Reply to comments

We are pleased to reply to the preceding comments of Gaymans and Dijkstra, and take this opportunity to explain more fully and show more clearly the validity of our percolation model for brittle–tough transition in polymer blends[1].

PERCOLATION THRESHOLD

As stated in our paper[1], we distinguish two thresholds: the onset of brittle–tough transition ϕ_{bc} (i.e. the brittle–tough threshold, which is a mechanical property) and the onset of connectivity of stress volumes ϕ_{sc} (i.e. the percolation threshold, which is a geometrical property). The two thresholds may or may not exactly coincide with each other, because brittle–tough transition may require a certain multiple-connectivity density of stress volumes above what is attained at the percolation threshold. This is a special feature of the toughness phenomenon, as we explicitly discussed before[1].

To be general, we thus allow a small difference δ between the two thresholds[1]:

$$\delta = \phi_{bc} - \phi_{sc}$$

Since the degree of connectivity increases enormously beyond the percolation threshold, the δ should be relatively small. Furthermore, the δ permits us to account for some additional physical realities, discussed below.

In our model, rubber particles are assumed to be randomly distributed. In real samples however, the particle distribution may not be completely random. This may occur, for instance, because of the method used to prepare the samples, or because of interparticle attraction which may cause the formation of certain ordered or network structures.

Our samples have similar chemical compositions and were prepared by the same method. Therefore, the δ should be a *small constant*. More importantly, the δ also allows us to examine the critical scaling behaviour *within* as well as above the brittle–tough transition zone, i.e. to include the brittle data below ϕ_{bc} and above ϕ_{sc}, further discussed later.

The exact level of multiple-connectivity density required for the onset of brittle–tough transition is unknown *a priori* at this time. The δ may be treated as an adjustable parameter, or simply set as $\delta = 0$ (i.e. $\phi_{bc} = \phi_{sc}$). In either case, the essence of our model is unaffected. However, we prefer the δ to be a small constant, chosen so that one or two brittle data just below the brittle–tough transition at each constant rubber volume fraction ϕ_r are above the percolation threshold. As mentioned before, this will enable us to examine the critical scaling behaviour *within*, as well as above the brittle–tough transition zone. This is particularly important, since the brittle–tough transition region is our primary interest. We thus let $\delta = 0.1$, which meets all the above physical requirements.

This choice of δ value gives us four brittle data below ϕ_{bc} but above ϕ_{sc} in our nylon/rubber blends. Brittle failure occurs below ϕ_{bc}, since not all stress volumes can yield here[1]. This is because the levels of connectivity density required for tough behaviour are not reached below ϕ_{bc}. The fracture mechanisms below and above ϕ_{bc} are different. Therefore, to examine the critical scaling law, we corrected the toughness of these four brittle data to correspond to the case where all stress volumes yield, i.e. tough behaviour, discussed before[1]. The four corrected brittle data are marked as a, b, c and d in our present *Figures 1* and 2.

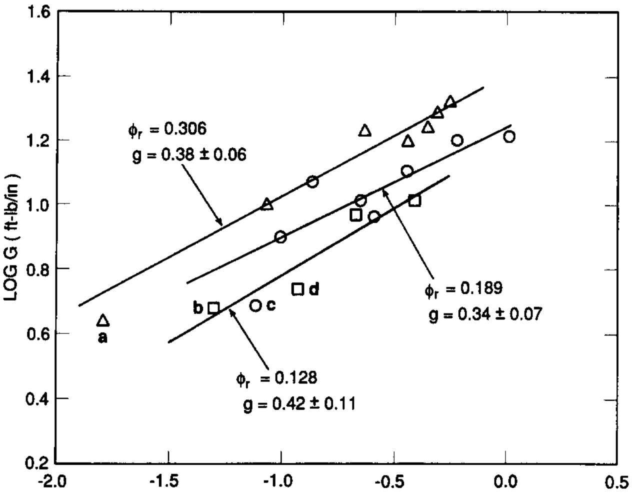

Figure 1 Notched Izod toughness G *versus* excess critical stress volume fraction $(\phi_s - \phi_{sc})$ at constant rubber volume fraction ϕ_r for nylon-66/rubber blends. △, $\phi_r = 0.306$; ○, $\phi_r = 0.189$; □, $\phi_r = 0.128$. The data points marked as a, b, c, d are the corrected tough data between ϕ_{bc} and ϕ_{sc}; see text and reference 1 for details

Thus, equation (4) of our previous paper[1] is more explicitly written as

$$\phi_{rc}(S_c/d_c)^3 = \phi_{sc} + \delta$$

For nylon/rubber blends, we thus used experimental data for ϕ_{rc}, τ_c and d_c in the above relation to obtain $\phi_{bc} \simeq 0.52$ and $\phi_{sc} \simeq 0.42$, as we reported before[1].

As explained below, interestingly our choice of δ gives the critical exponent g for brittle–tough transition as $g = 0.40$–0.45, which is practically equal to the theoretical β exponent for site and continuum percolations[1].

Qualitatively, it is immaterial whether ϕ_{sc} is 0.52 (for $\delta = 0$) or 0.42 (for $\delta = 0.1$). The critical threshold values are known to be different for different physical properties[2–7]. The important points are: *first*, the ϕ_{sc} values are constant for the samples in question; and *second*, the ϕ_{sc} values are physically reasonable, i.e. in the present case, between the two limiting values, 0.36 (for monodisperse particles) and 0.65 (for close-packed spheres). As shown in Figure 5 of our previous paper[1], our ϕ_{sc} values are indeed constant and well within the acceptable range of 0.36–0.65.

Therefore, the concept of percolation threshold is valid in interpreting the brittle–tough transition.

CRITICAL SCALING LAW

If brittle–tough transition is a percolation phenomenon, the toughness data in the vicinity above the percolation

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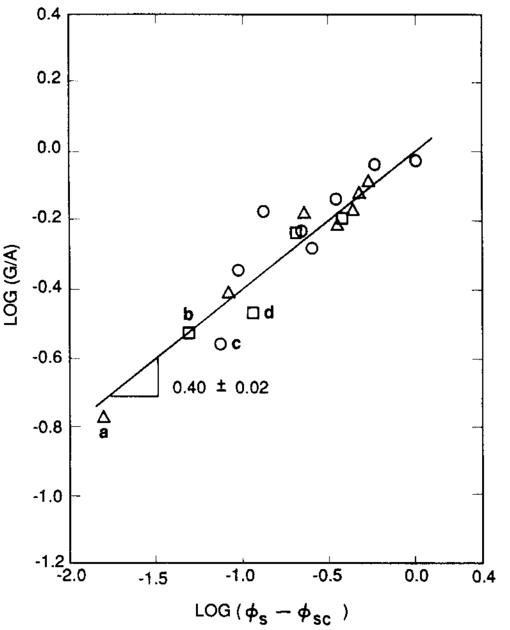

Figure 2 Normalized notched Izod toughness (*G/A*) *versus* excess critical stress volume fraction ($\phi_s - \phi_{sc}$) for nylon-66/rubber blends. △, $\phi_r = 0.306$; ○, $\phi_r = 0.189$; □, $\phi_r = 0.128$. The data points marked as a, b, c, d are the corrected data between ϕ_{bc} and ϕ_{sc}; see *Figure 1*

threshold should obey[1]

$$G = A(\phi_s - \phi_{sc})^g$$

where G is the toughness, A the prefactor, $\phi_s - \phi_{sc}$ the excess critical stress volume fraction, and g the critical exponent.

We hasten to caution that the above scaling law is valid only in the immediate vicinity above the percolation threshold, and must not be used indiscriminately without regard to *mechanical saturation*. In the regions sufficiently *far* above the brittle–tough transition, the toughness will become independent of stress–volume fraction, because of the mechanical saturation. This will occur when the stress volumes occupy the entire matrix phase, and so new stress volumes cannot be created from 'virgin' matrix by changing the particle size or the rubber volume fraction. Any apparent increase of stress–volume fraction arises from the overlapping of stress volumes, rather than from the creation of new stress volumes from the virgin matrix. Therefore, the toughness becomes independent of stress–volume fraction in this region. These mechanically saturated data should not be used to fit the critical scaling law.

The mechanical saturation appears to be reached in the few (3 or 4) data points having small particle sizes ($d \leqq \sim 0.52\,\mu$m) in the $\phi_r = 0.306$ series, as can be seen in the upper left region of Figure 1 in our previous paper[1]. They should not be used to fit the critical scaling law, as discussed above.

It is known that both the modulus and the yield stress of nylon/rubber blends are dependent on rubber volume fraction ϕ_r, but independent of rubber particle size, as ably reported elsewhere by Borggreve *et al.*[8]. Thus, the prefactor A varies with ϕ_r, but is constant for a series of samples with constant ϕ_r.

Therefore, we note that for a series of samples with constant ϕ_r, a straight line should be obtained, when $\log G$ is plotted *versus* $\log(\phi_s - \phi_{sc})$. On the other hand, when several series of samples with different ϕ_r values are plotted, a family of parallel straight lines should be obtained. Each line corresponds to a given ϕ_r value, and displaced from each other by $\Delta(\log A)$. This is indeed found to be true, as shown in our present *Figure 1*. The lines are parallel well within experimental scatter.

Interestingly, similar to our present *Figure 1*, Gaymans and Dijkstra also obtained parallel straight lines at constant ϕ_r values, i.e. the solid lines in their plot. But, their slopes are smaller than ours, because of two shortcomings in their plot, discussed below. Qualitatively however, the magnitude of the slope is *unimportant*. The important aspect is that parallel straight lines are obtained at constant ϕ_r values. Therefore, their plot actually *confirms* the validity of our percolation model.

There are two shortcomings in the way Gaymans and Dijkstra plotted our data, which gave them smaller slopes. First, they did not consider the effect of mechanical saturation. In their plot, the three or four data points at the right-hand end of the solid line for $\phi_r = 0.306$ are independent of particle size, and so are mechanically saturated. These few data points should not have been used.

Second, they did not include the brittle–tough transition zone in their constant ϕ_r plots (shown as solid lines). They omitted the four corrected brittle data between ϕ_{bc} and ϕ_{sc}. As already mentioned, these four corrected brittle data are marked a, b, c and d in our present *Figures 1* and *2*. In other words, their constant ϕ_r lines do not cover the brittle–tough transition zone, which is the most important region of interest. Instead, for these four data points, they drew a smoothed broken line without showing the data points in their plot. These four data points have different ϕ_r values, and are moreover too few to be statistically meaningful. Despite this, they compared their solid lines with the broken line. Such a comparison is improper.

On the other hand, we note that when normalized toughness (G/A) is plotted *versus* ($\phi_s - \phi_{sc}$) bilogarithmically, the family of straight lines should superimpose to form a single *universal* straight line for a given system. This is indeed true, as shown below.

As already shown in *Figure 1*, we first plot all the data above the percolation threshold (including the four corrected brittle data) at constant ϕ_r to obtain by least squares the A value at each constant ϕ_r. These A values are then used to obtain the normalized toughness (G/A).

Next, as shown in *Figure 2*, we plot the normalized toughness (G/A) *versus* ($\phi_s - \phi_{sc}$) bilogarithmically. This indeed gives a single *universal* straight line for the present system. This confirms the universality of the critical scaling law. The critical exponent is found to be $g = 0.40 \pm 0.02$.

Note that the scatter of data (see *Figure 1*) is such that it is statistically permissible to construct a single straight line in the $\log G$ *versus* $\log(\phi_s - \phi_{sc})$ plot using all the tough data (up to mechanical saturation) regardless of the ϕ_r values, as we did previously[1]. This simplified plot gave $g = 0.45 \pm 0.06$, which is practically identical to the present value of $g = 0.40 \pm 0.02$ obtained by the more strict normalized plot.

It is known that different physical properties have different critical exponents, depending on the relationship between the geometrical connectivity and the physical property in question. For instance, the critical exponent is $0.40 \sim 0.44$ for site and continuum percolations[6,7],

~1.7 for conductivity[2,3], ~3.8 for Young's modulus[4,5] and ~0.32 for magnetic induction[6]. Our critical exponent g pertains to the toughness, and is thus a mechanical exponent, not necessarily equal to the β exponent (0.40–0.44) for site and continuum percolations.

However, as already mentioned, it is interesting to note that our g exponent (0.40–0.45) is practically equal to the β exponent (0.40–0.44) for site and continuum percolations[1]. This suggests a direct proportionality between the toughness above the brittle–tough transition (up to mechanical saturation) and the connectivity density of the stress volumes. We emphasize here again that the similarity of g and β values is not our primary concern. The important aspect is that the functional form of the critical scaling law is *universal* with a constant critical exponent, whatever its numerical value.

Therefore, the brittle–tough transition is well described by the critical scaling power law.

CONCLUSIONS

We have explained in greater detail, and shown more clearly that the brittle–tough transition in nylon/rubber blends is well described by our percolation model. We have also shown that the plot of Gaymans and Dijkstra in their preceding comments actually confirms the validity of our percolation model.

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