

Mechanical and Thermal Properties of High-Density Polyethylene Toughened with Glass Beads

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ABSTRACT: Glass beads were used to improve the mechanical and thermal properties of high-density polyethylene (HDPE). HDPE/glass-bead blends were prepared in a Brabender-like apparatus, and this was followed by press molding. Static tensile measurements showed that the modulus of the HDPE/glass-bead blends increased considerably with increasing glass-bead content, whereas the yield stress remained roughly unchanged at first and then decreased slowly with increasing glass-bead content. Izod impact tests at room temperature revealed that the impact strength changed very slowly with increasing glass-bead content up to a critical value; thereafter, it increased sharply with increasing glass-bead content. That is, the Izod impact strength of the blends underwent a sharp transition with

increasing glass-bead content. It was calculated that the critical interparticle distance for the HDPE/glass-bead blends at room temperature (25°C) was 2.5 μm . Scanning electron microscopy observations indicated that the high impact strength of the HDPE/glass-bead blends resulted from the deformation of the HDPE matrix. Dynamic mechanical analyses and thermogravimetric measurements implied that the heat resistance and heat stability of the blends tended to increase considerably with increasing glass-bead content. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2102–2107, 2003

Key words: polyethylene (PE); blends; mechanical properties; thermal properties

INTRODUCTION

In general, it is known that the toughness of thermoplastic can be improved markedly via blending with a rubber or elastomer.^{1–10} However, the introduction of a rubber or elastomer into a thermoplastic can lead to a considerable reduction in thermoplastic stiffness, thermal stability, and so forth, thereby limiting its further application. Therefore, in recent years, considerable research efforts have been directed toward the

toughening of thermoplastics with rigid particles.^{11–22} Thermoplastics toughened with rigid particle possess high impact strength, high stiffness, high thermostability, and low cost. In comparison with elastomer or rubber particles, rigid particles are more difficult to use to toughen thermoplastics because of their large size and extremely low voiding ability.²³ For ductile thermoplastic/rigid particle blends to be obtained, the rigid particles must be small enough, or the temperature must be high enough.

Inorganic rigid particles (CaCO_3 particles, glass beads, SiO_2 , etc.) are usually employed to toughen thermoplastics. For examples, Bartczak and coworkers^{11–14} and Fu and Wang^{15,16} used CaCO_3 particle to toughen nylon, high-density polyethylene (HDPE), and polypropylene (PP) and found that Young's modulus of both HDPE and nylon increased continuously with increasing CaCO_3 content, whereas the tensile stress decreased considerably with increasing CaCO_3 content. Their Izod impact tests showed that the HDPE/ CaCO_3 blend was tough if the interparticle distance was smaller than a critical value, that is, the critical interparticle distance (ID_c). Otherwise, the blend was brittle. Similar results for PP/glass-bead blends were obtained by Liang and Li.¹⁹ Moreover, organic polymers with high stiffness can also be selected as toughening agents for thermoplastics. More

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TABLE I
Main Properties of the Glass Beads

Mean diameter (μm)	Density (g/cm^3)	Young's modulus (10^6 psi)	Rigidity modulus (10^6 psi)	Hardness (Moh)	Softening point ($^{\circ}\text{C}$)
4.0	2.5	10.0	4.3	6.0	704

recently, a liquid-crystalline polymer was successfully used to toughen PP.²² The results showed that PP toughened with the liquid-crystalline polymer had both high toughness and high stiffness.

Furthermore, thermal stability and heat resistance are the main thermal properties that determine whether a thermoplastic can be used as an engineering material. It is generally known that the thermal properties of thermoplastics can be improved by the introduction of rigid particles. In this study, we attempted to use glass beads to toughen HDPE, and we investigated the mechanical and thermal properties of the resultant blends.

EXPERIMENTAL

Materials

HDPE type 7750 was produced by Liaoyang Petrochemical Fiber Co. (Liaoyang, China). Its density, melting temperature, and melt-flow index (5 kg) were $0.952 \text{ g}/\text{cm}^3$, 132°C , and $1.6 \text{ g}/10 \text{ min}$, respectively. The filler glass beads, treated with coupling agents, were acquired from Potters Industries (6000 CP-01, USA). Their main properties are listed in Table I.

Sample preparation

HDPE pellets and glass-bead blends with different glass-bead contents were mixed with a Brabender-like apparatus at a capacity of 55 cm^3 (XSS-300, Rheocoder, Shanghai, China) and at 195°C for 4 min. The roller speed used for blending was 40 rpm. The temperature, mixing time, and roller speed remained unchanged for all blends. For Izod impact tests, plaques with dimensions of $160 \text{ mm} \times 63 \text{ mm} \times 3.0 \text{ mm}$ were prepared by mold pressing at 180°C under a pressure of $90 \text{ kg}/\text{cm}^2$, and they then were naturally cooled up to room temperature under a certain pressure. Izod impact specimens with dimensions of $63 \text{ mm} \times 12 \text{ mm} \times 3.0 \text{ mm}$ were cut from the plaques. For tensile tests, the blends were molded directly into dogbone-shaped tensile specimens (30-mm gauge length, 15-mm width, and 1-mm thickness). Their molding pressure and temperature were the same as those mentioned previously.

Mechanical measurements

Tensile tests were carried on an Instron 1121 tester at a deformation rate of $50 \text{ mm}/\text{min}$ at room temperature.

Izod impact specimens were tested with an XJ-40A Izod impact tester (Wuzhong, China) at room temperature (25°C). These specimens were sharply notched with a 45° V-shape knife. The notch depth was 2.5 mm. The impact strength was obtained from the value of G/S , where G is the impact energy and S is the cross-section area of notched sample.

The dynamic mechanical properties of the samples were studied with a Netzsch DMA 242C (Germany). The test temperature range was 25 – 115°C at a heating rate of $5^{\circ}\text{C}/\text{min}$ and at a fixed frequency of 5 Hz. The temperature sweep was carried out in the autostrain mode.

Thermal analysis

Thermogravimetric analysis was carried out on a PerkinElmer 7 series thermal analysis system (United States). The thermogravimetric analysis scans were recorded at $10^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere from 30 to 550°C .

Differential scanning calorimetry (DSC) for samples with various glass-bead contents was studied on a PerkinElmer 7 series thermal analysis system. The samples underwent three heating–cooling–heating procedures for the elimination of the thermal history. Both heating and cooling scans were carried out at a rate of $20^{\circ}\text{C}/\text{min}$.

Morphological observations

Scanning electron microscopy (SEM; JXA-840, Japan) was used to study the morphologies of the fracture surfaces of impact test specimens. The specimens were coated with a thin layer of gold before the SEM observations.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the variation of the relative Young's modulus (E_b/E_m) with the glass-bead content for the HDPE/glass-bead blends; E_b and E_m are the test moduli for the blend and pure HDPE, respectively. It reveals that the modulus of the HDPE/glass-bead blends increases considerably with increasing glass-bead content. For the blend containing 8.7 vol % glass beads, the relative modulus is 250% higher than that of the pure polymeric matrix. The variation of the yield stress of the HDPE/glass-bead blends with the

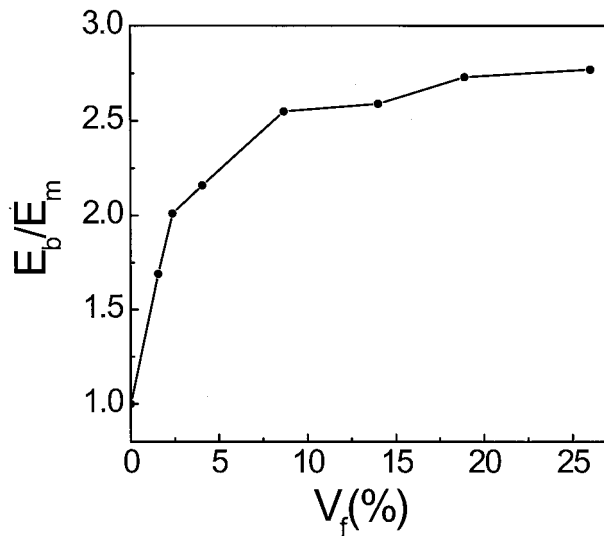


Figure 1 Variation of E_b/E_m with the glass-bead content (V_f) for the HDPE/glass-bead blends.

glass-bead content is depicted in Figure 2. The yield stress of the blends increases slightly with the glass-bead content increasing up to 1.5 vol %; thereafter, it decreases with increasing glass-bead content.

Figure 3 shows the Izod impact strength versus the glass-bead content for the HDPE/glass-bead blends. The impact strength changes very slowly with increasing glass-bead content up to a critical value; thereafter, it increases sharply with increasing glass-bead content. That is, the Izod impact strength of the blends undergoes a sharp transition with increasing glass-bead content. The critical glass-bead content (V_{fc}) is 12.5 vol %. According to the interparticle distance model proposed by Wu,¹⁰ ID_c can be calculated with the following formula:

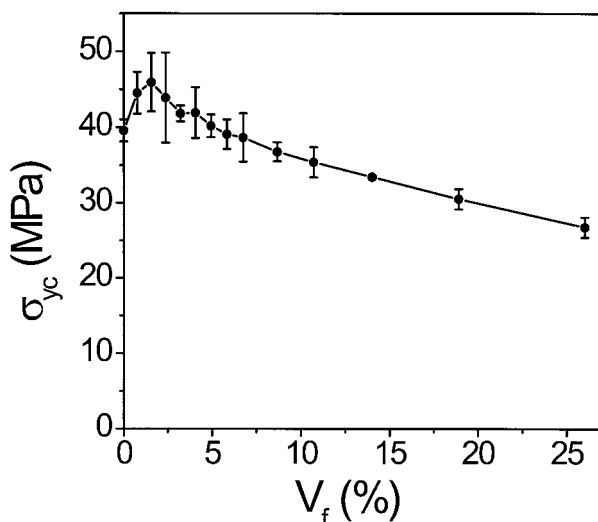


Figure 2 Variation of the yield strength (σ_{yc}) with the glass-bead content (V_f) for the HDPE/glass-bead blends.

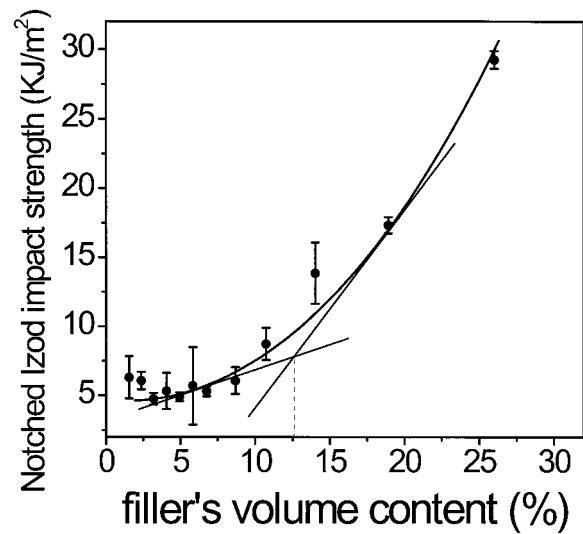


Figure 3 Variation of the notched Izod impact strength with the glass-bead content at 25°C.

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

where d is the average dispersed particle diameter, V_{fc} is the critical volume fraction of dispersed particles, and k is equal to 1 for the cubic lattice. In this study, for $d = 4.0 \mu\text{m}$, $V_{fc} = 12.5\%$, and $k = 1$, it is calculated that $ID_c = 2.5 \mu\text{m}$ for the HDPE/glass-bead blends at room temperature. This value is less than that of Fu and Wang¹⁵ (ca. $5 \mu\text{m}$) but is higher than that of Argon et al.¹¹ (ca. $0.6 \mu\text{m}$) for HDPE/ CaCO_3 blends. This result further implies that ID_c , as proposed by Wu,¹⁰ is not a constant value: it depends on the polymeric matrix material,²⁴ the dispersed-phase material,^{25,26} the temperature,^{27,28} and so forth.

Figure 4 shows SEM micrographs of Izod impact fracture surfaces of samples with various glass-bead contents at 25°C. These micrographs reveal that the fracture surfaces of Izod samples at 25°C are relatively smooth for lower glass-bead contents, whereas they are much more deformed for higher glass-bead contents. It is generally known that glass beads cannot be deformed during impact tests because of their high stiffness. In other words, no energy can be absorbed by glass beads during impact tests. Therefore, the impact energy is mainly absorbed by the deformation of the HDPE matrix for the ductile fracture.

Thermal properties

Figure 5 shows the DSC results for HDPE blends with various glass-bead contents. It is known that the melt temperature of the HDPE used in this study is 133°C. Moreover, the introduction of glass beads has less effect on this temperature.

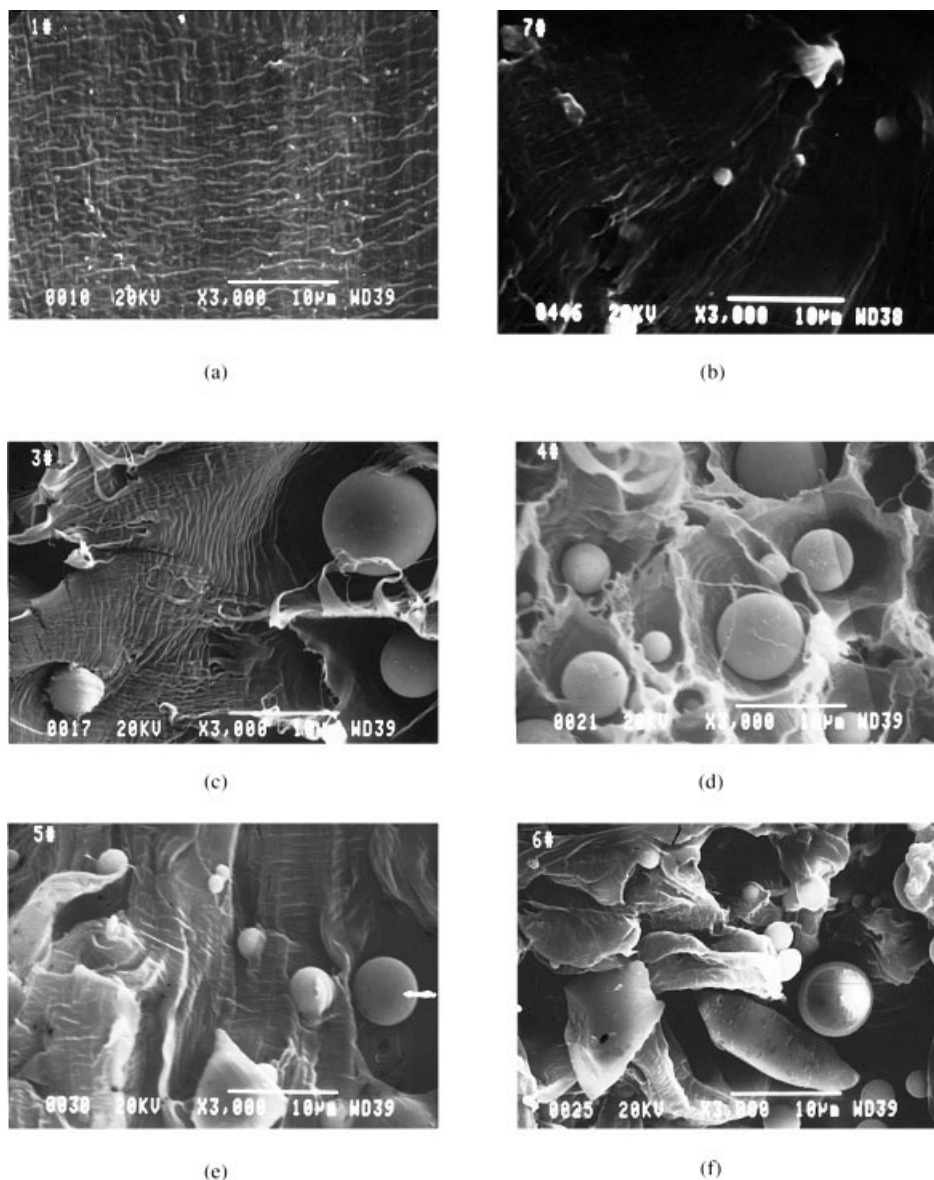


Figure 4 SEM photographs of the fractured surfaces of specimens after impact testing. HDPE was filled with (a) 0, (b) 4, (c) 14, (d) 20, (e) 30, and (f) 48 wt % glass beads.

It is generally known that the heat-deflection temperature of HDPE is very low. Figure 6 shows the variation of the storage modulus (E') with the temperature for the HDPE/glass-bead blends with various glass-bead contents. From Figure 6, it is known that the HDPE E' value at 40°C is 0.82 GPa. To evaluate the heat resistance of the blends, we define the temperature at $E' = 0.82$ GPa as $T_{E' = 0.82}$. From Figure 6, we know that $T_{E' = 0.82} = 56^\circ\text{C}$ for the blend containing 20 wt % glass beads and $T_{E' = 0.82} = 82^\circ\text{C}$ for the blend containing 48 wt % glass beads. These results reveal that the heat-deflection temperature of HDPE can be much improved by the incorporation of glass beads.

Figure 7 shows the weight loss versus the temperature for the HDPE matrix and its blends. It is clear that the weight-loss curve shifts to higher tempera-

tures with increasing glass-bead contents; this indicates that the thermal stability of the HDPE/glass-bead blends is improved considerably with increasing glass-bead contents. The variation of the 5% weight-loss temperatures ($T_{-5\%}$) with the glass-bead content is shown in Figure 8. The results demonstrate that the decomposition temperature of HDPE is increased from 319 to 382°C with the glass-bead content increasing from 0 to 48 wt %.

CONCLUSIONS

The mechanical and thermal properties of glass-bead-toughened HDPE have been studied. Static tensile measurements have shown that the modulus of HDPE/glass-bead blends increases considerably with

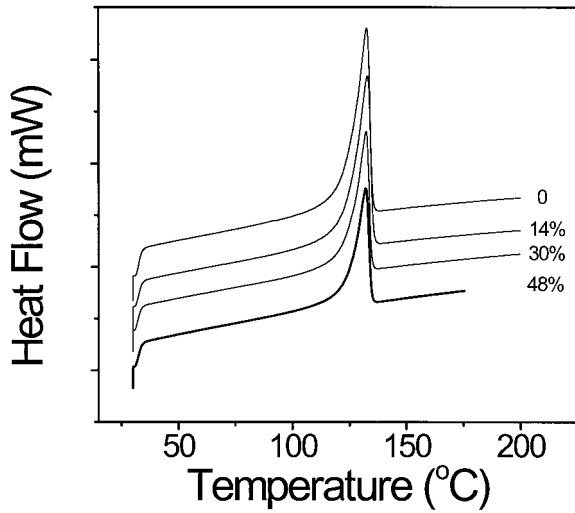


Figure 5 DSC results for HDPE blends with various glass-bead contents.

increasing glass-bead contents, whereas the yield stress remains roughly unchanged at first and then decreases slowly with increasing glass-bead contents. Izod impact tests at room temperature reveal that the Izod impact strength of the blends undergoes a sharp transition with increasing glass-bead contents. On the basis of Wu's¹⁰ interparticle distance model, it is calculated that ID_c for the HDPE/glass-bead blends at room temperature (25°C) is 2.5 μm . SEM observations indicate that the high impact strength of HDPE/glass-bead blends results from the deformation of the HDPE matrix. Dynamic mechanical analyses and thermogravimetric measurements imply that the heat-deflection temperature and decomposition temperature of HDPE can be much improved by the incorporation of glass beads.

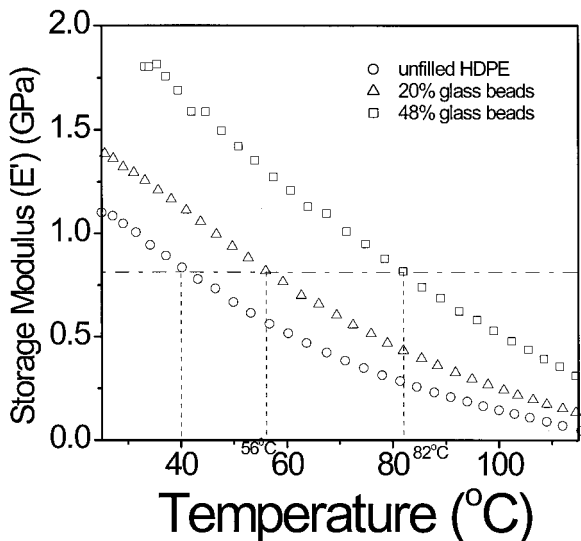


Figure 6 E' spectra for HDPE and HDPE/glass-bead blends.

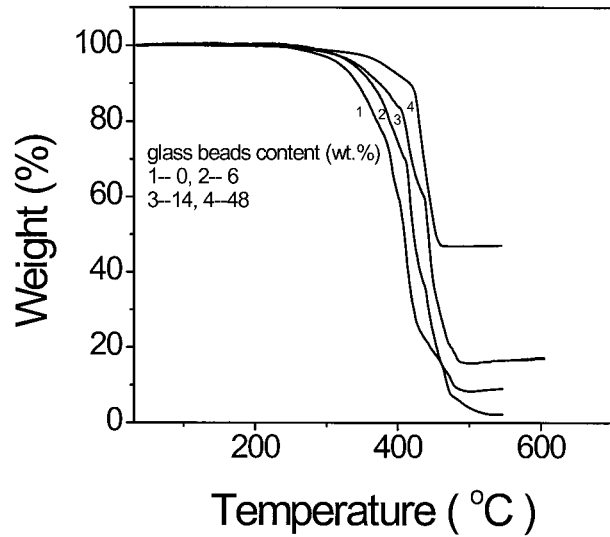


Figure 7 Weight loss versus the temperature for HDPE and HDPE/glass-bead blends.

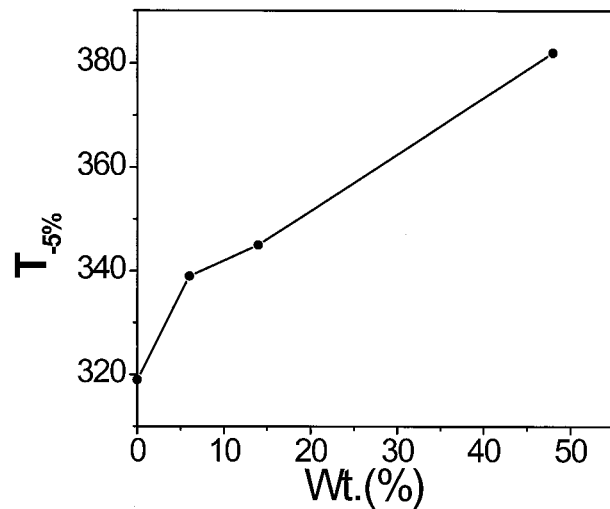


Figure 8 Variation of $T_{-5\%}$ with the glass-bead content.

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