Polymeric Composite Systems with Two Continuous Phases

LAWRENCE E. NIELSEN, *Monsanto Company, St. Louis, Missouri 63166*

Synopsis

A general mixture rule, which has the correct type of phase symmetry, is proposed for estimating the properties of composites having two continuous phases. The form of this equation is different from the equations used to predict the properties of composites with one continuous phase and one dispersed phase. The proposed equation for property P is

$$P^n = P_A{}^n \phi_A + P_B{}^n \phi_B$$

where the volume fractions of components A and B are ϕ_A and ϕ_B, respectively, and n is a constant. A simple model is used to correlate the morphology of systems having two continuous phases with the parameter n of the mixture rule. The connectivity of the phases varies with concentration. The properties, such as elastic modulus, depend primarily upon the modulus of the material with the higher modulus. In general, the properties depend very little on the morphology of the system.

INTRODUCTION

For composite systems consisting of one continuous phase (matrix) and one dispersed phase, accurate predictions can be made of various properties for many shapes and orientations of the dispersed particles. Typical properties which can be predicted are elastic moduli, thermal and electrical conductivity, and dielectric constant. Polymeric systems consisting of two continuous phases rather than a single continuous phase are of practical importance. Typical examples include semicrystalline polymers, block polymers, some polyblends, interpenetrating networks, and filled open-celled foams. However, no theory has been developed for predicting the properties of such composites in terms of the morphology of the systems.

The mixture rules or equations used to predict the properties of composites with one continuous phase should not be used to predict the properties of systems with two continuous phases. Equations for the systems with two continuous phases should be symmetrical with regard to the two phases since neither phase can be called the sole continuous phase or the dispersed phase. No such symmetry requirement is needed for the equations used to calculate the properties of the usual composites which contain a dispersed phase or filler.

THEORY AND A MODEL

A general mixing equation which satisfies the symmetry requirements for composites consisting of two continuous phases is
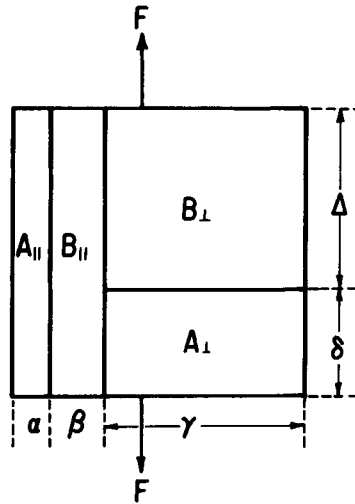
Fig. 1. Model for composites with two continuous phases consisting of materials A and B. F = Applied force or field.

$$P^n = P_A{}^n\phi_A + P_B{}^n\phi_B, \qquad -1 \le n \le +1 \qquad (1)$$

P is some property such as elastic modulus or thermal conductivity. The phases consist of materials A and B with volume fractions ϕ_A and ϕ_B, respectively. The constant n is some function of the morphology of the system and possibly the type of property being measured. It is the purpose of this work to gain some insight into the factors, especially the morphology of the system, which determine the value of n in eq. (1). When $n = 1$, one obtains the ordinary rule of mixtures. When $n = -1$, the inverse rule of mixtures is obtained. The logarithmic rule of mixtures is obtained when $n = 0$.

For a long time, it has been known that the elastic modulus of many block polymers and polyblends follows the logarithmic rule of mixtures quite accurately.[1] Davies[2,3] suggests that $n = \frac{1}{3}$ for the dielectric constant and $n = \frac{1}{5}$ for elastic modulus. Any effects due to morphology were neglected in these works. Recently, a value of $n = \frac{1}{5}$ was found to hold quite accurately at temperatures above the glass transition temperature for the elastic modulus of crystalline polymers as a function of the degree of crystallinity.[4] The morphology seemed to have only a secondary effect on the modulus. Morphologic changes and heat treatments can change the modulus by about a factor of 2, while the degree of crystallinity can change it by a factor of 10^4.

Takayanagi[5] developed models for predicting the moduli of crystalline polymers and polyblends, and Nielsen[6] used a similar type of model for predicting the permeability of filled polymers. Prevorsek and Butler[7] tried to relate the characteristics of the Takayanagi model to the morphology of a composite, but their results are of limited success when compared to what other theories of composites can do.[8-11] A limitation of the Takayanagi models is that they should apply only to composites which have one continuous phase. However, a slight modification of the Takayanagi models makes them applicable to composites with two continuous phases.
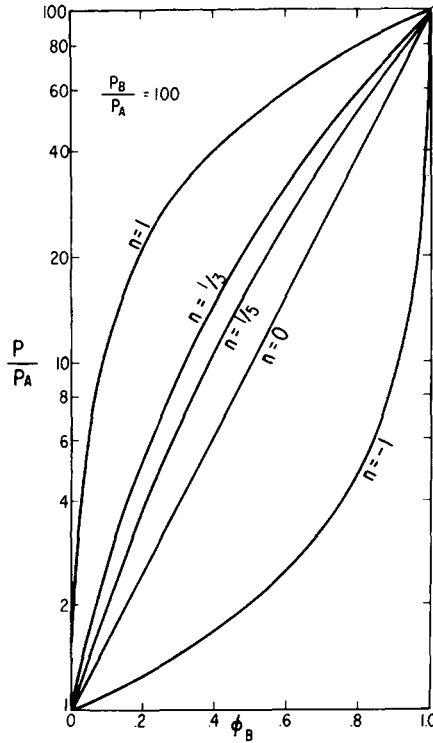
Fig. 2. Relative property P/P_A as a function of volume fraction ϕ_B of material B for different values of n in eq. (1).

The new model is illustrated in Figure 1. The following set of equations apply to this model:

$$P = P_A\phi_{A\|} + P_B\phi_{B\|} + \frac{P_A P_B(\phi_{A\perp} + \phi_{B\perp})}{P_A\phi_{B\perp} + P_B\phi_{A\perp}} \quad (2)$$

$$\phi_A = \phi_{A\|} + \phi_{A\perp}, \phi_B = \phi_{B\|} + \phi_{B\perp}, \phi_A + \phi_B = 1 \quad (3)$$

$$\begin{aligned} \phi_{A\|} &= \alpha, & \phi_{A\perp} &= \delta\gamma \\ \phi_{B\|} &= \beta, & \phi_{B\perp} &= \Delta\gamma \end{aligned} \quad (4)$$

The symbols have the following practical significance: $\phi_{A\|}$ is the volume fraction of material A which behaves as though it is a continuous phase. An analogous meaning applies to $\phi_{B\|}$. $\phi_{A\perp}$ is the volume fraction of material A which behaves as though it is a dispersed phase to some force F (mechanical, electrical, thermal, etc.) applied to the model as illustrated in Figure 1. The morphology of the system is related to the concept of the connectivity of the phases. The definitions of connectivity (C_A or C_B) of the phases are

$$C_A = \phi_{A\|}/\phi_A = \alpha/\phi_A$$

$$C_B = \phi_{B\|}/\phi_B = \beta/\phi_B \quad (5)$$

Equation (1) is plotted in Figure 2 for several values of n for the case where $P_B/P_A = 100$. If the property P is the elastic modulus, then the material B is 100 times as rigid as material A, for example.

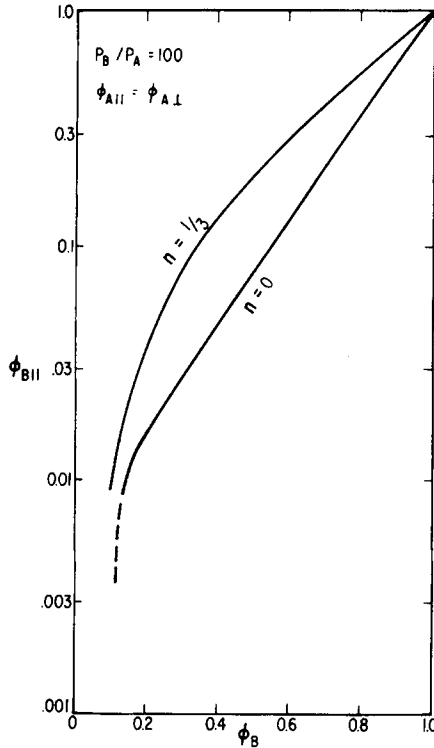The model in Figure 1 was forced to fit eq. (1) for $n = 0$ and $n = \frac{1}{3}$ for the case

Fig. 3. Volume fraction of material B which appears to be a continuous phase for $n = 0$ and $n = \frac{1}{3}$.

$P_B/P_A = 100$, while at the same time the connectivity of the soft phase A was held at about 0.5. Thus, the volume fraction $\phi_{B\parallel}$ of the hard phase which behaved as a continuous phase was calculated by the equation

$$\phi_{B\parallel} = \frac{(P_B{}^n\phi_B + P_A{}^n\phi_A)^{1/n}}{P_B} - \frac{P_A}{P_B}\phi_{A\parallel} - \frac{P_A(\phi_{A\perp} + \phi_{B\perp})}{P_A\phi_{B\perp} + P_B\phi_{A\perp}} \tag{6}$$

The results as a function of concentration are shown in Figure 3. As would be expected, the volume fraction $\phi_{B\parallel}$ approaches 1.0 as ϕ_B approaches 1.0. Less expected was the very rapid approach of $\phi_{B\parallel}$ toward zero as ϕ_B approaches zero. This indicates a strong tendency for B to become a dispersed phase at low concentrations. Even at $\phi_B = 0.5$, less than $\frac{1}{6}$ of the B phase behaves as though it is continuous when $n = 0$. This value increases to 40% of phase B that is present when $n = \frac{1}{3}$. Instead of holding $\phi_{A\parallel}/\phi_A$ constant as in the above calculations, a more realistic case would be to let $\phi_{A\parallel}/\phi_A$ decrease as ϕ_A decreases. However, as shown by other calculations, unless very drastic changes in the ratio $\phi_{A\parallel}/\phi_A$ are allowed to occur, very little change in the calculated property will be found as long as $\phi_{B\parallel}$ is constant for any given value of ϕ_B.

The model indicates that the value of property P is determined primarily by the amount of the hard phase B that acts as a continuous phase, i.e., by $\phi_{B\parallel}$. Morphologic changes involving the ratio $\phi_{A\parallel}/\phi_{A\perp}$ have very little effect, except in extreme cases of this ratio. This is illustrated in Figure 4. In this example, $\phi_B = 0.5$ and $\phi_{B\parallel}$ is held at 0.3, but the morphology as represented by $\phi_{A\parallel}/\phi_{A\perp}$

$P = 26.7$

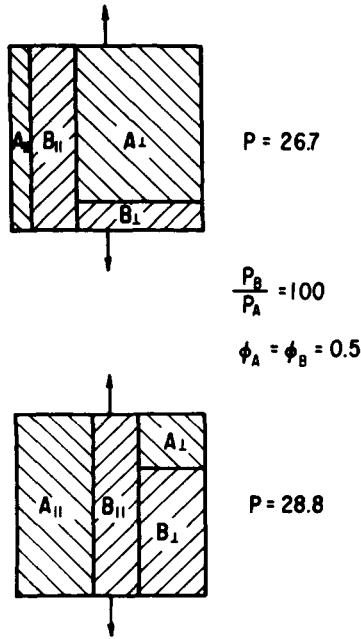$\dfrac{P_B}{P_A} = 100$

$\phi_A = \phi_B = 0.5$

$P = 28.8$

Fig. 4. Effect of morphology of material A on the properties of models.
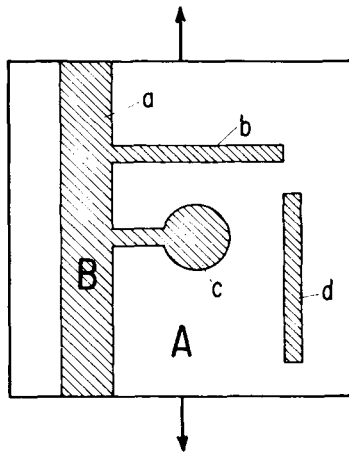

Fig. 5. Some morphologic factors affecting the continuity of phase B in a model. Arrows indicate direction of externally applied field or force.

is allowed to change from $\frac{1}{4}$ to 4.0. Even though the two models in Figure 4 look very different, the property P only changes from 26.7 to 28.8.

   Other calculations have been made to get results analogous to those shown in Figure 3. On the basis of these results, certain general conclusions can be made. If P_B/P_A is much greater than 10, the effect of morphology as defined by $\phi_{A\parallel}/\phi_A$ is unimportant, and the morphology only manifests itself in terms of the ratio $\phi_{B\parallel}/\phi_B$. At ratios of $P_B/P_A < 10$, the effect of morphology becomes much more important, and the role of $\phi_{B\parallel}$ becomes much less important. At intermediate and high values of ϕ_B and at large values of P_B/P_A, the connectivity of phase B (or $\phi_{B\parallel}/\phi_B$) becomes relatively independent of P_B/P_A for any given

value of n greater than zero. Since $\phi_{B\parallel}$ at a given concentration depends largely on n, the greatest effect of changing the morphology of phase B appears to manifest itself in changes in the value of n. However, from the practical standpoint, these changes must not be great, since the range of n in nearly all cases lies between zero and $\frac{1}{3}$.

A few comments need to be made regarding the concept of connectivity. Not all the material attached to a continuous, through-going phase needs to behave as the continuous phase, but it may actually act as a dispersed phase. This point is illustrated in Figure 5. The part of material B labeled "a" certainly behaves as a continuous phase for forces applied in the direction of the arrows. However, material in the parts marked "b" and "c" behaves primarily as a dispersed phase. Likewise, some material which is not a part of a continuous phase may behave as though it were continuous. Long rods or fibers, such as the material labeled "d" in Figure 5, may behave as a continuous phase to forces acting parallel to their long dimension. Thus, in Figure 5, the volume fraction of B is that fraction of the total square which is made up of parts "a" through "d," while $\phi_{B\parallel}$ is only that fraction of the square made up of parts "a" and possibly "d." If all the material of phase B is through-going and oriented in the direction parallel to the applied force, then the value of n in eq. (1) approaches a value of 1.0. However, if the force is applied perpendicular to the through-going phase, the value of n approaches -1.0. If all the material in a composite is through-going but randomly oriented, then a value of n near zero would be expected. Obviously, anisotropic materials can have different values of n depending upon the direction of the applied force or field.

References

1. L. E. Nielsen, *Rheol. Acta,* **13**, 86 (1974).
2. W. E. A. Davies, *J. Phys.,* **D4**, 318, 1176, 1325 (1971).
3. W. E. A. Davies, *J. Phys.,* **D7**, 1016 (1974).
4. L. E. Nielsen, *J. Appl. Polym. Sci.,* **19**, 1485 (1975).
5. M. Takayanagi, in *Proc. 4th Int. Congr. Rheology,* Providence, vol. 1, 1965, p. 161.
6. L. E. Nielsen, *J. Macromol. Sci. (Chem.),* **A1**, 929 (1967).
7. D. Prevorsek and R. H. Butler, *Int. J. Polym. Mater.,* **1**, 251 (1972).
8. E. H. Kerner, *Proc. Phys. Soc.* (London), **B69**, 808 (1956).
9. S. W. Tsai, U.S. Dept. of Commerce Rept. AD834851, 1968.
10. J. C. Halpin, *J. Composite Mater.,* **3**, 732 (1969).
11. L. E. Nielsen, *J. Appl. Phys.,* **41**, 4626 (1970).