Toughening Mechanism of Polymer Blends: Influence of Voiding Ability of Dispersed-Phase Particles

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SYNOPSIS

The parameters which effect the cavitation strain of polymer blends toughened with a shear yield mechanism have been studied by analysis of the stress acted on the equatorial plane of dispersed-phase particles. As a result, the cavitation strain of polymer blends depends on the Young's modulus and the Poisson's ratio of the dispersed-phase particles and the matrix and also on the break stress of dispersed-phase particles. We tried to provide a criterion for selecting the materials used as dispersed-phase particles which can effectively enhance the toughness of polymer blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The toughness of many glassy polymers can be enhanced by the addition of rubber. The toughening mechanisms in elastomeric-filled polymers include crazing and shear yielding. It is well recognized that for the ductile matrix, such as polycarbonate (PC)[1] and nylon,[2] the major toughening mechanism is thought to be the cavitation of rubber particles and shear yield of the matrix. The presence of many closely packed particles which can cavitate enable the local buildup of hydrostatic tension produced by localized (constant volume) shear processes to be relieved. Thus, possibly soon after the development of some initial shear yielding, the constrained conditions are relieved and even relatively thick bulk specimens may behave as if the matrix were everywhere under a plane-stress condition. Yee et al.[1] determined the fracture toughness of PC and core–shell rubber blends using the J integral analysis. They confirmed that cavitation of the rubber particle really occurs followed by enhanced shear yielding. Huang and Wood[3] determined the fracture toughness of nylon and EPR blends using the J integral analysis. They concluded that the increase of the

degree of cavitation of rubber correlated with increase of the toughness of blends. Gaymans et al.[2] correlated the strain at the onset of cavitation in slow-speed tensile tests in various toughened nylon-6 blends with the ductile–brittle transition (DBT) temperature in Izod. The blends with high strains to cavitate also had high DBT temperatures. They suggested that cavitation was essential to the toughening process in order to relieve the triaxial tension at the crack tip and to promote massive yielding.

Gent and Tompkins[4,5] stated that rubber cavitation under triaxial tension is due to the elastic instability of precavities in the rubber and therefore depends only on the elastic modulus of the elastomer. But it failed to describe the correlation between the "blend cavitation strain" and the initial Young's modulus of polyethylene (PE) and Arnite (a thermoplastic elastomer used by Gaymans et al.[2]) used as dispersed-phase particles in blends with nylon-6.

It is not clear now which parameters of dispersed-phase particles and the matrix determine the voiding process in the blend. The purpose of this article was to analyze the cavitation ability of dispersed-phase particles through calculating stress acted on the dispersed-phase particles. We tried to give a criterion for selecting the materials used as dispersed-phase particles in polymer blends toughened with a shear yield mechanism.

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ANALYSIS

The Cause of Voiding of Dispersed-phase Particles

The dispersed-phase particles embedded in an isotropic elastic matrix, which is subjected to an applied uniaxial tensile stress remote from the particle, will sustain tensile stress or compress stress depending on the % wt of the modulus and the Poisson's ratio of the dispersed-phase particles and the matrix. A dispersed-phase particle with a low modulus and a high Poisson's ratio, such as addition of rubber into plastic, always sustain tensile stress. The analysis of elastic-stress distribution in particle-dispersed blends has been made on the following assumptions: (a) dispersed particles are spherical; (b) the interaction among particles is neglected; and (c) the constituents are perfectly bonded together at the interface.[6-8] According to the analysis, stress acts on the equatorial plane, the maximum stress acted by the matrix, of a particle dispersed in a matrix under tensile stress through the differences of the Young's modulus and the Poisson ratio between the dispersed sphere (E_2, ν_2) and the matrix (E_1, ν_1). The stress is given as follows:

$$\sigma = [(3\lambda_2 + 2\mu_2)F + 2\mu_2 GM]_\varepsilon \qquad (1)$$

where ε is the strain of the material:

$$M = -\tfrac{1}{3}(1 + \nu_1)$$

$$F = (1 - 2\nu_1)(\lambda_1 + 2\mu_1)/(4\mu_1 + 3\lambda_2 + 2\mu_2)$$

$$G = 15\,\mu_1(\lambda_1 + 2\mu_1)/$$

$$[2\mu_2(3\lambda_1 + 8\mu_1) + \mu_1(9\lambda_1 + 14\mu_1)]$$

$$\mu_1 = E_1/2(1 + \nu_1)$$

$$\mu_2 = E_2/2(1 + \nu_2)$$

$$\lambda_1 = \nu_1 E_1/(1 + \nu_1)(1 - 2\nu_1)$$

$$\lambda_2 = \nu_2 E_2/(1 + \nu_2)(1 - 2\nu_2)$$

Here, we will rewrite eq. (1) as

$$\sigma = S_\varepsilon \qquad (2)$$

where $S = (3\lambda_2 + 2\mu_2)F + 2\mu_2 GM$

From eq. (2), the stress σ, acted on the equatorial plane of a dispersed-phase particle, will increase in proportion to the strain ε of the blends. There exists two possible cases as follows: (1) The interfacial adhesive strength σ_{AS} is weaker than the break stress σ_B of the dispersed-phase particles. If the tensile stress acting on the dispersed-phase particle exceeds the interfacial adhesive strength, the dispersed-phase particle will detach from the matrix. In this case, the voiding of the blends can be attributed to the detachment of the dispersed-phase particle from the matrix, and the strain at which voiding in the blend starts (cavitation strain) can be expressed as follows:

$$\varepsilon_{cav} = \sigma_{AS}/S \qquad (3)$$

ε_{cav} is the cavitation strain of the polymer blends. (2) The interfacial adhesive strength σ_{AS} is strong enough. If the tensile stress acting on the dispersed-phase particle exceeds the break stress σ_B of the dispersed-phase particle, the dispersed-phase particle will be broken. So, in this case, the voiding in the blends will be due to internal rubber cavitation rather than to detachment of the dispersed-phase particle from the matrix. Cavitation strain can be expressed as follows:

$$\varepsilon_{cav} = \sigma_B/S \qquad (4)$$

Analysis of Cavitation of Dispersed-Phase Particles

If $\sigma_{AS} < \sigma_B$, the detachment of dispersed-phase particles from the matrix will take place first. The cavitation strain can be expressed as eq. (3). It seems that poor interfacial adhesive between the dispersed-phase particles and the matrix will result in a low cavitation strain. According to Gaymans et al.'s observation, blends with a lower cavitation strain will also have a lower ductile–brittle transition (DBT) temperature. But we must not forget that for blends with poor interfacial adhesive there exists high interfacial tension between the two phases, which will lead to a coarse domain size. It will also lead to a high DBT temperature; because $ID < ID_c$ (ID and ID_c are, respectively, the interparticle distance and the critical interparticle distance), the DBT criterion proposed first by Wu[9] would not easily hold for a coarse domain size system. The blends tend to be broken by brittle fracture.

To obtain blends with low interfacial tension and improved mechanical properties, the graft or block copolymers that act as a compatibilizer formed *in situ* through reactive extrusion or added as a third component separately are needed in blends. The presence of the copolymer results in a low interfacial tension and a fine domain size. At the same time, the interfacial adhesive strength is also improved.

Table I Data Used by Gaymans et al.[2][a]

Impact Modifier	E Modulus (MPa)	σ_{max} (MPa)
EPDM K740	4.8	3.8
XX1201 (EPM)	31.9	7.4
Keltaflex N35	189.0	4.8
Polyethylene	265.0	9.7
Arnifel EL740	960.0	36.4
Arnifel E315	35.6	17.4

[a] Included are the Initial Young's modulus (strain rate 10% min$_{-1}$), maximum stress, and elongation at break (strain rate 250% min$_{-1}$) of impact modifiers used in this study. For PE and Arnitel E740, the maximum stress is the yield stress; the other maximum stresses are stresses at break.

So, for most of the blends with improved mechanical properties, it is reasonable to think that the interfacial adhesive is strong enough and that the dispersed-phase particle will be broken before detachment from the matrix. In this case, the voiding in the blends is due to internal rubber cavitation. The cavitation strain can be expressed as eq. (4). From eq. (4), it is clear that the low break stress of the dispersed-phase particle is beneficial for voiding at low strain the toughened polymer with the shear-yield mechanism. But it is not the only parameter controlling the cavitation strain of polymer blends. The cavitation strain ε_{cav} also depends on parameter S, the stress acting on the dispersed phase particle for $\varepsilon = 100\%$. The value of S depends on the modulus and the Poisson's ratio of the dispersed-phase particle (E_2, ν_2) and the matrix (E_1, ν_1). So, cavitation strain ε_{cav} also depends on the modulus and the Poisson's ratio of the dispersed-phase particle and the matrix.

Now, we use the experimental data of Gaymans et al. (see Table I) for illustrating the relation of S with (E_2, ν_2) and (E_1, ν_1). Figures 1 and 2 are the relations of S with E_1 and ν_1 (where $E_2 = 4.8$ MPa, $\nu_2 = 0.4997$; they are the values of E_2 and ν_2 of EPDM[2,10]). The value of S increases with increase of the matrix modulus and decreases with increase of the matrix Poisson's ratio. According to eq. (4), the high matrix modulus and low matrix Poisson's ratio is advantageous to the cavitation of dispersed-phase particles at low strain.

From Figure 3, we can see that the curve of E_2 dependence of S is a parabola. There exists an E_2 at which S reaches the maximum value S_{max}. For a higher modulus of a dispersed-phase particle, $E_2 > E_2'$, the value of S decreases with increase of E_2. So, it is better to chose $E_2 \le E_2'$ to obtain a low cavitation strain. In the region of $E_2 \le E_2'$, it seems
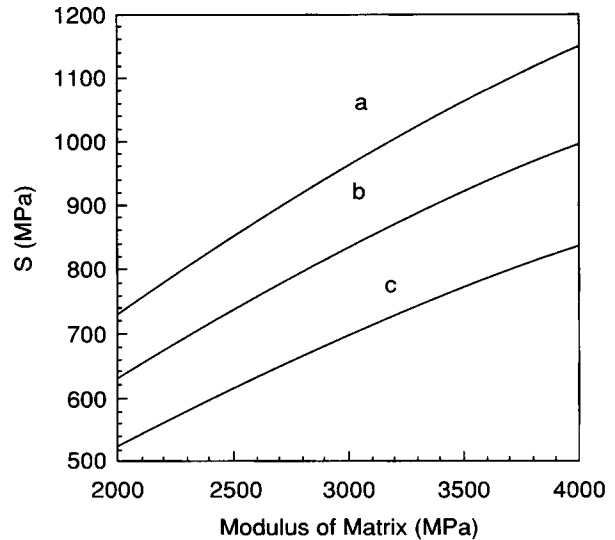

Figure 1 The relation of parameter S with the modulus of the matrix: $E_2 = 4.8$ MPa, $\nu_2 = 0.4997$; (a) $\nu_1 = 0.33$; (b) $\nu_1 = 0.40$; (c) $\nu_1 = 0.48$.

that the higher the E_2, the bigger the S, or the lower the ε_{cav}. But, in general (but not always), the material with a high modulus will also be broken at high tensile stress, i.e., high σ_B. So, to get a lower cavitation strain, according to eq. (4), the value of the modulus of a dispersed-phase particle must be chosen carefully.

Figure 4 shows the relation of S with the Poisson's ratio of dispersed-phase particles (where $E_1 = 2500$ MPa and, $\nu_1 = 0.43$, which is the value of the modulus
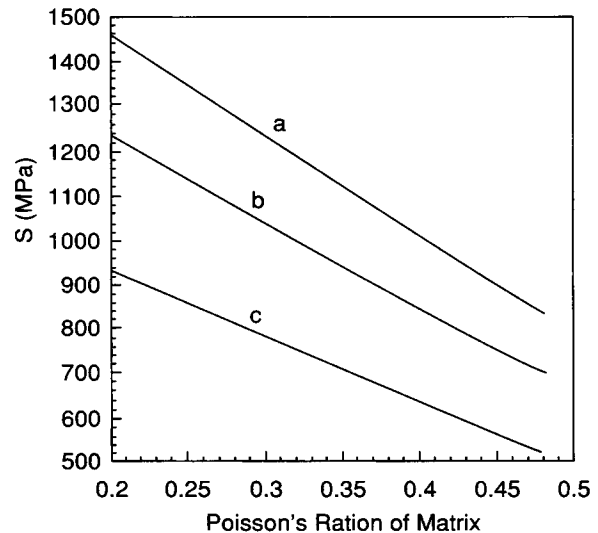

Figure 2 The relation of parameter S with the Poisson's ratio of the matrix: $E_2 = 4.8$ MPa; $\nu_2 = 0.4997$; (a) $E_1 = 4000$ MPa; (b) $E_1 = 3000$ MPa; (c) $E_1 = 2000$ MPa.
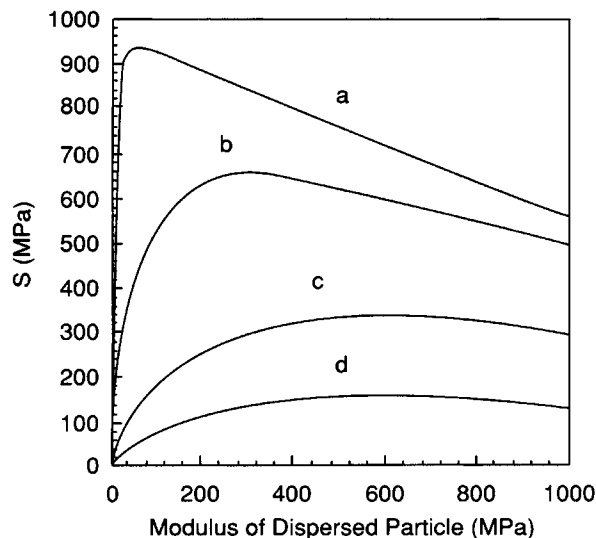
Figure 3 The relation of parameter S with the modulus of the dispersed particle: $E_1 = 2500$ MPa; $\nu_1 = 0.43$; (a) $\nu_2 = 0.4997$; (b) $\nu_2 = 0.49$; (c) $\nu_2 = 0.45$; (d) $\nu_2 = 0.40$.

and the Poisson's ratio of nylon-6 used by Gaymans et al.). ν_2 is taken from 0.3 to 0.4999; the Poisson's ratio of plastic and rubber are in this region. In Figure 4, the value of S increases with increase of the Poisson's ratio of the dispersed-phase particles for blends with different moduli of dispersed-phase particles. But, for low E_2 [here, curves a, b, and f for EPDM K740, XX1201(EPM), and Arnitel E315 respectively], the values of S are very low for $\nu_2 \leq 0.49$ and sharply increase for $\nu_2 \geq 0.49$. This means that dispersed-phase particles with a low modulus sustain a very weak force if $\nu_2 \leq 0.49$ and cannot be broken at low strain. If $\nu_2 = 0.49$–0.4999, which is in the region of rubber, the dispersed-phase particle will sustain a strong tensile force and the blends tend to be caved at low strain.

Now, we pay attention to curves b and f, corresponding to XX1201(EPM) and Arnite E315 as dispersed-phase particles. The two curves are close to each other because of almost the same moduli of the dispersed-phase particles. But the cavitation strain for blends with Arnite E315 and XX1201 as dispersed-phase particles are about 6.5 and 4%, and the BT temperatures are about 30 and $-10°$C, respectively. The difference of cavitation strain can be attributed to the different break stress and the Poisson's ratio of Arnite E315 and XX1201. According to the experimental data of Gaymans et al.,[2] (see Table I), the break stress of XX1201, $\sigma_{SXX} = 7.4$ MPa, and the break stress of Arnite E315, $\sigma_{SAr} = 17.4$ MPa,

$$\sigma_{SXX} < \sigma_{SAr} \qquad (5)$$

Since XX1201(EPM) is a rubber, its Poisson's ratio is reasonable in the region 0.49–0.4999. Since Arnite E315 is a thermoplastic elastomer, it is expected that the Poisson's ratio of Arnite E315 is smaller than 0.49. So, according to curves b and f in Figure 4,

$$S_{XX} > S_{Ar} \qquad (6)$$

where S_{XX} and S_{Ar} are the S values of XX1201 and Arnite E315, respectively. According to eq. (4) and combining eq. (5) with eq. (6), we have

$$\varepsilon_{cavXX} < \varepsilon_{cavAr} \qquad (7)$$

ε_{cavXX} is the cavitation strain of XX1201 and ε_{cavAr} is the cavitation strain of Arnite E315.

It is clear now that nylon-6 blends with Arnite E315 as a dispersed-phase particle exist at higher cavitation strains compared to that of nylon-6 blends with XX1201 as the dispersed-phase particle because of the high break stress and the low Poisson's ratio of Arnite E315 compared to that of XX1201.

Similarly, although curves c and d are close to each other, nylon-6 blends with Keltaflex (a thermoplastic elastomer used by Gaymans et al., see Table I) as the dispersed-phase particle (curve c) exists at a lower cavitation strain compared to that of ny-
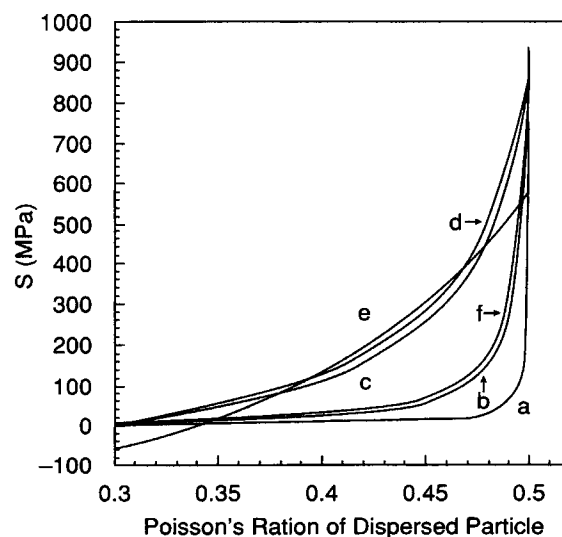

Figure 4 The relation of parameter S with the Poisson's ratio of the dispersed particle: $E_1 = 2500$ MPa; $\nu_1 = 0.43$; (a) $E_2 = 4.8$ MPa; (b) $E_2 = 31.9$ MPa; (c) $E_2 = 189$ MPa; (d) $E_2 = 265$ MPa; (e) $E_2 = 960$ MPa; (f) $E_2 = 36.5$ MPa.

lon-6 blends with PE as the dispersed-phase particle (curve d).

Curves c and f, because Keltaflex and Arnite are both thermoplastic elastomers, show that they have almost the same Poisson's ratio value. Keltafex, a dispersed-phase particle with a high modulus, will sustain stronger tensile stress compared to Arnite E315 as the dispersed-phase particle (Fig. 4). So, Keltaflex with a low break stress will break at a low strain compared to Arnite E315 with a high break stress.

CONCLUSIONS

The cavitation strain of polymer blends toughened with a shear-yield mechanism depends on the modulus and the Poisson's ratio of the matrix and the dispersed-phase particle and break stress of dispersed phase particles. In general, the higher the matrix modulus, the lower the Poisson's ratio value of the matrix; the higher Poisson's ratio value of the dispersed-phase particle and the lower breaking stress of the dispersed phase particle should be beneficial for a lower cavitation strain of polymer blends. The selection of the modulus of the dispersed-phase particle must be careful. We must combine the modulus of materials with their break stress and Poisson's ratio for selecting material as a dispersed-phase particle which can enhance the toughness of polymer blends effectively. In general, materials with low break stress, high modulus, such as Keltaflex, and low break stress, low modulus, and high Poisson's ratio, such as EPDM, are all effective materials that act as dispersed-phase particles.

REFERENCES

1. D. S. Partker, H.-J. Sue, J. Huang, and A. F. Yee, *Polymer,* **31,** 2267 (1990).
2. R. J. M. Borggreve, R. J. Gaymans, and H. M. Eichenwald, *Polymer,* **30,** 78 (1989).
3. D. D. Huang and B. A. Wood, *Polym. Prepr.,* **33,** 629 (1992).
4. A. N. Gent, in *Science and Technology of Rubber,* Academic Press, Orlando, FL, 1978, p. 419.
5. A. N. Gent and D. A. Tompkins, *J. Polym. Sci. A-2,* **7,** 1483 (1969).
6. J. M. Dewey, *J. Appl. Phys.,* **16,** 55 (1945).
7. J. M. Dewey, *J. Appl. Phys.,* **18,** 132 (1947).
8. J. M. Dewey, *J. Appl. Phys.,* **18,** 578 (1947).
9. S. Wu, *Polymer,* **26,** 1855 (1985).
10. J. Jancar, A. DiAnselmo, and A. T. DiBenedetto, *Polymer,* **34,** 1684 (1993).