Predicting Elastic Moduli of Heterogeneous Polymer Compositions

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Synopsis

A new method for predicting elastic moduli M of heterogeneous polymer compositions is proposed. It is based on a phenomenological adjustment between parallel and series models for upper and lower bound moduli M_U and M_L. Thus,

$$M = \phi_H{}^n(n\phi_S + 1)(M_U - M_L) + M_L$$

where ϕ_H is the volume fraction of hard phase, ϕ_S is the volume fraction of soft phase, and n is the only adjustable parameter since the upper and lower bound moduli are given by

$$M_U = \phi_H M_H + \phi_S M_S$$

and

$$M_L = (\phi_H/M_H + \phi_S/M_S)^{-1}$$

where M_H and M_S are the moduli of the pure hard and soft phases, respectively. Predicted values of M are in agreement with measured values in a number of systems which include polyblends and composite materials of fixed morphology. The significance of n is discussed relative to concentrations in the area of a phase transition for the polyblends *or* relative to phase morphology in the case of fixed morphology compositions. Interestingly, the relationship, by analogy, is in agreement with measured values of polyblend melt viscosities.

INTRODUCTION

Many methods for predicting elastic properties of heterogeneous materials have been used. They have been applied to such systems as filled resins, filled rubbers, fiber-reinforced resins, block polymers, polyblends, and interpenetrating or interstitially polymerized network structures. Earlier methods were based on a modulus–viscosity analogy using Einstein's relation for the viscosity[1] of a suspension of rigid spheres in a fluid. Examples of this are found in work by Smallwood,[2] Guth,[3] and Mooney.[4] The last of these introduced a crowding factor to account for the effects of packing. Later, Kerner[5] devised a theory based on the effect of hydrostatic stresses on a single spherical particle imbedded and well bonded to its matrix. Hashin and Shtrikman[6] have also proposed relationships

based on spherical particulate geometry. In the Kerner-type formulations, the imbedded spheres are no longer rigid; they have finite elastic properties and can even be softer than the matrix. Kerner's equations were recast as the Halpin-Tsai[7] equations which accommodated nonspherical particulate geometry. Lewis and Nielsen[8] then applied a packing or crowding factor similar to that of Mooney to the Halpin-Tsai equations.

The above models all assume that a discrete particulate phase is dispersed in a continuous matrix phase. If phase geometry is not known, the Kerner equations and their like can be used to predict upper and lower limits by assuming the hard phase continuous or the soft phase continuous. Upper and lower limits calculated in this way, for a given composition containing hard and soft phases, are somewhat closer together than calculations of the elementary series and parallel models.

More recently, Davies[9] has proposed a new relationship which is thought to be suited for systems in which both phases are continuous at all concentrations of hard or soft phase. This relationship states volume additivity of shear moduli raised to the $\frac{1}{5}$ power. The relationship is simple and describes well the relation between composition and modulus in some instances.[10] However, it is limited again to specific phase geometry.

A more general approach has been taken by Takayanagi et al.[11] It was assumed that a two-phase material can be treated as a mixture of series and parallel elements. Two models were used. Each model was treated in two dimensions. Rectangular areas were taken as a volume. Generally, for each composition, fitting parameters relating to model geometry are evaluated. These parameters then vary with hard/soft composition. Thus, the value of this approach for predicting the properties of various compositions is doubtful.

As Nielsen has pointed out, in systems of block polymers and polyblends, the phase morphology changes with composition.[12] In these cases, such parameters as packing factors and various methods of handling domain–domain interactions lose meaning. Continuous materials containing no voids can be made at any ratio of hard phase to soft phase. Both phases of such compositions are frequently in the liquid state during preparation. Morphologic accommodation is then completely facilitated.

In this report, an approach to predicting moduli of compositions of systems wherein the phase morphology is a function of hard or soft volume fraction is described. The approach is merely a phenomenological adjustment between the parallel and series models for upper and lower limits of modulus. The treatment was developed for rubber/resin polyblends but is applicable to most other types of systems.

THEORY

When two polymers are mixed in the melt and then cooled, the resulting composition generally comprises two phases. One phase largely consists of one polymer; the other phase largely consists of the other polymer. If the elastic moduli of the two polymers differ, the phase morphology can be such that the hard phase can be continuous, the soft phase can be continuous, or both phases can be continuous. Now it is agreed that the modulus (either Young's or shear) of the mixture must be between the parallel model upper bound, M_U, and the series model lower bound, M_L, given by the equations
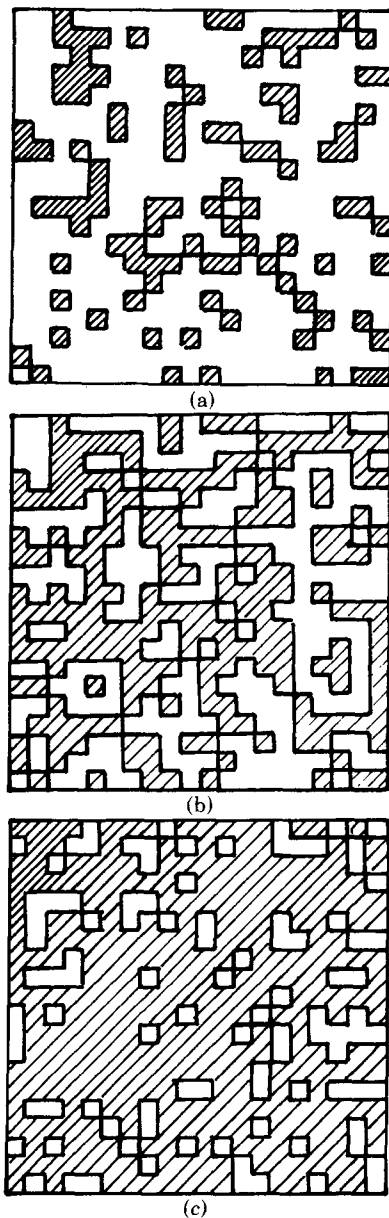
Fig. 1. Cross sections of idealized compositions: (a) $\phi_H = 0.25$; (b) $\phi_H = 0.5$; (c) $\phi_H = 0.75$. Dark area represents hard phase.

$$M_U = \phi_H M_H + \phi_S M_S \qquad (1)$$

and

$$M_L = (\phi_H/M_H + \phi_S/M_S)^{-1} \qquad (2)$$

where M_H and M_S are the moduli of the pure hard and soft phases, and ϕ_H and ϕ_S are the volume fractions of the hard and soft phases, respectively. The modulus M of the two-phase composition or composite can then be written

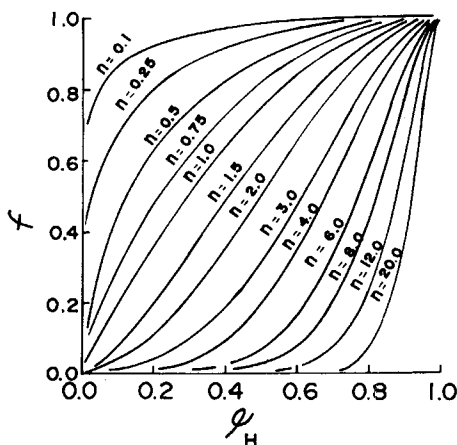$$M = f(M_U - M_L) + M_L \qquad (3)$$

Fig. 2. Parameter f as a function of n and volume fraction of hard component.

where the parameter f can vary between zero and unity. The value of f would be a function of phase morphology. If only the soft phase were continuous, f would be low; if only the hard phase were continuous, f would be closer to unity. Likewise, the case of interpenetrating phases, wherein both phases are continuous, would be characterized by intermediate values of f.

The phase morphology of mixtures frequently varies with ϕ_H or ϕ_S. This is especially true when compositions are prepared by mixing the two polymers at such a temperature that both are molten. A common type of change in phase morphology with ϕ_H is illustrated by the idealization of Figure 1. Here monodispersed cubic particles of hard material are randomly placed in a cubic lattice of a soft matrix. In Figure 1a, ϕ_H is 0.25; the soft phase is essentially continuous and the hard phase is dispersed. The series model M_L is favored, and f has a low value. In Figure 1b, both phases are largely continuous; f may be near 0.5, and M may be near the arithmetic mean of M_U and M_L. Similarly, in Figure 1c, ϕ_H is 0.75, and the soft phase is essentially dispersed in the continuous hard phase. Thus, the parallel model M_U is approached, and f is near unity.

In the case of Figure 1, f is clearly a function of ϕ_H or ϕ_S. The value of f will most rapidly change with ϕ_H where ϕ_H is 0.5, which corresponds to a phase transition or inversion. This can be approximated by

$$\frac{df}{d\phi_H} = 6\phi_H\phi_S \tag{4}$$

which integrates to

$$f = 3\phi_H{}^2 - 2\phi_H{}^3 \tag{5}$$

since ϕ_S is $1 - \phi_H$. A more general case, wherein the transition can occur other than where $\phi_H = 0.5$, is

$$f = \phi_H{}^n(n\phi_S + 1) \tag{6}$$

If n is 2.00, the case of eq. (5) is realized. Figure 2 illustrates how f can vary with ϕ_H and n.

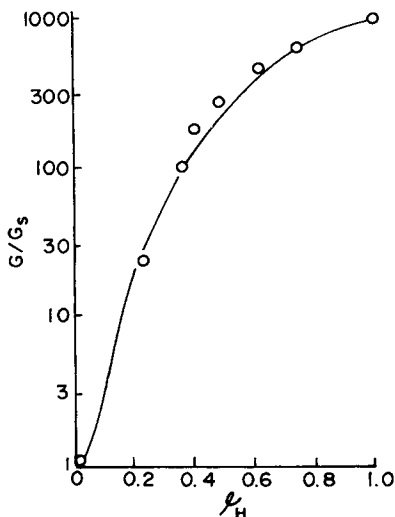Combining eq. (6) with eq. (3), we now write

Fig. 3. Relative shear modulus of EPDM/polypropylene polyblends. Circles are experimental observations; solid line is calculated.
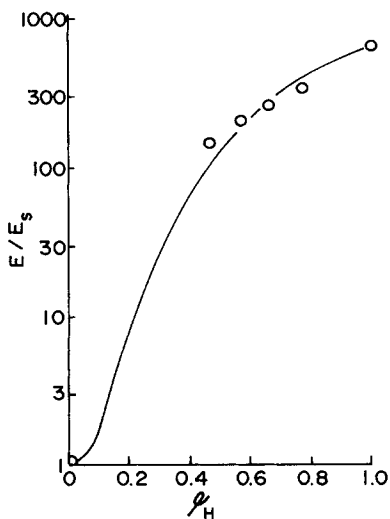

Fig. 4. Relative Young's modulus of ABS compositions. Circles are experimental observations; solid line is calculated.

$$M = \phi_H{}^n(n\phi_S + 1)(M_U - M_L) + M_L \qquad (7)$$

When M lies between M_L and M_U, it is expressed as a function of only one fitting parameter, n. The parameter n, then, must contain aspects of dispersed particulate shape, wetting, molecular interpenetrability, thermodynamic compatibility, interdomain interference, etc.

Certain statements about the nature or significance of the parameter n can be made from inspection of the equations. In the case of aligned continuous fiber morphology, the longitudinal Young's modulus would be characterized by a value of zero for n. Equation (7) then reduces to M_U or the volume rule of mixtures.
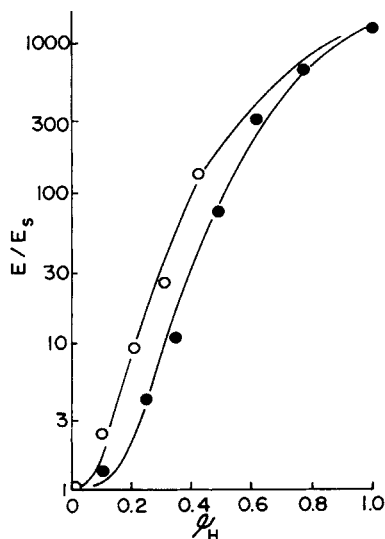
Fig. 5. Relative Young's modulus of polystyrene/rubber blends and triblock copolymers. Circles are experimental observations; solid lines are calculated.

Transverse Young's modulus for aligned laminated plate morphology would be characterized by an infinite value for n. Since the change in f in respect to ϕ_H is greatest when ϕ_H is $(n - 1)/n$, $(n - 1)/n$ would be related to a packing volume (ϕ_m) of the type used by Lewis and Nielsen. This, of course, could only apply to systems of fixed phase morphology in which nonmelting hard particles of fixed shape are dispersed in a continuous soft phase. In the case of melt-mixed polyblends and block polymers in which phase morphology depends on ϕ_H or ϕ_S, the composition where ϕ_H is equal to $(n - 1)/n$ could be viewed as a point of transition or phase inversion.

In addition to predicting moduli, the method of eq. (7) might be used to predict viscosities of mixtures of molten polymer phases. By analogy,[2] then, eq. (7) would be written

$$\eta = \phi_v{}^n(n\phi_{fl} + 1)(\eta_U - \eta_L) + \eta_L \qquad (8)$$

where ϕ_v = the volume fraction of the more viscous phase, ϕ_{fl} = the volume fraction of the more fluid phase, $\eta_u = \phi_v\eta_v + \phi_{fl}\eta_{fl}$, $\eta_L = (\phi_v/\eta_v + \phi_{fl}/\eta_{fl})^{-1}$, η_v = viscosity of the more viscous phase, and η_{fl} = the viscosity of the more fluid phase.

APPLICATION OF THE THEORY

Examples taken from elsewhere will be used to demonstrate the application of the theory to experimental results. Figure 3 is an example of a polyblend system.[13] Polypropylene was melt blended with EPDM rubber. Shear moduli of compression-molded sheets were determined at 25°C using a torsion pendulum. A value of 2.0 was selected for n to give the best fit of the data. This would indicate that, as ϕ_H is increased, a transition or inversion occurs near where ϕ_H is 0.5. In this case, the maximum change in f in respect to ϕ_H, at ϕ_H = 0.5, is likely due to a rapidly changing phase morphology with changes in ϕ_H. The
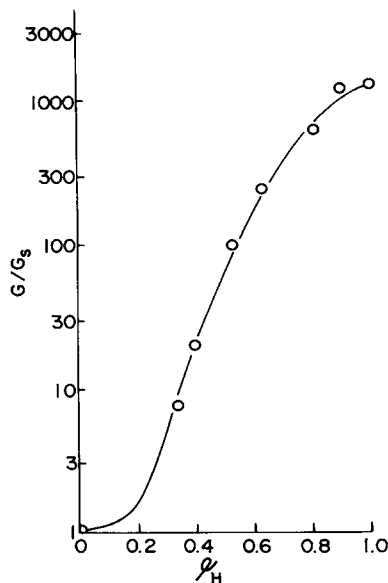
Fig. 6. Relative shear modulus of nylon 6/polyether block polymers. Circles are experimental observations; solid line is calculated.

situation could be similar to the idealization of Figure 1. At any rate, the theory fits the data reasonably well.

An example of an acrylonitrile–butadiene–styrene (ABS) polymer system reported by Uemura and Takayanagi[14] is illustrated by Figure 4. Here, the dynamic Young's modulus is plotted against the volume fraction of the hard acrylonitrile–styrene (An–St) polymer. A value of 2.5 was selected for n to give the best fit of the data. Again, eq. (7) fits the data reasonably well. Since morphology can vary with ϕ_H, the significance of the hard phase concentration, $\phi_H = 0.60$, corresponding to the maximum rate of change in f with ϕ_H is not known.

Figure 5 shows a contrast between a block copolymer system and a blend system. In both cases, the hard polymer is polystyrene, and the soft phases are similar, styrene–butadiene rubber (SBR) in the blend and polybutadiene in the block copolymer. The data relating to the blends are due to Kraus,[15] and the data relating to block polymers are in respect to a series of styrene–butadiene–styrene (SBS) triblock polymers reported by Holden et al.[16] and discussed by Nielsen.[12] A value of 2.95 was required to fit the case of blends, while a value of 4.5 was appropriate for the copolymer case. This would correspond to value of ϕ_H in the region of transition of 0.66 for the blend, but 0.78 for the copolymer. It is thus apparent that the changes in morphology with ϕ_H are quite different for the copolymers than for the blends. Possible morphologies of these two systems have been discussed by Nielsen.[12] Importantly, again the data are consistent with eq. (7).

A series of nylon 6/polyether block polymers is treated in Figure 6.[17] The values were measured at $-10°C$. As in the case of the SBS copolymers, n is a high value; in this case, it is 5.1. Though the segments of the SBS and the nylon 6/polyether system are vastly different, it is indicated that morphology changes with ϕ_H in each case in a similar fashion. It remains to be demonstrated, however, that all block polymers give high values of n.
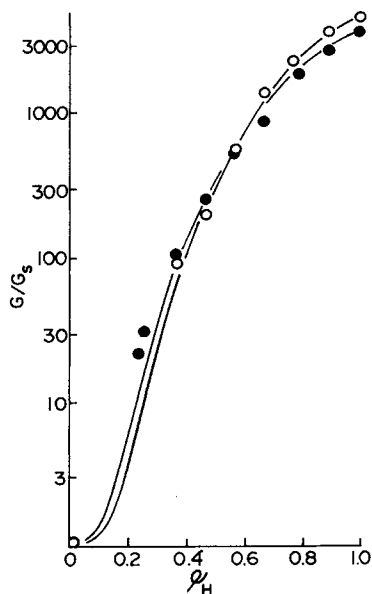
Fig. 7. Relative shear modulus of composites formed by interstitial polymerization of PAN/ure-thane and PMMA/urethane. Circles are experimental observations; solid lines are calculated.

Another type of system which has given high values of n is illustrated by Figure 7. These data relate to composites formed by interstitial polymerization of vinyl monomers in polyurethane elastomers reported by Allen et al.[10] Here, the ingredients for forming urethane elastomer networks are mixed with either methyl methacrylate or acrylonitrile. The urethane network forms, and then the vinyl monomer polymerizes. Both the poly(methyl methacrylate) (PMMA) and the polyacrylonitrile (PAN) systems give higher values of n, similar to those obtained for the block polymers. Morphologic studies indicated that the composites consisted of roughly spherical hard domains in a continuous elastomer matrix. However, it was further indicated that interactions as interconnections between the hard domains did, in fact, exist. It should be noted also that the Davies[9] equation which assumes interpenetrating phases fits the modulus–composition data fairly well. The rather large value of n needed to fit data relating to both the interstitial composites of Allen et al. and the block copolymer data as well may be related to a wide range of ϕ_H over which the phases are each interconnected.

The ability of eq. (8) to predict the viscosities of molten compositions is demonstrated by the plotted values in Figure 8. The data relate to melted blends of polyethylene and the more viscous polybutene-1 studied by Uemura and Takayanagi.[14] Again, the agreement between observed and calculated values is good. The value of n selected to fit the data was 3.0. This is similar to the values of n used to fit modulus data in the polyblends considered above.

In addition to the above systems which can be of variable morphology, systems of fixed morphology were studied. Composites of fixed morphology are those in which only one of the phases can flow during preparation of fabrication. Systems of fixed morphology include resin/fiber composites, glass bead/resin composites, ribbon/resin composites, graphite flake/resin composites, and the like.
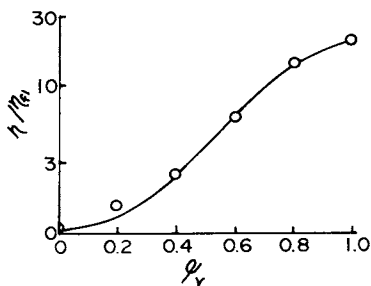
Fig. 8. Relative viscosity of molten polyblends of polyethylene and polybutene-1. The polybutene-1 phase is the more viscous, hence ϕ_v is the volume fraction of polybutene-1. Circles are experimental observations; solid line is calculated.
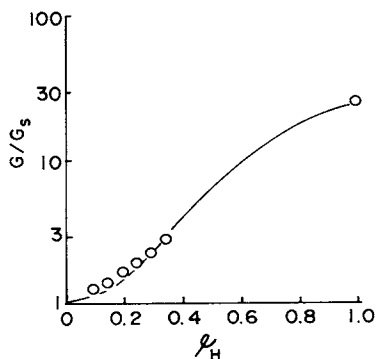

Fig. 9. Relative shear modulus of glass bead/epoxy resin composites. Circles are experimental observations; solid lines are calculated.

The case of glass beads in epoxy resin is given by Figure 9. These data were taken from Lewis and Nielsen.[8] Here, a value of 2.5 for n was required. This corresponds to a value of 0.60 for ϕ_H where f increases most rapidly with ϕ_H. This is not far from the value of ϕ_m (0.64), the maximum packing fraction used by Lewis and Nielsen to fit their data to the modified Halpin-Tsai equation.

Figure 10 contains data of Hirai and Klein.[18] It relates to graphite flake–epoxy resin composites. Here, a value of 0.75 was required for n. This would indicate a large interaction or connectivity between the flakes. The parallel model M_U is somewhat favored. The data of Figure 11 relate to aligned continuous carbon fiber/epoxy resin composites. The work was reported by Adams and Bacon.[19] For Young's modulus, a value of 0.6 was used for n. This again indicates a preference for the parallel model M_U. It would have been expected that n approach zero in this case, since the specimens were carefully prepared and the volume rule of mixtures should have been realized. These authors discuss to some extent the deviation of their data from the volume rule of mixtures.

Figure 11 also contains Adams and Bacon's data for shear moduli of the aligned carbon fiber composites. In this case, a value of 4.7 was required for n. In the case of the longitudinal shear modulus of aligned composites, as opposed to the case of longitudinal Young's moduli, a packing effect should be meaningful. The value of 4.7 for n gives a value of 0.79 for ϕ_H where f changes most rapidly with ϕ_H. The value 0.79 is of the magnitude expected for the close packing of rods. It should be noted that Adams and Bacon reported results relating to several
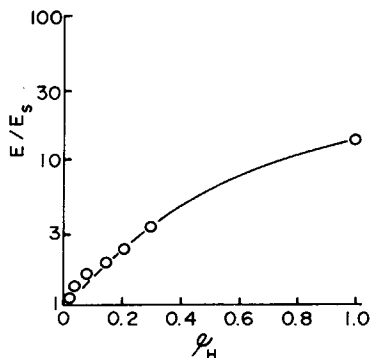
Fig. 10. Relative modulus of graphite flake/epoxy resin composites. Circles are experimental observations; solid line is calculated.
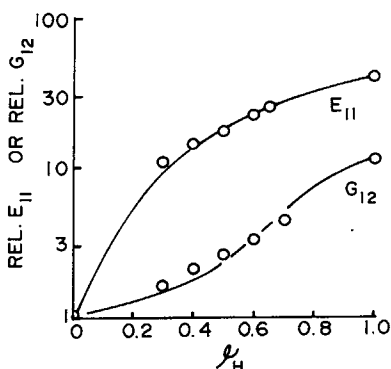

Fig. 11. Moduli of graphite fiber/epoxy resin composites. Circles are experimental observations; solid lines are calculated.

series of carbon fiber composites. Average values corresponding to each level of ϕ_H were used in Figure 11.

The application of the theory to experimental data is summarized in Table I. The agreement between observed properties (P) and calculated properties (P_{calc}) is indicated by the coefficients of variations (S_p). These are standard errors of estimating properties expressed as fractions of the calculated values. Thus,

$$S_p = \sqrt{\frac{\Sigma[(P - P_{calc})/P_{calc}]^2}{N}} \tag{9}$$

where N is the number of data points excluding, of course, the points corresponding to properties of pure components, which can be determined only experimentally. The number of degrees of freedom for error, values of which also are in Table I, is $N - 1$.

The coefficient of variation is 21% overall, with 54 degrees of freedom for error. This indicates good agreement since the range of data points is about $2\frac{1}{2}$ decades on the average. In addition, Table I indicates the possibility of broad application of the theory since values of shear modulus, Young's modulus, and viscosity were predicted for a wide variety of systems. It should be noted here that essentially all the data analyzed prior to this writing were used. Considering the simplistic

TABLE I
Summary of Applications

Type of composition	Hard phase	Soft phase	Morphological description	Property measured	n	$\frac{n-1}{n}$	Coefficient of variation, % (degrees of freedom/range of data, decades)	Ref./ Fig. no.
Blend	polypropylene	EPDM rubber	variable	G	2	0.5	20 (5/3.0)	13/3
Graft	AN–St	polybutadiene	variable	E	2.5	0.6	24 (3/2.8)	14/4
Blend	polystyrene	SBR	variable	E	2.95	0.66	28 (3/3.1)	15/5
Block co-polymer	polystyrene	polybutadiene	variable	E	4.5	0.78	25 (5/3.1)	16/5
Block co-polymer	nylon 6	polyether	variable	G	5.1	0.80	14 (5/3.1)	17/6
Interstitial composite	PMMA	urethane	polydisperse hard spheres in soft rubbery matrix	G	4.5	0.78	16 (5/3.7)	10/7
Interstitial composite	PAN	urethane	polydisperse hard spheres in soft rubbery matrix	G	4.0	0.75	39 (7/3.5)	10/7
Molten blend	polybutadiene	polyethylene	variable	η	3.0	0.67	10 (3/1.3)	14/8
Composite	glass	epoxy	glass spheres in epoxy matrix	G	2.5	0.5	9 (5/1.4)	8/9
Composite	graphite	epoxy	graphite flakes in epoxy matrix	E	0.75	—	11 (5/1.1)	18/10
Composite	carbon fiber	epoxy	aligned fiber in epoxy matrix	E	0.6	—	9 (4/1.6)	19/11
Composite	carbon fiber	epoxy	aligned fiber in epoxy matrix	G	4.7	0.79	15 (4/1.1)	19/11

nature of the theoretical approach, the breadth and quality of agreement are remarkable, if not fortuitous.

It is interesting that both systems of variable and fixed morphology are described by eqs. (7) and (8). However, the interpretations of the significance of the parameter n are different in the variable and fixed systems. In systems of variable morphology, $(n - 1)/n$ probably indicates the approximate center of a range of concentrations ϕ_H wherein a transition or inversion occurs. It is interesting that in the polyblends, n is 2 to 3 corresponding to transition or inversion concentrations for ϕ_H of 0.5 to 0.67. However, in copolymer heterophase systems, the transition or inversion occurs near where ϕ_H is about 0.8. Composites formed by interstitial polymerizations give transitions at about the same values of ϕ_H as for the copolymers.

As stated before, $(n - 1)/n$ in systems of fixed morphology can correspond to a packing volume. However, when n is near 1.0 or less, this interpretation becomes meaningless. This occurs as the parallel model is approached. In the case of aligned fiber composites, ideally, the volume rule of mixtures is achieved in respect to longitudinal Young's modulus. In such cases, indeed, the concept of packing volume loses relevance since hard domains essentially do not move in respect to one another during deformation.

It should be noted that the type of morphology cannot be determined from n. Different types of systems can give the same value of n for different reasons. On the other hand, if the morphology is fixed and known, it is possible that n could be estimated from the packing fraction.

Regardless of the interpretation of the significance of n, in principle, only one mixed composition must be tested for its determination. If the properties of the pure components and one mixture are known, then properties of other mixtures can be estimated by the present method.

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