Tensile Properties of Hollow Glass Bead-Filled Polypropylene Composites

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ABSTRACT: The tensile properties of polypropylene (PP) filled with hollow glass beads have been measured at room temperature to identify the effects of the particle contents, size and its distribution on them in the present article. The mean diameters of the fillers were 11, 35, and 70 μm, and they were named as TK10, TK35, and TK70 respectively. The surface of these particles was pretreated with silane coupling agent. The results showed that the yield stress (σ_y) decreased gently for PP/TK70 systems, whereas decreased relatively obviously for PP/TK35 systems with increasing the volume fraction (ϕ_f) of the fillers. When ϕ_f was less than 5%, the tensile strength at break (σ_b) of the composites increased with the increase of ϕ_f. When ϕ_f was more than 5%, σ_b was almost a constant for PP/TK70 systems, while σ_b decreased linearly for PP/TK35 systems. The tensile fracture strain (ε_b) of the composites decreased suddenly when ϕ_f was less than 5%, and then decreased slightly with increasing ϕ_f. When ϕ_f was 10%, σ_y and σ_b increased while ε_b decreased with the increase of the bead diameter. Furthermore, the σ_y was predicted by means an equation proposed in the previous work, and good interfacial adhesion was shown between the hollow glass beads and the matrix. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1697–1701, 2007

Key words: polypropylene; inorganic hollow bead; composites; tensile properties

INTRODUCTION

In general, the properties of polymeric materials depend mainly upon their inner 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 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 mechanical properties and some important behavior, such as tensile strength, stiffness, impact toughness, and brittle–ductile transition, are quite significant, in addition to the interfacial adhesion between the matrix and the filler particles.[4–7]

It is well-known that a lot of useful information about final performances, such as Young's modulus, tensile yield stress, elongation at break, and tensile fracture energy, of materials can be gained by tensile tests.[8] For rigid inorganic particulate-filled polymer composites, the interfacial adhesion between the filler particles and the matrix is also an important factor affecting tensile strength and toughness of materials.[9–14] Jancar and Kucera[10] pointed out that poor interfacial adhesion between polypropylene (PP) and calcium carbonate ($CaCO_3$) accounted for a decrease of the tensile yield stress with increasing the volume fraction of $CaCO_3$. Maiti and Mahapatro[11] found that the surface treatment of $CaCO_3$ particles with a titanate coupling agent LICA12 enhanced the interfacial adhesion between the fillers and the matrix, leading to further modifying strength properties. However, in the case of ''perfect'' interfacial adhesion of PP filled with $CaCO_3$ particles, the tensile yield strength only is enhanced slightly with the increase of the filler volume fraction.[12] It suggests that there should be a suitable interfacial adhesion between the filler and the matrix for the mechanical strength and toughness of polymer composites.

Glass bead is a kind of small solid spherical particle with smooth surface. Polymer filled with glass beads has less interface stress, good mechanical and processing properties. Recently, the authors[14] investigated the effects of the filler content and surface treatment on the tensile properties of glass-bead-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 are a new kind of fillers in rubber, plastics, and coating materials for produc-

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tion of light or thermal insulation products with smooth surface and stiffness. Compared with solid glass beads, hollow glass bead (HGB) has 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 this work, the effects of the particle size and content of the fillers on the tensile properties of hollow glass-bead-filled PP composites, such as yield strength, tensile stress at break and strain at break, are in particular investigated at room temperature.

EXPERIMENTAL

Materials

An injection grade of polypropylene (PP) with trademark of CJS-700, supplied by Guangzhou Petrochemical, was used as the matrix; 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 hollow glass beads (HGBs), HGB TK10, HGB TK35, and HGB TK70, with different size used as the fillers in this work were supplied by Eco. and Chimie (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, respectively. The surface of the particles was pretreated with 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 in Zhuhai city, China.

Sample preparation

After mixing, the PP resin and the HGBs 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 rpm, and then the extrudate was granulated to produce the composites. The volume fractions of the HGBs were 5, 10, 15, and 20%. Finally, the dumbbell sheets for tensile tests were molded by using an injection molding machine in temperature range of 160–240°C. The geometry of the tensile bars was according with ASTM D638-91 standard.

Apparatus and methodology

The instrument for tensile tests was an electronic universal materials test machine (Model CMT6104) supplied by New Sans Machinery in Shenzhen city, China. The tensile tests were carried out according with ASTM D638-91 standard, and the speed of cross-head was 50 mm/min. The tensile properties of the composites were measured at room temperature. Each group of specimens contained five pieces, and the average values of the tensile properties were determined from the measured data.

RESULTS AND DISCUSSION

Particle size distribution

It is generally believed that the effects of the filler particle size and size distribution on the mechanical properties of composites are very important, in addition to the filler surface treatment. Figure 1 shows the diameter distribution of HGB TK10, HGB TK35, and HGB TK70. It can be seen that the diameter distribution of the filler particles is exhibited roughly normal distribution, and the mean diameter for HGB TK10, HGB TK 35, and HGB TK 70 are about 11, 35, and 70 μm, respectively; where λ is the differential distribution, which is an important parameter for characterizing the size distribution of the filler particles. In the same particle diameter scope, the higher the value of λ, the narrower particle size distribution. Relatively, for the diameter distribution of HGB TK 70 is the widest, while HGB TK 10 is the narrowest. For TK10, the diameter concentrates are in a range from 7.09 to 18.09 μm, and the cumulative distribution is about 73%. For TK35, the diameter concentrates are in a range from 21.14 to 39.5 μm, and the cumulative distribution is about 62%. For TK70, the diameter concentrates are in a range from 53.9 to 100.6 μm, and the cumulative distribution is about 46%.

Stress–strain curves

Figure 2 demonstrates the tensile stress–strain curves of PP/TK35 composites. It can be seen that the PP resin exhibits significant yield and necking behavior in tensile process, while the composites do not present any yield and necking behavior in tensile pro-

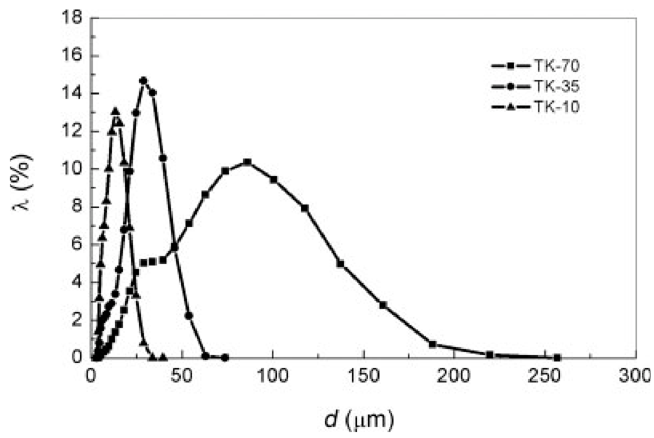

Figure 1 Particle size distribution of HGBs.

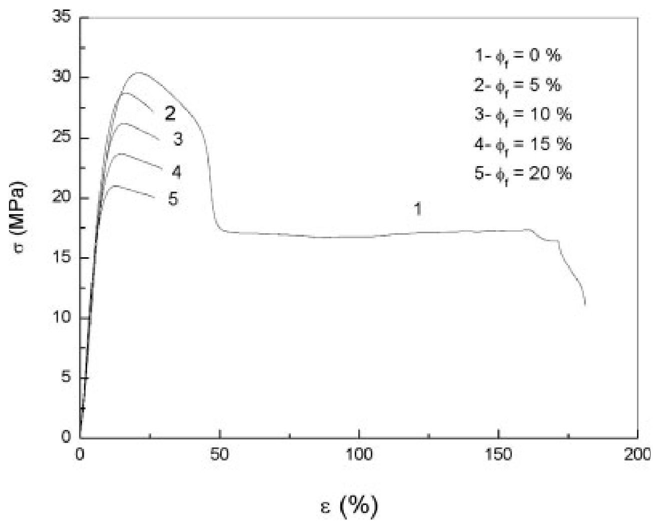

Figure 2 Tensile curves of PP/TK35 systems.

cess, and the tensile elongation at break of the unfilled PP is much longer than that of the composites. Furthermore, the tensile strength of the composites decreased with increasing the filler contents. Figure 3 shows the tensile stress–strain curves of PP/TK70 composites. Similarly, the unfilled PP exhibits obvious tensile yield and necking behavior, whereas the composites do not present any yield and necking behavior in tensile process, and the tensile strain at break of the unfilled is much greater than that of the composites. Furthermore, the tensile strength of the composites decreased with the increase of the filler contents.

Yield stress

Figure 4 displays the relationship between the tensile yield stress (σ_y) of the PP/HGB composite materials and the volume fraction (ϕ_f) of the HGB. It can be seen that the σ_y decreases slightly with increasing ϕ_f for PP/TK70 composite system, while the σ_y decreases relatively quickly with increasing ϕ_f for PP/TK35 composite system. Under the same filler content, the σ_y values for PP/TK70 composite system are greater than those for PP/TK35 composite system, and the difference in σ_y between both the two composites increases with increasing ϕ_f.

As stated earlier, the tensile strength of filled polymeric composites depends, in much extent, upon the interfacial adhesion between the filler and the matrix. For spherical particles with no adhesion to the polymer matrix, which fail by random fracture, Nicolais and Narkis[15] proposed a tensile strength equation as follows:

$$\sigma_c = \sigma_m\left(1 - 1.21\phi_f^{2/3}\right) \quad (1)$$

where σ_c and σ_m are the tensile strength of the composite and the matrix resin, respectively.

In fact, there is somewhat interfacial adhesion strength between filler particles and resin matrix. On the basis of the assumption of cubic array of spherical particles, therefore, Liang and Li[16] introduce a concept of interfacial bonding angle (θ) and derived a modified equation:

$$\sigma_c = \sigma_m\left(1 - 1.21\sin^2\theta\phi_f^{2/3}\right) \quad (2)$$

where θ is a parameter for characterization of the interfacial adhesion between the filler particle and the matrix. When $\theta = 0°$, the interfacial adhesion is good, whereas the interfacial adhesion is poor when

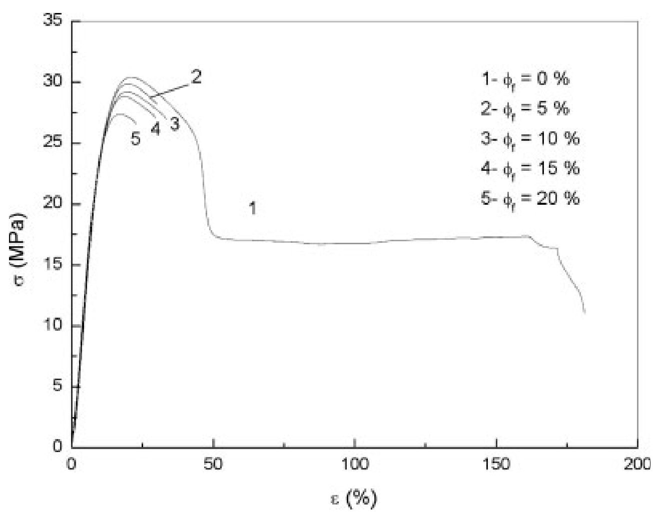

Figure 3 Tensile curves of PP/TK70 systems.

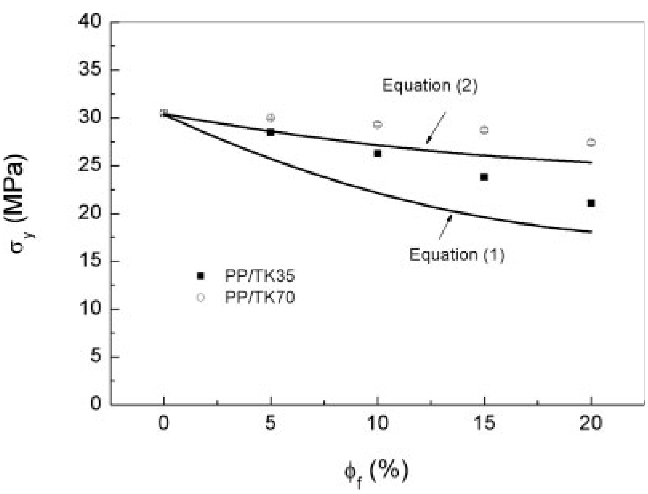

Figure 4 Relationship between tensile yield stress and hollow glass bead volume fraction.

$\theta = 90°$. For most particulate-filled polymer composites, therefore, $\theta = 0–90°$. In this study, θ is taken 40°. Substituting ϕ_f into eqs. (1) and (2), respectively, we may estimate the tensile yield stress of the composites, and the results are shown in Figure 4. It can be seen that the predictions of σ_y by using eq. (2) are relatively closer to the measured data from the experiments of PP/TK35 and PP/TK70 systems. It means that the interfacial adhesion between the HGBs and the PP matrix of the composites is good, especially for PP/TK70 system.

Tensile stress at break

Figure 5 shows the dependence of the tensile stress at break (σ_b) of the materials on the volume fraction of the HGB. It can be seen that the σ_b increases quickly with increasing ϕ_f for both the two filled systems when ϕ_f is less than 5%. When ϕ_f is more than 5%, the σ_b decreases linearly with the addition of ϕ_f for PP/TK35 composites, while the σ_b decreases very slightly with the increase of ϕ_f for PP/TK70 composites. This suggests that the tensile fracture strength of PP filled with HGB composites is enhanced, especially at lower concentration of the filler particles. Similarly, under the same filler content, the σ_b values for PP/TK70 composite system are greater than those for PP/TK35 composite system, and the difference in σ_b between both the two composites increases with increasing ϕ_f.

Figure 6 displays the effect of the filler particle size on the tensile stress of these composites when the volume fraction of the hollow glass beads is 10%. With the addition of the mean diameter of the fillers, the σ_y and σ_b increase. This illustrates that the bigger particles are beneficial to enhance the tensile strength of the composites for these hollow spheres.

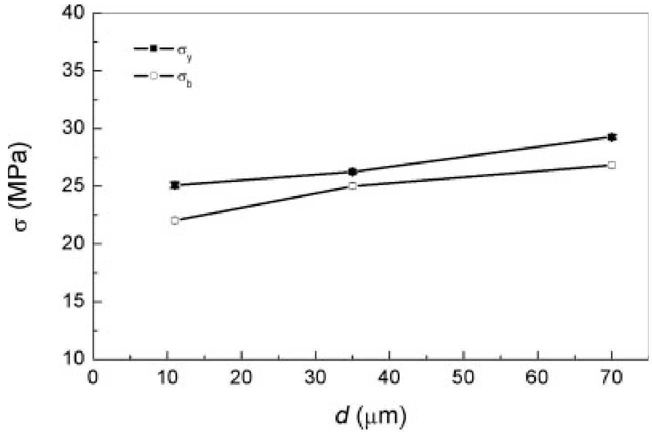

Figure 6 Influence of particle size on tensile stress.

Tensile strain at break

Tensile elongation at break (ε_b) is an important parameter for characterization of the tensile fracture toughness of materials. Figure 7 shows the dependence of ε_b of the composite materials on the volume fraction of the HGB. It can be seen that the ε_b of the composites drops down quickly with increasing ϕ_f when ϕ_f is less than 5%, then it decreases quite slowly with an addition of ϕ_f.

Figure 8 illustrates the influence of the filler particle size on the tensile fracture elongation of the composites when the volume fraction of the hollow glass beads is 10%. It can be seen that the ε_b value for PP/TK10 system is greater than that for PP/TK35 and PP/TK70 systems. However, the ε_b value for PP/

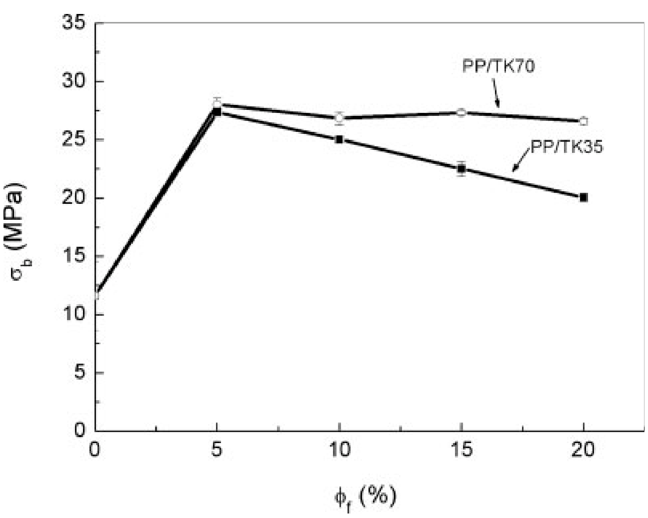

Figure 5 Dependence of tensile stress at break on hollow glass bead volume fraction.

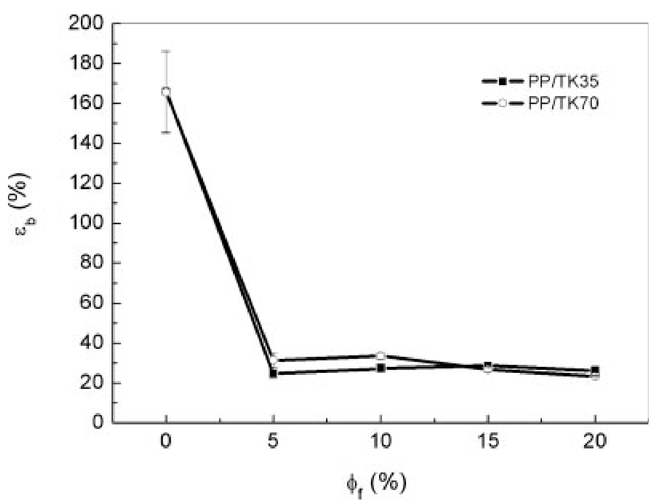

Figure 7 Tensile strain at break versus hollow glass bead volume fraction.

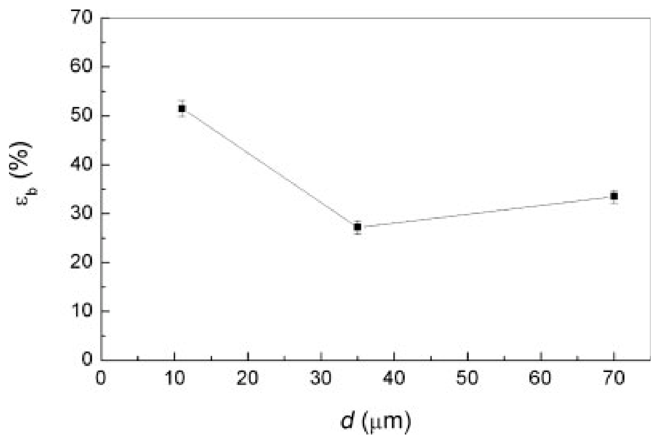

Figure 8 Influence of particle size on tensile fracture elongation ($\phi_f = 10\%$).

TK70 system is slightly greater than that for PP/TK35 system.

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, the matrix around the particles will be yield first and more elastic deformation energy will be absorbed by these crazes in tensile process, leading to improve the tensile fracture elongation (Fig. 8).

The mechanical properties, especially for tensile properties, of inorganic particulate-filled polymer composites depend, to some extent, upon the interfacial morphology, such as interfacial layer thickness, the distribution and dispersion of the fillers in the resin matrix, as well as the interfacial adhesion between the matrix and the inclusions. The experimental measurement results show that the interfacial adhesion between the PP matrix and the hollow glass beads is good, especially for PP/TK70 system.

CONCLUSIONS

There was somewhat reinforced effect for hollow glass-bead-filled polypropylene (PP) composites especially at low particle concentration. When ϕ_f was less than 5%, the tensile strength at break (σ_b) of the composites increased with the increase of ϕ_f. When ϕ_f was more than 5%, σ_b was almost a constant for PP/TK70 systems, while σ_b decreased linearly for PP/TK35 systems. The σ_b of both PP/TK35 and PP/TK70 systems was greater than that of the unfilled PP resin.

Good interfacial adhesion was shown between the HGB and the PP matrix. The yield stress (σ_y) was predicted by means an equation proposed in the previous work, and the results showed that the estimations were roughly close to the measured data of σ_y from both PP/TK35 and PP/TK70 systems when the interfacial adhesion angle was about 50°.

When the volume fraction of HGBs was 10%, both σ_y and σ_b increased with the addition of the particle diameter. Furthermore, the ε_b was the highest for PP/TK10 system in these three filled systems when ϕ_f was also 10%.

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References

1. Wu, S. Polym Eng Sci 1990, 30, 753.
2. Narkis, M.; Nicolais, L. J Appl Polym Sci 1971, 15, 469.
3. Jiang, W.; Liu, C. H.; Wang, Z. G.; An, L. J.; Liang, H. J.; Jiang, B. Z.; Wang, X. H.; Zhang, H. X. Polymer 1998, 39, 3285.
4. Ahmed, S.; Jones, F. R. Composites 1990, 21, 81.
5. Jancar, J.; Kucera, J. Polym Eng Sci 1990, 30: 714.
6. Mitsui, S.; Kihara, H.; Yoshimi, S.; Okamoto, Y. Polym Eng Sci 1996, 36, 2241.
7. Tszeng, T. C. Composites B 1998, 29, 299.
8. Liang, J. Z.; Li, R. K. Y.; Tjong, S. C. Polym Compos 1999, 20, 413.
9. Pukanszky, B. Composites 1990, 21, 255.
10. Jancar, J.; Kucera, J. Polym Eng Sci 1990, 30, 707.
11. Maiti, S. N.; Mahapatro, P. K. J Appl Polym Sci 1991, 42, 3101.
12. Jancar, J; Dibenedetto, A. T.; Dianselmo, A. Polym Eng Sci 1993, 33, 559.
13. Ou, Y. C.; Yu, Z. Z. Polym Int 1995, 37, 113.
14. Liang, J. Z.; Li, R. K. Y. Polym Int 2000, 49, 170.
15. Nicolais, L.; Narkis, M. Polym Eng Sci 1971, 11, 194.
16. Liang, J. Z.; Li, R. K. Y. Polym Compos 1998, 19, 698.