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Impact fracture toughness of hollow glass bead-filled polypropylene composites

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Abstract The notched Izod impact properties of polypropylene (PP) filled with hollow glass beads (HGB) have been measured at room temperature to identify the effects of the particle contents, size and its distribution on them in the present paper. The mean diameters of the particles were 11, 35, and 70 μm, and named TK10, TK35 and TK70 respectively. The surface of the particles was pretreated with silane coupling agent. The results showed that the notched Izod impact strength (σ_I) of the filled systems increased gently with increasing the volume fraction (ϕ_f) of the fillers when ϕ_f was less than 15%, and then it decreased. When ϕ_f was 10%, σ_I decreased with an increase of the mean diameter of the particles. Furthermore, the impact fracture surface of the specimens was observed by using a scanning electron microscope (SEM). The improvement of the impact toughness of the composites might be mainly attributed to the shear yielding first of the matrix around the beads to absorb relevant deformation energy under impact load.

Introduction

In general, the mechanical properties of polymeric materials depend mainly upon their internal morphology and structure. For a neat polymer, molecular aspects of craze/yield behavior are controlled by two chain parameters: entanglement density and the characteristic ratio of the chain [1]. In addition, the influence of outside circumstance and operation conditions (e.g. temperature, strain rate, the form and time of applied force, etc.) on the mechanical properties are also quite important [2, 3]. For particulate-filled polymer composites, the effects of the filler shape, content, particle size and its dispersion in the matrix on the physical properties, especially for some important mechanical behavior, such as tensile strength, stiffness, impact toughness and brittle-ductile transition (BDT), are quite significant, in addition to the interfacial adhesion between the matrix and the filler particles [4–7].

For a rigid inorganic particulate-filled polymer composites, the interfacial adhesion between the filler particles and the matrix is also an important factor affecting impact toughness of materials [8–13]. It suggests that there should be a suitable interfacial adhesion between the filler and the matrix for the mechanical strength and fracture toughness of polymer composites.

Polypropylene (PP) is extensively used in automobile and electronic appliance applications. However, its application is somewhat limited due to its high shrinkage rate, and relatively poor impact resistance at room or low temperatures. To improve its impact toughness and dimensional stability, PP filled with rigid inorganic particles is widely used in industry, such as calcium carbonate, mica, talcum powder, and so on. Glass bead (GB) is a kind of small solid spherical particle with smooth surface. Polymer filled with GBs has less internal stress, good mechanical and processing properties. Recently, the authors [14] investigated the

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effects of the filler content and surface treatment on the tensile properties of GB-filled PP composites, and found that the tensile strength of the composite filled with the pretreated fillers was slightly greater than that of the composite filled with the raw fillers, while the tensile fracture toughness of the latter was better than that of the former.

Hollow glass beads (HGBs) are a kind of fillers in rubber, plastics and coating materials for production of light or thermal insulation products with smooth surface and stiffness. Compared with solid GBs, HGBs have some specialists, such as small density, thermal insulation and sound insulation. Therefore, if it is used as filler, some cellular composites with corresponding functions (e.g. thermal insulation and sound insulation) can be made. In the previous work, the author [15] measured the tensile and flexural properties of HGB-filled ABS composites. Mouzakis et al. [16] investigated the fracture behavior of PP/GB elastomer composites by using the essential work-of-fracture method, and found that the GBs induced matrix cavitation, which triggered the yielding of the PP matrix, especially in the presence of a finely dispersed elastomer phase. In this work, the effects of the particle size and content of HGBs on the Izod notched impact fracture behavior of the filled PP composites are in particular investigated at room temperature.

Experimental

Materials

An injection grade of PP with trade mark of CJS-700, supplied by Guangzhou petrochemical Co. Ltd in China, was used as the matrix resin, the density and melt flow index (230 °C, 2.16 kg) of the resin were 0.91 g/cm^3 and 12 g/10 min, respectively.

Three kinds of HGB with different size used as the fillers in this work were supplied by Eco. & Chimie Co. Ltd. (Guangzhou, China). The mean diameters of the fillers were 11, 35 and 70 μm, and the density was 1.2, 0.68 and 0.21 g/cm^3, the fillers were called respectively as TK10, TK35 and TK70. The surface of the particles was pretreated with a silane coupling agent by the supplier. The particle size distribution of the fillers was measured by means of a laser size instrument (Model LS-C (I) supplied by Omik Co. Ltd in Zhuhai city, China.

Sample preparation

After mixing simply, the PP resin and the HGB with different proportions were compounded in a twin-screw extruder. The blending was conducted in a temperature range of 160–230 °C and screw speed of 25 r/min, and then the extrudate was granulated to produce the composites. The volume fractions of the HGB were 0, 5, 10, 15 and 20%. The specimens for Izod impact tests were molded by using an injection-molding machine in temperature range of 160–240 °C after drying the composites. The geometry of the impact specimens was made according with ASTM D256-93 standard.

Apparatus and methodology

The V-notched Izod impact tests of the composites were carried out by means of a Ceast pendulum impact tester (Ceast Code 6545/000). The impact tests were conducted according to ASTM D256-93 standard. The impact properties of the specimens were measured also at room temperature. Each group of specimens contained 5 pieces, and the average values of the tensile properties were determined from the measured data.

The fracture surface from the Izod impact test specimens were examined by means of a scanning electron microscope (SEM) in order to observe the interfacial debonding, interlayer structure morphology, and the dispersion or distribution of the filler particles in the PP matrix. The SEM (model S440) was supplied by Leica Cambridge (UK). These samples were gold coated before the SEM examination.

Results and discussion

Particle size distribution

It is generally believed that particle size and size distribution of fillers are important parameters for affecting mechanical properties of composites. Differential distribution (λ) is an important parameter characterizing the particle size distribution of fillers. The higher the value of λ in a given range of particle diameter, the narrower particle size distribution. Figure 1 shows the particle size distribution of the three kinds of fillers. It can be seen that the size distribution of TK10 is the most narrow, white the size distribution of TK70 is the widest, TK35 has a medium size distribution. For TK10, the diameter concentrates in a range from 7.09 to 18.09 μm and the cumulative distribution is about 73%. For TK35, the diameter concentrates in a range from 21.14 to 39.5 μm and the cumulative distribution is about 62%. For TK70, the diameter concentrates in a range from 53.9 to 100.6 μm and the cumulative distribution is about 46%.

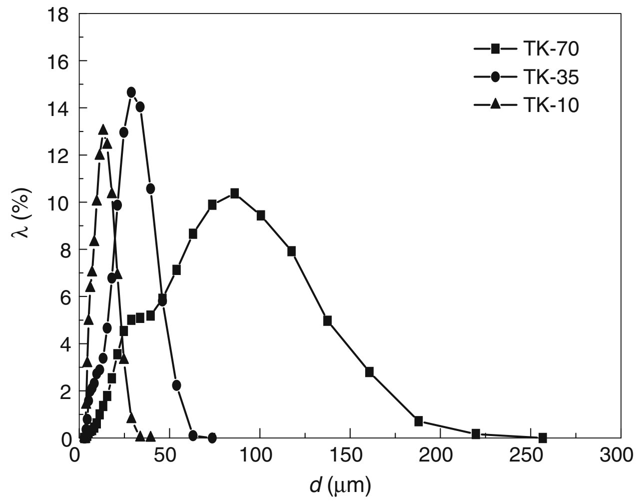

Fig. 1 Particle size distribution of HGB

Relationship between impact strength and filler content

In general, the impact fracture toughness of materials is characterized by impact strength. Figure 2 shows the dependence of the notched Izod impact strength (σ_I) of the PP/TK35 and PP/TK70 systems on the volume fraction (ϕ_f) of the HGB. It can be seen that σ_I increases slightly with an addition of ϕ_f when ϕ_f is less than 15%, and then it decreases somewhat when ϕ_f is more than 15%. This indicates that the impact fracture toughness of the composites is improved at lower concentration of the beads. Under the same conditions, the values of σ_I for PP/TK35 system are higher than those of PP/TK70 system except individual data point. This means that small size HGBs are beneficial to improve impact fracture toughness of the filled PP composites.

Dependence of impact strength on particle size

Figure 3 demonstrates the dependence of impact strength on particle size of the three filled systems when ϕ_f is 10%. It can be seen that σ_I decreases roughly linearly with an increase of the mean diameter of the beads. That is

$$\sigma_I = \alpha + \beta d \tag{1}$$

where α and β are the parameters related to impact fracture toughness of composites, and they may be determined by means of a linear regression analysis method from experimental data. The results show that the values of α and β are respectively 5.07175 and –0.01012, and the absolute value of linear corresponding coefficient is 0.9946. In this work, the impact strength (in kJ/m^2) is given by:

$$\sigma_I = \frac{W}{h \cdot b_N} \times 10^3 \tag{2}$$

where W is the corrected impact energy absorbed by the fractured specimen in J, h is the specimen thickness in mm, and b_N is the ligament width in mm, which is equal to the width of the specimen minus the V-notch depth. In this test, h was 8 mm and b_N was 4 mm.

In general, the smaller the size of filler particles, the more their number is. Therefore, the interfacial ligament between neighboring two particles decreases with

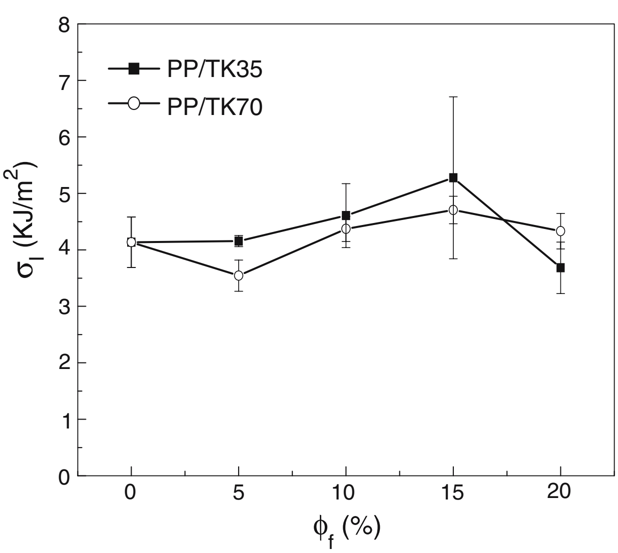

Fig. 2 Notched impact strength of PP/HGB composites

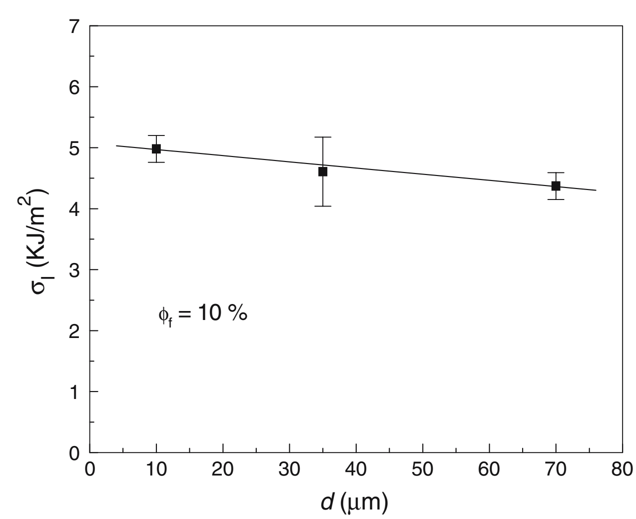

Fig. 3 Effect of particle size on notched impact strength of PP/HGB composites

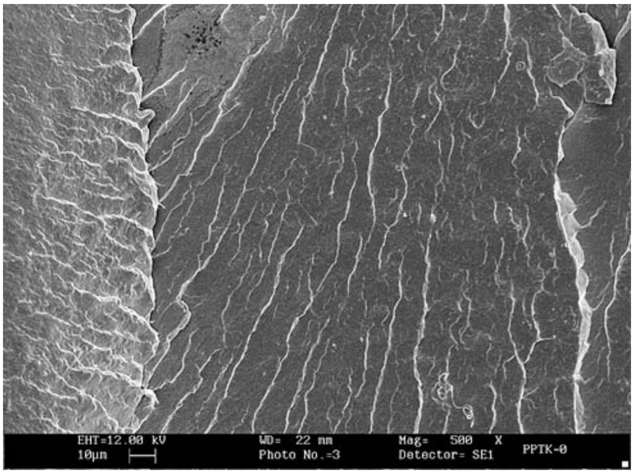

Fig. 4 Scanning electron micrograph of impact fracture surface of unfilled PP

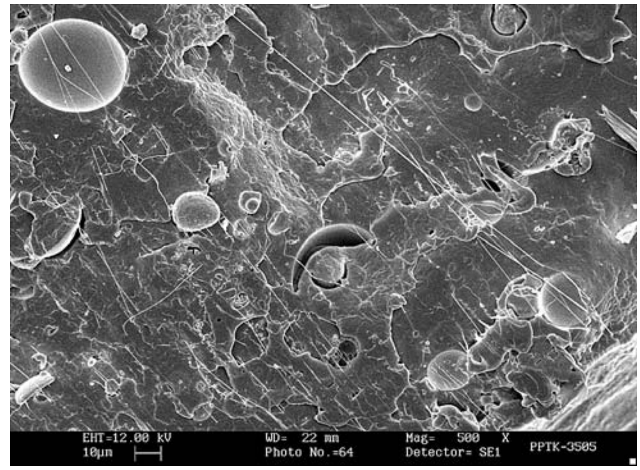

Fig. 5 Scanning electron micrograph of impact fracture surface of PP/TK35 (ϕ_f = 5%)

reduction of the particle size at the same volume fraction of the fillers when the dispersion of the particles is uniform, leading to changing relatively easily from plane strain to plane stress. In this case, the matrix around the particle will reach shear yield firstly and absorb impact deformation energy. Consequently, the impact toughness of the composite is improved.

Morphology

Figure 4 is a scanning electron micrograph of impact fracture surface of unfilled PP. It can be seen that the impact fracture surface is relatively smooth. This because that the specimen of the PP resin might fracture along the V-notch as a crack when it is subjected to impact load, and the crack expands quickly owing to its bad impact toughness, leading to generation of smooth fracture surface of the specimen. In this test, the SEM pictures are taken just in the vicinity of the notch, and the position of the notch is on the left of the SEM picture.

Figure 5 shows a scanning electron micrograph of impact fracture surface of PP/TK35 composite when ϕ_f is 5%. It illustrates that there are some look-like fibrils on the impact fracture surface, and these fibrils are along the impact direction. When the specimen is subjected to impact load, the interfacial layer between the HGBs and the PP resin is acted with shear stress and yields first due to stress concentration around the beads, it will generate obvious plastic deformation and crazing correspondingly, leading to production of these fibrils.

Figure 6 is a scanning electron micrograph of impact fracture surface of PP/TK35 composite when ϕ_f is 10%. Similarly, there are some look-like ribbons on the impact fracture surface of the specimen. These fibrils absorb a number of impact deformation energy during impact process, resulting in an increase of impact strength of the filled PP system (see Fig. 2).

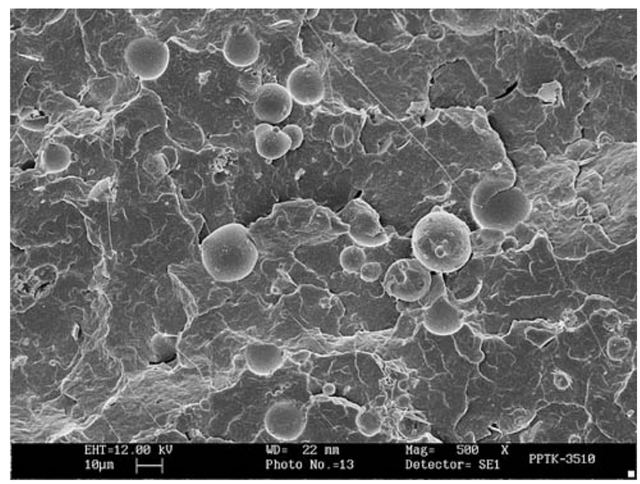

Fig. 6 Scanning electron micrograph of impact fracture surface of PP/TK35 (ϕ_f = 10%)

Figure 7 displays a scanning electron micrograph of impact fracture surface of PP/TK70 composite when ϕ_f is 10%. It can be seen that the impact fracture surface is uneven, whereas there are no any look-like ribbons on the impact fracture surface of the specimen. It means that the toughening mechanisms of this composite system are somewhat different from PP/TK35 composite system in impact fracture.

Figure 8 is a scanning electron micrograph of impact fracture surface of PP/TK10 composite when ϕ_f is 10%. It can be seen that the impact fracture surface is similar to those of PP/TK35 composite systems (see Figs. 5 and 6). Namely, there are some look-like fibrils on the

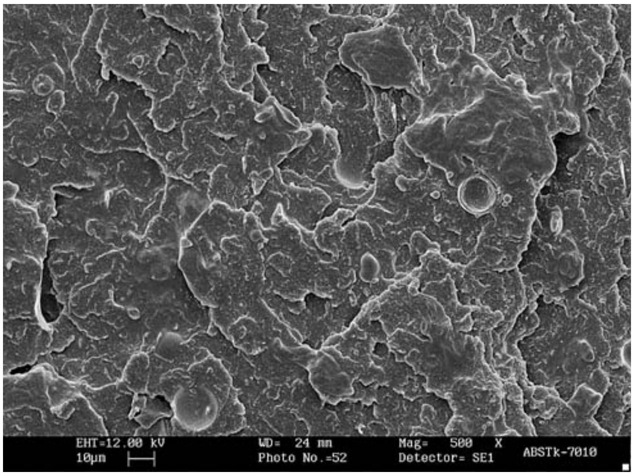

Fig. 7 Scanning electron micrograph of impact fracture surface of PP/TK70 (ϕ_f = 10%)

impact fracture surface of the specimen. In addition, the number of the HGB of PP/TK10 system in the same area limit is more than that of PP/TK35 system. In this case, the stress concentration around the hollow micro-spheres might be more than the latter, resulting in obvious toughening effect (see Fig. 3).

Discussion

Under the conditions of the same surface treatment and content of the filler particles, the effects of the particle size and its contribution on the mechanical properties of filled composites are quite important. In general, smaller fillers are beneficial to induce more crazes in the matrix around the particles due to stress concentration under action of impact load, the matrix around the particles will be yield first and more elastic deformation energy will be absorbed in impact process in addition to these crazes, leading to improve the impact fracture toughness (see Fig. 3).

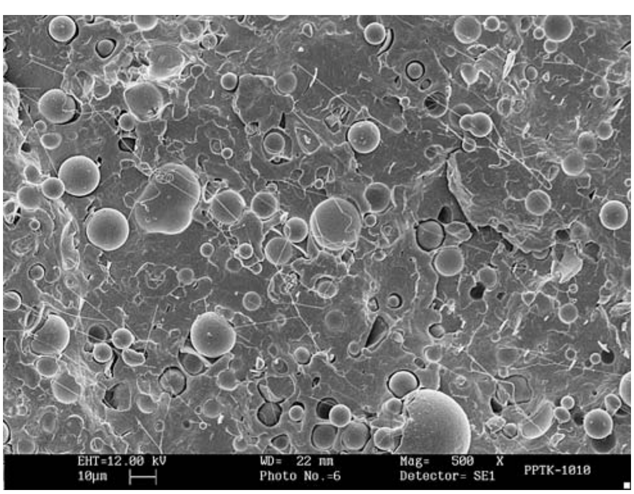

Fig. 8 Scanning electron micrograph of impact fracture surface of PP/TK10 (ϕ_f = 10%)

As shown in Fig. 1, the particle size distribution of the bigger hollow micro-spheres (e.g. HGB TK70) are wider than that of smaller filler (e.g. HGB TK35 and TK10). In general, the bigger filler particles with wider size distribution have higher pile up density. Thus, in the case of a polymer filled with this kind of particles, the agglomeration phenomenon of the particles in the matrix might occur. In other wards, smaller filler particles with narrower size distribution are relatively beneficial to improve their dispersion (or distribution) in the matrix, and are relatively beneficial to enhance the impact strength of polymer composites (see Fig. 3).

As stated above, the smaller the size of filler particles, the more their number is. The particle number is proportional to the filler volume fraction and is inversely proportional to the cubic of the particle diameter, and the relationship between them is expressed as follows:

$$N_f \propto \frac{\phi_f}{d^3} \tag{3}$$

where N_f and d are the number and diameter of filler particles, respectively.

Wu [17, 18] proposed a concept of the critical matrix ligament thickness (L_c) for BDT of materials, which was defined as the nearest distance between two neighboring particles in the matrix based on the studies of the impact strength of rubber modified Nylon-66. L_c is given by:

$$L_c = d_c\left[k\left(\frac{\pi}{6\phi_f}\right)^{\frac{1}{3}} - 1\right] \tag{4}$$

where d_c is the critical particle diameter, k is the geometric constant. For cubic lattice, k is equal to 1.

For $\phi_f = 0.1$, by substituting respectively the HGB mean size d = 10, d = 35 and d = 70 μm in Eq. 4, L_c = 7.36, L_c = 25.78 and L_c = 51.55 μm can be derived correspondingly. Therefore, the interfacial ligament between neighboring two particles decreases and tends to L_c owing to increasing quickly N_f with reduction of the particle size at the same volume fraction when the dispersion of the particles in the matrix is uniform, leading to changing relatively easily from plane strain to plane stress [19]. Based on the SEM pictures in Figs. 5 and 6 both these distance requirements are satisfied and a complex crazing-yielding mechanism might be considered. In this case, the matrix around the particle will reach shear yield first besides the crazes generated around the beads due to stress concentration, to generate some look-like fibrils and to absorb impact deformation energy, and the BDT may occur. Similar phenomenon could be observed in the experiments reported by Mouzakis et al. [16]. Consequently, the impact toughness of the composite is improved. On the other hand, the aggregation phenomenon of the fillers in the matrix might happen with increasing further the particle concentration, resulting in reduction of impact strength (see Fig. 2).

Conclusions

The impact fracture toughness of PP might be improved by filling HGBs. The results illustrated that the notched Izod impact strength (σ_I) of PP/HGB composites increased with increasing the volume fraction (ϕ_f) of the fillers when ϕ_f was less than 15%, and then it decreased. The values of σ_I for PP/TK35 system were approximately higher than those of PP/TK70 system under the same conditions. When ϕ_f was 10%, σ_I decreased roughly linearly with an increase of the mean diameter of the beads.

Furthermore, the scanning electron micrographs of the impact fracture surface of the impact specimens of the smaller bead-filled systems (PP/TK35 and PP/TK10) showed that there were some look-like fibrils on the fracture surface. These fibrils were generated duo to the crazing and the shear yielding first of the matrix around the bead when the specimen subjected to impact load. The critical matrix ligament thickness for BDT of the composites were 7.36, 25.78 and 51.55 μm respectively for TK10, TK35 and TK70 when ϕ_f = 10%. These were satisfied with DBT requirement and the impact toughening might be considered as a complex crazing-yielding mechanism.

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