Phase structure and adhesion in polymer blends: A criterion for rubber toughening*

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The effects of rubber particle size and rubber–matrix adhesion on notched impact toughness of nylon–rubber blends are analysed. A sharp tough–brittle transition is found to occur at a critical particle size, when the rubber volume fraction and rubber–matrix adhesion are held constant. The critical particle size increases with increasing rubber volume fraction, given by $d_c = T_c\{(\pi/6\phi_r)^{1/3} - 1\}^{-1}$, where d_c is the critical particle diameter, T_c the critical interparticle distance, and ϕ_r the rubber volume fraction. The critical interparticle distance is a material property of the matrix, independent of rubber volume fraction and particle size. Thus, the general condition for toughening is that the interparticle distance must be smaller than the critical value. Van der Waals attraction gives sufficient adhesion for toughening. Interfacial chemical bonding is not necessary. Even if there is interfacial chemical bonding, a polymer–rubber blend will still be brittle, if the interparticle distance is greater than the critical value. The minimum adhesion required is about 1000 J m^{-2}, typical for van der Waals adhesion. In contrast, chemical adhesion is typically 8000 J m^{-2}. The present criterion for toughening is proposed to be valid for all polymer–rubber blends which dissipate the impact energy mainly by increased matrix yielding.

(Keywords: polymer blends; impact toughness; particle size; interfacial tension; interfacial thickness; adhesion; rubber toughened nylon)

INTRODUCTION

Rubber particle size and rubber–matrix adhesion are two important factors determining the toughness of polymer–rubber blends. These two factors are, however, interrelated; changing one will change the other. Therefore, when studying the two factors, they must be carefully controlled. Earlier work on the effects of particle size and adhesion on toughness has often given inconsistent results, apparently because the two factors were not adequately controlled, as pointed out by Bucknall[1].

In this work, we studied the effects of rubber particle size on the notched impact toughness of nylon–rubber blends while keeing the adhesion constant. It has thus been found that the blends undergo a sharp tough–brittle transition, when the interparticle distance is at a critical value. This critical interparticle distance is shown to be the only characteristic parameter which determines whether a blend will be tough or brittle. This toughening criterion should be valid for all polymer blends which are toughened by increased shear yielding of the matrix, such as the present nylon–rubber blends whose impact fracture mechanism has been analysed recently[2]. The minimum adhesion required for toughening is also discussed.

EXPERIMENTAL

Materials

The matrix is a nylon 66 resin ($M_n = 17\,000$ and $M_w = 35\,000$). Two hydrocarbon rubbers are used as the dispersed particles. They have essentially the same chemical compositions and molecular weights. However, one contains a small amount of a reactive group and adheres strongly to nylon; the other contains no reactive groups and adheres weakly to nylon.

The reactive rubber ($M_n = 15\,000$, $M_w = 66\,000$ and $T_g = -52°\text{C}$) contains less than 1% by weight of a reactive polar group; adheres strongly to the matrix through interfacial chemical bonding (adhesive fracture energy $G_a = 8100$ J m^{-2}); and is designated as the PR rubber. The nonreactive rubber ($M_n = 21\,000$, $M_w = 79\,000$ and $T_g = -52°\text{C}$) contains no reactive group; has otherwise identical chemical composition as the PR rubber; adheres weakly to the matrix through nonpolar attraction ($G_a = 140$ J m^{-2}); and is designated as the NR rubber.

These nylon–rubber blends are similar to those used in the analysis of impact fracture mechanisms, reported recently[2].

Preparation of blends

Nylon–rubber blends of varying rubber particle sizes were prepared by melt extrusion at two constant levels of adhesion ($G_a = 8100$ and 140 J m^{-2}) and three rubber contents (25, 15 and 10% by weight, or 30.6, 18.9 and 12.8% by volume). The particle size was varied by using different extrusion conditions. The melt temperature (300°–325°C) and the residence time (1–2 min) were carefully controlled, so that all blends had similar thermal history.

Structure and size of rubber particles

During melt extrusion, the rubber was dispersed as discrete spheroids. No rubber particles contain droplets of the nylon. During injection moulding of test specimens

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the rubber particles were slightly elongated up to about 10% in the direction of flow.

The rubber particle size was determined by scanning electron microscopy (SEM). Injection-moulded specimens[2] were cut at the centre, transverse to the longitudinal axis. The cut surfaces were then smoothed by shaving with a glass microtome, and etched in boiling toluene for 1 h to dissolve the rubber particles. The etched surfaces were next vacuum-plated with gold-platinum for s.e.m. The s.e.m. photomicrographs were scanned with an image analyser to obtain the particle size distribution.

The microtomed surfaces cannot always cut through the centre of each rubber particle. If the particles are randomly distributed, the true particle size distribution function $F(a)$ is related to the observed apparent particle size distribution function $f(r)$ by

$$f(r)=\int_0^\infty F(a)g(r,a)\mathrm{d}a \qquad (1)$$

where r is the observed apparent radius, a the true radius, and

$$g(r,a)=(r/a)(a^2-r^2)^{-1/2} \qquad \text{for } r<a$$

$$=0 \qquad \text{for } r>a$$

Inversion of equation (2) gives the true particle size distribution function $F(r)$. For spheres of equal radius a, the observed average radius $\bar{r}$ is given by $\bar{r}=(\pi/4)a$.

Figure 1 shows the histogram of rubber particle size distribution for a typical blend containing 15% by weight of PR rubber with a number-average particle diameter of 0.70 μm and a notched impact toughness of 632 J m^{-1} (11.9 ft-lb in^{-1}). *Figure 2* shows that the distribution fits the log-normal distribution. In fact, all blends were found to have log-normal distributions of rubber particles. The ratio of the area-average to the number-average particle size ranges from 1.8–2.1.

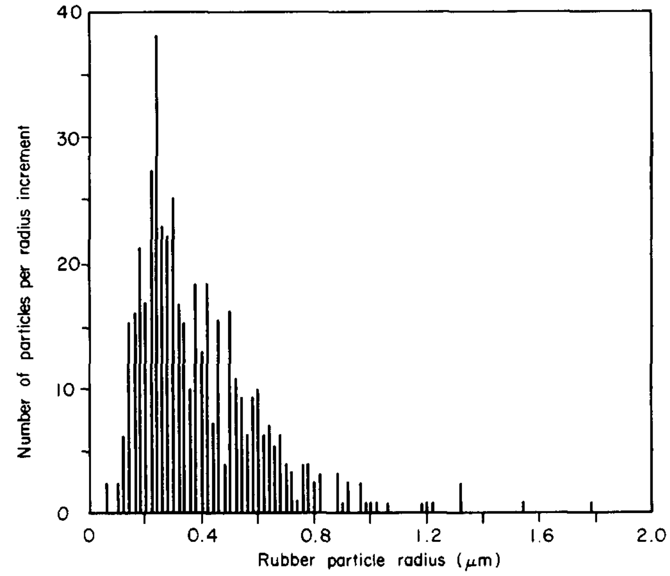

Figure 1 Particle size distribution histogram for the tough composition nylon–PR-rubber blend 85/15 weight ratio, d_n = 0.70 μm and notched Izod impact strength 632 J m^{-1} (or 11.9 ft-lb in^{-1}), coded 2.10 in *Table 2*

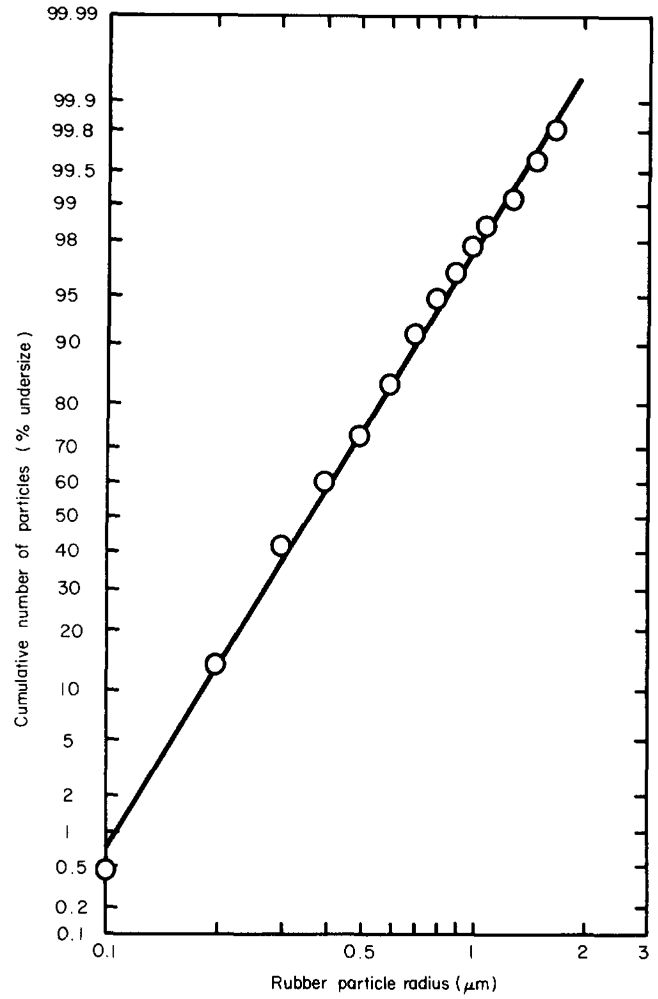

Figure 2 Log-normal distribution plot for the nylon–PR-rubber blend of *Figure 1*

In this work, the number-average particle diameter d_n is used throughout. Other averages may be used without affecting the essential features of the results, since various averages are uniquely interrelated in the log-normal distribution[3].

Nylon–rubber interface and adhesion

During melt extrusion, the reactive PR rubber molecules are grafted onto the nylon matrix within an interfacial zone of 500 Å thickness, determined by electron microscopy and solvent extraction. The interfacial tension between the PR rubber and nylon is thus calculated to be 0.25 dyne cm^{-1} at the extrusion temperature (300°C–325°C) by using[4]

$$\gamma_{12}=55\lambda^{-0.86} \qquad (2)$$

where γ_{12} is the interfacial tension (dyne cm^{-1}) and λ the interfacial thickness (Å). On the other hand, no chemical reaction occurs between the nonreactive NR rubber and nylon. The interfacial tension between the NR rubber and nylon is 8.8 dyne cm^{-1} at 325°C with a temperature coefficient $\mathrm{d}\gamma_{12}/\mathrm{d}T=-0.020$ dyne cm^{-1} deg^{-1}. The interfacial thickness in this case is calculated to be only about 8 Å.

There is no known satisfactory method for measuring the adhesion between rubber particle and matrix *in situ* at the impact speed. However, *in situ* measurement is not necessary, since the adhesive fracture energy G_a is independent of geometry, although dependent on rate[4]. We thus used a peel test to evaluate the nylon–rubber adhesion. Theory and experimental methods for the measurement of adhesion have been discussed elsewhere[4].

In the peel test, the adhesive fracture energy G_a is given by[4]

$$G_a = (\chi - \cos\theta)P \qquad (3)$$

where χ is the extension ratio of the flexible member (the rubber), θ the peel angle and P the peel force per unit width. Since G_a is rate-dependent, the peel test should strictly be made at the impact speed (3.46 m s^{-1}). However, for convenience, a peel rate of 0.085 cm s^{-1} was used. This is much slower than the impact rate, however, it should provide relative measures of adhesion.

A 2.5 cm wide and 0.5 mm thick rubber strip was backed with a 0.1 mm thick polyester-cotton fabric, and bonded to a 0.32 cm thick, rigid nylon adherend at 180°C and 2.8 MPa pressure for 12 min. The bonds were peeled at 180° angle at 0.085 cm s^{-1} rate. The fabric backing restricted the extension of the rubber strip during the peeling, so that $\chi \simeq 1$. The peel force was found to be independent of the rubber thickness in the ranges tested.

Structure of nylon matrix

The nylon matrix has 42% crystallinity of α-triclinic crystals, which does not change with the type and amount of added rubber. Details of nylon matrix structure and morphology have been analysed and discussed before[2].

Weight fraction versus *volume fraction*

The volume fraction of rubber ϕ_r was calculated from the weight fraction w_r by

$$\phi_r = \rho_m w_r / \{(\rho_m - \rho_r) w_r + \rho_r\} \qquad (4)$$

here ρ_m and ρ_r are the densities of nylon (1.44 g cm^{-3}, 42% crystalline) and the rubber (0.850 g cm^{-3}) at 20°C[2]. For the present work, $w_r = 0.10$ corresponds to $\phi_r = 0.128$; $w_r = 0.15$ corresponds to $\phi_r = 0.189$; $w_r = 0.25$ corresponds to $\phi_r = 0.306$.

Testing of impact toughness

The notched Izod impact strength was tested at the room temperature using an ASTM D-256. The impact speed was 3.46 m s^{-1}. Toss energy was corrected in all cases. Specimens (6.35 × 1.27 × 0.317 cm) were cut from the mid sections of injection moulded standard flex bars (12.7 × 1.27 × 0.317 cm), as discussed before[2]. A notch of 0.0254 cm radius was machined on all specimens. The notched impact strength of the present rubber toughened nylon is practically independent of notch radius, tested over 2.5×10^{-4} to 0.1 cm radii[2,5].

RESULTS AND DISCUSSION

Tables 1, *2* and *3* tabulate the particle size, adhesion and impact toughness for all blends. As shown, the nylon matrix (without rubber) is rather brittle, having a notched impact toughness of 18.6 J m^{-1} (0.35 ft-lb in^{-1}). Addition of rubber increases the toughness variously up to a factor of about 60. The effects of particle size and adhesion on notched impact toughness are analysed below. Details of impact fracture mechanisms have been discussed elsewhere[2].

Effect of particle size

Figure 3 shows the notched impact toughness *versus* the particle size at three PR rubber contents and a constant adhesion of 8100 J m^{-2}. A sharp tough-brittle transition is found to occur at a critical particle size for a given rubber content and constant adhesion. The critical particle diameter d_c is 0.48 μm for 10% by weight of rubber; 0.76 μm for 15% by weight of rubber; 1.73 μm for 25% by weight of rubber. The d_c increases with increasing rubber content. We show later that the d_c is related to the rubber content through a single parameter. The tough–brittle transition at a critical particle size should be a

Table 1 Particle size, adhesion and impact toughness of nylon–rubber blends containing 25% by weight (30.6% by volume) of rubber

Code	Particle diameter d_n (μm)	Notched Izod impact toughness	
		(J m^{-1})	ft-lb in^{-1}
Nylon 66 (without rubber)			
1.0	—	18.6	0.35
Nylon–NR-rubber blends: Adhesion $G_a = 140$ J m^{-2}			
1.1	24	20.2	0.38
1.2	25	28.6	0.35
1.3	25	19.1	0.36
1.4	26	26.5	0.31
Nylon–PR-rubber blends: Adhesion $G_a = 8100$ J m^{-2}			
1.5	0.32	1080	20.4
1.6	0.45	1130	21.2
1.7	0.51	1070	20.2
1.8	0.52	1080	20.4
1.9	0.63	1130	21.3
1.10	0.64	1140	21.4
1.11	0.68	1050	19.7
1.12	0.72	941	17.7
1.13	0.81	850	16.0
1.14	1.03	920	17.3
1.15	1.70	537	10.1
1.16	2.32	191	3.6

Note: 1 ft-lb in^{-1} = 53.2 J m^{-1} (specimen width = 1 cm)

Table 2 Particle size, adhesion and impact toughness of nylon–rubber blends containing 15% by weight (18.9% by volume) of rubber

Code	Particle diameter d_n (μm)	Notched Izod impact toughness	
		J m^{-1}	ft-lb in^{-1}
Nylon–NR-rubber blends: Adhesion $G_a = 140$ J m^{-2}			
2.1	24	24.4	0.46
2.2	25.	23.9	0.45
2.3	26	25.5	0.48
2.4	26	24.4	0.46
Nylon–PR-rubber blends: Adhesion $G_a = 8100$ J m^{-2}			
2.5	0.31	882	16.6
2.6	0.40	856	16.1
2.7	0.50	686	12.9
2.8	0.57	494	9.3
2.9	0.60	553	10.4
2.10	0.70	632	11.9
2.11	0.80	154	2.9
2.12	1.00	96	1.8
2.13	1.13	122	2.3
2.14	1.50	149	2.8
2.15	1.67	85	1.6
2.16	2.27	85	1.6

Note: 1 ft-lb in^{-1} = 53.2 J m^{-1} (specimen width = 1 cm).

Table 3 Particle size, adhesion and impact toughness of nylon–rubber blends containing 10% by weight (12.8% by volume) of rubber

Code	Number-average particle diameter d_n (μm)	Notched Izod impact toughness J m^{-1}	ft-lb in^{-1}
Nylon–NR-rubber blends: Adhesion $G_a = 140$ J m^{-2}			
3.1	24	25.5	0.48
3.2	24	19.7	0.37
3.3	24	19.7	0.37
3.4	25	26.6	0.50
Nylon–PR-rubber blends: Adhesion $G_a = 8100$ J m^{-2}			
3.5	0.35	523	10.4
3.6	0.42	500	9.4
3.7	0.48	83	1.6
3.8	0.54	75	1.4
3.9	0.75	76	1.4
3.10	0.86	92	1.7
3.11	0.92	59	1.1
3.12	1.22	82	1.6
3.13	1.43	60	1.1
3.14	1.67	53	0.99
3.15	1.84	44	0.83
3.16	2.42	54	1.0

Note: 1 ft-lb in^{-1} = 53.2 J m^{-1} (specimen width = 1 cm).

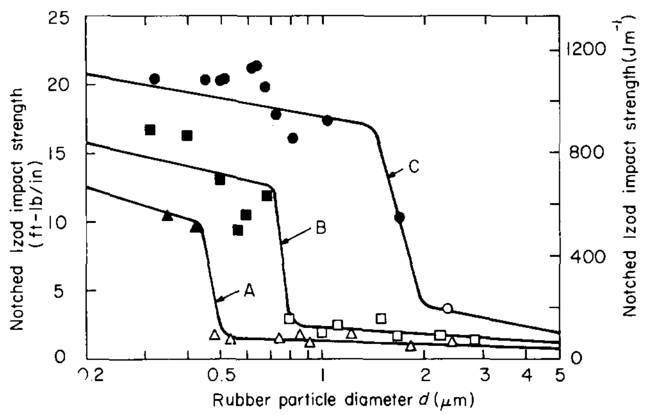

Figure 3 Notched Izod impact strength *versus* PR-rubber number-average particle diameter d_n at constant adhesion $G_a = 8100$ J m^{-2} and constant rubber contents curve A: 10%; curve B: 15%; and curve C: 25% by weight. Solid symbols are for tough fracture; open symbols are for brittle fracture

general phenomenon for all polymer blends which are toughened mainly by increased matrix yielding.

The tough–brittle transition is very sharp. All specimens are either tough (with impact toughness above 500 J m^{-1} or 9 ft-lb in^{-1}) or brittle (with impact toughness below 200 J m^{-1} or 4 ft-lb in^{-1}). No specimens were found to have an intermediate behaviour, i.e., having an impact toughness between 200 and 500 J m^{-1} (4 and 9 ft-lb in^{-1}).

It should be noted that all compositions in *Figure 3* have the same strong nylon–rubber adhesion of 8100 J m^{-2} due to interfacial grafting. However, some blends are tough and some are brittle. Thus, strong adhesion alone is not sufficient for toughening; the particle size must also be smaller than the critical size to achieve a tough behaviour.

Nylon matrix (without rubber) is very brittle, having a notched impact toughness of 19 J m^{-1} (0.35 ft-lb in^{-1}). All the brittle blends have notched impact toughness from 44 to 191 J m^{-1} (0.83–3.6 ft-lb in^{-1}). Thus, the rubber increases the toughness of brittle blends by a factor of 2–10. This is a significant improvement, but the blends remain to have brittle behaviour in impact. On the other hand, the tough blends have notched impact toughness of 494–1140 J m^{-1} (9.3–21.4 ft-lb in^{-1}), which is an improvement by a factor of 27–61, and the blends are changed to have tough behaviour in impact.

Thus, it is important to distinguish between tough and brittle behaviours. Although the rubber increased the toughness of brittle blends by a factor of 2–10, the blends are still brittle. On the other hand, the rubber increases that of the tough blends by a factor of 27 to 61, and the blends acquire tough behaviour. Thus, the rubber *toughens* the tough blends, but only *increases the toughness* of the brittle blends without making them tough. In other words, toughening is the major change from brittle to tough behaviour, while the variations of toughness among brittle or tough blends are considered as secondary effects which have mechanisms different from the major change, i.e., tough–brittle transition.

Modes of impact fracture

In *Figure 3*, the specimens in the upper legs of the sigmoid curves [(●), (■), (▲)] are tough (above 500 J m^{-1} or 9 ft-lb in^{-1}). They break in a tough fashion with about 75% of the impact energy dissipated by matrix yielding and about 25% by crazing[2]. SEM photomicrographs of the fracture surfaces show extensive matrix yielding, characteristic of tough failure (*Figure 4*). No rubber particles are visible on the fracture surfaces. To confirm that the rubber particles are indeed not exposed, the fracture surfaces were etched with boiling toluene for one hour and re-examined by s.e.m. The etched surfaces retained the same morphology as the un-etched ones (*Figure 4*). If the rubber particles had been exposed on the fracture surfaces, they would have been dissolved away by the boiling toluene, leaving hemispherical holes. Thus, the tough fracture proceeds entirely within the nylon matrix without exposing rubber particles.

On the other hand, the specimens in the lower legs of the sigmoid curves [(○), (□), (△)] (*Figure 3*) are brittle (below 200 J m^{-1} or 4 ft-lb in^{-1}). They break in a brittle fasion. S.e.m. photomicrographs of the fracture surfaces show little matrix yielding, characteristic of brittle failure (*Figure 5*). The fracture surfaces are relatively smooth, having many hemispherical bumps, which are exposed rubber particles. These hemispherical bumps are easily dissolved away with boiling toluene, leaving hemispherical holes on the etched fracture surfaces (see *Figure 5*). The rubber particles are however firmly attached to the nylon matrix, because of the strong adhesion ($G_a = 8100$ J m^{-1}). If the adhesion was weak, the rubber particles would have been dislodged from the matrix during the impact fracture, such as in the case of NR rubber which has a weak adhesion ($G_a = 140$ J m^{-2}) (see *Figure 6*). Thus, the brittle fracture follows a relatively straight path, slicing across rubber particles in the fracture path.

Analysis of tough–brittle transition

The critical particle size at the point of tough–brittle transition varies with rubber volume fraction, increasing with increased rubber volume fraction. In other words, if the rubber particles are large, larger amount of rubber will be needed to achieve toughening, and *vice versa*. A relation between critical particle size and

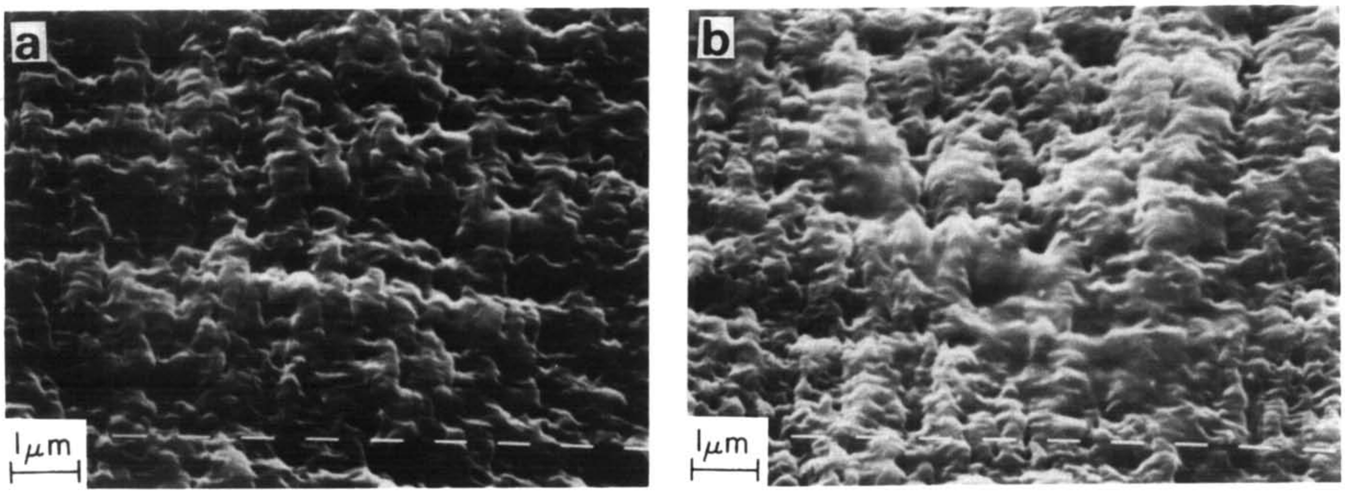

Figure 4 Scanning electron photomicrographs of a notched impact fracture surface for a tough nylon–PR-rubber blend ($d_n = 0.31\ \mu m$, $G_a = 8100\ J\ m^{-2}$, notched Izod impact strength = 882 $J\ m^{-1}$ or 16.6 ft-lb in^{-1}, code 2.5 in *Table 2*), showing tough fracture. (a) Photomicrograph showing the original fracture surface; (b) photomicrograph showing the fracture surface etched with boiling toluene (scale bars = 1 μm)

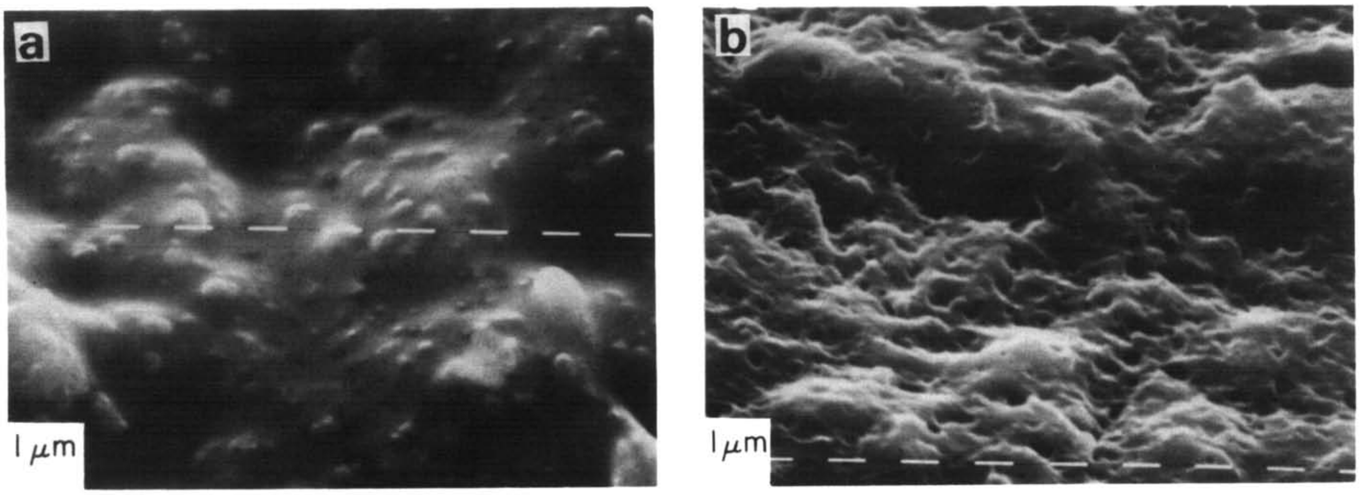

Figure 5 Scanning electron photomicrographs of a notched impact fracture surface for a brittle nylon–PR-rubber blend with strong adhesion ($d_n = 1.50\ \mu m$, $G_a = 8100\ J\ m^{-2}$, notched impact strength = 149 $J\ m^{-1}$ or 2.8 ft-lb in^{-1}, code 2.14, *Table 2*), showing brittle fracture. (a) Photomicrograph shows the original fracture surface; (b) photomicrograph showing the fracture surface etched with boiling toluene. (Scale bars = 1 μm)

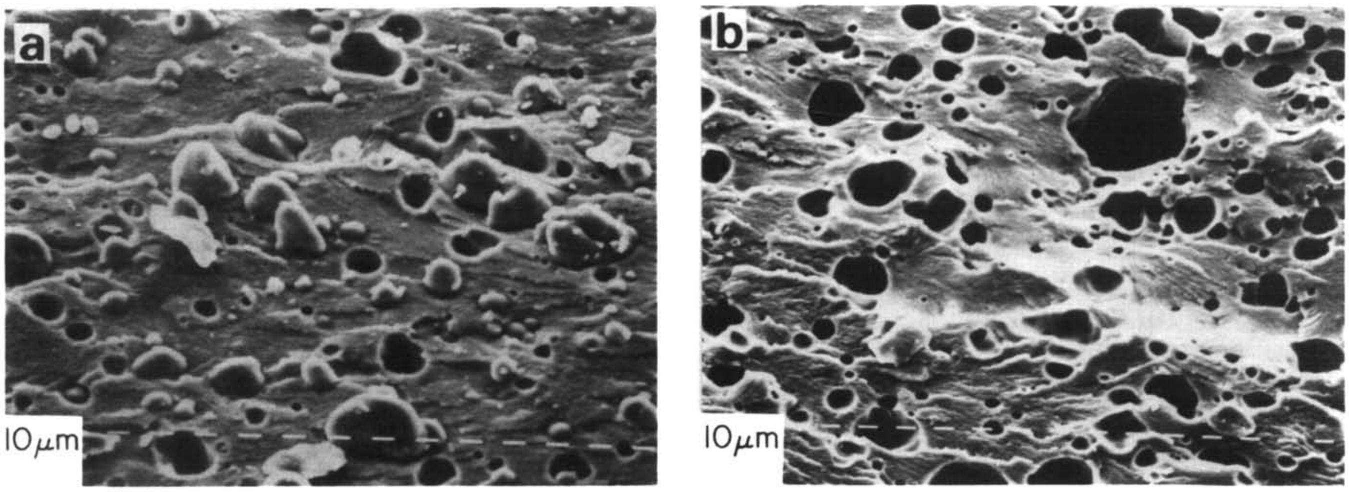

Figure 6 Scanning electron photomicrographs of a notched impact fracture surface for a brittle nylon–PR-rubber blend with weak adhesion ($d_n = 26\ \mu m$, $G_a = 140\ J\ m^{-2}$, notched impact strength = 25.5 $J\ m^{-1}$ or 0.48 ft-lb in^{-1}, code 2.3, *Table 2*), showing brittle fracture. (a) Photomicrograph showing the original fracture surface; (b) photomicrograph showing the fracture surface etched with boiling toluene. (Scale bars = 10 μm)

rubber volume fraction is established below. Three models are examined: the interfacial area model, the particle concentration model, and the critical interparticle distance model. It will be shown that the critical interparticle distance model predicts the tough–brittle transition very well.

In the models, the rubber particles are assumed to be spherical, of the same size, and arranged in a cubic lattice to simplify the arithmetics. Of course, this is strictly not the case. However, the simplification does not affect the essential features of the analysis. The effects of particle shape, size distribution and spatial distribution can be taken into account in more detailed analysis, but will not change the essential features of the present analysis.

(*a*) *Interfacial area model*

In this model, the tough–brittle transition is assumed to occur when the rubber–matrix interfacial area per unit volume of the blend is at a critical value. The critical particle diameter d_c is given by

$$d_c = 6\phi_r / A_c \qquad (5)$$

where ϕ_r is the rubber volume fraction, and A_c the critical interfacial area per unit volume. The parameter A_c is by definition independent of ϕ_r and d_c. A linear relation between d_c and ϕ_r is predicted.

Figure 7 compares the experimental (○) and theoretical ((·····); $A_c = 1.51\ \mu m^{-1}$) d_c values as a function of ϕ_r. As can be seen, this model is inadequate.

(b) *Particle concentration model*

In this model, the tough–brittle transition is assumed to occur when the number of particles per unit volume of the blend is at a critical value. The d_c is given by

$$d_c = \{(6\phi_r)/(\pi N_c)\}^{1/3} \qquad (6)$$

where N_c is the critical number density of the rubber particles for the onset of tough–brittle transition. A linear relation between d_c and $\phi_r^{1/3}$ is predicted.

Figure 7 compares the experimental (○) and the theoretical ((-----); $N_c = 0.831\ \mu m^{-3}$) d_c values as a function of ϕ_r. As can be seen, this model is also inadequate.

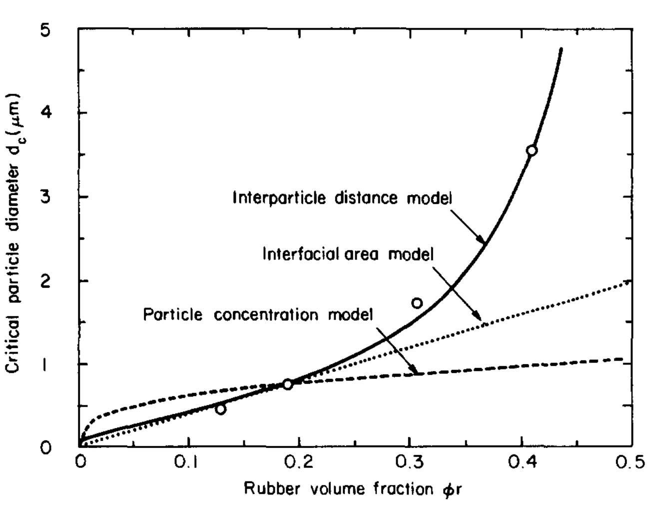

Figure 7 Critical particle diameter for toughening in notched impact *versus* rubber volume fraction. The lines ((———); (·····); (-----)) are theoretical results; (○) experimental results. $T_c = 0.304\ \mu m$; $N_c = 0.831\ \mu m^{-3}$; $A_c = 1.508\ \mu m$

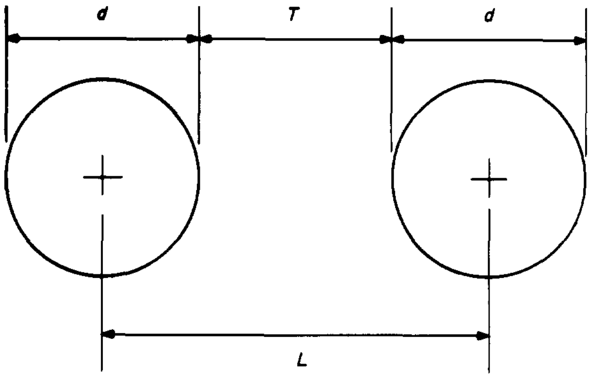

Figure 8 Model for (surface-to-surface) interparticle distance T, (centre-to-centre) particle separation L, and rubber particle diameter d

Table 4 Experimental and calculated critical particle size for the onset of tough–brittle transition for notched Izod impact fracture based on the interparticle distance model

Rubber weight fraction, w_r	Rubber volume fraction, ϕ_r	Critical particle diameter, d_c (μm)	
		Calculated[a]	Experimental
0.10	0.128	0.51	0.48
0.15	0.189	0.76	0.76
0.25	0.306	1.58	1.73
0.34	0.408	3.57	3.60

[a] $T_c = 0.304\ \mu m$, calculated by equation (7) using the experimental d_c value at $w_r = 0.15$

(c) *Interparticle distance model*

In this model, the tough–brittle transition is assumed to occur when the interparticle distance between two nearest neighbouring particles is at a critical value. The d_c is given by

$$d_c = T_c\{(\pi/(6\phi_r))^{1/3} - 1)\}^{-1} \qquad (7)$$

where T_c is the critical interparticle distance between the surfaces of two nearest neighbouring particles, defined in *Figure 8*. The T_c is by definition independent of d_c and ϕ_r.

Figure 7 compares the experimental (○) and the theoretical ((———); $T_c = 0.304\ \mu m$) d_c values as a function of ϕ_r. As can be seen, this model gives a very good prediction of d_c. *Table 4* lists the experimental and the predicted d_c values at several rubber contents. Good agreement can be seen.

The onset of tough–brittle can be more vividly seen by plotting the impact toughness *versus* the interparticle distance, shown in *Figure 9*. The sharp tough–brittle transition is seen to occur at the interparticle distance of 0.304 μm, independent of rubber volume fraction. In the tough region, the impact toughness increases with increasing rubber volume fraction and decreasing interparticle distance (or smaller particle size). This is due to secondary effects already mentioned before, whose mechanisms are not our concern here. Our primary concern is the major change from brittle to tough behaviour at the critical interparticle distance.

We can therefore propose that the critical interparticle distance is the only parameter that determines the onset of tough–brittle transition in polymer–rubber blends. A blend will be tough, if the interparticle distance is smaller

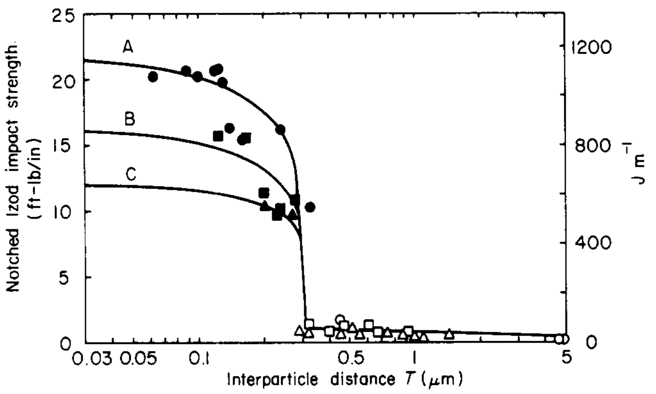

Figure 9 Notched impact toughness *versus* (surface-to-surface) interparticle distance T, showing that the tough–brittle transition occurs at the critical value T_c, independent of rubber volume fraction. Rubber contents; curve A: 25 wt%; curve B: 15 wt%; curve C: 10 wt%

than the critical value. A blend will be brittle, if the interparticle distance is greater than the critical value.

Equation (7) can be rearranged in an alternative form to show that there is a critical volume fraction at which a tough–brittle transition will occur for a series of blends having the same particle size but varying rubber contents, i.e.,

$$\phi_{rc} = (\pi/6)\{1 + (T_c/d)\}^{-3} \tag{8}$$

where ϕ_{rc} is the critical rubber volume fraction for the onset of tough–brittle transition, and d the particle diameter. For a series of blends having $d \simeq 3.6$ μm, the ϕ_{rc} is calculated to be 0.41 volume fraction (or, 0.34 weight fraction), in good agreement with the experimental value of 0.35 weight fraction, shown in *Figure 10*.

Origin of the critical interparticle distance

When rubber particles are greatly separated, the stress field around a particle is only slightly affected by the presence of other particles. The stress field in the matrix is simply a superposition of those around isolated particles, and the polymer blend will remain brittle. However, when the particles are sufficiently close together, the stress field is no longer simply additive, and the field around neighbouring particles will interact considerably. This will result in enhanced matrix yielding, and a transition to tough behaviour. We propose that this is the origin of the tough–brittle transition.

We have found experimentally that the tough–brittle transition occurs when the surface-to-surface interparticle distance between nearest neighbouring particles T is equal to the critical value T_c. This may be explained as follows. The interaction and enhancement of stress field in a matrix with many rubber particles has not been theoretically analysed, due to the mathematical complexity[1]. However, some understanding of the problem is provided by Matsuo and coworkers[6].

Mastuo and coworkers[6] observed the crazing of polystyrene with two embedded large rubber balls (3–5 mm diameter). They found that matrix crazing occurs predominantly at the equator of the balls, where the stress is the highest. When the two balls are far apart, matrix crazing around one ball is not affected by the other. However, when the two balls are placed in close proximity ($L/d < 1.45$), matrix crazing is greatly enhanced in the regions between the two balls. Note here that L is the centre-to-centre particle distance, defined in *Figure 8*. This indicates that strong interaction and enhancement of stress field start to occur at $L/d = 1.45$.

In a matrix with many rubber particles, the enhancement of stress field will be even more pronounced. In a semi-brittle matrix such as nylon, the stress-field interaction will result in enhanced shear yielding. Since we have found that tough–brittle transition occurs at the critical interparticle distance T_c, it is suggested that stress-field enhancement occurs when the surface-to-surface interparticle distance equals the critical value in a matrix with many rubber particles.

Alternatively, the onset of tough–brittle transition may be specified in terms of a critical centre-to-centre particle separation L_c. The critical ratio $(L/d)_c$ is then given by

$$(L/d)_c = (T/d)_c + 1 \tag{9}$$

$$= \{\pi/(6\phi_r)\}^{1/3} \tag{10}$$

Equation (9) is plotted in *Figure 11*. Note that $(L/d)_c$ is dependent on ϕ_r, but not on d, whereas T_c is independent on both ϕ_r and d.

Consider Matsuo and coworkers' case of two rubber balls embedded in a polystyrene matrix. Since the stress field interaction and enhanced crazing occur in the region between the two balls, it is reasonable to assume that the local stress fields are active over a volume of $2L \times L \times L$.

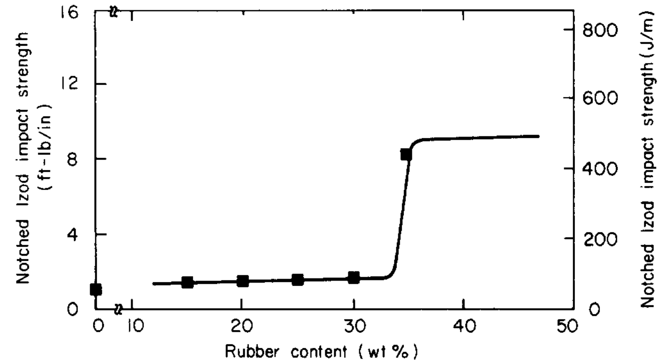

Figure 10 Notched Izod impact strength *versus* rubber content at constant particle size ($d_n \sim 3.6$ μm) and constant adhesion ($G_a = 8100$ J m^{-2}), showing a tough–brittle transition at a critical rubber content

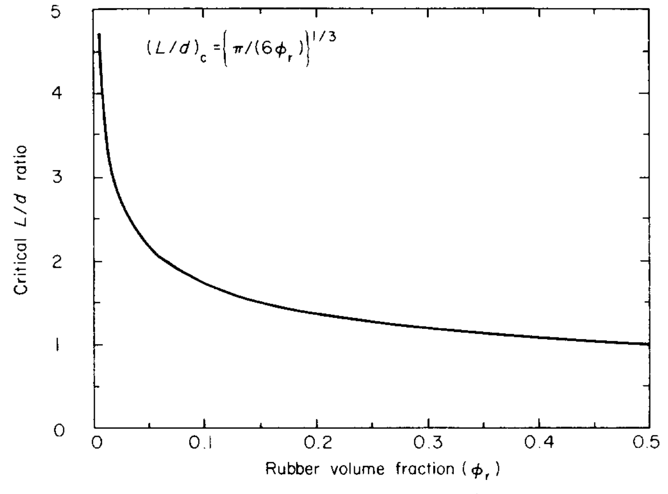

Figure 11 Critical L/d ratio *versus* rubber volume fraction ϕ_r, according to equation (9). Note that $(L/d)_c$ is a function of rubber volume fraction, but T_c is independent of rubber volume fraction

The rubber volume fraction within this active space is thus $\phi_r = 0.172$. The $(L/d)_c$ is thus calculated to be 1.45 by equation (10), which surprisingly agrees exactly with the experimental value of 1.45 for the onset of craze interaction and enhancement found by Matsuo and coworkers.

Effect of rubber–matrix adhesion

As already mentioned, strong adhesion alone does not ensure toughening. The interparticle distance must also be smaller than the critical value to achieve a transition from brittle to tough behaviour. Even if the rubber particles are chemically bonded to the matrix, a polymer blend will still be brittle, if the interparticle distance is greater than the critical value. What then is the minimum adhesion required for toughening?

All the blends having weak adhesion of $G_a = 140\ \mathrm{J\ m^{-2}}$ are brittle (*Tables 1, 2* and *3*). However, in these blends, the rubber particles ($\sim 25\ \mu$m) are much larger than the critical size for toughening. Furthermore, the rubber particles are dislodged from the matrix during impact fracture (*Figure 6*). Therefore, both the large particle size and the weak adhesion appear to have caused the brittleness. The adhesion of $G_a = 140\ \mathrm{J\ m^{-2}}$ is thus too low for toughening in impact.

The minimum adhesion required should be that the rubber particles are not detached from the matrix during fracture. Since the rubber particles are not detached from the matrix when the adhesion is $8100\ \mathrm{J\ m^{-1}}$ (*Figures 4* and *5*), the minimum adhesion required must be between 140 and $8100\ \mathrm{J\ m^{-2}}$. This minimum adhesion should be about equal to the tear energy of the rubber. A typical lower limit of tear energy is about $1000\ \mathrm{J\ m^{-2}}$. We thus suggest that the minimum adhesion required for toughening should be about $1000\ \mathrm{J\ m^{-2}}$. This level of adhesion can be obtained from van der Waals adhesion alone without chemical bonding[4].

CONCLUSION

Impact energy may be dissipated by crazing, yielding or both[1,2]. There are two types of polymers: Type I (brittle, with crazing as the main fracture mechanism) such as polystyrene and poly(methyl methacrylate), and Type II (ductile, with yielding as the main fracture mechanism) such as nylon, poly(ethylene terephthalate) and polycarbonate. Type I polymers have low crack initiation and low crack propagation energies in impact. Therefore, they have low unnotched and low notched impact strengths. They are rubber-toughened mainly by increased matrix crazing. On the other hand, Type II polymers have high crack initiation energy, but low crack propagation energy in impact. Therefore, they have high unnotched impact strength, but low notched impact strength. They are rubber-toughened mainly by increased matrix yielding[2]. Both types of polymers break by brittle fracture in both unnotched and notched impacts. However, rubber particles have different effects on these two types of polymer matrices, as discussed below. The present work concerns the Type II matrix.

In Type I matrices, earlier work on the effect of particle size on impact toughness has often given conflicting results, probably because the adhesion was not strictly controlled in all cases. The toughness was found to increase with increasing particle size in ABS[1,7-9], polystyrene[9,10] and epoxy resin[11]. But it was also found to increase with decreasing particle size in polystyrene[12], polypropylene[12] and epoxy resin[14], or to be independent of particle size in epoxy resin[14]. The highest toughness was said to occur at an optimum particle size occurred in polystyrene (2–5 μm)[15-18], poly(styrene–acrylonitrile) (0.1–1 μm)[19] and poly(methyl methacrylate) (0.3 μm).

However, it is usually recognized that there is an optimum particle size at which the toughness is the greatest for the Type I matrix. This appears to be because craze termination is important in the toughening of Type I matrix, and small particles give more termination sites per unit volume but with lower efficiency at each site. Interestingly, the optimum particle size is comparable to the craze thickness, for instance, in polystyrene[16,17,20], poly(styrene–acrylonitrile)[19,20] and poly(methyl methacrylate)[21]. It has also been generally recognized that strong adhesion involving interfacial chemical bonding is necessary to achieve impact toughness in Type I matrix, because craze termination cannot operate if the rubber particles are detached from the matrix[1,22,23].

In Type II matrices, however, we have found that there is a sharp tough–brittle transition occurring at a critical particle size at constant adhesion and constant rubber content. The critical particle size increases with increasing rubber volume fraction, but is uniquely related to the rubber volume fraction through a single characteristic parameter. This is the critical surface-to-surface interparticle distance T_c, which is independent of particle size and rubber volume fraction, and is characteristic of a given matrix. The condition for toughening is established as that the interparticle distance must be smaller than the critical value T_c. That is, a polymer–rubber blend will be tough, when the interparticle distance is smaller than the critical value. A polymer–rubber blend will be brittle, when the interparticle distance is greater than the critical value.

Strong adhesion alone is not sufficient for toughening. The interparticle distance must also be smaller than the critical value. The critical parameter is viscoelastic in nature, and so should depend on loading mode and rate. For nylon–rubber blends, T_c is found to be 0.304 μm for notched Izod impact fracture. The minimum adhesion required for toughening is proposed to be about $1000\ \mathrm{J\ m^{-2}}$, typical for van der Waals adhesion.

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