

A Generalized Criterion for Rubber Toughening: The Critical Matrix Ligament Thickness

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Synopsis

The thickness of matrix ligament is shown to be the single parameter determining whether a polymer/rubber blend will be tough or brittle. The matrix ligament is defined as the region of the matrix between two neighboring rubber particles. Specifically, the ligament thickness is the surface-to-surface interparticle distance. When the average ligament thickness is smaller than a critical value, a blend will be tough; when greater, it will be brittle. In other words, a sharp brittle-tough transition occurs at the critical ligament thickness. This critical parameter is independent of rubber volume fraction and particle size, and is characteristic of the matrix for a given mode, temperature and rate of deformation. What is important is the matrix ligament, not rubber particles. The single matrix parameter explains the effects of phase morphology, rubber volume fraction, particle size, particle-size polydispersity, and particle flocculation on toughness.

INTRODUCTION

Recently, we found that a sharp brittle-tough transition occurs when the average surface-to-surface interparticle distance is smaller than a critical value in nylon/rubber blends.¹ This critical value is independent of rubber volume fraction and particle size, and is the property of the matrix alone. We thus proposed that the surface-to-surface interparticle distance is the single parameter determining whether a blend will be tough or brittle for pseudo-ductile matrices.

We would like to reinterpret this finding, show that the important factor is the matrix ligament rather than the rubber particles, and extend the concept to polymer/rubber blends with brittle matrices.

POLYMER MATRICES

There are two types of polymer matrices: pseudoductile and brittle. This classification is not rigorous, since time-temperature-geometry effects are ignored. However, it gives a convenient basis for our discussion.

Pseudoductile polymers tend to shear yield, have a high crack initiation energy but a low crack propagation energy, and so have a high unnotched but a low notched impact strength. Examples are nylons, thermoplastic polyesters, and polycarbonate. Matrix yielding is the main mechanism of energy dissipation in such polymer/rubber blends.^{2,3}

Brittle polymers tend to craze, have a low crack initiation, and a low crack propagation energy, and so have both a low unnotched and a low notched

impact strength. Examples are polystyrene and poly(methyl methacrylate). Matrix crazing is the main mechanism of energy dissipation in such polymer/rubber blends.^{2,3} On the other hand, however, recent work of Gilbert and Donald⁴ showed that matrix yielding does occur after crazing. Only when this occurs, will a blend be very tough, as further discussed later.

BLENDS WITH PSEUDODUCTILE MATRICES

Critical Matrix Ligament Thickness

Figure 1 shows schematics of two rubber particles in a matrix, where d is the particle diameter, τ the surface-to-surface interparticle distance (i.e., the matrix ligament thickness) and L the center-to-center interparticle distance. Figure 2 shows the notched Izod impact strength (ASTM D-256, 25°C) versus the number-average particle diameter at constant rubber contents (10, 15, and 25% by weight) for nylon-66/rubber blends, where the rubber is a carboxylated ethylene-propylene rubber.¹ All blends have the same strong nylon/rubber adhesion through interfacial grafting ($G_a = 8100 \text{ J/m}^2$, where G_a is the adhesive fracture energy).¹ A sharp brittle-tough transition occurs at critical particle diameters, which vary with the rubber volume fraction.

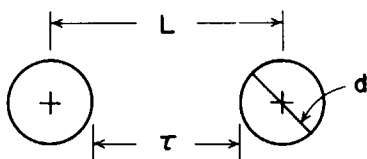


Fig. 1. Schematics of rubber particles and matrix ligament.

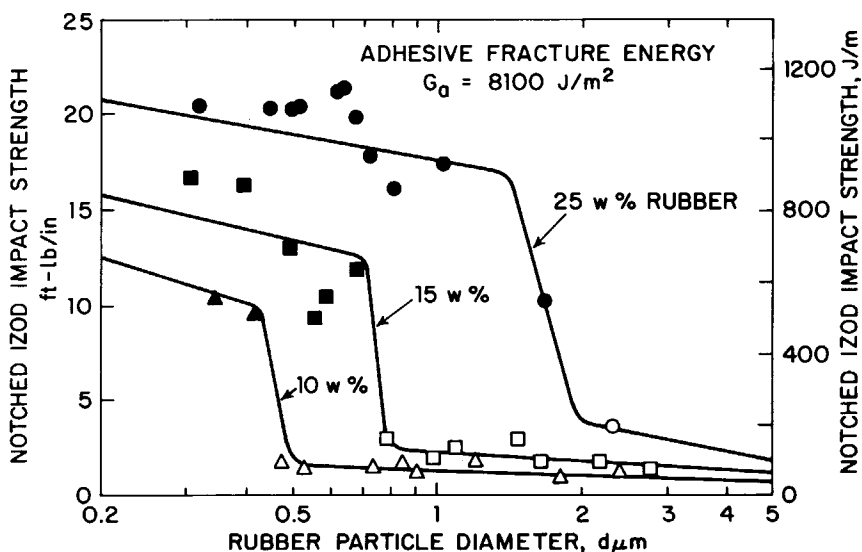


Fig. 2. Notched Izod impact strength vs. number-average diameter of rubber particles for nylon-66/rubber blends (ASTM D-256, 25°C). After Ref. 1.

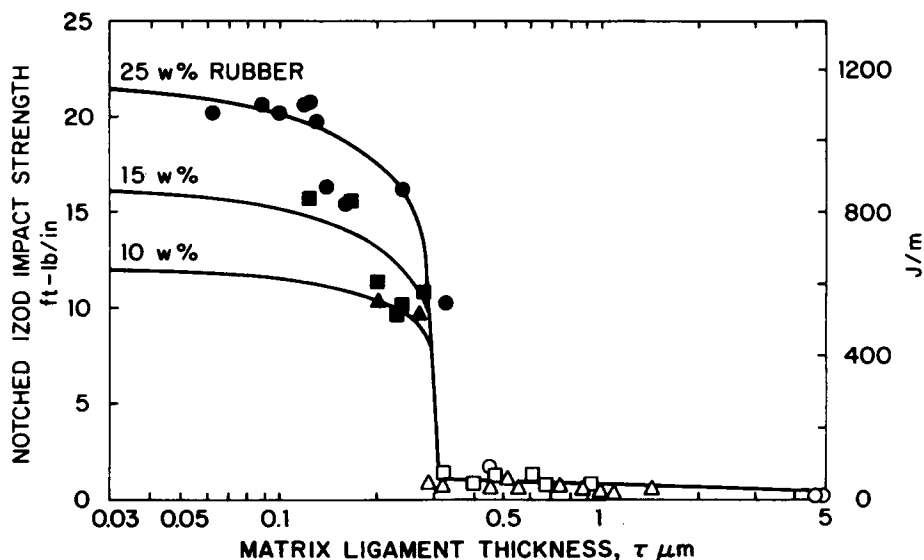


Fig. 3. Notched Izod impact strength vs. matrix ligament thickness for nylon-66/rubber blends. Replotted from Figure 1. Tough: (●) 25 w%; (■) 15 w%; (▲) 10 w% rubber; Brittle: (○) 25 w%; (□) 15 w%; (△) 10 w% rubber. After 1.

However, when plotted versus the average surface-to-surface interparticle distance, shown in Figure 3, the transition is found to occur at a single critical value τ_c , which is independent of rubber volume fraction and particle size.¹

Therefore, the condition for rubber toughening for blends with pseudoductile matrices is simply,

$$\tau < \tau_c \quad (1)$$

where τ is the average matrix ligament thickness (i.e., surface-to-surface interparticle distance) and τ_c the critical matrix ligament thickness for the onset of brittle-tough transition. The τ_c is independent of rubber volume fraction and particle size, and is characteristic of the matrix alone at a given mode, temperature and rate of deformation. For blends with dispersed spherical particles, we have¹

$$d_c = \tau_c \left[k(\pi/6\phi_r)^{1/3} - 1 \right]^{-1} \quad (2)$$

where d_c is the critical rubber particle diameter, ϕ_r the rubber volume fraction, and k a geometric constant, i.e., $k = 1$ for cubic lattice, $(2)^{1/3}$ for body-centered lattice and $(4)^{1/3}$ for face-centered lattice. Figure 4 shows that the spatial packing of rubber particles in nylon/rubber blends is well described by a cubic lattice ($k = 1$), wherein the symbols are experimental and the lines are drawn to Eq. (2). The τ_c is 0.30 μm for nylon/rubber blends.

We have also observed similar critical phenomenon in blends with other pseudoductile matrices, such as thermoplastic polyesters. For instance, we

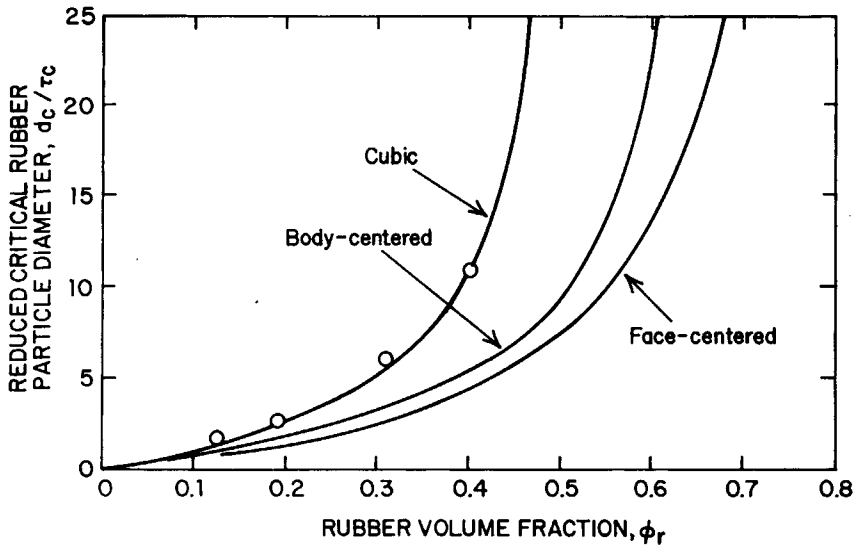


Fig. 4. Reduced critical rubber particle diameter vs. rubber volume fraction for cubic, body-centered, and face-centered lattices. Symbols are experimental for nylon/rubber blends. Lines are theoretical.

found that for PETG/rubber blends, $\tau_c = 0.44 \mu\text{m}$ for notched Izod impact strength, where PETG is an amorphous copolyester of ethylene glycol, 1,4-cyclohexanedimethanol and terephthalic acid. We thus propose that the critical phenomenon is general with pseudoductile matrices.

Note that the critical quantity is the surface-to-surface interparticle distance. In fact, the center-to-center interparticle distance is not important. The term "interparticle distance" tends to focus on the rubber particles. However, what is important is not the rubber particles but rather the thickness of the matrix ligament. The matrix ligament thickness is, by definition, the surface-to-surface interparticle distance for blends with dispersed particles, as shown in Figure 1. The condition for toughening is thus "the matrix ligament thickness must be smaller than the critical value τ_c ." This reinterpretation properly shifts the focus from rubber particles to the matrix ligament. The concept can now explain the effects of phase morphology (spheroids, rods, platelets, and networks), size polydispersity and particle flocculation, and may also be extended to blends with brittle matrices.

Origin of Critical Phenomenon

During impact fracture, rubber particles cavitate to relieve the triaxial stresses in the matrix ligament; see Note. If the matrix ligament is thinner than τ_c , a plane-strain to plane-stress transition would occur; the ligament would shear yield, and the blend would be tough. On the other hand, if the ligament is thicker than τ_c , such transition could not occur, and the matrix ligament would fail in a brittle fashion.

In a real blend, there is a distribution of thin and thick ligaments. However, if the number-average ligament thickness is smaller than τ_c , the thick liga-

ments would be surrounded by enough thin ones, so that the yielding of thin ones would cause a plane-strain to plane-stress transition in thick ones, causing them to yield eventually. The matrix yielding would propagate, and the blend would be tough. On the contrary, if the number-average ligament thickness is greater than τ_c , there would not be enough thin ones to surround the thick ones, so that matrix yielding could not propagate, and the blend would be brittle.

Effect of Size Polydispersity

In a real blend, rubber particles have a range of different sizes. We have shown that rubber-particle size obeys the log-normal distribution,¹ given by⁵

$$f = \frac{1}{(2\pi)^{1/2}(\ln \sigma_g)} \exp \left[\frac{-(\ln x - \ln \bar{x}_g)^2}{2(\ln \sigma_g)^2} \right] \quad (3)$$

where f is the frequency, \bar{x}_g the geometric mean size ($= \bar{x}_m$, the median size by count) and σ_g the geometric mean standard deviation. The σ_g is a measure of the breadth of distribution. For monodispersity (uniform size), $\sigma_g = 1$; for polydispersity, $\sigma_g > 1$. For nylon/rubber blends, σ_g varies from ~ 1.4 to ~ 2 .¹

Figure 5 shows the log-normal distribution of rubber particle radius (r) for a nylon/rubber blend.¹ The size at 50% is equal to \bar{x}_g , and the "slope" (i.e.,

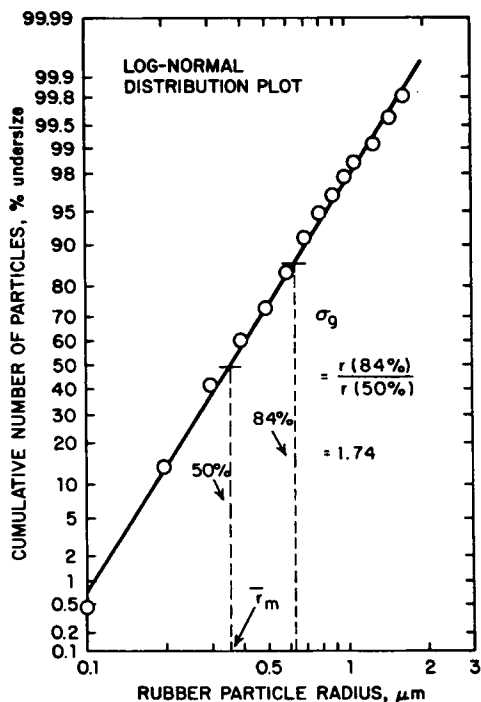


Fig. 5. Log-normal distribution of rubber particles in a nylon/rubber blend.

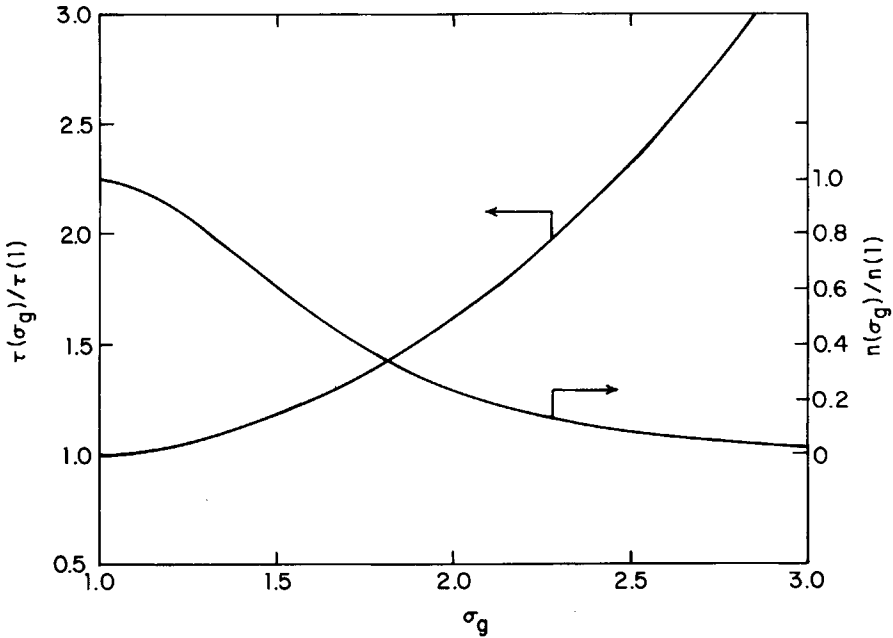


Fig. 6. The plots of $n(p)/n(1)$ and $\tau(p)/\tau(1)$ vs. σ_g for rubber particles conforming to log-normal distributions.

the ratio of size at 84% to size at 50%) is equal to σ_g . For the blend shown, $\bar{x}_m = 0.35 \mu\text{m}$, and $\sigma_g = 1.74$.

The effect of size polydispersity can be seen in the ratio of the number of particles per unit volume in the polydisperse sample $n(\sigma_g)$ to that in the monodisperse sample $n(1)$, and the ratio of the average matrix ligament thickness in the polydisperse sample $\tau(p)$ to that of the monodisperse sample $\tau(1)$. For log-normal distributions, at the same rubber volume fraction and average size \bar{x}_m , we have

$$n(\sigma_g)/n(1) = \exp[-3(\ln \sigma_g)^2] \quad (4)$$

and

$$\tau(\sigma_g)/\tau(1) = \exp[(\ln \sigma_g)^2] \quad (5)$$

Figure 6 plots Eqs. (4) and (5), showing that as the size polydispersity increases, the number of particles decreases, and the average ligament thickness increases rapidly. Thus, uniform particle sizes are more effective than heterogeneous sizes in rubber toughening.

Effect of Particle Flocculation

The present concept predicts that particle flocculation will greatly reduce the toughening efficiency, consistent with experience in the art. Figure 7

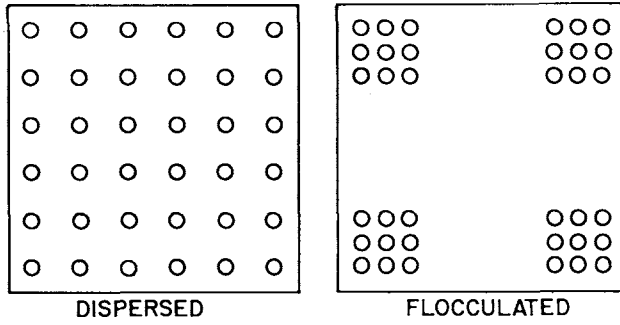


Fig. 7. Schematics of particle dispersion and flocculation.

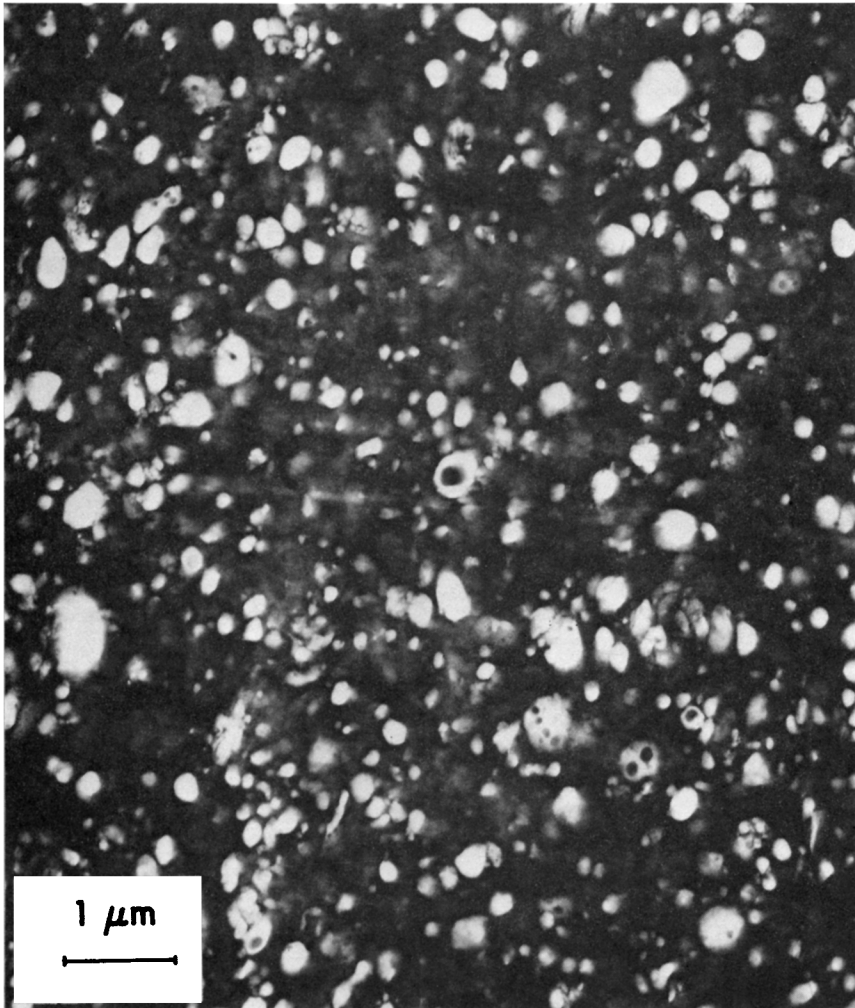


Fig. 8. Nylon-66/rubber blends (15% by weight of rubber) with well-dispersed rubber particles (high notched impact strength of 15 ft-lb/in.). Transmission electron photomicrograph of a microtomed section stained in 1% aqueous phosphotungstic acid.

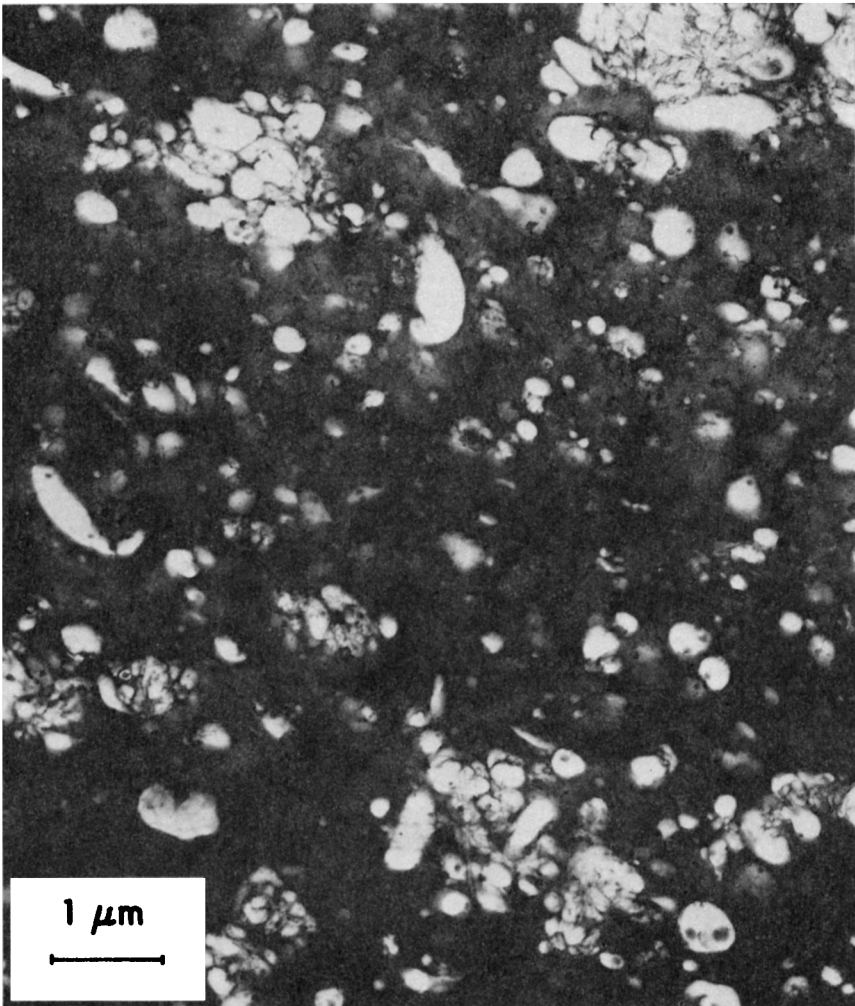


Fig. 9. Nylon-66/rubber blends (15% by weight of rubber) with flocculated rubber particles (low notched impact strength of 2.5 ft-lb/in.). Transmission electron photomicrograph of a microtomed section stain with 1% aqueous phosphotungstic acid.

illustrates dispersed and flocculated particles; each case has 36 particles. Flocculation forms clusters of particles. Within a cluster, the ligaments are thin, but the clusters are surrounded by very thick ligaments. Therefore, ligament yielding cannot propagate, and the blend is brittle. On the other hand, in well-dispersed cases, ligaments are much thinner and more uniformly distributed. Therefore, ligament yielding can propagate, and the blend is tough.

Figures 8 and 9 show two examples for nylon-66/rubber blends. Each case contains 15% by weight of the rubber of similar particle sizes. However, the blend shown in Figure 8 has well-dispersed particles, a high notched Izod impact strength (ASTM D256, 25°C) of 15 ft-lb/in. (i.e., 790 J/m), and is tough, while the blend shown in Figure 9 has flocculated particles, a low notched impact strength of 2.5 ft-lb/in. (i.e., 130 J/m), and is brittle.

Minimum Particle Size

At a given rubber volume fraction, the ligament thickness decreases with decreasing particle size. Thus, small particles are more effective in toughening than large ones. However, very small rubber particles might not cavitate such as shown in epoxy,⁶ and so their effectiveness could diminish. However, this has not been observed with the smallest particles ($\sim 0.1 \mu\text{m}$) available.

COMMENTS AND PERSPECTIVE

We would like to emphasize that we found the brittle-tough transition and the critical parameters (i.e., critical particle size and surface-to-surface interparticle distance, which is renamed here as the matrix-ligament thickness) experimentally without recourse to any specific fracture mechanisms (1).

We then suggested that stress-field overlap might explain the origin of brittle-tough transition (1). However, we now believe that stress-field overlap may not account for the onset of brittle-tough transition, although it can enhance matrix yielding. The stress intensity is a function of L/d , i.e., L is proportional to d at constant L/d . Thus, it would predict that the center-to-center interparticle distance L is the critical parameter, and that large particles are more effective in toughening than small ones. Both predictions are incorrect.

We now propose that the present mechanism of rubber cavitation, stress-state transition, ligament yielding and propagation through connectivity of "thin" ligaments is the correct one. Enhanced matrix yielding due to rubber cavitation was suggested to toughen ABS (7) and polycarbonate (8). However, prior to our work, it was not known that the matrix ligament must be thinner than the critical value τ_c for the ligament to yield, and that thin ligaments must have sufficient connectivity for the yielding process to propagate. In other words, the onset of brittle-tough transition may be formulated as a problem of the connectivity of thin ligaments.

Furthermore, we believe that having a lower modulus than the matrix, rubber particles need not cavitate to cause a stress-state transition (6), although cavitation will enhance it.

BLENDS WITH BRITTLE MATRICES

Matrix crazing has been shown as the main mechanism of energy dissipation in such blends.² However, recently Gilbert and Donald⁴ showed that matrix yielding can occur after crazing. Only when this occurs, will a blend be very tough.

Figure 10 shows schematically a stage during the fracture of a polystyrene/rubber blend, drawn after a scanning electron photomicrograph of Gilbert and Donald.⁴ Large rubber particles ($d > d_z$, where d_z is the minimum particle diameter for craze initiation) first initiate crazes, which start to break down on continued deformation. If the matrix ligament (Fig. 10) is thicker than a critical value τ_c , secondary crazes are found to form at the bases of the ligament, where the tensile stresses are the greatest. The secondary crazes continue to grow, and the ligament fails catastrophically in a brittle fashion. When this occurs, the blend is only marginally tough. On the

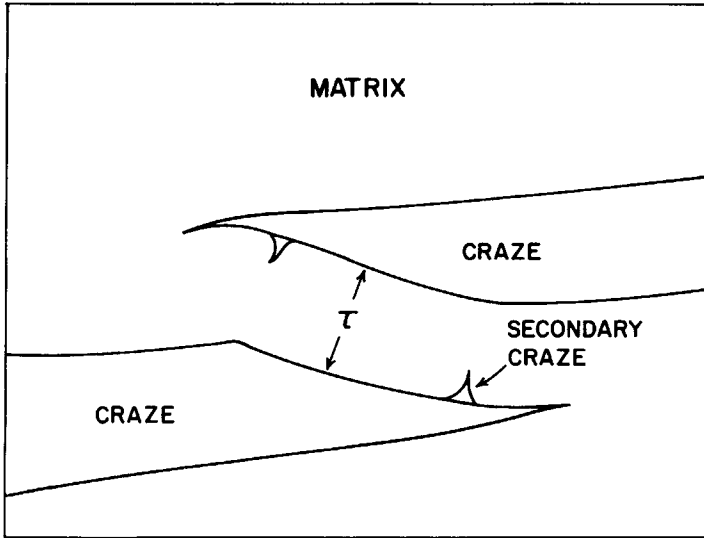


Fig. 10. Schematics of primary crazes, matrix ligament and secondary crazes in the fracture of a polystyrene/rubber blend. Drawn from Ref. 4.

other hand, if the matrix ligament is thinner than τ_c , secondary crazes are not formed; rather the ligament is found to yield. Only when this occurs, is the blend very tough.⁴

Thus, the condition for toughening, in the case of blends with brittle matrices, is

$$\tau < \tau_c \quad \text{and} \quad d > d_z \quad (6)$$

At constant rubber volume fraction, the matrix ligaments are thinner with smaller particles, but larger particles are more efficient for craze initiation. Therefore, there is an optimum rubber particle size at which the toughness is the greatest. If we crudely assume that the matrix ligament thickness may be approximated by the surface-to-surface interparticle distance, the optimum rubber particle size is then given by

$$d_0 \approx \tau_c \left[(\tau/6\phi_r)^{1/3} - 1 \right]^{-1} \quad (7)$$

where d_0 is the optimum diameter.

Experimentally, for polystyrene/rubber blends, $d_0 \approx 5 \mu\text{m}$ at $\phi_r \approx 0.15$.⁹⁻¹⁴ Using these in Eq. (7) gives $\tau_c \approx 2.5 \mu\text{m}$, which compares favorably with the observed value of $\sim 3 \mu\text{m}$ reported by Gilbert and Donald⁴ by in situ observation of the deformation of matrix ligament under scanning electron microscope.

CONCLUSION

Matrix ligament thickness is shown to be the most basic factor in rubber toughening. A sharp brittle-tough transition will occur when the average thickness of matrix ligaments is at the critical value. This single parameter

explains the roles of phase morphology, particle size, polydispersity, flocculation, and rubber volume fraction. There are variations in the toughness within brittle and tough regions. These are due to secondary effects, not dealt with here.

Matrix/rubber adhesion is also an important factor. The minimum adhesion required has been established before.¹ In all the blends discussed herein, the adhesion is above the minimum required level and is constant in each series.¹ Even if the adhesion is strong, through interfacial chemical bonding, the matrix ligament must be smaller than the critical value for a blend to be tough. Otherwise, it will still be brittle.

NOTE

The rubber particles cavitate during impact fracture of nylon-66/rubber blends. Figure 11 shows the transmission electron photomicrograph of an undeformed specimen, showing that the rubber particles are not cavitating

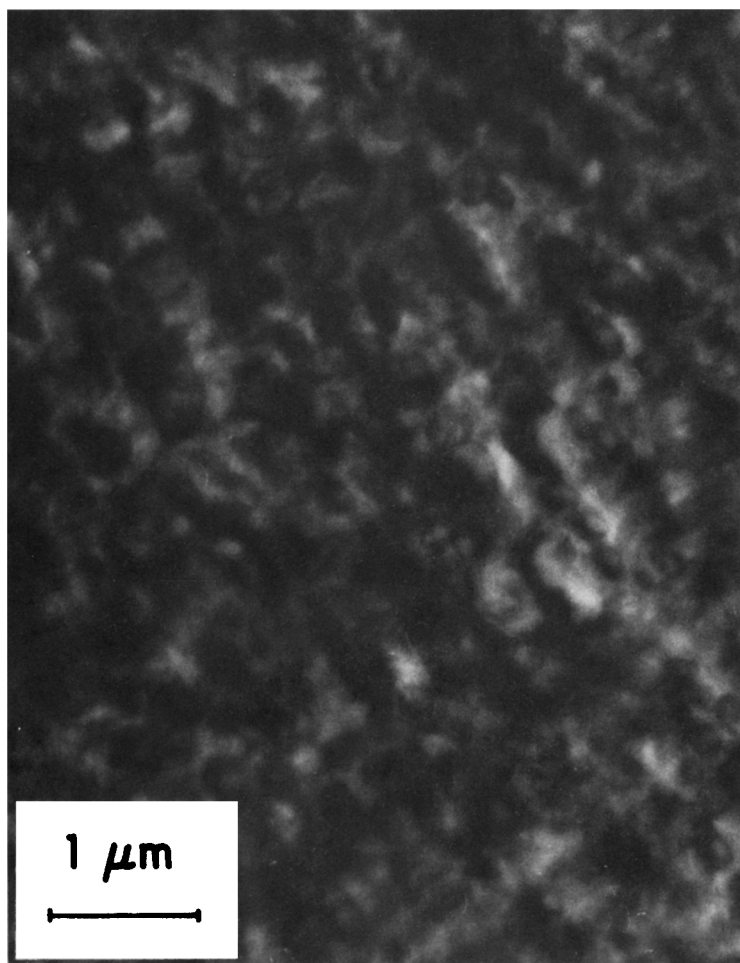


Fig. 11. Transmission electron photomicrograph (not stained) of a thin section of virgin undeformed specimen of toughened nylon-66/rubber blend (notched Izod 17 ft-lb/in or 900 J/m).

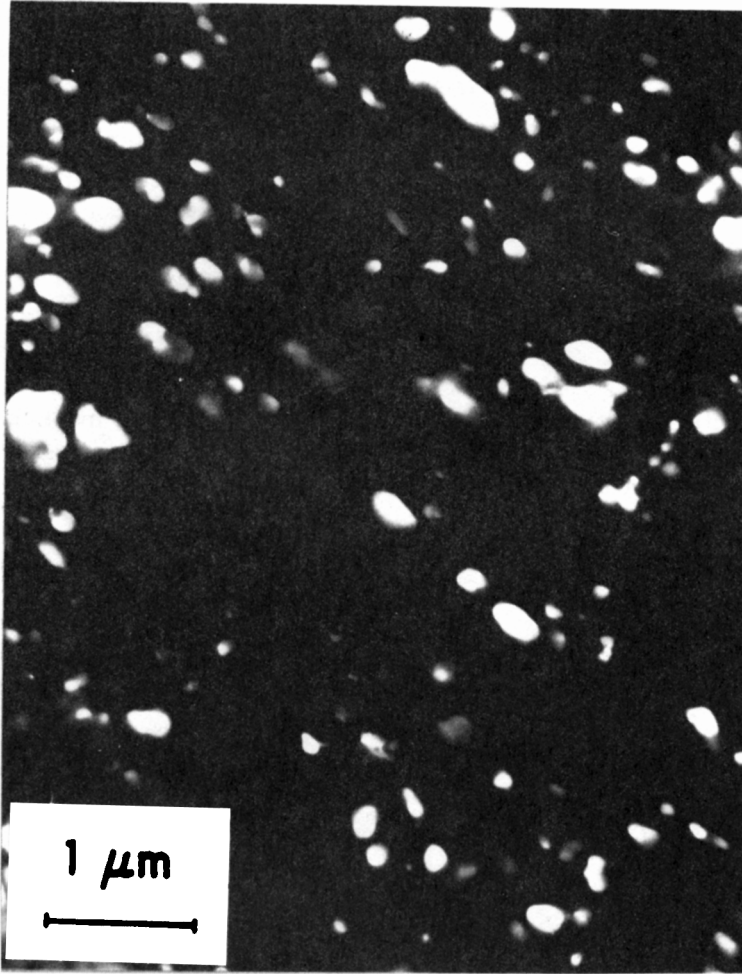


Fig. 12. Transmission electron photomicrograph (not stained) of a thin section of the energy dissipation zone (i.e., stress-whitened zone around the crack) of the same specimen as in Fig. 11 after impact fracture.

before impact. To better show the coherence of the specimen, the microtomed section was not stained to avoid enhancing the contrast between the two phases. Figure 12 shows a photomicrograph of the energy dissipation zone (i.e., stress-whitened zone around the crack) of the same specimen after impact fracture, showing that the rubber particles are extensively cavitated. The section was microtomed the same way, and was also not stained.

References

1. S. Wu, *Polymer*, **26**, 1855 (1985).
2. C. B. Bucknall, *Toughened Plastics*, Applied Science Publishers, London, 1977.
3. S. Wu, *J. Polym. Sci.: Polym. Phys. Ed.*, **21**, 699 (1983).
4. D. G. Gilbert and A. M. Donald, *J. Mater. Sci.*, **21**, 1819 (1986).
5. R. R. Irani and C. F. Callis, *Particle Size: Measurement, Interpretation and Application*, Wiley, New York, 1963.

6. J. N. Sultan and F. J. McGarry, *Polym. Eng. Sci.*, **13**, 29 (1973).
7. M. A. Maxwell and A. F. Yee, *Polym. Eng. Sci.*, **21**, 205 (1981).
8. A. M. Donald and E. J. Kramer, *J. Mater. Sci.*, **17**, 1765 (1982).
9. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum, New York, 1976.
10. A. M. Donald and E. J. Kramer, *J. Appl. Polym. Sci.*, **27**, 3729 (1982).
11. R. F. Boyer and H. Keskkula, in *Encyclopedia of Polymer Science and Technology*, Vol. 13, Edited by N. Bikales, Interscience, New York, 1970, pp. 375-394.
12. S. L. Rosen, *Polym. Eng. Sci.*, **7**, 115 (1967); *J. Elastoplast.*, **2**, 195 (1976).
13. R. P. Kambour, *J. Polym. Sci.: Macromol. Rev.*, **7**, 1 (1973).
14. D. J. Angier and E. M. Fettes, *Rubber Chem. Technol.*, **38**, 1164 (1965).

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