Application of percolation model on the brittle to ductile transition for polystyrene and polyolefin elastomer blends

Z. Guo, Z. Fang*, L. Tong

Institute of Polymer Composites, Zhejiang University, Hangzhou 310027, P. R. China

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Abstract. The percolation model was applied in the study of brittle to ductile transition (BDT) of polystyrene (PS) and polyolefin elastomer (POE) blends. Based on the interparticle distance and percolation model, stress volume (V_s) can be expressed by volume fraction (V_r) and ratio of the diameter of stress volume and the diameter of the domain (S/d). The percolation threshold (V_{sc}) varied from $\pi/6$ to 0.65. From the results of the Charpy impact strength of the blends, the percolation threshold for the brittle to ductile transition of PS/POE blend is 14 wt% POE, corresponding to $V_{sc} \approx 0.5$, which is consistent with the calculated value of $\pi/6$. Morphology observations show that the percolation point is correlated with the phase inversion of the blend.

Keywords: polymer blends and alloys, percolation phenomenon, brittle to ductile transition (BDT), polystyrene (PS), polyolefin elastomer (POE)

1. Introduction

The fracture toughness of polymeric materials is a decisive factor in material selection, which is one of the most important mechanical properties that determine whether a polymer can be used as an engineering material. Many effective toughening methods for polymeric materials have been developed in the last years. Rubber toughening is one of the methods successful in toughening brittle or notch sensitive polymers. A great amount of experimental data is available to reveal the toughening mechanism. Many aspects of fracture behavior in polymer blends have been explained phenomenologically on the basis of the Ludwik-Davidenkov-Orowan (L-D-O) hypothesis [1, 2]. On this basis, brittle fracture and plastic flow are viewed as independent processes, giving separate characteristic relations for the brittle fracture stress σ_b and the yield stress σ_y , and the intersection of the σ_b/σ_y

curves defines the brittle-ductile transition (BDT) point.

Jang et al. [3–7] attributed the fracture toughness of rubber toughened polymers to a competition between two deformation mechanisms: crazing and shear yielding. When the craze initiation stress σ_{cr} is lower than the shear initiation stress σ_{sh} the failure mode is crazing and brittle fracture occurs. Otherwise, when $\sigma_{sh} < \sigma_{cr}$ shear yielding will be the main deformation mechanism and large energy absorption takes place, resulting in a tough fracture. The test conditions where $\sigma_{sh} = \sigma_{cr}$ define the BDT of the material [8].

Compared with the dispersed particle content and dispersed particle size, Wu [9–12] and Borggreve [13–16] proposed the ‘interparticle distance (ID , also called matrix ligament thickness)’ model and found that ID is a more important morphology parameter that dominates the BDT of polymer

*Corresponding author, e-mail: zpfang@zju.edu.cn
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Figure 1. Definition of the interparticle distance (ID)

blends. The definition of ID is shown in Figure 1, and can be determined from:

$$ID = d \left[\left(\frac{k\pi}{6V_r} \right)^{1/3} - 1 \right] \quad (1)$$

where V_r is the rubber volume fraction, $k = 1$ for cubic packing, d is the rubber particle diameter. According to Wu, there is a critical value of the interparticle distance (ID_c) when supposing that d is independent of V_r , which can be expressed by:

$$ID_c = d \left[\left(\frac{\pi}{6V_{rc}} \right)^{1/3} - 1 \right] \quad (2)$$

If ID is smaller than ID_c , then the blend is tough, otherwise the blend is brittle, namely, the change in ID can induce the BDT of polymers. Generally, the ID_c not only depends on the properties of the matrix materials [11, 12, 14], but also depends on the properties of the dispersed phase [13, 15–17]. Moreover, ID_c is also dependent on temperature and rate of deformation [18–20]. At a given mode, rate and temperature of deformation, however, ID_c is independent of particle size and rubber volume fraction and is characteristic for a given matrix [21]. In spite of comprehensive experimental and theoretical studies, the causes why ID_c exist remains unexplained up to now.

Rubber toughened polystyrene has received much attention from both academia and industry for a number of years. [22–33] However, the study on percolation phenomenon of PS and their blends was seldom reported. In this paper, polyolefin elastomer (POE) toughened polystyrene (PS) was used as a model system to explain the percolation phenomenon. SEM and TEM were performed to show the morphology behaviors before and after the percolation threshold. The selective dissolution was used to determine the continuity of POE in the blends.

2. Experimental part

2.1. Materials

Polystyrene (PS, code 666D) was obtained from Yanshan Petrochemical Co. China with a density of 1.05 g/cm^3 ($M_w = 310\,000$; $M_n = 87\,000$; $M_w/M_n = 3.6$).

Polyolefin Elastomer (POE, code Engage 8150) is a copolymer of octylene and ethylene, obtained from Du Pont-Dow Chemical Co. America with a octylene content of 25% and a density of 0.868 g/cm^3 ($M_w = 382\,000$, $M_n = 134\,000$, $M_w/M_n = 2.9$).

All the materials and reagents were commercial products and were used without further purification.

2.2. Preparation of the PS/POE blends

Melt blending process was carried out with a twin-screw extruder. The temperatures of the feeding zone, the mix zone, the reaction zone, and the die were 150 , 170 , 180 and 175°C , respectively. The rotation speed of the screw was 30 rpm . The samples were evacuated at 80°C for one night for drying. Then, the blends were preheated at 170°C in a mold for 5 min followed by compression under 14 MPa for 5 min at the same temperature and subsequently cooled down to room temperature under this pressure.

2.3. Measurements of the mechanical properties

The impact strengths were measured with an XCI-4 impact instrument (Charpy) according to GB1043-93 (similar to ISO179-1993, $70 \times 6 \times 4 \text{ mm}^3$). All the tests were performed at 25°C . Results of five measurements for each sample were averaged.

2.4. Morphological observations

An SIRION-100 (FEI, USA) scanning electron microscope (SEM) was used to observe the morphology development of PS/POE blends. The specimens were prepared by cryofracture in a liquid nitrogen cooling unit. Then they were covered with a layer of gold to avoid electrical charging to increase contrast during observation.

2.5. Selective dissolution and continuity calculation

The samples were compressed into slices and extracted with *n*-heptane at a bath temperature of 80°C for 48 h in order to dissolve the POE. After dissolution the samples were separated from the solution, dried in a vacuum oven at 70°C for 24 h, and then weighed. Three pieces of each sample were used to obtain an average value.

The percent continuity can be defined as the weight ratio of the POE phase involved in the continuous path divided by the total weight of the theoretical POE phase [34]. The POE phase involved in the continuous path is the dissolved phase:

$$\text{Continuity of POE [\%]} = \frac{\text{weight dissolved POE}}{\text{weight of initial POE}} \times 100 \quad (3)$$

where weight of dissolved POE is the weight difference of the sample before and after *n*-heptane dissolution.

3. Results and discussion

3.1. Theory

According to the theory of Wu, the ID_c as a critical thickness for the plane stress to plane strain transition [11]. If the sufficiently neighbored particles automatically lead to a stimulation of local plastic deformations due to overlapping of the local stress concentrations, the material between the particles is in plane stress resulting in macroscopically tough behaviors. However, the dimensions at which the plane stress to plane strain transition occur are of the order of millimeters [35] rather than fractions of a micron as implied by Wu. At sufficiently small particle distances, moreover, the transition from plane strain to plane stress in the matrix ligaments between the particles is also connected with the phenomena of cavitation for the rubber particles. In this context it has been shown by Borggreve and Sjoerdsma et al. [13–17] that cavitation inside the disperse phase and matrix/particle delaminations influence the toughness of the blend together. The original concept by Wu is only related to the matrix but not the characteristics of the disperse phase.

Therefore, the explanation of BDT by Wu's theory is not fully satisfactory. Based on the theory of interparticle distance, in 1988 Margolina [21] pro-

Figure 2. Schematics of stress volume around a rubber particle. The rubber particle is shaded

posed the percolation model for brittle-ductile transition in nylon/rubber blends. Margolina theory is based on the assumption that the critical stress necessary for initiation of plastic flow in the matrix is significantly reduced by transition from plane strain to plane stress inside the thin matrix ligaments. Each stress volume centers at a rubber particle and includes a concentric annular shell of the matrix of constant thickness $ID_c/2$, which is the critical ligament thickness, as defined before. When the volume fraction of stress volumes approaches the percolation threshold, stress volumes tend to overlap, allowing the yielding process to propagate and pervade over the entire matrix. Therefore, the diameter of a stress volume as shown in Figure 2 is

$$S = d + ID_c \quad (4)$$

where d is the diameter of the rubber particle, S is the diameter of a stress volume. Moreover, the volume fraction of the rubber particle (V_r) and the volume fraction of the stress volume (V_s) can be calculated by:

$$V_r = \frac{4}{3} \pi \left(\frac{d}{2} \right)^3 \quad (5)$$

$$V_s = \frac{4}{3} \pi \left(\frac{S}{2} \right)^3 \quad (6)$$

Therefore, V_s can be given as:

$$V_s = \left(\frac{S}{d} \right)^3 \cdot V_r \quad (7)$$

Continuum percolation of stress volumes will occur when the volume fraction of the stress volume is at its critical value (V_{sc}).

From Equation 2, 4 and 7, we can obtain

$$V_s = \left(\frac{\pi}{6V_{rc}} \right) V_r \quad (8)$$

when $V_r = V_{rc}$, V_s can obtain a critical value as $V_{sc} = \pi/6 \approx 0.52$ [36].

From Equation 7, we can also obtain that the V_{sc} values tend to vary with S/d rapidly. At $S/d = 1$, the V_{sc} increases to the limit value for random close packing (0.65), i. e. the saturated stress volume. Therefore, the percolation threshold V_{sc} varies from 0.52 to 0.65.

3.2. Brittle to ductile transition in PS/POE blends

Figure 3 reveals the relationship between the mechanical properties and the fraction of POE in PS/POE blends. As shown in the figure, an obvious brittle-ductile transition of PS/POE blends occurs in the Charpy impact tests with the increase of POE content. The value of impact strength nearly unchanged at first and then increased remarkable with increasing POE content. The point where the rubber content was 0.14 by weight, before and after which the impact strength enhanced about 3 folds, seems a critical point at which the transition from brittle to ductile behavior in PS/POE blends occurred.

PS and POE are immiscible. PS/POE blends show sea-island structure with PS matrix and POE domain. The volume fraction V_r of the POE can be given by

$$V_r = \frac{W_{POE}\rho_{PS}}{W_{POE}\rho_{PS} + W_{PS}\rho_{POE}} \quad (9)$$

where W_{POE} , ρ_{POE} and ρ_{PS} refer to the weight fraction of the POE rubber, density of the POE and

Figure 3. Variation of Charpy impact strength with the POE content [wt%] for PS/POE blends

Figure 4. Variation of Charpy impact strength with the fraction of stress volume (V_s)

density of the matrix, respectively. For PS/POE blends, $\rho_{POE} = 0.87 \text{ g/cm}^3$ and $\rho_{PS} = 1.05 \text{ g/cm}^3$. As shown in Figure 3, the point where the rubber content was 0.14 by weight is a critical point. Therefore, we can estimate from Equation 9 that $V_{rc} = 0.16$. Then, from Equation 8, a curve of the relation between impact strength and V_s can be achieved, as shown in Figure 4. According to the plots, it can be found that the critical V_s , i.e. the percolation threshold V_{sc} , is about 0.53, which is proximate to the theoretical value $\pi/6$, that is, the onset of percolation phenomenon will be observed when POE content was 14 wt%. Moreover, the rapid increase tendency of impact strength with V_s stopped at $V_s = 0.64$, corresponding to the limit value for random close packing (0.65). Thus it is believed that the percolation model is appropriate for the BDT behavior of PS/POE blends and the percolation threshold was between 0.53 and 0.64.

3.3. Morphology observations

There was an indication of heterogeneous phase structure of PS/POE blends. For this reason, such a blend can be considered as having two phases. Because of poor compatibility between PS and POE components, the dimensions of most POE droplets were big and the size distributions were very wide. The POE phase presents droplets with different sizes in the blend and poor adhesion between phases can be observed. The degree of shear yielding is relatively low; therefore, the crazing mechanisms contribute significantly to the deformation of PS/POE blends.

Figure 5. SEM micrographs of PS/POE blends: a) PS/POE = 90/10; b) and c) PS/POE = 80/20; d) PS/POE = 70/30; and e) PS/POE = 60/40

It can be seen for all blend compositions (Figure 5a–5d) that the phase structure of these blends is inhomogeneous and that the blend composition influences the extent of dispersion of the two phases. Figure 5a showed a micrograph of the surface of the 90/10 PS/POE blend. In this blend, PS forms a continuous phase, while the POE forms a discrete phase, indicating immiscible behavior of the blends. The POE phase presents droplets with different sizes in the blend and poor adhesion between phases can be observed. Figure 5b and 5c depicts the morphology of 80/20 PS/POE blend. It can be seen that the POE phases change partially continuous long fibrils and the POE domain size becomes bigger. The micrograph revealed a change in the distribution of the dispersed POE particles, with many of them starting to form aggregate-like elongated structures. According to the differences of the structure and shape between Figure 5a, 5b and 5c, therefore, when POE content is about 20 wt%, the

volume fraction of stress volumes has already exceeded the percolation threshold, and the stress volume has overlapped. With the composition of PS/POE increasing to 70/30 (Figure 5d), the aggregates were more obvious and the fiber diameters were coarser. The percolation phenomenon went on in the blends. However, when POE content increased to 40%, POE phase became completely continuous and PS/POE blends showed the co-continuous structures, as shown in Figure 5e.

3.4. The continuity of POE

POE can be well dissolved in *n*-heptane and PS is not dissolved in *n*-heptane. Therefore, the continuous POE phase in PS/POE blends can be extracted by *n*-heptane and we can calculate the continuity of POE from Equation 3. Figure 6 presents the evolution of the continuity of POE with the composition of the PS/POE blends. At 90/10 PS/POE the level

Figure 6. Continuity of POE phase as a function of the composition after solvent dissolution

of continuity of POE is nearly zero, consisting with the typical matrix-droplet structure in morphology as shown in Figure 5a. As the content of POE increasing, the continuity is also increasing, reflecting in morphology (Figure 5c and 5d) as the POE particles elongating. When the content of POE is about 40%, the continuity has been beyond 50%, corresponding to the co-continuous morphology structure in Figure 5e. The content of 20% POE seems a threshold of continuity increasing dramatically, indicating that the percolation phenomenon has already started. This result gives the additional evidence to the morphology observation for the gradual coarsening of fiber diameters up to the phase inversion region.

4. Conclusions

The percolation model has been applied to the study on brittle to ductile transition (BDT) of the PS/POE blends. According to the interparticle distance theory and percolation model, the relations of stress volume (V_s), volume fraction (V_r) and S/d were achieved. It was predicted that the percolation threshold (V_{sc}) varied from $\pi/6$ to 0.65. The curve of Charpy impact strength and content of POE showed a typical brittle to ductile transition phenomenon. The 14 wt% POE content was a critical point at which the BDT in PS/POE blends was induced and the percolation threshold of PS/POE blends was showed within 0.53 ~ 0.64, corresponding to the theoretical value. It was well shown the percolation point and phase inversion through morphology observations of SEM and TEM and continuity of POE by selective dissolution.

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