

On the Modulus of Three-Component Particulate-Filled Composites

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Synopsis

Modulus-composition data obtained on a model three-component particulate composite comprising a finely divided dispersed rubber phase and inorganic glass beads in a poly(methyl methacrylate) (PMMA) matrix cannot be represented appropriately in terms of the multicomponent form of the well-known Kerner equation. The data are more nearly in accord with a model based on the assumption that the dispersed rubber phase and the PMMA matrix, taken together, constitute an effective matrix for the glass bead filler. Interparticle interactions are discussed in terms of a maximum packing fraction for each filler species; interspecies interactions are found to be minor for the system studied.

INTRODUCTION

Most theoretical and experimental work on the modulus of particulate-filled polymer composites has been restricted to binary systems. This work has been reviewed by Nielsen¹ and by Hashin.² A number of additional pertinent references are listed in Dickie.³ Some work⁴⁻⁸ has also been reported on ternary systems containing a structured particulate filler such as a layered sphere or a particle containing multiple inclusions. The present paper discusses the properties of a composite material comprising two different species of particulate filler in a polymer matrix.

THEORETICAL

In previous papers,^{3,8,9} we have discussed the dependence of dynamic Young's modulus (E^*) and elastic Young's modulus (E) on composition and morphology. It was reported that an acceptable representation of data on a number of two-phase acrylic polyblends could be obtained by modifying the well-known Kerner equation for modulus¹⁰ to account for interparticle interactions. Additional corrections for copolymerization effects and partial phase inversion (to produce a dispersed phase containing subinclusions of matrix material) were introduced for specific systems. None of these modifications changes the basic form or functional dependence of Kerner's equation, however.

Kerner's original treatment¹⁰ was written for an n -component system; after some algebra, eq. (8) of ref. 10 can be written in the form

$$n_0 = G_0/G_1 = \frac{1 + \sum \frac{v_i(n_i - 1)}{1 + \alpha n_i}}{1 - \alpha \sum \frac{v_i(n_i - 1)}{1 + \alpha n_i}} \quad (1)$$

where $n_i = G_i/G_1$ and $\alpha = 2(4 - 5\nu_1)/(7 - 5\nu_1)$. Here, G is shear modulus, ν is Poisson's ratio, v is volume fraction, and subscripts 0, 1, and i refer to the properties of the composite, the matrix, and filler species i , respectively. Summations are carried out over all filler species.

For a binary composite, the Halpin-Tsai equation^{11,12} is

$$n_0 = G_0/G_1 = (1 + \zeta\eta v_f)/(1 - \eta v_f) \quad (2)$$

where $\eta = (n_f - 1)/(n_f + \zeta)$, subscript f refers to the (single) filler species, and ζ is a measure of reinforcement. Equation (2) reduces to the two-component form of eq. (1) if $\zeta = 1/\alpha$. Ashton, Halpin, and Petit¹¹ have suggested that, if two or more reinforcements are uniformly mixed in a common matrix, one should compute $(n_0)_a$ for reinforcement "a" using eq. (2), then incorporate reinforcement "b" into the composite calculation through a second application of eq. (2), employing $(n_0)_a$ as the effective matrix modulus. There does not appear to be a theoretical basis on which

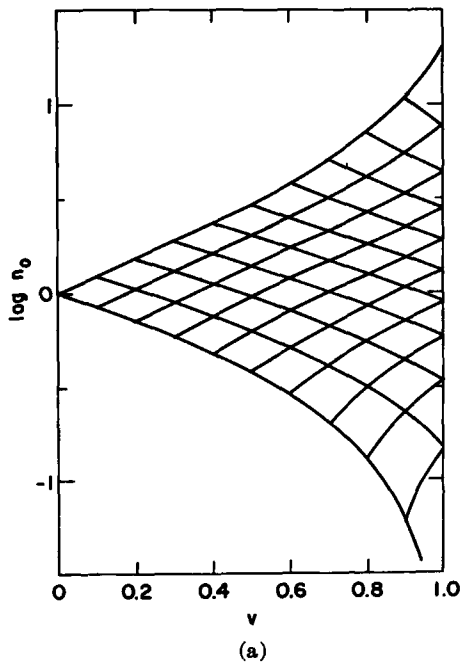
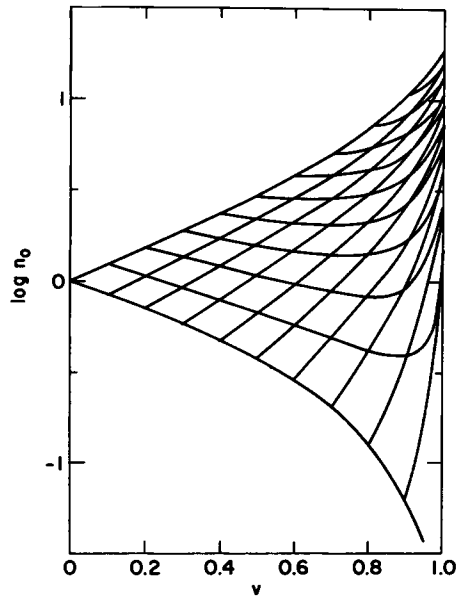
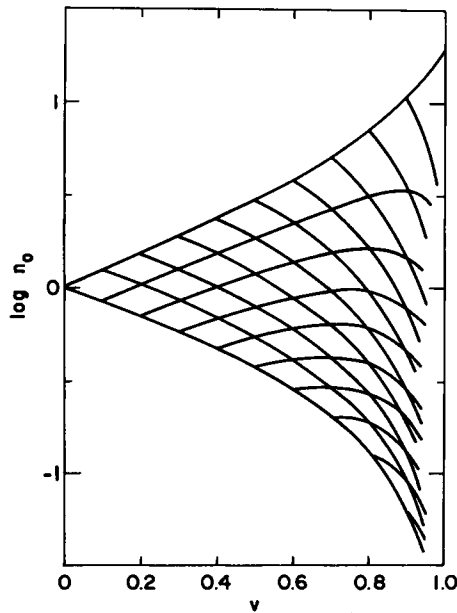


Fig. 1 (continued)



(b)



(c)

Fig. 1. Dependence of modulus ratio $n_0 \equiv G_0/G_1$ on total filler concentration v for three-component composite comprising a matrix of unit modulus and two particulate fillers of modulus 4×10^{-4} and 20: (a) computed according to eq. (1); (b) and (c) computed by successive application of eq. (2), assuming (for B) soft filler in an effective matrix of hard filler in unit modulus material and (for c) a hard filler in an effective matrix of soft filler in unit modulus material.

to choose the order in which this two-stage calculation should be carried out, although the expressions obtained for n_0 by successive application of eq. (2) are not symmetric with respect to the order of addition of fillers and are not equivalent to eq. (1) written for a ternary composite. However, the numerical difference between the two methods of application of eq. (2) are inconsequential if the two fillers have similar moduli, or if one or both filler volume fractions are small.

Significant differences among the three possible treatments for a ternary particulate composite do arise when the two filler species have substantially different moduli. To illustrate qualitatively these differences, calculations have been performed assuming a matrix of unit modulus containing two particulate fillers of modulus 4×10^{-4} and 20 (arbitrary units). These values correspond to what might be observed for a two-phase rubber-modified polymer system (such as high-impact polystyrene) containing a particulate inorganic filler (such as glass beads, clay, or a pigment).

Figure 1a represents results obtained for the modulus of this system as a function of total filler volume fraction v , by application of eq. (1). Figures 1b and 1c present results obtained by successive application of eq. (2). Isoleths connecting points of constant filler volume fraction have been constructed for each filler species at 0.1 increments of volume fraction. In Figure 1a, both sets of volume fraction isopleths are monotonic functions of concentration and roughly parallel the appropriate $v_i = 0$ isopleth. In Figure 1b, the soft-filler isopleths are monotonically increasing, but the hard-filler isopleths display a pronounced minimum. In Figure 1c, hard-filler isopleths are monotonically decreasing, whereas the soft-filler isopleths display a maximum. Thus, at sufficiently high values of total filler volume fraction, there are qualitative as well as quantitative differences among the three methods of computation.

Packing fraction effects have not been included in these calculations. However, barring strong interspecies interactions, the effect of such terms should be essentially to compress the concentration scale for each species. Packing fraction effects have previously been accounted for^{8,9} by replacing volume fraction v by an effective volume fraction, v_{eff} , assumed to be a function of maximum packing fraction v_m . In general, v_m will not be the same for two different filler species, so it is to be expected that an experimentally determined modulus-composition diagram will be somewhat distorted as well as compressed along the concentration axis.

EXPERIMENTAL

Materials

Polymers used were rubber-modified poly(methyl methacrylate) compositions prepared as described elsewhere.⁸ These materials (referred to as HLP1's in ref. 8) are based on heterogeneous latex particles prepared by emulsion polymerization of methyl methacrylate on a cross-linked acrylic rubber seed latex (monomer composition: 95 mole-% butyl

acrylate, 5 mole-% 1,3-butylene dimethacrylate). The phase structure of the heterogeneous particles is sufficiently stable to allow fabrication of composites having a uniform spatial distribution of rubbery inclusions by compression molding. A comparable poly(methyl methacrylate) homopolymer (PMMA), prepared by emulsion polymerization, was also used.

Glass beads (Potter Brothers 325-) were washed in isopropanol; iron filings were removed magnetically. No attempt at fractionation was made. Glass beads were incorporated into the finely powdered polymers by ball milling; sheets were prepared by compression molding. Volume concentration of glass beads was determined by density measurement.

Modulus Measurement

Values of tensile modulus were obtained using an Instron Universal Testing Machine equipped with an x-y recorder and an Instron 0.5-in.-gauge-length, 10%-maximum-strain, clip-gauge extensometer. Tensile specimens were of the usual dog-bone shape (reduced gauge section 0.250 in. wide, 0.08 in. thick, nominal parallel gauge length 1.0 in.) and were pulled at a cross-head speed of 0.04 in./min. Modulus measurements are based on the initial slope at strains less than about 0.3%; stress-strain curves displayed substantial nonlinearity at strains greater than about 0.5%.

RESULTS AND DISCUSSION

Four sets of composites varying in glass bead concentration from $v = 0$ to $v \approx 0.45$ were prepared from PMMA and three HLP1 compositions; the latter contained 0.27, 0.53, and 0.77 volume fraction acrylic rubber. The results of modulus determinations on these materials are presented in Figure 2 plotted at constant polymer phase composition versus v_G , the volume fraction of glass beads. Since the polymer phase composition is constant along each of the four curves drawn in the figure, the value of v_R , the volume fraction of rubber in the composite v , decreases with increasing v_G along each curve:

$$v_R = (v_R)_{v_G=0} (1 - v_G) \quad (3)$$

In order to construct a modulus-composition diagram comparable to those presented in Figure 1, vertical sections (at constant values of v_G) are constructed through the curves of Figure 2. Values of v_R are computed from eq. (3), and a plot of tensile modulus as a function of v_R at constant values of v_G is prepared (Fig. 3). Now, by taking vertical sections through the curves of Figure 3, the required modulus-composition diagram (Fig. 4) can be prepared and v_R and v_G isopleths constructed for comparison with Figure 1. There is a strong qualitative similarity between Figure 4 and Figure 1c (note the maximum in the v_R isopleths), implying that eq. (1), the multicomponent form of the Kerner equation, is not appropriate for representation of these data and that, empirically, the proper treatment

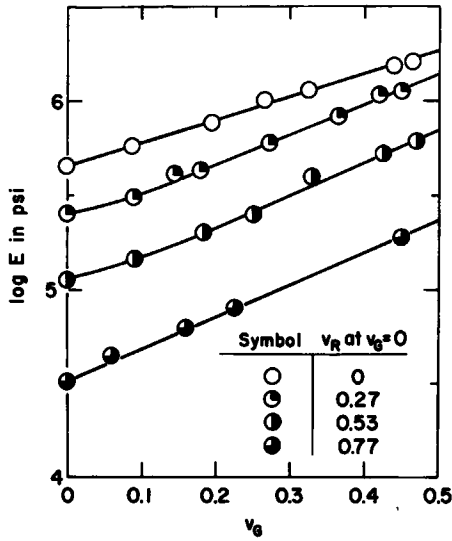


Fig. 2. Dependence of tensile modulus on volume fraction of glass beads for PMMA and three HLP1's.

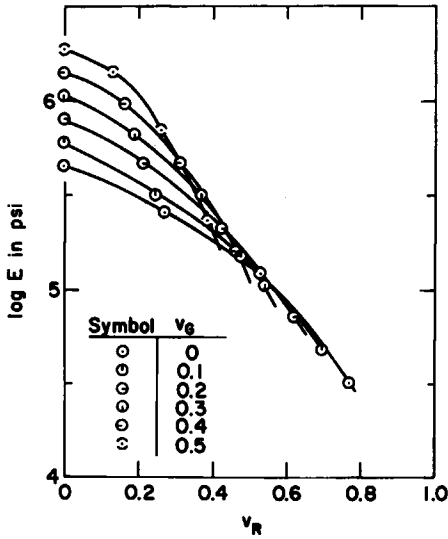


Fig. 3. Dependence of tensile modulus on volume fraction of rubber at constant values of v_g . Derived from Fig. 2 as explained in text.

is a two-stage calculation employing eq. (2) with the dispersed rubber phase and PMMA matrix taken together considered an effective matrix for the glass bead filler.

Quantitatively, the dependence of modulus on concentration is somewhat more pronounced than predicted. However, this is just what is expected from interparticle interactions (maximum packing fraction ef-

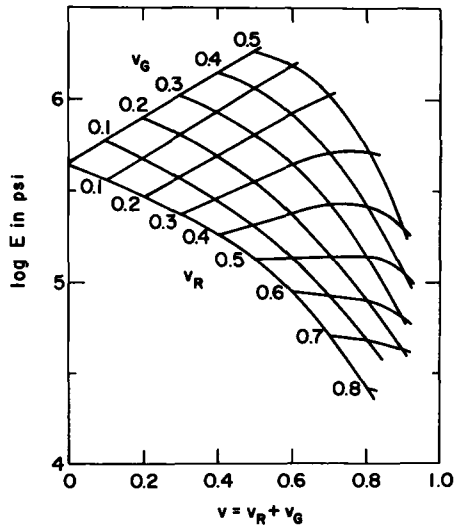


Fig. 4. Dependence of tensile modulus on total filler concentration. Derived from Fig. 3 as explained in text.

fect). It is by no means clear how the concept of maximum packing fraction should be introduced for ternary composites in general. A number of factors can be expected to play a role: for each filler species independently, size distribution and filler particle deformability are important; the ratio of filler to matrix modulus may also be important (unpublished data of the author indicate that maximum packing fraction may pass through a shallow maximum as the filler-matrix modulus ratio goes through unity). When two filler species are present, additional factors enter, including relative size and stiffness of the two species.

In the present case, the filler species differ by about three orders of magnitude in diameter and by about four orders of magnitude in modulus. Also, the qualitative dependence of modulus on concentration indicates that the glass beads effectively "see" a uniform matrix. We therefore expect little interspecies interparticle interaction effect.

In ref. 8, it was found that the dependence of modulus on concentration for rubber-modified materials of the type used in this study could be described in terms of eq. (1) (written for a binary composite), provided that the volume fraction of filler v_f was replaced by an effective volume fraction, v_{eff} , a function of v_m , the maximum packing fraction, and, of course, also of v_f . The form assumed for v_{eff} was one proposed by Nielsen¹³:

$$v_{eff} = [1 + v_f(1 - v_m)/v_m^2] v_f. \quad (4)$$

A value of 0.8 to 0.83 was assigned to v_m . There are cogent reasons^{8,13} for selecting a form such as eq. (4) for v_{eff} ; however, these reasons are based primarily on expected modulus (or viscosity) behavior at small

volume fractions of filler. For the data presently available on the HLP1's used in this and our previously reported work,^{8,9} a nearly equivalent representation is obtained simply by assuming that the effective volume fraction v_{eff} is given by v_f/v_m , with $v_m = 0.85$. In Figure 5a are plotted values of v_{eff} (calculated from observed moduli and the two-component form of eq. (1) with v_{eff} substituted for v_f) as a function of v_R .

A similar analysis of data has been undertaken on the glass bead-filled materials, using the data presented in Figure 2. Calculated values of v_{eff} are plotted in Figure 5b as a function of v_G . These data are reasonably well represented by $v_{eff} = v_f/v_m$ with $v_m = 0.65$, or somewhat less accurately by eq. (4) with $v_m = 0.6$.

The effect of rubbery filler on v_m is apparently minor; the best slopes through individual groups of points give values of v_m from 0.6 to 0.7. These

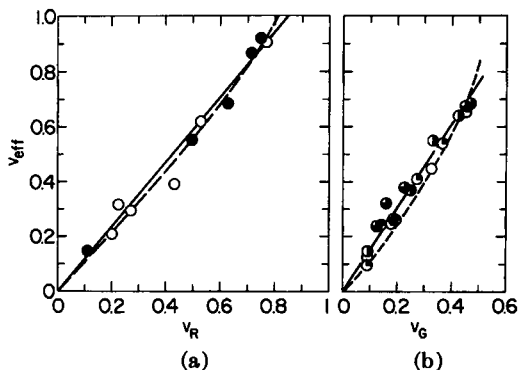


Fig. 5. Dependence of v_{eff} on v : (a) For rubber in HLP1's; filled points, data from ref. 8; open points, data from this work; solid line, $v_{eff} = v_f/0.85$ broken line v_{eff} calculated from eq. (4) with $v_m = 0.83$. (b) For glass heads in PMMA and three HLP1 compositions; key as for Fig. 2; solid line, $v_{eff} = v_f/0.65$; broken line, v_{eff} calculated from eq. (4) with $v_m = 0.6$.

differences may be due to differences in matrix modulus or to slight differences in agglomeration of beads.

Although only minor, if any, interspecies interactions can be inferred from the present data, this result is probably specific to composites of the same general type, i.e., those containing a relatively large, hard particulate filler, and a relatively small, soft dispersed rubber phase in a polymer matrix. Preliminary measurements on the dynamic mechanical properties of composites containing two particulate polymeric fillers of different T_g indicate that such a system may exhibit stronger interspecies interactions than seen in the present work.

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