Design of Impact Modifiers for Thermoplastic Polymers Based on Micromechanics

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ABSTRACT: Efficient impact modifiers for lowering the ductile–brittle transition temperature of thermoplastic blends have been designed by modeling the stress distribution near the notch of an Izod impact test sample and the nature of stresses in spherical particle-filled polycarbonate. The model considers the inhomogeneity of a soft phase inside a relatively rigid phase, particle interaction, and the effects of thermal residual stresses imposed as a consequence of processing and differences in matrix and particle thermal coefficients of expansion. Polycarbonate blends are used as an example for the modeling. The predictions of the ductile–brittle transition temperature of blends provide guidelines for selection of impact modifier type. The model predicts that there is no further advantage in toughening by increasing the ratio of the moduli of matrix and rubber particle more than 1000. The model also predicts that the glass–rubber transition temperature, T_g, and the nature of transition (i.e., sharp or smooth transition) dominate the ductile–brittle transition temperature of blends. An energy criterion for yielding is proposed to be an improved necessary condition for the yielding of polymer instead of the Von Mises stress-yielding criterion. The energy creterion can be used to predict an optimal volume fraction of rubber particles for ductility. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2209–2216, 1997

Key words: impact modification; thermoplastic polymer; stress analysis; micromechanics; ductile–brittle transition temperature

INTRODUCTION

Plastics toughened by introducing two-phase structure into the solid has been extensively discussed for many years, and several books have been published on this topic by the American Chemical Society.[1–3] The enhancements of impact toughening in polymers are usually explained from either physical or mechanical perspectives. From a physical perspective, the addition of rubber particles is considered to accelerate the relaxation processes of the polymer matrix. A mechanistic viewpoint considers plane strain–plane stress transition, particle interaction, and Poisson's ratio effect. Many criteria for toughness have been proposed based on these models, for example, interfacial size, particle concentration, interparticle distance, matrix ligament thickness, mean particle radius, etc. The large variety of these criteria highlights the complexity of the problem and, correspondingly, the limitation of each criterion. Furthermore, given the very large range of possible performance attributes of various impact modifiers through changes in density, molecular weight, crystalline content, etc., it is desirable to try to develop quantitative models for the selection of desirable attributes of an impact modifier in a given matrix, rather than through laborious empirical efforts using statistical experimental design.

A model based on the local stress analysis of spherical particle-filled polycarbonate is reported

in this article. The model considers the inhomogeneity of the soft phase inside a relatively rigid phase, particle–particle interaction, and the effects of thermal residual stresses imposed as a consequence of processing and differences in matrix and particle thermal coefficients of expansion. The consequent predictions on the effects of the physical properties of impact modifier on the ductile–brittle transition temperature of blends give certain guidelines for the selection of an impact modifier. Polycarbonate blends are used as examples of the utility of the model. It should be emphasized that impact modifiers can be designed according to the chemical structure (e.g., by grafting), morphology (e.g., core–shell structure), or physical properties. In this article, only the physical properties of the impact modifier are discussed. Thermoplastic polymer toughening by designing the morphology of the toughening agent will be addressed in the future.

MODELING OF THE TWO-PHASE SYSTEM

Thermal Residual Stress

The effect of thermal stresses on the toughness of a two-phase system that are due to processing has been discussed for plastic[4] and ceramic materials.[5–9] The mismatch between the linear thermal expansion coefficients (α) and elastic modulus (E) in the matrix and rubber particle results in the generation of residual stresses in the particles and surrounding matrix during cooling after processing. These residual matrix stresses can be expressed as[6,10]:

$$\sigma_r = \Delta T(\alpha_p - \alpha_m)/\{[(1 + \nu_m)/2E_m]$$
$$+ [(1 - 2\nu_p)/E_p]\}$$
$$\sigma_\theta = -\sigma_r/2 \quad (1) \tag{1}$$

where the subscripts p and m refer to the particle and matrix, respectively, ν is the Poisson's ratio, and ΔT is the temperature range from solidification of matrix to the testing temperature. In this study, the parameters for rubber particles and matrix are taken as $\alpha_p = (12 \times 10^{-5})°C^{-1}$, $\alpha_m = (6.8 \times 10^{-5})°C^{-1}$, $\Delta T = T_g - T$, where T_g is the glass transition temperature of the matrix (150°C), and T is the test temperature. For polycarbonate, the T_g can be taken as the solidification temperature, and $\nu_m = 0.4$, and $\nu_p = 0.49$. The temperature dependence of E_m and E_p are deter-
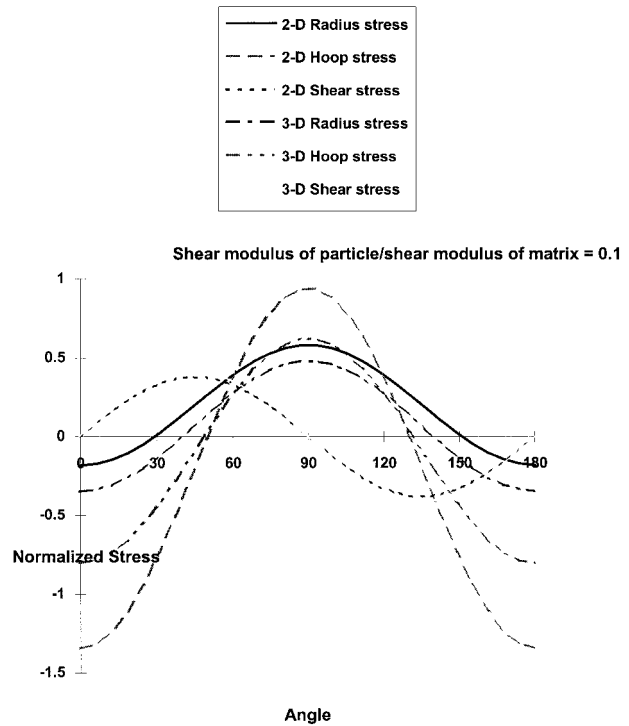

Figure 1 The comparison of normalized stress components in the matrix around a particle evaluated using the solution of the 2D plane strain (a slice through a cylinder) and 3D (a sphere).[10]

mined by the experiment. By introducing the above parameters to eq. (1), the thermal residual stress caused by the mismatch of thermal expansion coefficients can be calculated and is found to be about 1/3 of yielding stress of polycarbonate, i.e., $\sim$ 20 MPa at room temperature at the particle boundary.

The Problem of Structural Inhomogeneity

The problem of an isolated sphere inclusion embedded in another media was considered by Goodier.[10] The stress components in the matrix around a particle have been evaluated using the solution of the 2D plane strain (a slice through a cylinder) and 3D (a sphere) to see if the easier 2D solution can be employed. The calculations show that only the values of the shear stress of the 2D model are nearly equivalent to those of the 3D model. The other stress components (radial and hoop stresses) are quite different (see Fig. 1). Because it is known that shear stress is not the only component responsible for toughening, the 2D plane strain model is insufficient for calculating the component of stress around a particle.
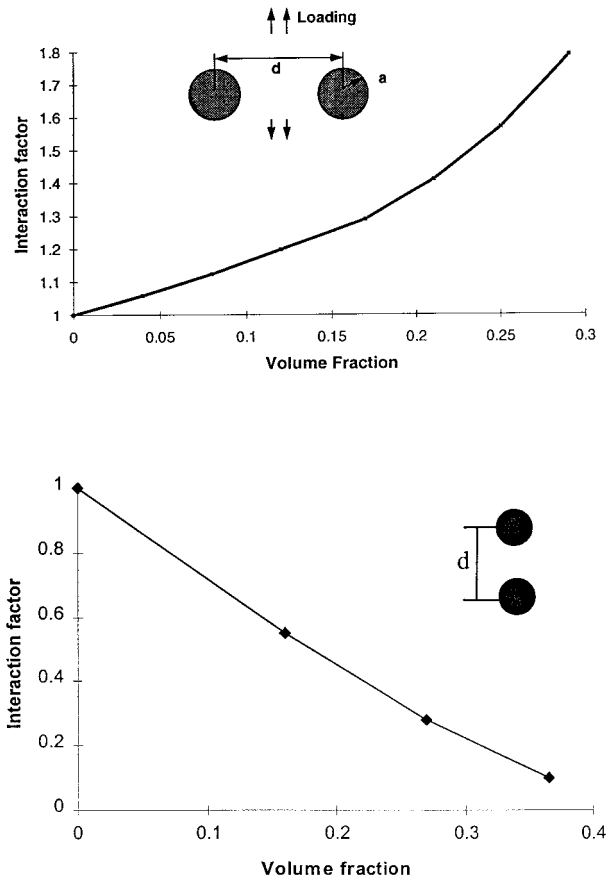
Figure 2 The numerical result of the stress amplification factor due to the interaction between two rubber particles: (a) the particles are packed perpendicular to the loading direction; (b) the particles are packed parallel to the loading direction.

In this study, the 3D solution of an isolated sphere embedded in matrix was used in our calculations.

Rubber Particles Interaction

The elastic stress–field interaction between particles has been considered as an important determinant for toughening. Most of the work to date is based on the early work of stress distribution of a particle embedded in another media by Goodier.[10] The problem of an infinite region containing two spherical cavities was discussed based on the Boussinesq stress–function approach.[11,12] Separately, the interaction of finite gas bubbles in a solid was discussed by Wills and Bullough.[13] More recently, the problem of particle interaction was analyzed by finite element method.[14,15] However, due to the complexity of the problem, all published solutions were based on some numerical calcula-

tion and given in the numerical form of a two-void interaction. Considering that the void is the limiting case of an elastic particle when the Young's modulus approaches zero, it is conservative to use the data of voids interaction for the interaction of elastic particles. Therefore, the function representing the stress changing due to the interaction of two particles is obtained by smoothing the numerical data of refs. 12 and 14.

The stress interaction between two particles depends on the packing direction and loading direction (Fig. 2). When the packing direction is perpendicular to the loading direction, the stress at the particle wall will increase as the distance between them decreases. This is called amplification. Conversely, the stress at the particle wall will decrease as the distance decreases if the packing direction is parallel to the loading direction. This is called shielding. For real systems, there is a complex mixture of amplification and shielding effects that may vary in ratio depending on the nature of the particle packing, which itself depends on particle volume fraction and particle shape.

Modeling of Izod Impact Test and the Ductile–Brittle Transition

The notched Izod impact test is widely used to measure the impact strength and determine the ductile brittle transition of rubber-toughened blends. It is known that the failure of a sample is controlled by the stress field near the notch tip because of stress concentration. A sketch of the notched Izod impact test sample is shown in Figure 3. Because of the complexity of the problem, we introduce four assumptions to the consider-
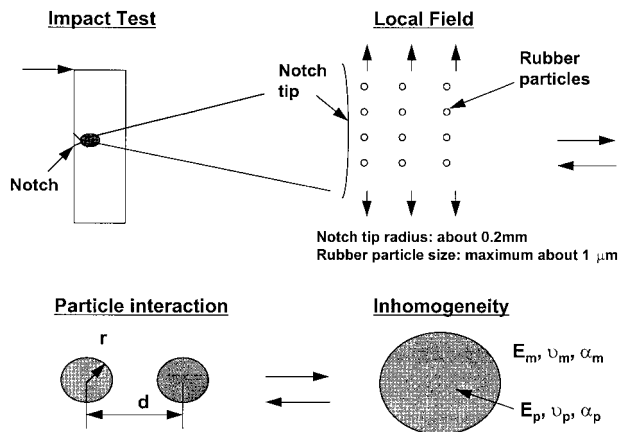

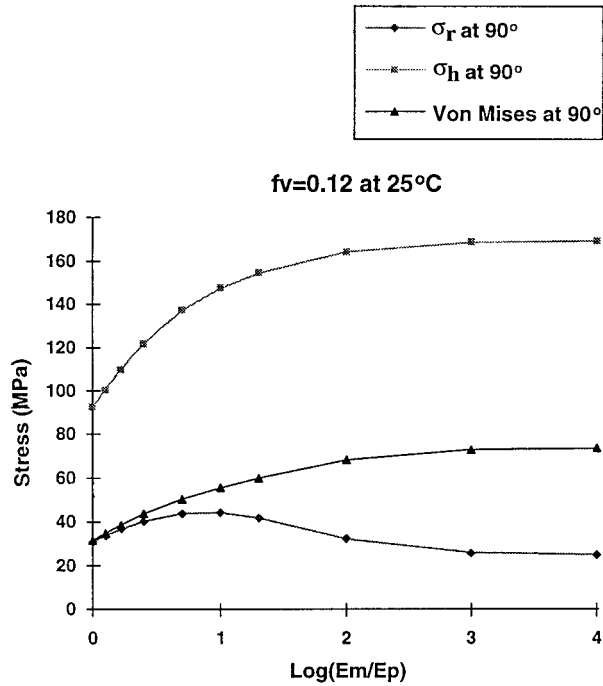**Figure 3** Sketches of the Izod impact test sample.

Figure 4 The Von Mises, radial, and hoop stress at the equator as functions of the ratio of moduli of matrix and rubber particle.

ation of a ductile–brittle transition: (1) it is assumed that at the initial point of failure, if a ductile failure mechanism is enabled the entire specimen will fail by a ductile mechanism. Alternatively, if a brittle crack is initiated, then the entire specimen will fail in a brittle manner. (2) According to the ASTM standard test method for impact resistance of plastics,[16] the radius of the notch tip of the sample is 250 μm. In our case the diameter of the rubber particle is less than 1 μm, so the notch tip radius is about 250 times larger than the size of particles. Thus, on the scale of the rubber particle near the notch tip, the notch tip will be flat. Because failure (shear yielding, microcracking, or crazing) usually occurs first in the vicinity of the notch tip, it is reasonable to assume the remote loading for the particles is uniaxial tension. (3) The remote loading occurs with a maximum stress given by an effective yielding stress (see Fig. 3). The effective yielding stress has been discussed by Ishai and Cohen.[17] With an increase in the volume fraction of soft particles, there will be an increase in the effective yielding stress under a constant loading condition. The standard notched Izod impact test is essentially a constant rate of displacement test. (4) The interfacial strength of the matrix and particle is larger than the matrix strength.

The total stress around the boundary of the particles can be obtained by superimposing the stress due to remote loading, the thermal residual stress, and the particle interaction. So the stress in the matrix near the particle can be expressed as:

$$\sigma = f(d/a)[\sigma^{\text{load}}(E_m, E_p, \phi, \sigma_y, \nu_m, \nu_p)$$
$$+ \sigma^{\text{thermal}}(T, \alpha_m, \alpha_p, E_m, E_p, \nu_m, \nu_p)] \quad (2)$$

where σ^{load} is the stress distribution of a spherical inhomogeneity in an infinite region,[10] σ_y is the yield stress of matrix, and $f(d/a)$ is the interaction function, depending on the packing arrangement, and is obtained by smoothing the function shown in Figure 2. The stress induced by temperature changes (σ^{thermal}) is shown in eq. (1). The ratio of d/a can be presented according to body centered cubic (BCC) packing,[18] and cubic packing[19] as follows:

$$d/a = 2\{3^{1/2}/2[\pi/(3\phi)]^{1/3} - 1\} \quad \text{for BCC packing}$$
$$d/a = 2\{[\pi/(6\phi)]^{1/3} - 1\} \quad \text{for cubic packing} \quad (3)$$
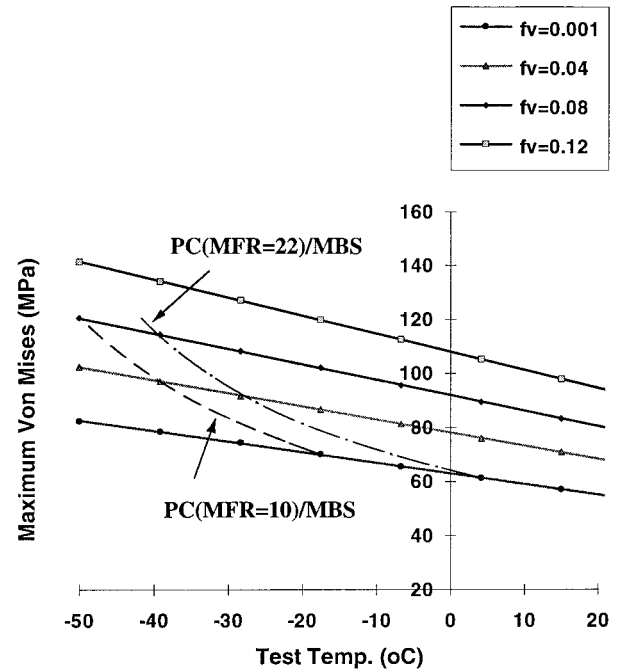

Figure 5 The maximum Von Mises stress as a function of volume fraction of impact modifier and temperature. The experimental results of ductile–brittle transition temperature of PC/MBS blends are also shown for comparison.
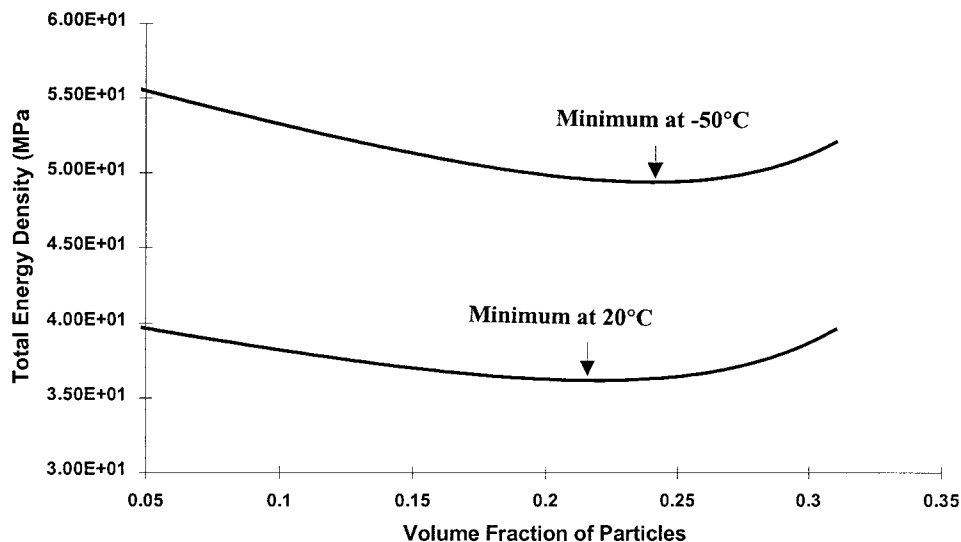
Figure 6 The total energy density of the representative volume vs. the volume fraction of rubber particles.

where ϕ represents the volume fraction of the spherical rubber particles.

YIELDING CRITERIA FOR POLYCARBONATE

Von Mises Yielding Criteria

It was first suggested by Bowden and Jukes[20] that the Von Mises stress can be considered as a yielding criterion for plastics. The criterion stated that yielding will take place if the Von Mises stress reaches the shear yielding strength of the material. The Von Mises stress around a given particle can be calculated by combining the stress fields arising from the inhomogeneity problem, the thermal stress, and particle interaction [see eq. (2)]. The results show that at the equator, we have a maximum value of Von Mises stress, and so the Von Mises stress at this point is chosen to check the suitability of this criterion of yielding as it relates to the ductile–brittle transition.

The dependence of Von Mises stress, radial stress, and hoop stress on the E_m / E_p is shown in Figure 4. These stresses increase as the ratio of moduli of the matrix and rubber particle increases. However, after E_m / E_p approaches 1000, stresses approach a constant value. This suggests that it is not necessary to increase E_m / E_p to more than 1000 to get higher stress concentration. Because shear yield or craze initiation is controlled by local stress distribution, a similar stress distribution should lead to a similar failure mechanism.

The ratio of E_m / E_p is mainly affected by the T_g of the rubber particle. A lower T_g rubber particle will have a better chance to have a higher E_m / E_p ratio throughout the service temperature range. This leads to the conclusion that a low T_g of the rubber particle will contribute to a lower ductile–brittle temperature transition of the blends.

The results of calculations also show that the Von Mises stress increases with decreasing elastomer density at a given volume fraction. If we further assume that the ductile–brittle transition is given by the intersection of the Von Mises stress with various temperatures with the projected yield strength of polycarbonate, then the lower density elastomer should produce a lower ductile–brittle transition. However, when we tried to compare the experimental Izod impact data of blend of poly(bisphenol A carbonate), polycarbonate (PC), and methylmethacrylate–butadiene–styrene (MBS) core shell rubbers with the prediction by the Von Mises yielding criterion, we quickly realized that we must consider the effect of matrix molecular weight (see Fig. 5). The experimental results of ductile–brittle transition temperature (DBTT) of PC/MBS blends show different curves when the molecular weight of the matrix changes from MFR = 10 to MFR = 22. It is known that the yielding stress of PC does not depend on the molecular weight in this molecular weight range. Hence, although the Von Mises criterion for yielding is considered a necessary condition for yielding, it is insufficient to predict the changes in
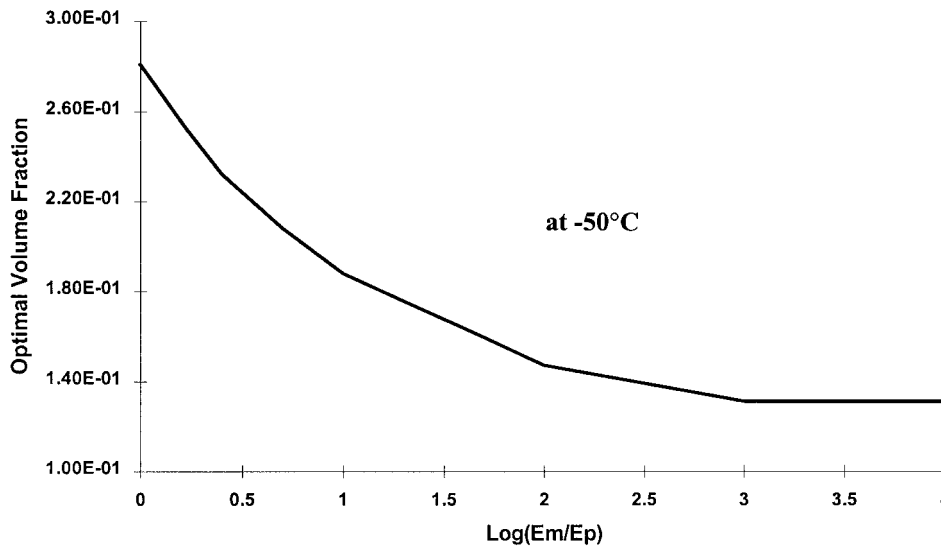
Figure 7 The effect of the ratio of the modulus of polycarbonate over the modulus of the elastomers on the optimal volume fraction at the ductile–brittle transition points.

the ductile–brittle transition in polymers with changes in the impact modifier type and content.

Energy Criteria for Yielding

An energy criterion for yielding has been proposed in recently published work[21] that describes the drawing (yielding) process of polycarbonate as a phase transition process. The drawing process will only take place when there is a certain stress level as well as enough energy input. The energy criterion for yielding in this article is discussed by using a similar concept. A representative volume is taken as that volume that contains only one rubber particle. The size of the representative volume as the function of the volume fraction can be obtained from eq. (3). The effective volume of the matrix, V_{eff}, will be the difference between the representative volume and the volume of particle.

The energy criterion can be stated as follows: if the average total energy density needed to fully yield the polycarbonate in the effective volume is smaller than the input energy density, yielding will take place; otherwise, the sample may fracture in a brittle fashion. This criterion can be illustrated in the following equation:

$$(W + \gamma)V_{eff}/V = (W + \gamma)(1 - \phi) = C \quad (4)$$

where W is the strain energy density, γ is the plastic energy needed to fully draw the polycarbonate and can be expressed as $\gamma = \sigma_{tr}(\lambda - 1)$, σ_{tr} is the drawing stress, and λ is the drawing ratio

of polycarbonate. The input energy density, C, is taken as a constant considering the nature of the Izod impact test. Because the Young's modulus of the rubber particle is much smaller than that of polycarbonate, the energy spent to deform the rubber particle to the yield strain of the polycarbonate matrix is ignored.

The results of the total energy density as a function of the volume fraction of rubber particles are shown in Figure 6. There is a minimum of total energy density at a specific volume fraction of rubber particles. The specific volume fraction of rubber particles at which this minimum total energy density occurs changes with the test temperature. The minimum in the total energy density comes from the effects of a decreasing effective volume and an increase of stress interaction as the volume fraction of rubber particle increases. The physical meaning of this minimum energy can be interpreted as the best chance that polycarbonate will yield at this temperature and volume fraction of impact modifier. Therefore, this optimal volume fraction may be considered as a parameter related to the ductile–brittle transition. Of note, optimal volume fractions have been determined experimentally (converted from the findings of a critical interparticle distance) in Nylon-EPDM,[22,23] and directly correlated to the ductile–brittle transition temperature.[23]

The effects of material parameters on the optimal volume fraction of rubber particle are shown in Figures 7 and 8. The result shows that the optimal volume fraction decreases as the ratio of
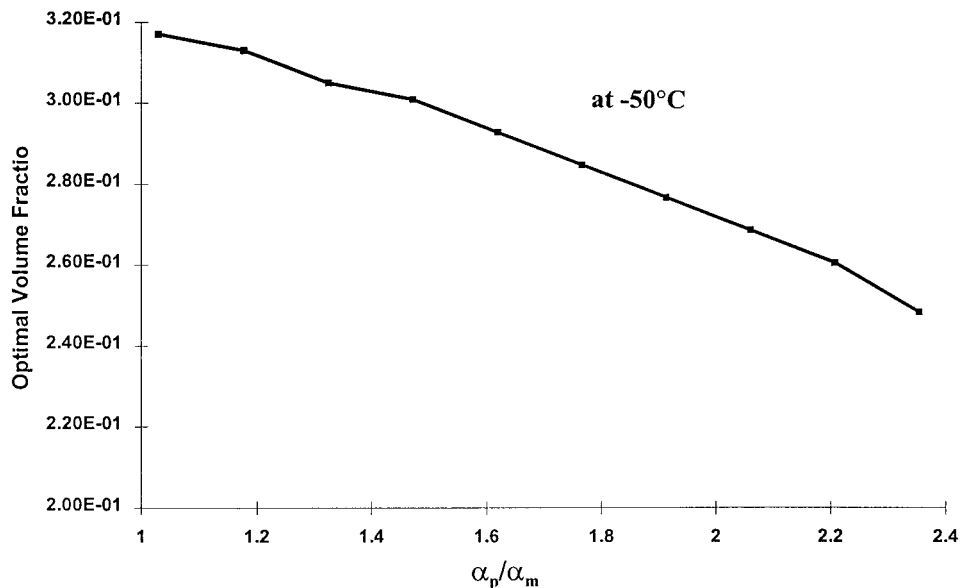
Figure 8 The effect of the ratio of the thermal expansion coefficient of the elastomer over the thermal expansion coefficient of polycarbonate on the optimal volume fraction at the ductile–brittle transition points.

the modulus of polycarbonate to the modulus of the elastomers increases. Interestingly, after this ratio of moduli is larger than 1000, the results change little, which indicates there is no advantage in reducing the modulus of rubber particles below about 10^6 Pa for impact modification of glassy polymers with modulus $\sim 10^9$ Pa. Similarly, the results show that the optimal volume fraction of rubber particle decreases as the thermal expansion coefficient of elastomers increases.

volume fraction of particles should be obtained through statistical means. The effect of the distribution of rubber particles on impact properties has been assumed to be that more uniform distribution of particles results in better impact performance. However, recent publications have indicated that a cocontinuous structure rather than uniformly distributed particle morphology may lead to higher impact toughness in certain polymers.[24]

DISCUSSION

This model predicts the importance of the material properties of the rubbery phase in the determination of the impact performance of the blend. It is specific to spherical particles and does not consider the energy dissipation or mechanisms after failure initiation. In selecting thermoplastic elastomers as impact modifiers, the elements of shape and shape control are important to consider also. The effect of particle shape on the impact properties of blends can be predicted within the model, although other considerations must be taken into account.

In real blends systems, the rubber particles may not be packed in cubic or body-centered cubic packing, especially in the case of a high-volume fraction. The relationship between the size and

CONCLUSIONS

Selection of an impact modifier type and content for a lower ductile–brittle transition temperature of thermoplastic blends has been made by modeling the stress distribution near the notch of an Izod impact test sample and the nature of stresses in spherical particle-filled polycarbonate. The model predicts that there is no advantage in reducing the modulus of rubber particles beyond where the ratio of the moduli of the matrix and the rubber particle is larger than 1000. The model also predicts that the glass–rubber transition temperature, T_g, and the nature of the transition dominate the ductile–brittle transition temperature of the blends.

An energy criterion for yielding is proposed to be an improved necessary condition for the yield-

ing of polycarbonate instead of the Von Mises stress yielding criterion, and can be used to predict an optimal volume fraction of rubber particles for ductility.

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