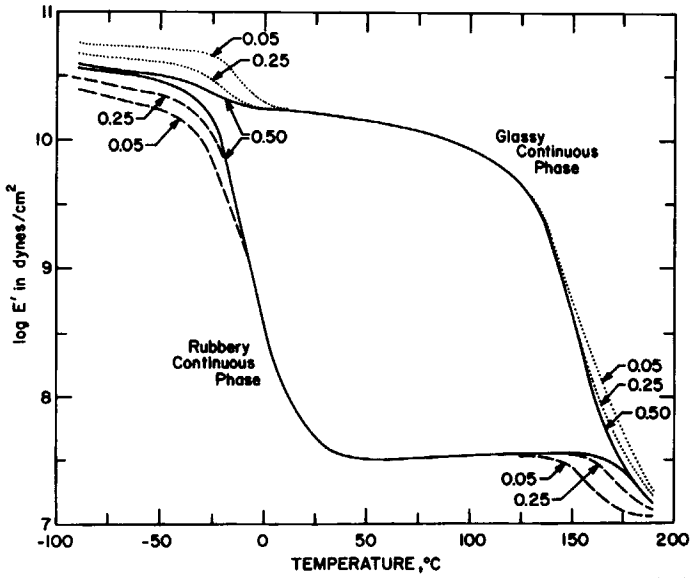
Fig. 10. Dependence of E' on overall composition and morphology assuming constant dispersed-phase volume fraction. Dispersed-phase volume fraction = 0.5. Labels indicate overall volume fraction glass for the rubber continuous-phase curves, and overall volume fraction rubber for the glass continuous-phase curves.
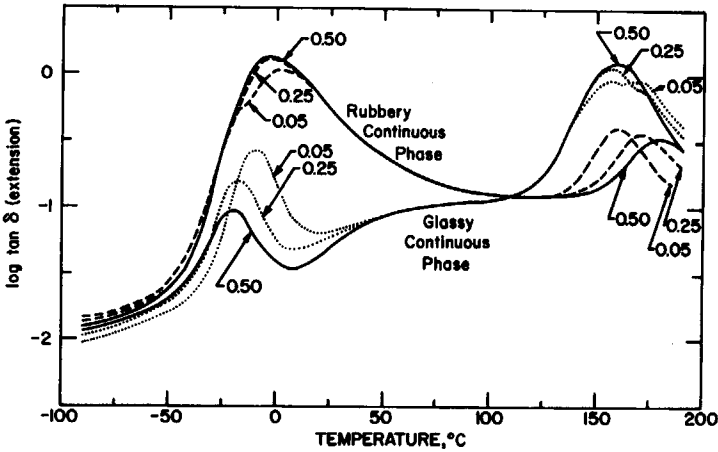

Fig. 11. Dependence of tan δ on overall composition and morphology assuming constant dispersed-phase volume fraction. Key as for Fig. 10.

dispersed phase over this temperature range. Below the transition region of the rubber and above the transition region of the glass, E' of the composite does become composition dependent; in these regions, the moduli of the two phases are more nearly comparable.

The dispersed-phase loss tangent maximum is, on the other hand, highly composition dependent. The effect is most pronounced for materials

having a continuous glassy phase, and for these materials it is seen that the magnitude of the low-temperature loss peak can be substantially *increased* by *decreasing* the overall rubber content at constant dispersed-phase volume fraction.

An implicit assumption of the calculations presented for composite inclusions is that the inclusions are uniform in composition and properties. The composite inclusions in real materials would probably vary widely in composition (as in Fig. 4). Such a distribution in composition would be expected to result in broadened transitions, analogous to those observed for copolymers which are not strictly uniform in composition.

Other Changes in Effective Properties

The foregoing model calculations have served to illustrate the effect on the dynamic mechanical properties of changes in effective phase properties due to changes in morphology. There are numerous other ways in which deviations of effective properties from the properties of the bulk constituents can arise; copolymerization effects (in the case of interpolymers) or immobilization (or plasticization) of some fraction of material in the vicinity of phase boundaries immediately come to mind. Copolymerization effects in particular should be reflected in changes in the location, intensity, and breadth of the observed transitions such as are well documented in the case of "random" copolymers; it should be possible to account for such effects by introduction of data on appropriate copolymers into the calculations.

Appendix I

Equation (6a) can be separated into real and imaginary parts to yield explicit expressions for E' (the in-phase component of E^*, or storage modulus) and for E'' (the out-of-phase component of E^*, or loss modulus). An expression can also be written for the loss tangent ($\tan \delta = E''/E'$). We obtain

$$E' = E_m'(A/C) - E_m''(B/C) \tag{I-1}$$

$$E'' = E_m''(A/C) + E_m'(B/C) \tag{I-2}$$

where

$$A = (1 - c)(1 + \alpha c)\gamma(E_m^{2'} + E_m^{2''}) + (1 - c)(\alpha + c)\,\alpha\beta^2\gamma(E_i^{2'} + E_i^{2''})$$
$$+ [(1 - c)^2\alpha + (\alpha + c)(1 + \alpha c)]\beta\gamma(E_m'E_i' + E_m''E_i'') \tag{I-3}$$

$$B = \beta\gamma(\alpha + 1)^2c(E_i''E_m' - E_m''E_i') \tag{I-4}$$

$$C = (1 + \alpha c)^2(E_m^{2'} + E_m^{2''}) + (1 - c)^2\alpha^2\beta^2(E_i^{2'} + E_i^{2''})$$
$$+ 2(1 + \alpha c)(1 - c)\alpha\beta(E_i'E_m' + E_m''E_i'') \tag{I-5}$$

also

$$\tan \delta = E''/E' = \frac{(B/A) + (\tan \delta)_m}{1 - (\tan \delta)_m(B/A)}. \tag{I-6}$$

The second term in the denominator will generally be small; thus, the loss tangent of the composite will be approximately equal to the matrix loss tangent plus the term B/A, which may be written as

$$B/A = c(\alpha + 1)^2[(\tan \delta)_i - (\tan \delta)_m]/\{(1 - c)(1 + \alpha c)[1 + (\tan \delta)_m{}^2](E_m{}'/\beta E_i{}')$$

$$+ (1 - c)(\alpha + c)\alpha\beta[1 + (\tan \delta)_i{}^2](E_i{}'/E_m{}')$$

$$+ [(1 - c)^2\alpha + (\alpha + c)(1 + \alpha c)][1 + (\tan \delta)_m(\tan \delta)_i]\}. \quad \text{(I-7)}$$

Equivalent expressions for G' and G'' can be obtained by substituting shear moduli for Young's moduli throughout and letting $\beta = \gamma = 1$.

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