Three-Dimensional Models for Predicting the Modulus and Yield Strength of Polymer Blends, Foams, and Particulate Composites

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Two models are introduced to predict mechanical properties of two-component isotropic systems: (i) the cross orthogonal skeleton (COS) with co-continuous components and (ii) the cubic orthogonal skeleton (three perpendicular plates—3PP) with one component continuous and one discontinuous. Simultaneous prediction of the modulus and yield (or tensile) strength is based on phase continuity parameters (calculated for the two models) which serve as input data in an equivalent box model. At yielding (or breaking), the upper and lower bounds are distinguished which are related, respectively, to interfacial adhesion sufficient and insufficient for the transmission of stress inducing plastic deformation. The moduli and the upper bound of yield (or tensile) strength of the COS model, which is applied to polymer blends, are monotonic functions of composition. If partial or complete debonding occurs before yielding (or breaking), the corresponding strength passes through a minimum as a function of composition. The 3PP model renders an approximate prediction of the modulus and yield strength of closed-cell foams and particulate composites. Predicted dependences reasonably agree with those of other models and/or with experimental data from literature.

INTRODUCTION

Preparation of polymer blends and composites ranks among the most cost-effective ways of upgrading existing polymers. It is thus desirable to anticipate the values or limits of their mechanical properties, e.g., modulus E_b, yield strength S_{yb}, or tensile strength S_{ub} (subscript b stands for binary systems). When looking for an appropriate model, one should take care that the selected model meets all requirements concerning phase continuity, geometry of phases, symmetry of properties, etc., of the material under consideration. The available models are not versatile, but usually are suitable only for one or two of the three main categories of polymeric materials, i.e., fiber composites, particulate composites, and heterogeneous blends.

As for theory, it has achieved its highest level (1–11) for composites with continuous fibers. Mechanical properties of orthotropic laminae with uniaxially oriented fibers are usually calculated by the linear mixing rule (along the fibers) and the Halpin-Tsai equations (1, 5, 12–15) (across the fibers). The latter equations are only formally analogous to those of Kerner and Nielsen (7) or McGee and McCullough (16) for isotropic particulate composites. They are also in-dispensable for calculating elastic properties of the composites with uniaxially oriented short fibers or other non-isometric reinforcing elements. To calculate properties of composites with short fibers randomly oriented in a plane, a procedure called laminate analogy (1) gives satisfactory results. The strength of composites with continuous fibers is routinely evaluated by using criteria of maximum stress or maximum strain or maximum work (5), while the Halpin-Kardos equations (12–14) are used for short-fiber composites. Linear mixing rules, valid for parallel or series coupling of components, e.g. in laminae, are sometimes used as first approximations of the upper or lower bound of physical properties of isotropic heterogeneous blends, e.g., of modulus (16–20), yield strength (17, 20–22), tensile strength (7, 20), and permeability (23, 24). Obviously, these bounds lie far apart (25), and their application cannot be justified (26) from the viewpoint of the phase structure of blends.

Theoretical apparatus developed for particulate polymer composites consisting of a continuous matrix and a discontinuous filler (isometric reinforcement) is frequently modified for polymer blends, because both types of materials rank among heterogeneous isotropic materials. The modulus of particulate composites

can be calculated by means of several models (7, 16, 25, 27–31) which usually take into account the maximum achievable volume fraction of the dispersed phase. S_{yb} is frequently of primary importance because it represents the limit of allowable (tensile) stress. Several simple equations have been proposed (7, 17, 32–37) for S_{yb} of the particulate systems with poor interfacial adhesion where the discontinuous component merely reduces the cross section of the matrix transmitting the external load. If the term expressing the matrix cross section reduction is combined (37, 38) with an empirical exponential term, it is possible to fit (but not to predict) the experimental data on yield and tensile strength of both particulate composites and polymer blends. For particulate composites with interfacial adhesion strong enough to transmit acting stress up to fracture, the shear-lag analysis (originally used to predict tensile strength of short-fiber composites) was modified (39) for S_{ub} of composites with spherical particles. We have shown (40) that the derived formula also fits the dependence of yield strength of composites consisting of functionalized polypropylene and calcium carbonate. However, this approach is not applicable for ordinary polymer blends.

Polymer blends that are typical heterogeneous isotropic materials differ from particulate composites in two aspects: (i) their components are co-continuous over a wide interval of compositions; (ii) respective mechanical properties of polymer constituents are much closer to each other than properties of matrices and reinforcements in composites. The equations for the modulus or for the yield (or tensile) strength derived for particulate systems can be used also for blends, but only in the marginal composition intervals where the minority polymer is discontinuous. Thus, it is quite evident that models of mechanical properties intended for polymer blends have to allow for (i) respective properties of all components, (ii) a wide interval of co-continuity (phase duality) of constituents (41–43), and (iii) strength of interfacial adhesion. Recently, we have proposed (44) a new scheme for simultaneous prediction of the modulus and yield (or tensile) strength of binary blends that meets all these requirements. Our predictive scheme employs a two-parameter equivalent box model (EBM) and the data on the continuity of constituents acquired from general equations based on the percolation theory of two-component systems (45, 46). The predictive scheme was also successfully used for the prediction of permeability of binary polymer blends (47). The concept of phase continuity was used with regard to the fact that there is a lot of experimental evidence (7, 18, 48–51) that elastic, yield, and ultimate properties of blends are profoundly affected by the degree of continuity of constituents, though these properties are related to the phase structure in diverse ways. Let us point out that earlier the EBMs were viewed only as a convenient framework for systematic phenomenological description of elastic behavior of various systems (19, 52–56); the parameters (volume fractions) of the

EBMs were not predicted, but adjusted *a posteriori* by fitting experimental data.

The objective of this paper is to introduce two types of single-parameter models for binary *isotropic* systems with (i) both components co-continuous or (ii) one component continuous and the other discontinuous (throughout the whole composition range). The models assume the maximum achievable degree of phase continuity in three dimensions for (i) two or (ii) one component. Thus, they make possible the prediction of the modulus and yield (or tensile) strength for idealized structures approximating polymer blends with two co-continuous components, polymer foams with discontinuous pores or particulate composites. An important feature of the predictive scheme is that the simultaneously predicted mechanical properties are related to the same phase structure.

MODEL CONSIDERATIONS

The prediction of mechanical properties will be implemented in two steps: 1) the equations will be derived for properties under consideration in terms of the EBM (*Fig. 1*); 2) the volume fractions v_{ij} occurring in the EBM will be calculated for the cross orthogonal skeleton (COS) (*Fig. 2a*) and the cubic orthogonal skeleton, i.e., the model consisting of three perpendicular plates (3PP) (*Fig. 2b*). The COS and 3PP models are fully defined by the volume fractions of complementary components. To predict modulus or yield (or tensile) strength, both models require only respective val-
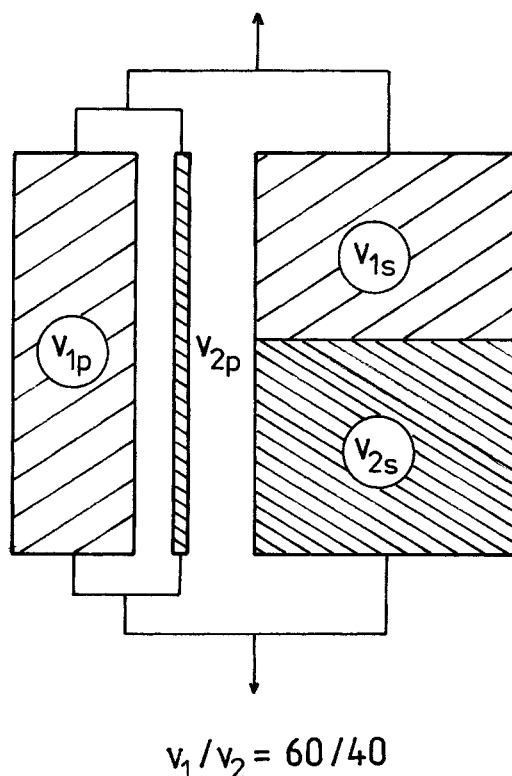

$$v_1 / v_2 = 60/40$$

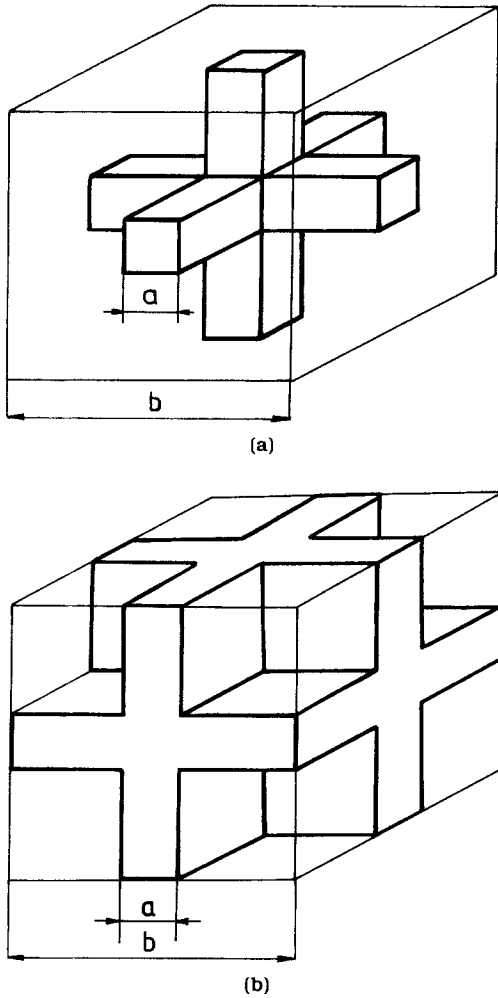*Fig. 1. Equivalent box model for a binary blend 60/40.*

Fig. 2. (a) Cross orthogonal skeleton model and (b) three perpendicular plates model (cubic orthogonal skeleton).

ues characterizing the components; other data, e.g., Poisson's ratio ν and bulk modulus, are not needed.

Equivalent Box Model: Equations for Modulus and Yield (or Tensile) Strength

The concept of the phase continuity (or connectivity) used in this paper is related to the well-known parallel and series box (or block) models (7, 15, 19, 28, 29). The parallel coupling of components implies that the strain of all constituents is equal (the isostrain model) and that the contribution of each component to the final value of a mechanical property is given by the (linear) rule of mixing. As all constituents (phases) are continuous in the direction of the acting force, the phase continuity degree, C_i, of each component can be considered equal to unity in this direction. The lines of force do not cross any interface so that the resulting mechanical properties of the composite system are independent of the interfacial adhesion. In the series coupling, all components are discontinuous in the direction of the acting force (the isostress model); thus, their continuity can be regarded as zero. Contributions of constituents to a system property are

expressed by the inverted rule of mixing. As all stress is transmitted through the present interfaces, interfacial adhesion between constituents is of primary importance.

Mechanical properties of isotropic heterogeneous materials cannot be accurately represented by a simple parallel or series model, but more complex models are required (44, 56). The EBM in *Fig. 1* is a two-parameter model as of four volume fractions v_{ij} only two are independent. The dimensions of blocks indicate which volume fractions of each constituent can be regarded as coupled in parallel or in series relative to the acting force so that the EBM response to loading may be equivalent to that of the modeled system. The fractions of either component coupled in parallel (subscript p) or in series (subscript s) are interrelated as follows:

$$v_{1p} = v_1 C_1; \quad v_{1s} = v_1(1 - C_1); \quad (1a)$$

$$v_{2p} = v_2 C_2; \quad v_{2s} = v_2(1 - C_2), \quad (1b)$$

where C_1 and C_2 are the phase continuity parameters. (It should be noted that "phase continuity" or "phase connectivity" may have different meaning in other papers, e.g., in ref. 41, 42, 46, 57). Besides, the following relations hold:

$$v_p = v_{1p} + v_{2p}; \quad v_s = v_{1s} + v_{2s};$$

$$v_1 = v_{1p} + v_{1s}; \quad v_2 = v_{2p} + v_{2s};$$

$$v_1 + v_2 = v_p + v_s = 1. \quad (2)$$

The effective moduli of the parallel and series branches of the EBM are expressed by following equations (44):

$$E_p = (E_1 v_{1p} + E_2 v_{2p})/v_p; \quad (3a)$$

$$E_s = v_s/[(v_{1s}/E_1) + (v_{2s}/E_2)]. \quad (3b)$$

The modulus of a binary system consisting of two immiscible components is then given as the sum $(E_p v_p + E_s v_s)$:

$$E_b = (E_1 v_{1p} + E_2 v_{2p}) + (v_s^2/[(v_{1s}/E_1) + (v_{2s}/E_2)]). \quad (4)$$

"Perfect" adhesion between constituents and a linear stress-strain relationship indispensable for modulus measurements can be granted only at low strains, typically $<1\%$, where almost all polymer systems show interfacial adhesion sufficient for the transmission of the acting (very low) stress. At higher strains, tensile stress exceeds the linearity limit and attains (usually at 4%–6%) the value of yield strength, thus inducing plastic deformation. If the material does not show any yielding, the stress-strain curve proceeds monotonically until the tensile strength is achieved. We have shown (44, 58–60) that the EBM can be also used for the calculation of S_{yb} (or S_{ub}). Obviously, the EBM cannot be employed for the prediction of mechanical properties if the mixing process

produces a significant change in the structure of a constituent (e.g., crystallinity) or a new mechanism (e.g., enhancement of toughness due to the matrix multiple crazing induced by elastomer inclusions).

In our previous papers (44, 58–60) we have derived the following equation for S_{yb} (or S_{ub}) of the EBM visualized in *Fig. 1*:

$$S_{yb} = (S_{y1}v_{1p} + S_{y2}v_{2p}) + AS_{y1}v_s, \qquad (5)$$

where S_{y1} and S_{y2} characterize parent polymers and A the extent of interfacial debonding. Two limiting values of S_{yb}, identified with the lower or upper bound, can be distinguished by means of *Eq 5*: (i) Interfacial adhesion is so weak that complete debonding (dewetting) occurs at the yield stress between the fractions of constituents coupled in series ($A = 0$). Consequently, the series branch does not contribute to the resulting S_{yb} and the lower bound is therefore equal to the contribution of the parallel branch. (ii) Interfacial adhesion is strong enough to transmit the yield stress between constituents so that no debonding appears ($A = 1$); then the contribution of the series branch is added to that of the parallel branch (the effect of slightly different strain rates in the two branches on S_{y1} and S_{y2} is neglected). However, if two components differing in the yield strength are coupled in series, the branch will yield at S_{y1} or S_{y2}, whichever is lower ($S_{y1} < S_{y2}$ is assumed in *Eq 5*). Replacing S_{y1} and S_{y2} by the tensile strengths S_{u1} and S_{u2}, respectively, we obtain the bounds of S_{ub} of binary systems.

Cross Orthogonal Skeleton Model (COS)

The COS model (*Fig. 2a*) consists of three orthogonal bars (cross section a^2) of component 2 ("reinforcement") embedded in a unit cube (volume b^3) where the remaining volume is occupied by component 1 ("matrix"). If $f = a/b$, then the volume fractions coupled in parallel and in series to the acting force are:

$$v_{2p} = a^2b/b^3 = f^2, \qquad (6a)$$

$$v_{2s} = (2a^2b - 2a^3)/b^3 = 2f^2(1 - f). \qquad (6b)$$

Volume fraction of component 2 is

$$v_2 = (3a^2b - 2a^3)/b^3 = f^2(3 - 2f). \qquad (6c)$$

Analogously, for component 1 holds:

$$v_{1p} = 4b(b/2 - a/2)^2/b^3 = (1 - f)^2, \qquad (7a)$$

$$v_{1s} = 8a(b/2 - a/2)^2/b^3 = 2f(1 - f)^2, \qquad (7b)$$

$$v_1 = (1 - f)^2(1 + 2f). \qquad (7c)$$

Figure 3a shows that the dependences of v_{1p} and v_{2p} or v_{1s} and v_{2s} on composition are symmetrical, which means that the components 1 and 2 are interchangeable. Thus the COS model can be viewed as an approximation of polymer blends with co-continuous ("interpenetrating") components. By differentiating *Eqs 6* and *7* we can easily show that v_p or v_s passes
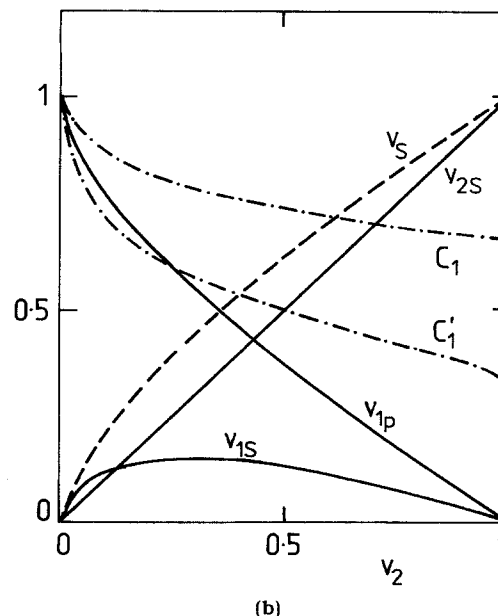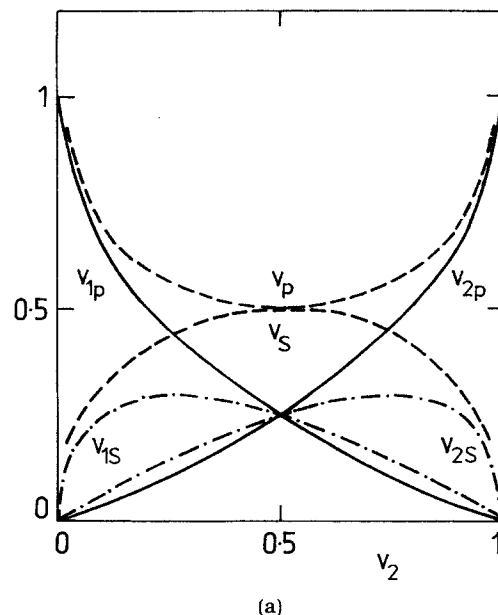

(a)

(b)

Fig. 3. Effect of composition on volume fraction of components (subscript 1,2) coupled in parallel (subscript p) or in series (subscript s) defined by Eqs 2: (a) the orthogonal skeleton model (Eqs 6 and 7); (b) the three perpendicular plates model (Eqs 11 and 12). Phase continuity parameters C_1 for the 3PP model and C_1' for the COS model are defined by Eq 1.

through a minimum or a maximum at $f = 0.5$, i.e., at $v_1 = v_2 = 0.5$. On the other hand, v_{1s} and v_{2s} show maxima at $f = 1/3$ and $f = 2/3$, respectively, assuming a value of 8/27; the maxima are located at $v_2 = 7/27$ and 20/27, respectively. For the sake of comparison of the COS and 3PP models, C_1' characterizing the COS model is given in *Fig. 3b*. For v_2 approaching 1, C_1' assumes a limiting value 1/3. The dependence C_2' for the second phase of the COS would be symmetrical to C_1'.

Inserting v_y from *Eqs 6* and *7* to *Eq 4* we obtain a formula for the modulus of the COS:

$$E_b = E_1(1 - f)^2 + E_2 f^2 + 2f(1 - f)/[(1 - f)/E_1 + (f/E_2)]. \quad (8)$$

Analogously, combining *Eqs 6, 7,* and *5* we receive an equation for the yield strength of the COS:

$$S_{yb} = S_{y1}(1 - f)^2 + S_{y2}f^2 + AS_{y1}2(f - f^2), \quad (9)$$

where $S_{y1} < S_{y2}$ is assumed. The effect of composition on modulus, upper bound S_{yb+} $(A = 1)$ and lower bound S_{yb-} $(A = 0)$ of yield strength is schematically visualized for the COS model in *Fig. 4a*. While E_b and S_{yb+} are monotonic functions of composition, S_{yb-} passes through a deep minimum, which is located closer to the component of lower S_y.
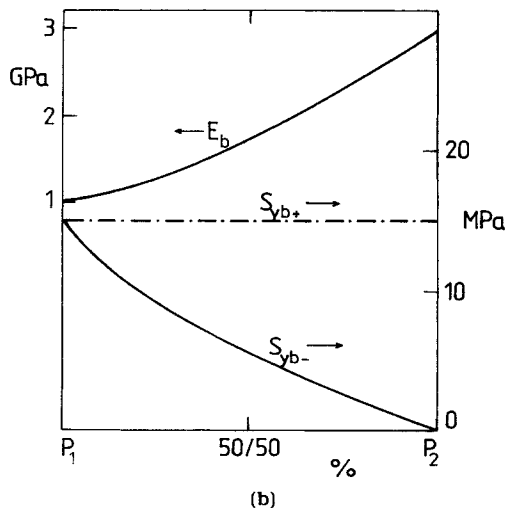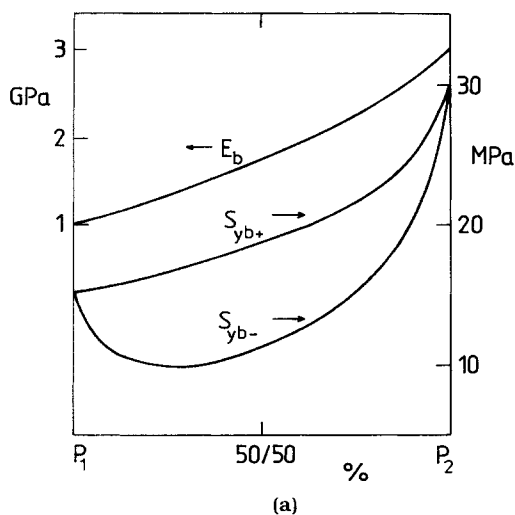

(a)

(b)

Fig. 4. Young's modulus E_b, upper bound of yield strength S_{yb+} and lower bound of yield strength S_{yb-} predicted by (a) the COS model (Eqs 8 and 9) and (b) the 3PP model (Eqs 13 and 14).

Differentiating *Eq 9* according to f we can show that yield strength exhibits a minimum at

$$f_{min} = S_{y1}(1 - A)/[S_{y2} - S_{y1}(2A - 1)]. \quad (10)$$

Obviously, S_{yb} passes through a minimum (as a function of composition) for $A < 1$, while a monotonic dependence occurs only if $A = 1$; for $A = 0$ we obtain $f_{min} = S_{y1}/(S_{y2} + S_{y1})$. In our previous paper (60), evaluating the extent of interfacial debonding in binary polymer blends by means of the EBM combined with the percolation approach, we illustrated the effect of A on the S_{yb} vs. v_2 dependences in a graphical manner (analytical solution of the obtained equations is hardly viable). Thus we can conclude that a minimum on the S_{yb} vs. composition dependence is a reliable symptom of (at least partial) interfacial debonding at stresses corresponding to the yield (or tensile) strength of a system.

Three Perpendicular Plates Model (3PP)

If the modulus E_2 of discontinuous component is comparable or higher than E_1 of the continuous phase (matrix), the 3PP model imitates blends or particulate composites; if $E_2 = 0$, it may represent an idealized foam with segregated cells. Volume fractions of the component 1 (matrix) are the following:

$$v_{1p} = (2ab^2 - a^2 b)/b^3 = f(2 - f), \quad (11a)$$

$$v_{1s} = 4a(b/2 - a/2)^2/b^3 = f(1 - f)^2, \quad (11b)$$

$$v_1 = [3ab(b - a) + a^3]/b^3 = 3f(1 - f) + f^3. \quad (11c)$$

Analogously, for the dispersed component 2:

$$v_{2p} = 0(\text{for } v_2 < 1), \quad (12a)$$

$$v_2 = v_{2s} = 8(b/2 - a/2)^3/b^3 = (1 - f)^3. \quad (12b)$$

The dependences of v_{1p}, v_{1s}, v_{2s}, and $v_s = v_{1s} + v_{2s}$ of the 3PP model on blend composition are given in *Fig. 3b*. v_{1s} passes through a maximum at $v_2 = 8/27$ assuming a value of $v_{1s} = 4/27$. For v_2 rising in interval $0 < v_2 < 1$, the phase continuity parameter C_1 decreases in the interval $1 < C_1 < 2/3$. On the other hand, $C_2 = 0$ at $v_2 < 1$ and $C_2 = 1$ at $v_2 = 1$.

The modulus of the 3PP model is given by *Eqs 4, 11,* and *12*:

$$E_b = E_1 f(2 - f) + (1 - f)^2/[f/E_1 + (1 - f)/E_2]. \quad (13)$$

Similarly enough, for $S_{y1} < S_{y2}$, *Eqs 5, 11,* and *12* provide

$$S_{yb} = S_{y1}f(2 - f) + AS_{y1}(1 - f)^2. \quad (14)$$

The modulus, upper bound $S_{yb+} = S_{y1}$ $(A = 1)$ and lower bound S_{yb-} $(A = 0)$ of yield strength simultaneously predicted by the 3PP model are given in *Fig. 4b*. As can be seen, the 3PP model displays a monotonic dependence of E_b on composition. In the case of poor interfacial adhesion, S_{yb-} is proportional v_{1p}.

For plastics/elastomer blends (with discontinuous elastomer phase) we have to consider $S_{y1} > S_{y2}$:

$$S_{yb}^* = S_y f(2 - f) + A S_{y2}(1 - f)^2. \qquad (15)$$

For $A = 0$, S_{yb-} from *Eq 14* and S_{yb-}^* from *Eq 15* are identical, which means that at "zero" interfacial adhesion the yield strength of the dispersed component is irrelevant. Similarly enough, if $S_{y1} \gg S_{y2}$, then S_{yb+}^* equals to S_{yb-}^* or S_{yb-} derived from *Eq 14*.

RESULTS AND DISCUSSION

Prediction of modulus and yield (or tensile) strength rendered by the presented models will be compared with experimental data and/or with the prediction of some other models so far used in the fields of (i) polymer blends, (ii) polymer foams, and (iii) particulate composites.

Polymer Blends

Experimental data for binary blends given in *Figs. 5a* and *b* were selected from the available literature in order to illustrate various combinations of the E_b and S_{yb} (or S_{ub}) patterns. In addition to the prediction based on the COS model, also the curves are given that were calculated with the aid of v_{ij} obtained from equations derived (44, 59, 60) on the basis of the percolation model (45, 46):

$$v_{1p} = [(v_1 - v_{1cr})/(1 - v_{1cr})]^{t_1}, \qquad (16a)$$

$$v_{2p} = [(v_2 - v_{2cr})/(1 - v_{2cr})]^{t_2}, \qquad (16b)$$

where v_{cr} is the critical volume fraction (the percolation threshold) and t is the critical universal exponent. "Universal" values (41, 42) of these parameters are $v_{cr} = 0.16$ and $t = 1.8$, but v_{1cr} and t_1 frequently differ from v_{2cr} and t_2 in binary blends, mainly because of different viscosities of components in the blended melt. Obviously, $v_{1cr} < v_1 < (1 - v_{2cr})$ is the interval of the co-continuity of constituents in which the phase inversion takes place. In the marginal zone $0 < v_1 < v_{1cr}$ (or $0 < v_2 < v_{2cr}$), where only component 2 (or 1) is continuous, it holds for the minority component that $v_{1p} = 0$, $v_{1s} = v_1$ (or $v_{2p} = 0$, $v_{2s} = v_2$).

In either series of blends in *Figs. 5a* and *5b*, the modulus vs. composition dependences of blends are well described by means of v_{ij} from *Eqs 16*. However, in both series $v_{2cr} = 0.30$ was to be adjusted, which differs from the "universal" theoretical value. The dashed curves corresponding to the COS model are necessarily somewhat higher because phase continuity parameters in real blends cannot attain those of the COS model. Whenever experimental data on S_{yb} or S_{ub} follow the upper bound corresponding to *Eq 5* for $A = 1$ (*Fig. 5a*), we can deduce that the interfacial adhesion is strong enough to transmit the stress achieved at tensile yielding or breaking. In this respect the COS-based prediction of S_{ub} *Eq 9* is distinctly higher than the experimental data in the interval $90 > \%$ PE > 30, which is mainly attributable to a high
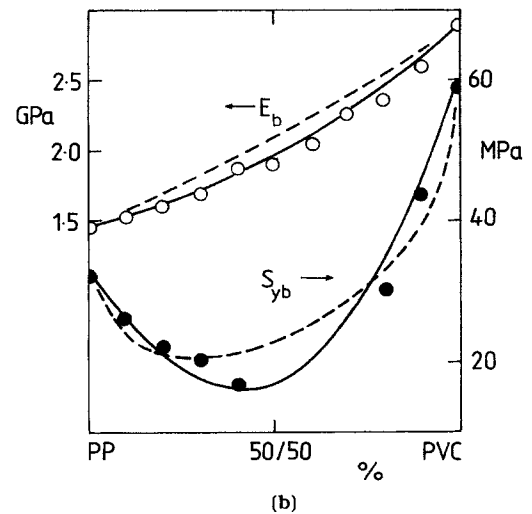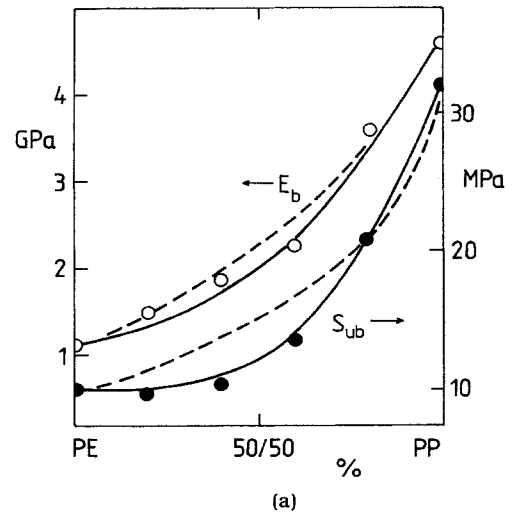

(a)

(b)

Fig. 5. Effect of composition on (a) tensile modulus (○) and tensile strength (●) of polyethylene/polypropylene blends (61) and on (b) tensile modulus (○) and yield strength (●) of polypropylene/poly(vinyl chloride) blends (62). Full lines calculated simultaneously from Eqs 4 and 5 by using volume fractions v_{ij} from the Eqs 16 derived for the percolation model. The input parameters are the following in both figures: $v_{1cr} = 0.16$; $v_{2cr} = 0.30$; $t_1 = t_2 = 1.8$. Dashed lines: Eq 8 for moduli; (a) Eq 9 with A = 1 for tensile strength; (b) Eq 9 with A = 0 for yield strength.

critical volume fraction of the PP component. In contrast, *Fig. 5b* brings data for blends whose yield strength passes through a minimum as a function of the blend composition. The experimental data correspond fairly well to the lower bounds ensuing from both the COS and percolation models. PVC is known to be immiscible with PP or PE (49), which is reflected in "zero" adhesion ($A = 0$) at yielding throughout the whole composition range. *Figure 5b* documents that while modulus indicates sufficient interfacial adhesion at small deformations, yield strength evidences poor adhesion insufficient to transmit stress inducing plastic deformation.

The experimental finding that *Eq 5* predicts both yield and tensile strengths can be linked to previous

experience that also the equations based on the reduction of load-bearing cross section have been successfully used for the evaluation of yield as well as tensile strength of particulate systems (7, 34–37). The well-evidenced applicability of the EBM to the estimate of S_{ub} implies that fracture mechanisms of individual components in blends are the same as in parent polymers and that they do not perceptibly affect each other.

Interestingly enough, also the 3PP model is appropriate for polymer blends. It follows from *Eq 12b* that

$$f = 1 - v_2^{1/3}; \qquad (17a)$$

consequently,

$$f(2 - f) = (1 - v_2^{1/3})(1 + v_2^{1/3}) = 1 - v_2^{2/3}. \qquad (17b)$$

Inserting these relations into *Eq 15* and assuming $A = 1$, we obtain the following equation

$$S_{yb} = S_{y1}(1 - v_2^{2/3}) + S_{y2}v_2^{2/3}, \qquad (18)$$

which is identical with the equation proposed earlier (7, 22) for polymer blends with a strong interfacial adhesion. Obviously, as the phase structure of real blends cannot coincide with the 3PP model, *Eq 18* can be only approximative. With regard to our previous papers (44, 59, 60), we believe that S_{yb} as a function of blend composition is plausibly described by *Eq 5* and v_{ij} from *Eqs 16*.

Polymer Closed-Cell Foams

The equations derived for the 3PP model can be modified for idealized closed-cell polymer foams (subscript f) by considering $E_2 = 0$ and $S_{y2} = 0$. Then *Eqs 13* and *14* for E_b and S_{yb} are formally identical, i.e.,

$$E_f/E_1 = f(2 - f), \qquad (19a)$$

$$S_{yf}/S_{y1} = f(2 - f). \qquad (19b)$$

Introducing the relative density of a foam

$$d_f/d_1 = v_1 = 1 - v_2 \qquad (20)$$

into *Eq 19a*, we obtain a relationship between modulus and density of foams:

$$E_f/E_1 = 1 - v_2^{2/3} = 1 - (1 - d_f/d_1)^{2/3}. \qquad (21)$$

Note that *Eq 21* is identical with the relationship derived earlier (63) for the modified "cube in cube" model imitating polymer foams. With regard to the analogous form of *Eqs 19a* and *19b*, E_f and S_{yf} are likely to follow similar patterns as functions of foam composition.

Many other equations can be found (22, 63) expressing the foam modulus as a function of the volume fraction of pores in foams. A square-power relationship between modulus and density for high-density foamed thermoplastics was derived earlier (30) and confirmed experimentally (63):

$$E_f/E_1 = (1 - v_2)^2. \qquad (22)$$

Another model used for predicting the modulus of foams is that of Kerner (27) in its original form, which does not account for the maximum packing volume of the dispersed component. The Kerner equation was modified (22) to the following form:

$$E_f/E_1 = \{1 + [15(1 - v_1)v_2]/[(7 - 5v_1)v_1]\}^{-1} \qquad (23)$$

Predictions of the modulus as a function of foam composition provided by *Eqs 21, 22*, and *23* are compared with experimental data in *Fig. 6*. While the dependences predicted by *Eqs 21* and *23* almost coincide, *Eq 22* predicts perceptibly lower values in the interval $0.3 < v_2 < 1$. However, available experimental data (64) located between the curves are not sufficient for unequivocal testing of the models.

Particulate Composites

The 3PP model can predict modulus E_c and yield strength S_{yc} of particulate composites where the maximum volume fraction of the dispersed component (filler) V_{max} can approach unity, which would be exceptional in real systems. Nevertheless, it is useful to confront the 3PP with other models disregarding V_{max}. The curves plotted in *Fig. 7* are predicted by *Eqs 24–26*, which were obtained by modifying the original equations for G modulus under the assumption that component 1 (a glassy polymer matrix) and component 2 (a filler) have the same Poisson's ratio v (22).

(i)   Hashin-Shtrinkman lowest upper bound (25)

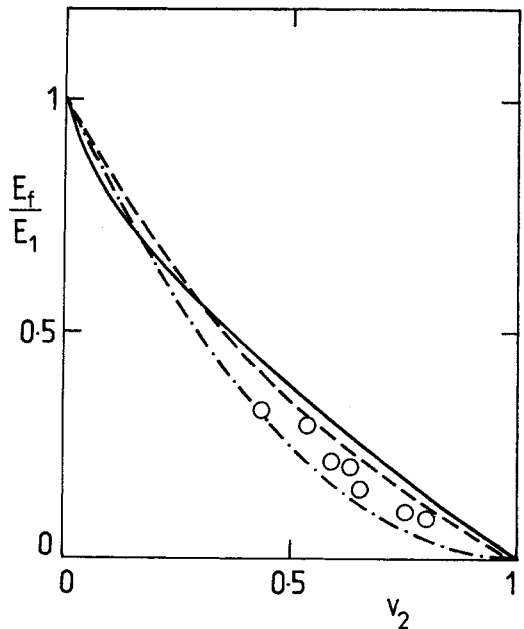$$E_{c+}/E_1 = E_2/E_1 + v_1/[E_1/(E_1 - E_2) + D(E_1/E_2)v_2] \qquad (24)$$

Fig. 6. Effect of volume fraction v_2 of cells on the relative modulus of polymer foams. Full line: Eq 19a; dashed line: Eq 23; dash and dot line: Eq 22; experimental data points from Gent and Thomas (64).
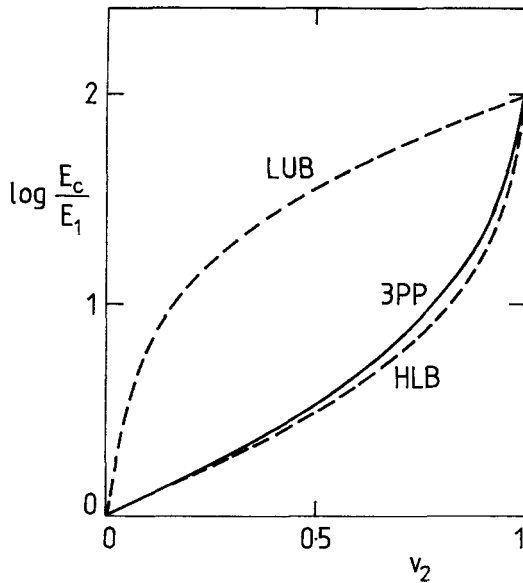
Fig. 7. *Effect of volume fraction v_2 of dispersed component on the relative modulus of particulate composites. Full line: prediction of the 3PP model, Eq 13; dashed lines: highest lower bound (HLB), Eq 25, coinciding with the prediction of Eq 26; lowest upper bound (LUB), Eq 24.*

where $D = 6(K_2 + 2G_2)/5(3K_2 + 4G_2)$. Modulus K_2 can be eliminated from D by using the following general relationship:

$$K = (2/3)G(1 + v)/(1 - 2v).$$

In our calculations we have assumed $v_1 = v_2 = 0.35$.

(ii) Hashin-Shtrinkman highest lower bound (25)

$$E_{c-}/E_1 = 1 + v_2/[E_1/(E_2 - E_1) + Dv_1] \quad (25)$$

where $D = 6(K_1 + 2G_1)/5(3K_1 + 4G_1)$.

(iii) Kerner equation (27) simplified to the following form (65):

$$E_c/E_1 = [(1 - v_2) + B(A + v_2)]/[(1 + Av_2)$$

$$+ AB(1 - v_2)] \quad (26)$$

where $A = (8 - 10v_1)/(7 - 5v_1)$ and $B = E_2/E_1$.

Figure 7 shows that the relative Young's modulus predicted by the 3PP model is slightly higher than the highest lower bound (25) (at $v_2 < 0.3$, the differences are not discernible in the scale of the figure); the latter bound coincides with the curve predicted by *Eq 26*, which is in conformity with previous analyses (65–67). Thus it is obvious that the 3PP model provides reasonable prediction very close to that of other well-established models.

As for the yield strength of particulate composites with strong interfacial adhesion, the 3PP model predicts, by *Eq 14*, a constant value S_{yc} equal to S_{y1} of the matrix as the only component undergoing plastic deformation in the system. For instance, the yield strength of functionalized polypropylene filled with

calcium carbonate was found to pass through a shallow maximum as a function of filler volume fraction, which was in conformity with the finite element simulation (68). The observed increase in S_{yc} with filler content is a likely manifestation of the immobilized layer of the matrix adhering to the filler surface.

As far as composites with "zero" adhesion ($A = 0$) are concerned, *Eqs 14* and *17b* predict

$$S_{yc-} = S_{y1}f(2 - f) = S_{y1}(1 - av_2^{2/3}) \quad (27)$$

with $a = 1$. This is so because V_{max} is presumed to achieve values as high as unity; however, if $V_{max} < 1$, then $a > 1$. Nielsen (7) *proposed* $a = (1/V_{max})^{2/3}$, which allows *Eq 27* to plausibly fit experimental data for various particulate composites with poor adhesion between the components.

CONCLUSIONS

Two models are introduced for simultaneous prediction of the modulus and yield (or tensile) strength of two-component isotropic systems: (i) the cross orthogonal skeleton (COS) with co-continuous components and (ii) the cubic orthogonal skeleton (three perpendicular plates—3PP) with one component continuous and one component discontinuous. The predictive scheme consists of two steps: 1) the COS or 3PP model renders phase continuity parameters used as input data for 2) the equivalent box model (EBM), for which the equations were derived expressing the modulus and yield (or tensile) strength as functions of system composition. There is no adhesion term in the equation for Young's modulus, since it is presumed that the adhesion is sufficient to transmit small stresses in the linear stress-strain region. However, at yielding (or breaking), the upper and lower bounds have to be distinguished. They are related, respectively, to interfacial adhesion sufficient and insufficient for the transmission of the stress inducing plastic deformation. The moduli of the COS and 3PP and the upper bound of yield (or tensile) strength of the COS are monotonic functions of composition. If partial or complete interfacial debonding occurs at yielding (or breaking), the COS model predicts that the yield (or tensile) strength passes through a minimum as a function of composition, which is in conformity with earlier model calculations (based on the percolation approach) and experimental findings for polymer blends. The 3PP model approximates fairly well experimental data on the modulus of closed-cell polymer foams and also proposes a formally analogous formula for their yield strength. Furthermore, the 3PP model is applicable to particulate composites: (i) the equation for modulus virtually coincides with the Hashin-Shtrinkman highest lower bound and the Kerner equation; (ii) the anticipated yield strength of particulate composites with good adhesion is independent of composition (being equal to that of the matrix as the only yielding component in the system); in the case of poor adhesion, the ensuing relationship is identical with that proposed earlier (22). The outlined predictive

scheme is advantageous in two aspects: (i) all predicted properties are related to the same phase structure; (ii) the prediction of modulus or yield (or tensile) strength requires only the respective values characterizing the components; no other data, e.g., Poisson's ratio and bulk moduli, are needed.

ACKNOWLEDGMENT

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Revised April 1997