ELSEVIER

Polymer 40 (1999) 3191–3195

polymer

Brittle–ductile transition in polypropylene filled with glass beads

Ji-Zhao Liang[a,b,*], R.K.Y. Li[a]

[a]Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, People's Republic of China
[b]Department of Chemical Machinery, South China University of Technology, Guangzhou 510641 People's Republic of China

Received 20 March 1998; accepted 9 July 1998

Abstract

The effect of surface treatment of glass beads with a silane coupling agent and the filler content on the notched Izod impact properties of the filled polypropylene (PP) composites has been investigated. It was found that the impact fracture energy of the composites, E_{IC}, increased with increasing the volume fraction of glass beads, ϕ_f; the influence of surface treatment of glass beads on E_{IC} was insignificant; the brittle–ductile transition (BDT) phenomenon occurred when ϕ_f was about 10%. A modified percolation model for BDT in thermoplastic–rigid particle blends is proposed under the basis of predecessors' work. The results show that the BDT of the composites in impact can be considered as a percolation process.

Keywords: Polypropylene; Glass bead; Composite

1. Introduction

For brittle or quasi-ductile polymeric materials, it is very important to enhance their toughness to extend their applications. The inclusion of fillings into these materials for modification is a widespread practise in industry. When they are modified with elastomer or rigid particulate, a brittle–ductile transition (BDT) phenomenon will occur under given conditions. The origin of BDT phenomenon or toughening mechanism in thermoplastic materials, such as polypropylene (PP), high density polyethylene (HDPE), polystyrene (PS) and polyamine etc., modified with rubber have been studied [1–11]. It is generally believed that the toughening of materials is attributable to deformation energy absorbed by crazing or shear yielding under the action of outside force. Therefore, the competition between crazing and shear yielding dictates the subsequent failure model. The dependence of BDT on the test and material parameters (such as temperature, strain rate, pressure, orientation, notching, and plasticizer) may be ascribed to the respective influence of these parameters on crazing relative to shear yielding [1,3]. Wu [2,4] proposed an interparticle distance model (i.e. the critical matrix ligament thickness) as a criterion of BDT for rubber toughening polymers, which is often used by other researchers. But Sjoerdsma [7], queried whether this model was suitable when the particle size was too small to induce plastic deformation. He derived a new criterion for BDT in rubber-modified polymers by assuming that the connectivity of volume elements that did not yield, determined the toughness. Liu et al. [12] studied the effect of morphology on the BDT of binary polymer blends, and presented a modified matrix ligament thickness equation for correlating morphological parameters of particles.

Margolina and Wu [5] investigated the BDT in nylon–hydrocarbon rubber blends, and noted that the BDT occurred when yielding process propagated through thin ligaments in which a plane-strain to plane-stress transition took place, this propagation could be modeled as a percolation phenomenon. However, this model is based on the assumption of the uniform distribution of the particles in the matrix. Considering the aggregation phenomenon of the inclusions in the matrix, Alberola and Mele [13] established a model describing the volume fraction of a percolated matrix.

In this paper, on the basis of investigating the effect of interfacial adhesion on the notched Izod impact properties for glass bead filled PP composites, we attempt to propose a modified model for the BDT in these composites.

2. Experimental

2.1. Materials

PP used in this test was a general purpose polypropylene, Himont Pro-fax® 6331, with improved processibility. The

* Corresponding author. E-mail: 95412028@plink.cityu.edu.hk

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00532-1

density and melt flow index were 0.9 g cm^{-3} and 12 g 10 min^{-1}, respectively.

Two types of glass beads (A-GLASS 3000) with the same mean diameter of 35 μm, one was surface pretreated with a silane coupling agent CP-03 (3000) and the other had no surface pretreatment (3000U), were selected as the fillers to identify the effect of surface treatment on the impact properties of the composites. The glass beads were small solid spherical particles (Potters Indust. Inc., USA), with the density of 2.5 g cm^{-3}.

The PP was blended with glass beads of volume fractions of 5%, 10%, 15%, 20%, 25% and 30%, using a Brabender twin screw extruder to produce the composites. The extrusion temperatures varied from 180°C to 220°C. The specimens for tensile mechanical test were molded with an injection molding machine, which the width and thickness were 13 and 3.2 mm, respectively. The injection temperatures were 190°C–230°C.

2.2. Apparatus and methods

The Izod impact tests of the notched specimens were conducted at room temperature employing an Ceast impact tester (Code 6545/000), according to ASTM D256-93a standard. The dimension of the specimens (length × width × thickness) was 63.50 × 13 × 3.20 mm.

To observe the morphological structure of the impact fracture surface for the notched specimens, a scanning electron microscope (SEM), the instrument being JSM-820 made by Jeol in Japan, was used.

3. Results and discussion

3.1. Impact fracture energy

Impact fracture energy is an important parameter characterizing toughness of materials. Fig. 1 displays the relationship between the notched impact fracture energy of the composites, E_{IC}, and ϕ_f. When $\phi_f < 10\%$, E_{IC} increases slightly with increasing ϕ_f. But E_{IC} increases significantly with ϕ_f when $\phi_f > 10\%$. It suggests that the critical volume fraction, ϕ_{fc}, which occurs at the phenomenon of brittle–ductile transition in the composites, is around $\phi_f = 10\%$ for the PP–3000U system and 7% for the PP–3000 system, respectively, under these conditions. In addition, the difference between PP–3000 and PP–3000U systems is small. It means that the effect of surface treatment of glass beads on the impact properties of the filled PP composites is not too significant.

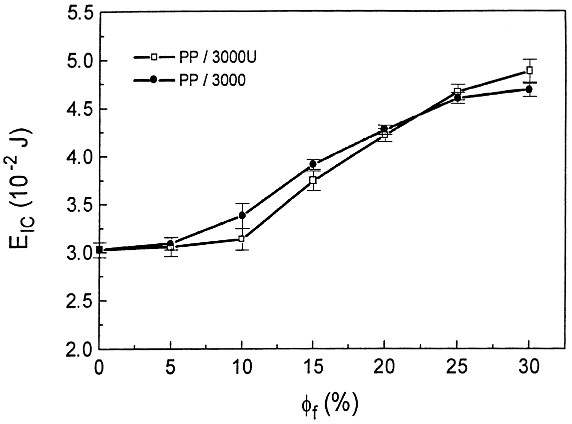

Fig. 1. E_{IC} as a function of ϕ_f.

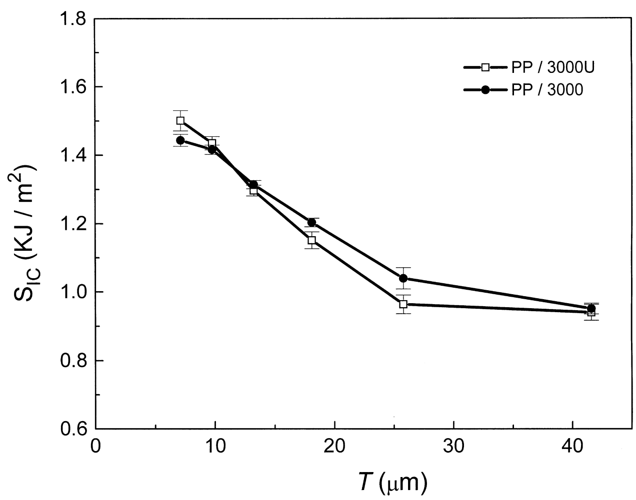

Fig. 2. S_{IC} vs matrix ligament thickness.

3.2. Matrix ligament thickness

Using an equation of the matrix ligament thickness, T, (i.e. surface-to-surface interparticle cluster distance) proposed by Wu [2] as follows:

$$T = d[(\pi/6\phi_f)^{1/3} - 1] \quad (1)$$

we can plot the curves of the notched impact strength of the composites, S_{IC}, against T from the results shown in Fig. 1, as shown in Fig. 2. Where d in Eq. (1) is the average diameter of the particle. It can be observed from Fig. 2, that S_{IC} decreases with increasing T, and S_{IC} remains constant when T is greater than 25.776 μm. It means that the critical matrix ligament thickness, T_c, is about 25.776 μm in this case. That is, the material will be ductile if T is smaller than T_c, and will be brittle when T is greater than T_c. This is because, when the matrix ligament is thinner than T_c, a plane-strain to plane-stress transition would occur; the ligament would shear yield, and the composite would be tough. On the other hand, if the ligament is thicker than T_c, such transition could not take place, and the matrix ligament would fail in a brittle fashion [4].

3.3. Morphology

Fig. 3 is SEM photograph of impact fracture cross-section of the specimen for the pure PP. One can see that the

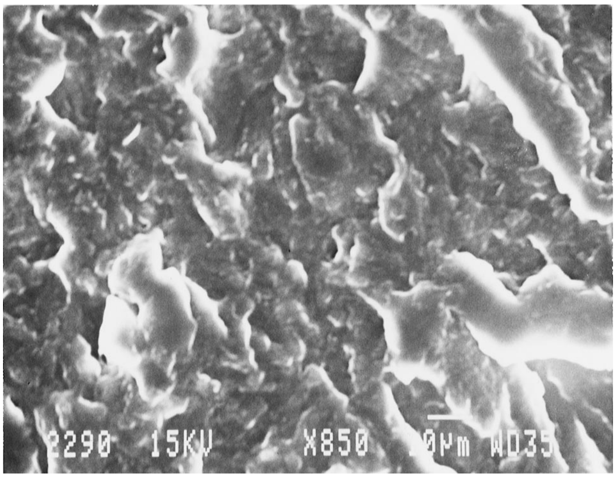

Fig. 3. SEM photograph of impact fracture cross-section of pure PP specimen.

morphology of the section is like a sea-wave, and the wave crest and the trough are very clear. In addition, the arrangement and direction of the waves are regular and perpendicular to the impact direction. It suggests that the crack (e.g. the notch), developed from crazes, will propagate towards the whole cross-section in a pattern of a wave until complete fracture of the specimen under the impact load, thus the specimen rapidly fractures.

Fig. 4 is a SEM photograph of impact fracture cross-section of the specimen for the PP–3000 system with $\phi_f = 15\%$. It can be seen that the regular wave shape section can not be observed, and a number of small pieces of the matrix with the beads are formed and distribute irregularly. The matrix layer around the particle will yield first, as a result of stress concentration, to form these pieces and absorb plastic deformation energy to enhance the toughness of the composites (see Figs 1 and 2). In addition, the aggregation phenomenon of glass beads in the PP matrix can be observed. That is, the dispersion of glass beads in the PP matrix is not uniform. On

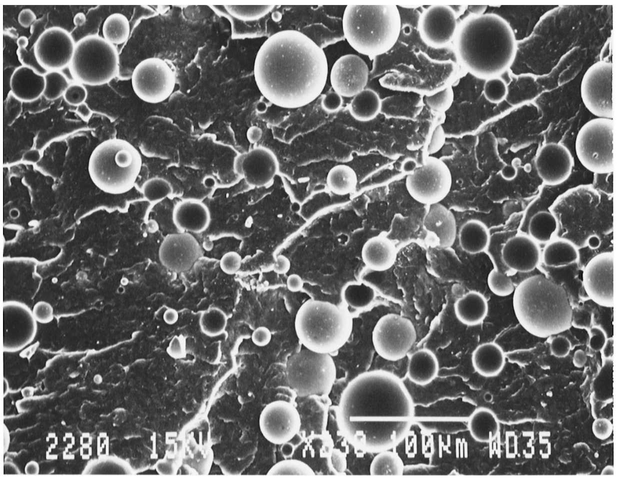

Fig. 4. SEM photograph of impact fracture cross-section of the PP–3000 ($\phi_f = 15\%$) specimen.

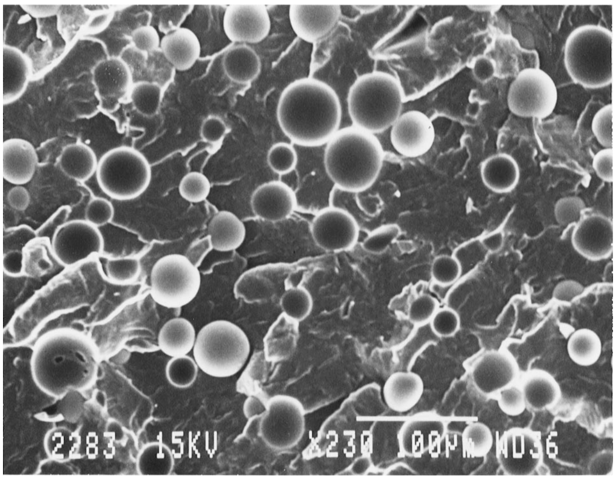

Fig. 5. SEM photograph of impact fracture cross-section of the PP–3000U ($\phi_f = 15\%$) specimen.

the other hand, the interfacial adhesion between the particle and the matrix is good.

Fig. 5 is a SEM photograph of impact fracture cross-section of the specimen for the PP–3000U system with $\phi_f = 15\%$. Similarly, a number of small pieces of the matrix with the beads are formed instead of a wave shape section, and the pieces are relatively large. Thus, the toughness is also improved (see Figs 1 and 2). In addition, the dispersion of glass beads in the matrix is also poor, and some phenomenon of agglomeration of glass beads in the matrix can be observed. But the interfacial adhesion between the fillers and the matrix is relatively poor.

For the unfilled PP, when the notched composite specimen carries out impact load, the crazes will rapidly develop into cracks, and will propagate towards whole cross-section to form the morphology-like regular arrangement of sea-waves (see Fig. 3), and result in fracture. But for the glass filled PP composites, a number of crazes of the matrix around the particle will be formed to absorb the impact deformation energy; on the other hand, the particle will block the propagation of the cracks developed from the crazes to enhance the toughness of the filled systems (see Fig. 2), and form small yielded pieces with an irregular arrangement of the matrix including glass beads (see Figs 3 and 4). Therefore, the cracks will propagate in a random fashion. In other words, the plastic deformation process may be a percolation phenomenon.

4. Analysis

As stated previously, Wu's model (Eq. (1)) is established on the basis of the hypothesis of the uniform distribution of particles in matrix. In fact, when there are more inclusions in the matrix, the aggregation phenomenon of the particles in the matrix may take place. Especially for glass beads, this aggregation phenomenon is more likely to occur as a result

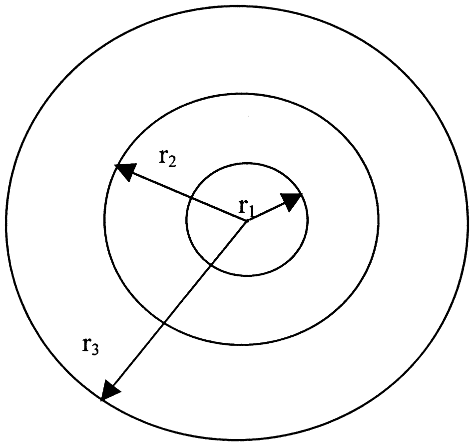

Fig. 6. Diagram of the mechanical model.

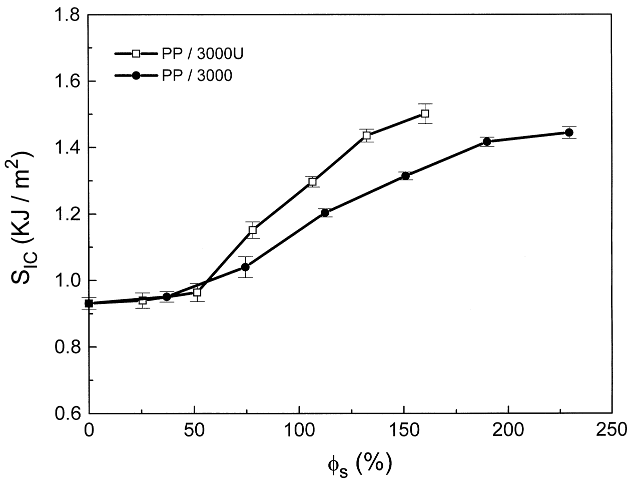

Fig. 7. Relationship between S_{IC} and ϕ_s.

of their smooth spherical surface. In this case, the matrix region encircled by a cluster of particles may not yield when other matrix yields (see Figs 4 and 5). In other words, this is an unpercolated matrix. It should be considered, therefore, when one analyses the percolation process of BDT of particulate filled thermoplastic composites.

A model of percolation in rigid particulate filled polymers is shown in Fig. 6, where the clitellum between r_2 and r_3 represents the percolated matrix; the clitellum between r_1 and r_2 stands for the cluster of particles; and the circle with r_1 is the unpercolated matrix. The relationship between the ratios of radii and relevant volume fraction is defined as follows:

$$\phi_1 = 1 - \left[\frac{r_1}{r_3}\right]^3 \quad (2)$$

$$\phi_2 = \frac{r_2^3 - r_1^3}{r_3^3} \quad (3)$$

$$\phi_3 = 1 - \left[\frac{r_2}{r_3}\right]^3 \quad (4)$$

and

$$r_3 = r_2 + T_c'/2 \quad (5)$$

where $\phi_1 = \phi_m$-ϕ_3, ϕ_m and ϕ_2 is the volume fraction of the matrix and particles, respectively (i.e. $\phi_2 = \phi_f$), and the critical matrix ligament thickness, T_c', is given by:

$$T_c' = 2r_2\left[\left(\frac{\pi}{6\phi_{2c}}\right)^{1/3} - 1\right] \quad (6)$$

Continuum percolation of stress sphere volumes will occur when the volume fraction of stress sphere volumes (ϕ_s) is at its critical value (ϕ_{sc}). Since $\phi_f \sim r_2^3$, and $\phi_s \sim r_3^3$. From the aforementioned, the volume fraction of stress sphere can be expressed:

$$\phi_s = \phi_f\left\{\left[\frac{r_3}{r_2}\right]^3 - \phi_1\right\} \quad (7)$$

Substituting the above relevant equations into Eq. (7), we have

$$\phi_s = \phi_f\left[\frac{\pi}{6\phi_{fc}} + \phi_f - \frac{6\phi_{fc}}{\pi}\right] \quad (8)$$

where ϕ_{2c} (or ϕ_{fc}) is the critical volume fraction of the particles.

If the brittle–ductile transition is a percolation phenomenon, then the following expression will be available from a scaling law in percolation theory:

$$S_{IC} \sim (\phi_s - \phi_{sc})^g \quad (9)$$

where ϕ_{sc} is also the percolation threshold, and g the critical exponent.

The dependence of S_{IC} on ϕ_s is shown in Fig. 7. It can be seen that the relationship between S_{IC} and ϕ_s is similar to the dependence of E_{IC} on ϕ_f shown in Fig. 1. When ϕ_s is greater than about 50%, S_{IC} increases significantly with increasing ϕ_s. It suggest that the critical values of volume fraction of stress sphere, ϕ_{sc}, are 60% for the PP–3000 system and 51%

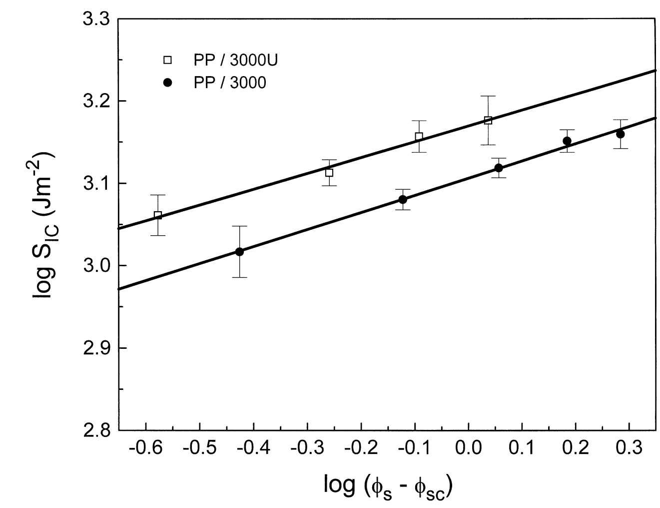

Fig. 8. Log S_{IC} vs log ($\phi_s - \phi_{sc}$).

for the PP–3000U system, respectively. Fig. 8 illustrates the plots of log S_{IC} vs log ($\phi_s - \phi_{sc}$) for the composites. It can be seen that the relationship between them is linear, and the values of g are 0.208 for the PP–3000 system and 0.192 for the PP–3000U system, respectively. It suggests that the brittle–ductile transition in the composites is a percolation process. The values of critical exponent g of the composites are lower than the critical 'geometrical' exponent β ($\cong$0.44) found for classical percolation in three dimensions [14]. It indicates that the toughening effect of the glass bead filled PP composites is not too significant, because the slope of the curve for log S_{IC} versus log ($\phi_s - \phi_{sc}$) is not great (see Fig. 7).

5. Conclusion

The results show that the notched Izod impact fracture energy of the composites, E_{IC}, increases with increasing the volume fraction of glass beads, ϕ_f, especially when $\phi_f >$ 10% the increase in notched Izod impact strength of the composites, S_{IC}, is more significant; it is attributable to the matrix layer around the particle yield firstly as a result of the stress concentration to absorb plastic deformation energy, and the development of cracks is blocked by the inclusions as well as the fact that the cracks propagate in a random fashion. The influence of surface treatment of glass beads with a silane coupling agent on E_{IC} or S_{IC} is insignificant.

The brittle–ductile transition phenomenon occurs when ϕ_f is about 10%. When the concentration of fillers is higher, the aggregation phenomenon of the particles in the matrix will occur more easily. A modified percolation model for brittle–ductile transition in thermoplastic–rigid particle blends is proposed under the basis of a predecessors' work. The results show that the notched Izod impact fracture of the glass bead filled PP composites can be considered as a percolation process.

Acknowledgements

This work was supported by a City University of Hong Kong Strategic Research Grant no. 7000649.

References

[1] Jang BZ, Uhlmann DR, Vander Sande JB. J Appl Polym Sci 1984;29:3409.
[2] Wu S. Polymer 1985;26:1855.
[3] Jang BZ, Uhlmann DR, Vander Sande JB. J Appl Polym Sci 1985;30:2485.
[4] Wu S. J Appl Polym Sci 1988;35:549.
[5] Margolina A, Wu S. Polymer 1988;29:2170.
[6] Chou CJ, Vijayan K, Kirby D, Hiltner A, Baer E. J Mater Sci 1988;23:2521.
[7] Sjoerdsma SD. Polym Comm 1989;30:106.
[8] Wu S. Polym Engng Sci 1990;30:753.
[9] Fu Q. Wang G, Shen J. J Appl Polym Sci 1993;49:673.
[10] Bagheri R, Pearson RA. Polymer 1995;36:4883.
[11] Liang H, Jiang W, Zhang J, Jiang B. J Appl Polym Sci 1996;59:505.
[12] Liu ZH, Zhang XD, Zhu XG, Qi ZN, Wang FS. Polymer 1997;38:5267.
[13] Alberola ND, Mele P. Polym Engng Sci 1997;37:1712.
[14] Stauffer D. Introduction to percolation theory. London: Taylor and Francis, 1985.