Percolation model for brittle–tough transition in nylon/rubber blends

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It is proposed that the brittle–tough transition in nylon/rubber blends occurs when the yielding process propagates through thin matrix ligaments in which a plane-strain to plane-stress transition takes place. This propagation process is modelled as a percolation phenomenon. The model explains the observed brittle–tough transition, and predicts that monodisperse and asymmetric particles are more effective in toughening than polydisperse and spherical ones.

(Keywords: brittle–tough transition; percolation theory; polymer blends; impact strength; rubber toughening; nylon/rubber blends)

INTRODUCTION

A key observation in rubber toughening of pseudo-ductile polymers was recently made, namely that a sharp brittle–tough transition occurs at a critical rubber particle size[1,2], shown in *Figure 1* for nylon/rubber blends. The critical particle size was related to the rubber volume fraction ϕ_r by[1]:

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

where d_c is the critical rubber particle diameter, and τ_c the critical surface-to-surface interparticle distance, or the critical matrix-ligament thickness[2], shown in *Figure 2*. The value of τ_c is independent of particle size and rubber volume fraction, and is a characteristic property of the matrix at a given mode, rate and temperature of deformation[1]. It is the single matrix parameter that determines the onset of brittle–tough transition in polymer/rubber blends with pseudo-ductile matrices[1]. Recently, Borggreve and coworkers[3] confirmed this concept, and reported the dependence of τ_c on temperature in nylon/rubber blends (see Note added in proof).

The term 'surface-to-surface interparticle distance' tends to focus our attention on rubber particles. However, the main mechanism of energy dissipation in polymer/rubber blends with pseudo-ductile matrices is the yielding of the matrix[4]. To focus our attention properly on the locus of energy dissipation, the surface-to-surface interparticle distance was renamed the matrix-ligament thickness[2]. *Figure 3* shows that a matrix ligament is defined as the region of the matrix between two neighbouring rubber particles. Thus, the condition for brittle–tough transition is that the average matrix-ligament thickness must be smaller than the critical value, τ_c.

MECHANISM

During impact fracture, rubber particles cavitate to relieve the triaxial dilative stress[2]. This tends to induce a plane-strain to plane-stress transition, leading to shear yielding in those ligaments which are thinner than the critical value[1,2]. Cavitation is, however, not always required. The dispersed phase (rubber) needs only to have a lower modulus than the matrix for the dilative stress to be relieved and the yielding of thin ligaments to occur[2].

There is a distribution of thick ($\tau > \tau_c$) and thin ($\tau < \tau_c$) matrix ligaments. During fracture, thin ligaments may yield, while thick ones may not. However, if the thick ligaments are surrounded by enough thin ones, the yielding of thin ones could also relieve the dilative stress and cause the thick ones to yield. When yielding thus propagates and pervades over the entire deformation zone, a tough behaviour is obtained. Thus, we may formulate the propagation of yielding process as the percolation (i.e. connectivity) of thin ligaments.

At the percolation threshold (i.e. the formation of the first percolation path), many thick ligaments may not be surrounded by sufficient numbers of thin ligaments, and so cannot yield. In this case, crazing will be favoured over yielding, and a brittle behaviour will be observed. For

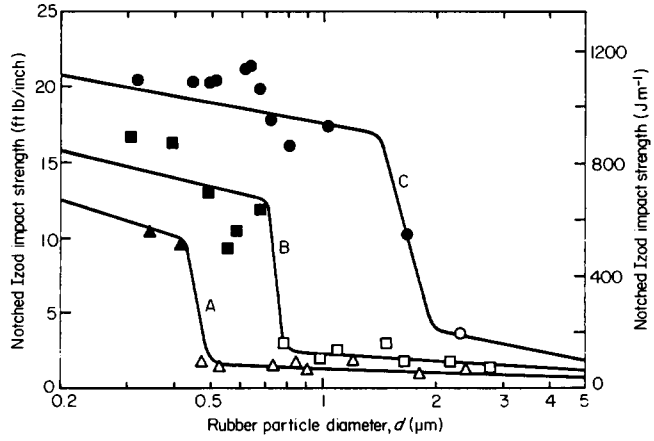

Figure 1 Notched Izod impact strength *versus* rubber particle size at constant rubber volume fractions for nylon/rubber blends: curve A, $\phi_r = 0.128$; curve B, $\phi_r = 0.189$; curve C, $\phi_r = 0.306$. Filled symbols are for tough specimens. Open symbols are for brittle ones. After Wu[1]

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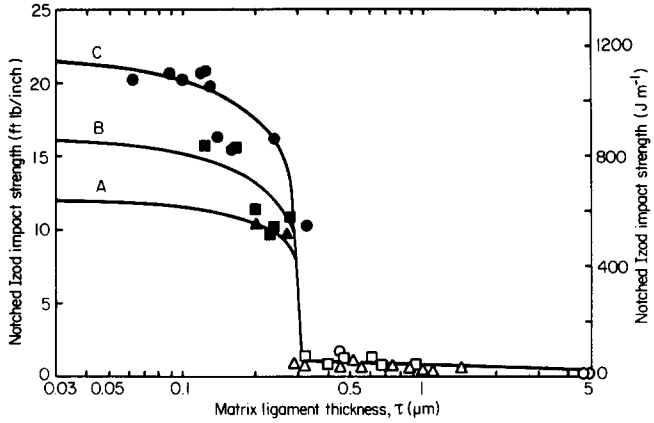

Figure 2 Notched Izod impact strength *versus* matrix-ligament thickness for nylon/rubber blends: curve A, $\phi_r=0.128$; curve B, $\phi_r=0.189$; curve C, $\phi_r=0.306$. Filled symbols are for tough specimens. Open symbols are brittle ones. After Wu[1]

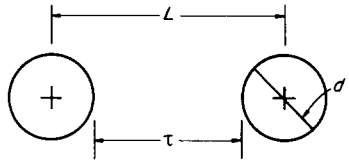

Figure 3 Schematics of rubber particles and matrix ligament

tough behaviour to occur, therefore, a certain level of multiple connectivity of thin ligaments must be attained. This is an important feature of the toughness problem, as opposed to the 'first-path' percolation treated in transport problems[5].

The exact level of multiple connectivity required is not known at this time. However, the connectivity is known to increase rapidly beyond the percolation threshold. Thus, the onset of tough behaviour will be only slightly different from the 'first-path' percolation threshold. In other words, the onset of observed tough behaviour may not exactly coincide with the 'first-path' percolation threshold. There is a small difference between the two. This small difference arises from the mechanical nature of fracture processes, which is recognized throughout this work, and does not detract from our analysis. Thus, we propose that the onset of brittle–tough transition occurs near the percolation threshold of thin ligaments. If, on the other hand, the percolation of thin ligaments cannot occur, fracture will proceed mainly by crazing, resulting in brittle behaviour.

PERCOLATION MODEL

Consider equal-sized rubber particles occupying a random lattice. The lattice sites can be linked with bonds to form tetrahedra so that the circumsphere of a tetrahedron contains no other sites. This can be done in such a way that the tetrahedra fill the space without overlap[6]. Each bond has length $L=d+\tau$. For the present purpose, it suffices to define the matrix ligament as the region of the matrix enclosing a lattice bond, and the matrix ligaments fill the matrix space. Thus, each matrix ligament is associated with one and only one lattice bond. The thickness of a matrix ligament τ is the part of the bond length between the surfaces of two neighbouring rubber particles (*Figure 3*).

Tough behaviour occurs when thin ligaments ($\tau<\tau_c$) are interconnected, allowing the yielding process to propagate and pervade over the entire matrix in the deformation zone. This corresponds to the phenomenon of bond percolation in the random lattice, which has been shown to be equivalent to continuum percolation of spheres[7]. As in customary use, the percolation threshold refers to the onset of the 'first-path' connectivity, which is, however, slightly below the actual onset of tough behaviour, as discussed before. This should be understood throughout this work. For simplicity, however, we shall not always specifically make such a distinction.

Our problem is thus recast as the percolation of spherical 'stress volumes' in the random lattice. Each stress volume centres at a rubber particle and includes a concentric annular shell of the matrix of constant thickness $\tau_c/2$, which is the critical ligament thickness, as defined before. Namely, the diameter of the stress volume is:

$$S=d+\tau_c \tag{2}$$

where S is the diameter of a stress volume, shown in *Figure 4*. Two neighbouring stress volumes are considered to be connected when $L<S$. At the percolation threshold, we have:

$$S_c=d_c+\tau_c \tag{3}$$

where the subscript 'c' denotes the critical condition. During tough fracture, the stress volumes will yield and propagate. However, in brittle fracture, crazing is favoured over yielding. Thus, the stress volumes will not yield, and the fracture will proceed mainly by crazing.

Continuum percolation of stress volumes will occur when the volume fraction of stress volumes (ϕ_s) is at its critical value (ϕ_{sc}). Since $\phi_r\sim d^3$ and $\phi_s\sim S^3$, we obtain the critical condition for brittle–tough transition as:

$$\phi_{rc}(S_c/d_c)^3=\phi_{sc} \tag{4}$$

where ϕ_{rc} is the rubber volume fraction at the critical condition.

At high rubber volume fractions, stress volumes tend to overlap. Therefore, the percolation threshold ϕ_{sc} tends to vary with d/S rapidly at high rubber fractions. The ϕ_{sc} values as a function of d/S have been numerically simulated for the case of monodisperse (equal-sized) spheres in a random lattice[8,9]. It was found that ϕ_{sc} is roughly constant ($\sim$0.36) for $d/S<0.8$, and increases rapidly to the limiting value for random close packing (0.65) at $d/S=1$ (ref. 8); see also *Figure 5*, and further discussions later.

It is interesting to note that (1) may be rearranged to

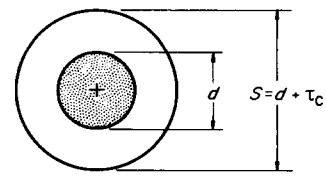

Figure 4 Schematics of stress volume around a rubber particle. The rubber particle is shaded

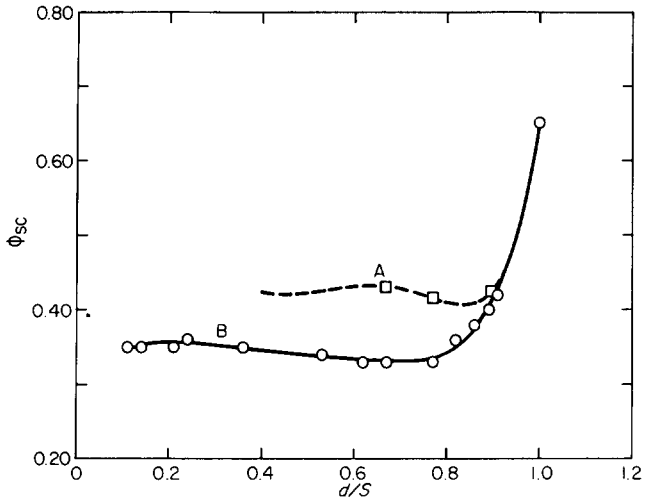

Figure 5 Percolation threshold ϕ_{sc} *versus* d/S: curve A, this work for polydisperse particles; curve B, theoretical curve for monodisperse particles by Bug and coworkers[8]

the form of (4), giving:

$$\phi_{rc}(L_c/d_c)^3 = \pi/6 \tag{5}$$

where L is the average random-lattice constant, defined as $n^3L = 1$ with n being the number density of lattice sites and L_c being its critical value. For equal-sized spheres, $\phi_{sc} \simeq 0.36$ (ref. 8), and for the polydisperse nylon/rubber blends of this work to be discussed below, $\phi_{sc} \simeq 0.42$, as compared with $\pi/6$ from equation (5).

APPLICATION

We apply the percolation model to analyse the impact toughness of nylon-6,6/rubber blends. Experimental data for impact toughness (notched Izod, ASTM D-256) at various rubber particle sizes and volume fractions have been reported in detail elsewhere[1]. In this system[1], it was found that $\tau_c = 0.30\,\mu$m, shown in *Figure 2*. This value is used in (4) to calculate the values of ϕ_{sc} as a function of d/S. The results are plotted in *Figure 5*, together with the theoretical curve of Bug and coworkers[8] for the case of monodisperse spheres.

It is satisfying to find that the brittle–tough threshold ϕ_{sc} *versus* d/S curve for the present system is similar to the theoretical percolation threshold curve for monodisperse spheres. At high rubber volume fractions ($d/S > \sim 0.9$), the two curves coincide with each other. In other regions, the ϕ_{sc} values for the present system (~ 0.42 for $d/S < \sim 0.8$) are shifted to somewhat higher values than those for monodisperse spheres (~ 0.36 for $d/S < \sim 0.8$). This difference may be due to (1) the disparity between the thresholds for brittle–tough transition and 'first-path' percolation as mentioned before, (2) particle-size polydispersity and (3) particle-shape asymmetry, discussed below.

The particles in the present system have polydisperse sizes, conforming to log-normal distributions with polydispersity (i.e. geometric-mean standard deviation σ_g) of 1.4 to 2 (refs 1, 2). The average matrix-ligament thickness increases significantly with increasing size polydispersity[2]. For the present system, σ_g is typically 1.7 (ref. 2), and so the average matrix-ligament thickness is about 50% greater than for the monodisperse case at the same average size and volume fraction[2]. Thus, we expect ϕ_{sc} to be greater for the polydisperse case than for the monodisperse one[10]. This appears to account for the main difference.

On the other hand, it is known that percolation threshold depends on particle shape, i.e. decreasing with increasing aspect ratio[11]. In other words, asymmetrical particles have lower threshold values, and thus should be more effective than spherical ones in toughening. However, in the present system, the particles are spheroidal with aspect ratios of only about 1.1 (ref. 1). Therefore, we expect the shape effect to be small.

If the brittle–tough transition is a percolation phenomenon, we further expect a scaling law above the percolation threshold ϕ_{sc}:

$$G \sim (\phi_s - \phi_{sc})^g \tag{6}$$

where G is the toughness, g the critical exponent and ϕ_s the stress volume fraction:

$$\phi_s = \phi_r(S/d)^3 = \phi_r[(d+\tau_c)/d]^3 \tag{7}$$

This provides a critical test to see if the brittle–tough transition is indeed a percolation phenomenon.

Figure 6 plots log G *versus* $\log(\phi_s - \phi_{sc})$ for the present system. Tough data are plotted as open squares; brittle data as open circles. The fracture mechanisms in tough (yielding) and brittle (crazing) behaviours are different. The brittle data plotted herein are in the region above the 'first-path' percolation threshold, but are below

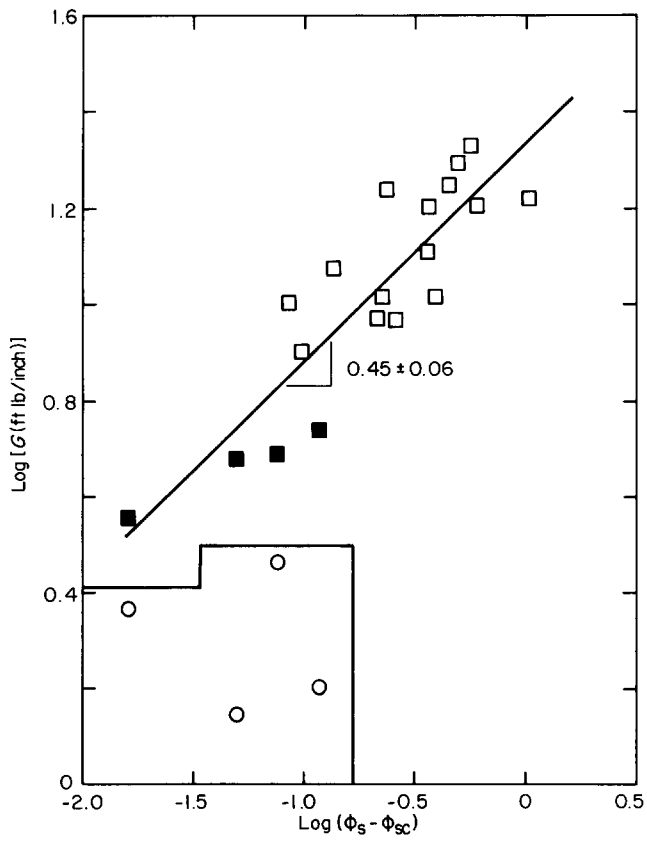

Figure 6 Log G *versus* $\log((\phi_s - \phi_{sc})$ for nylon/rubber blends, showing $g = 0.45 \pm 0.06$. Open squares are the data in the tough region. Filled squares are the estimated 'tough' strength in the brittle region. Open circles are the brittle strength in the brittle region. The tough strengths in both tough and brittle regions are used to obtain the correlation and the g value. The brittle strengths are plotted for reference only, and are not used

the multiple connectivity required for the onset of tough behaviour, as discussed before. Therefore, these brittle data must not be used with the tough data for determining the critical exponent g since the fracture mechanisms are different. Instead, we must use the 'tough' strength, if yielding were to occur in this 'brittle' region, discussed below.

A material may be considered to have both a brittle and a tough strength. In the brittle region, the brittle strength is weaker than the tough strength. This tough strength is equal to the strength that would be obtained if all the stress volumes were to yield in the absence of connectivity, i.e.:

$$G' = G_0 \phi_s \tag{8}$$

where G' is the 'tough' strength in the brittle region, and G_0 the toughness when the stress volumes just pervade over the entire deformation zone. For the present system, we have $G_0 \simeq 10$ ft lb/inch (i.e. 5.3 kJ m^{-2}). The 'tough' strength in the brittle region is thus calculated by (8), and plotted in *Figure 6* as filled squares. Using the tough data in both the tough and brittle regions, we obtain by least squares:

$$g = 0.45 \pm 0.06 \tag{9}$$

The fact that the data indeed obey the scaling law (equation (6)) further supports the concept of percolation for brittle–tough transition.

The critical exponent g is for the brittle–tough transition. Thus, it may be termed a critical 'mechanical' exponent. Interestingly, g ($\simeq 0.45$) is practically equal to the critical 'geometrical' exponent β ($\simeq 0.44$) found for classical percolation in three dimensions[5]. Our exponent g pertains to the toughness, which measures the dissipation of mechanical energy, and thus is a new mechanical exponent in percolation theory, not known before.

Furthermore, it is known that 'transport' exponents are affected by the distribution (polydispersity) of connecting-bond length, although 'geometrical' exponents are not[12]. Thus, we might expect that the 'mechanical' exponent g may also depend on particle polydispersity (or ligament length distribution).

CONCLUSIONS

The brittle–tough transition in polymer/rubber blends with pseudo-ductile matrices may be modelled as the percolation of matrix ligaments that are thinner than a critical value and in which a plane-strain to plane-stress transition and yielding take place. The onset of transition obeys an appropriate scaling law with a mechanical critical exponent $g \simeq 0.45$, which is interestingly practically equal to the classical critical exponent $\beta \simeq 0.44$ in three dimensions. The percolation threshold varies with d/S, particle size polydispersity and shape asymmetry, such that the toughening efficiency is predicted to be greater with monodisperse and highly asymmetrical rubber particles (i.e. rods, platelets and webs) than with polydisperse and spherical ones.

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REFERENCES

1 Wu, S. *Polymer* 1985, **26**, 1855
2 Wu, S. *J. Appl. Polym. Sci.* 1988, **35**, 549
3 Borggreve, R. J. M., Gaymans, R. J., Schuijer, J. and Ingen Housz, J. F. *Polymer* 1987, **28**, 1489
4 Wu, S. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 699
5 Stauffer, D. 'Introduction to Percolation Theory', Taylor and Francis, London, 1985
6 Zallen, R. 'The Physics of Amorphous Solids', Wiley, New York, 1983, p. 60
7 McCarthy, J. F. *Phys. Rev. Lett.* 1987, **58**, 2242
8 Bug, A. L. R., Safran, S. A., Grest, G. S. and Webman, I. *Phys. Rev. Lett.* 1985, **55**, 1896
9 Pike, G. E. and Seager, C. H. *Phys. Rev.* (*B*) 1974, **10**, 1421
10 Phani, M. K. and Dhar, D. *J. Phys.* (*A*) 1984, **17**, L645
11 Bug, A. L. R., Safran, S. A. and Webman, I. *Phys. Rev. Lett.* 1985, **54**, 1412
12 Feng, S., Halperin, B. I. and Sen, P. N. *Phys. Rev.* (*B*) 1987, **35**, 197
13 Flexman, E. A. *Polym. Eng. Sci.* 1979, **19**, 564
14 Hobbs, S. Y., Bopp, R. C. and Watkins, V. H. *Polym. Eng. Sci.* 1983, **23**, 380
15 Borggreve, R. J. M., Gaymans, R. J. and Luttmer, A. R. *Makromol. Chem., Macromol Symp.* 1988, **16**, 195

Note added in proof

Previously, Flexman[13] and Hobbs and coworkers[14] have also discussed impact fracture mechanisms of nylon/rubber blends. More recently, Borggreve and coworkers[15] independently suggested that stress-state transition in the matrix phase may account for the observed critical interparticle distance.