

Competing Effect Between Filled Glass Bead and Induced β Crystal on the Tensile Properties of Polypropylene/Glass Bead Blends

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ABSTRACT: The blends of the polypropylene (PP-1) with various glass bead contents were prepared via melt blending. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) results indicated that the β crystal existed in PP-1 and increased with increasing glass bead content up to 6 wt %. It was generally known that the stiffness of a polymer increased with introducing rigid particles, and the stiffness of the β crystal was less than that of the α crystal. This competing effect thus leads to the tensile modulus of PP-1/glass bead blend decreasing with increasing glass bead content up to 6 wt %; thereafter, it increased with increasing glass bead content. For the purpose of com-

parison, the polypropylene (PP-2) without the β crystal was employed to blend with glass bead. The tensile tests showed that the modulus of the PP-2/glass bead blend increased continuously with increasing glass bead content. This result further supported that the tensile modulus behavior of PP-1/glass bead blends resulted from the competing between the filled glass bead and the induced β crystal. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1729–1733, 2005

Key words: polypropylene (PP); blends; mechanical properties

INTRODUCTION

Filled polymers with inorganic particles possess advantageous properties, such as heat distortion temperature, hardness, toughness, stiffness, and mold shrinkage. Many studies have therefore been carried out with the aim of understanding the composition, structure, and morphology-property relationship of inorganic filled thermoplastics.^{1–6} Researchers have reported that the addition of fillers provoked an increase in modulus of elasticity.^{2,6}

It is well known that polypropylene is capable of crystallizing in three polymorphic forms.⁷ In melt-crystallized material, the predominant polymorph is the α or monoclinic form. However, unless using specific β -nucleating agents, the β or pseudohexagonal form generally occurs at levels of only a few percent, or the crystallization has occurred in a temperature gradient^{5,8} or in the presence of shearing force.^{9,10} In these latter cases, much higher levels of the β -phase material can be obtained and is always accompanied with α crystals. The third crystalline modification is

the γ or triclinic form, which is only observed in low-molecular-weight or stereoblock fractions that have been crystallized at elevated pressure.^{6,11} Recently, the mechanical properties, such as impact properties and fracture characteristics, of polypropylene including α and β -forms have been obtained. Shi and coworkers^{12–14} reported that the high-purity β -form sample had lower yield strength but higher impact strength than those of the α -form sample. Jacoby et al.¹⁵ reported that increasing the β -form content of melt-crystallized polypropylene also had a marked effect on certain physical properties, namely, high levels of the β -form led to lower values of the modulus and yield stress, but higher values of elongation at break. More recently, Karger-Kocsis and Varga¹⁶ obtained purely α -iPP and β -iPP specimens, and tested their tensile properties; the results indicated that no matter under static tensile tests or under dynamic tests, the elastic modulus (E') of β -iPP was lower than that of α -iPP. In addition to organic nucleating agents, mineral fillers, such as wollastonite, carbonate, talc, etc., can also be used to produce various levels of β -form crystallinity.^{3,17–19}

However, to the best of our knowledge, the competing effects between the matrix morphology structure and inorganic particles filling in the tensile properties of polypropylene remain unclear up to now. In this

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TABLE I
Main Properties of the Glass Bead

Mean diameter (μm)	Density ($\text{g} \cdot \text{cm}^{-3}$)	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

study, the crystal structure and composition-property relationship of PP/glass bead blends is investigated. The purpose is to correlate the polymorphic polymer and the strengthening of inorganic particles to their mechanical properties.

EXPERIMENTAL

Materials

There were two commercial grade polypropylenes used in this work; one was named PP-1 [type 5004, $M_w = 3.72 \times 10^5$, $M_w/M_n = 5.4$, density $\rho = 0.9 \text{ g cm}^{-3}$, and melt flow index = $3.3 \text{ g } 10\text{min}^{-1}$ with a load 5kg (ASTM D1238)], which was obtained from Liaoyang Petrochemical Fiber Co. (P. R. China); the other was named PP-2 [type Moplen EP 501L, $M_w = 3.01 \times 10^5$, $M_w/M_n = 5.2$, density $\rho = 0.9 \text{ g cm}^{-3}$, and melt flow index = $6 \text{ g } 10\text{min}^{-1}$ with a load 5kg (ASTM D1238)], which was supplied by Targor (BASF). The filler glass beads were produced by Potters Industries (USA). Their main properties are listed in Table I.

Sample preparation

The PP pellets and glass bead blends with different glass bead contents were mixed with a Brabender-like apparatus at a capacity of 55 cm^3 (Rheocoder XSS-300, made in 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 the tensile test, the blends were molded directly into dumbbell-shaped tensile specimens, 20 mm gauge length, 15 mm width, and 1 mm thickness at 180°C under the pressure of 90 kg/cm^2 , then were naturally cooled up to room temperature under a certain pressure.

Tensile tests

Tensile tests were carried out on a Shimadzu AG-I 20KN tensile machine at 1 mm/min crosshead speed at room temperature. At least five specimens of each composition were tested and the average values reported.

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction was performed on a Rigaku D/MAX 2500V PC X-ray diffractometer (Ja-

pan) in reflection mode using the monochromated $\text{CuK}\alpha$ radiation from a Rigaku generator operated at 40 KV and 200 mA. An angle range of $5\text{--}40^{\circ}$ was scanned at $4^{\circ}/\text{min}$ for every sample.

Differential scanning calorimetry (DSC)

A differential scanning calorimeter, Perkin-Elmer Diamond DSC, was used for thermal analysis. The Perkin-Elmer Diamond DSC instrument was equipped with intracooler 2P. The samples underwent heating-cooling-heating three procedures to eliminate the thermal history. Both heating and cooling scans were carried out in a nitrogen environment with a rate of $20^{\circ}\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Figure 1a shows the variations of yield stress and Young's modulus with glass bead content of PP-1/glass bead blends. The yield stress of the blends appears to decrease with increasing glass bead content as expected; whereas the Young's modulus of the blends first decreases with increasing glass bead content up to 6 wt %, and, thereafter, it increases linearly with increasing glass bead content. The tensile properties versus glass bead content for PP-2/glass bead blends are shown in Figure 1b. It is apparent that the yield stress of the blends decreases markedly with increasing glass bead content. However, different from PP-1/glass bead blends, the Young's modulus of PP-2/glass bead blend increases continuously with increasing glass bead content.

As observed in previous studies, inorganic particles would increase the stiffness of the blends¹⁻⁵ with increasing content of the rigid particle. On the other hand, it is generally known that polypropylene has two crystalline forms (α and β), each of which has different mechanical properties. The Young's modulus of the β -form is obviously lower than that of the α -form.¹²⁻¹⁶ The WAXD patterns of various glass bead contents are depicted in Figures 2a and b for PP-1/glass bead and PP-2/glass bead blends, respectively. The basic difference in these two figures is that the PP-2/glass bead system lacks the peak at about 16° , which belongs to β (300). This implies that two crystalline forms, α and β , exist simultaneously in the PP-1/glass bead blends at room temperature; but for PP-2/glass beads, only one crystalline form (α) exists.

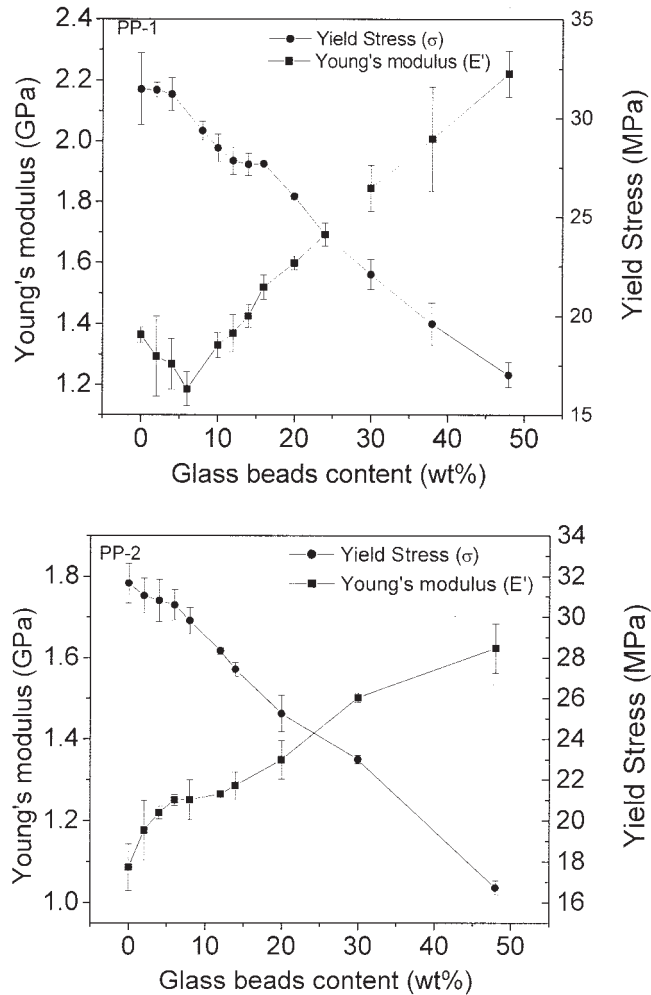


Figure 1 Variations of yield stress and Young's modulus with glass bead content for (a) PP-1/glass bead blends; (b) PP-2/glass bead blends.

Figures 3a and b show the DSC curves of the second heating procedure for PP-1/glass bead and PP-2/glass bead blends, respectively. Two peaks are observed in each sample of PP-1/glass bead blends. The temperature for the first peak is about 148°C, corresponding to the melting temperature of the β crystalline phase, while the temperature for the second peak is about 163°C, which belongs to the melting temperature of the α crystalline phase. For PP-2/glass bead blends, all the traces of DSC show only one peak, whose temperatures are about 164°C. DSC results indicate that the crystalline phases of the two systems are different, namely PP-1/glass bead blends have two crystalline phases (α and β), while PP-2/glass bead blends only have the α crystalline phase. The relative amount of the β and α forms present in PP could be measured according to an empirical parameter K as

$$K_{\beta} = \frac{H_{\beta}}{H_{\beta} + (H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3})} \quad (1)$$

where $H_{\alpha 1}$, $H_{\alpha 2}$, and $H_{\alpha 3}$ are the heights of the three strong equatorial α -form peaks, (110), (040), and (130), respectively, and H_{β} is the height of the strong single β -peak (300). From eq. (1) and Figure 2a, the K_{β} is obtained for PP-1/glass bead blends and listed in Table II. Moreover, the overall crystallinity of PP and PP/glass bead blends are obtained from DSC and listed in Table III; here the enthalpy of fusion for a fully crystalline PP is assumed to be 209 J/g. From Table III, it can be seen that the overall crystallinity of PP and PP/glass bead blends remains constant.

Thus, it can be ascertained that it's the competing effects between the β -form and the strengthening of inorganic particles that lead to the difference in Young's modulus for PP-1/glass bead and PP-2/glass bead blends. At low glass bead content for PP-1/glass bead blends (≤ 6 wt %), the effect of the β -form is stronger than that of the strengthening of the glass

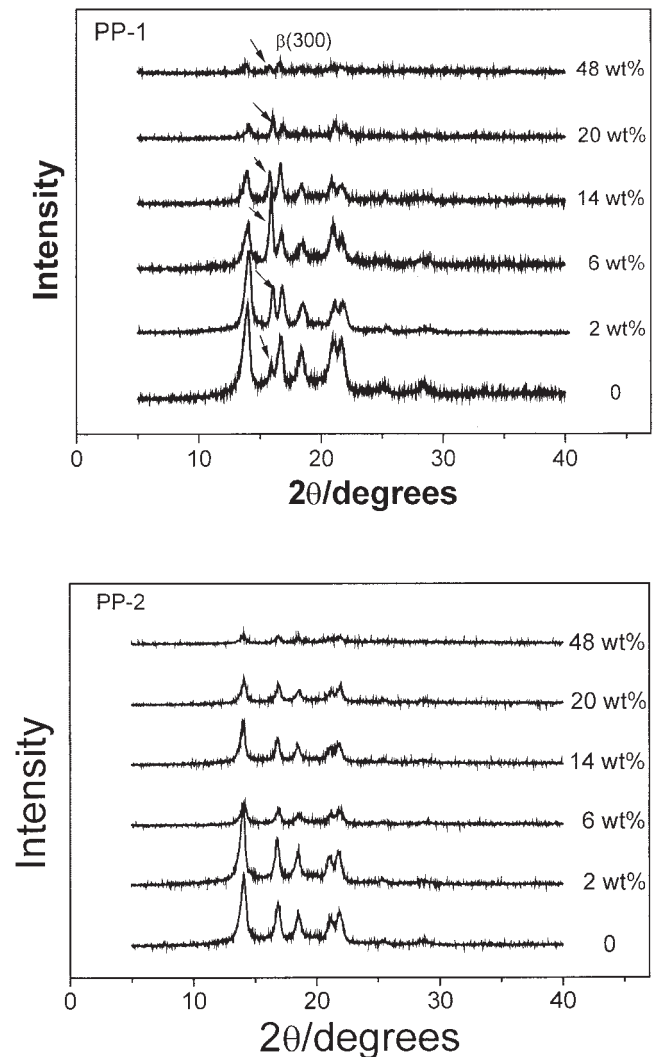


Figure 2 WAXD patterns for (a) PP-1/glass bead blends for various glass bead contents; (b) PP-2/glass bead blends for various glass bead contents.

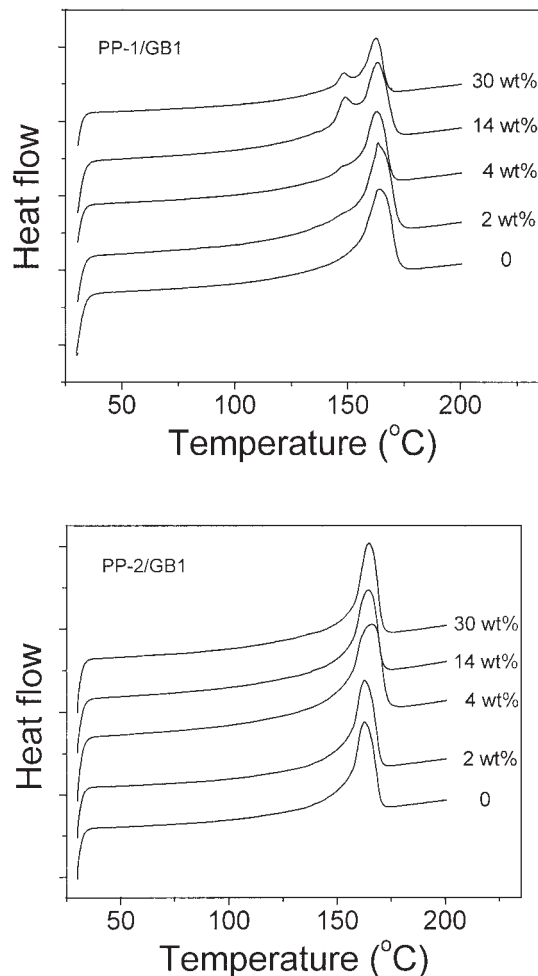


Figure 3 DSC thermograms (second heating run) of the (a) PP-1/glass bead blends for various glass bead contents; (b) PP-2/glass bead blends for various glass bead contents.

beads. The increasing content of β -form in the blends gives rise to the decrease of Young's modulus. When $\phi_f = 6$ wt %, $K\beta = 45.4\%$, the Young's modulus of the blends is the lowest (about 87% of the modulus of pure polypropylene). However, with increasing glass bead content (≥ 6 wt %), the strengthening of inorganic particles becomes the leading effect. The Young's modulus of the blends increases with increasing glass bead content. However, for PP-2/glass bead blends, there is only one crystalline form (the α -form), and the strengthening of the glass bead effect is decisive on the tensile properties of the blends. The Young's modulus of the PP-2/glass bead blends thus

TABLE II
The Relative Content of β -Form in PP-1/Glass Bead Blends

Glass bead content (wt %)	0	2	6	14	20	48
K_β (%)	16	22.5	45.4	24.8	45.6	23.6

TABLE III
The Overall Crystallinity of PP-1/Glass Bead Blends and PP-2/Glass Bead Blends

Glass bead content (wt %)	0	2	4	14	30
X_c (%) (PP-1 system)	42.9	43.3	42.8	43.7	43.3
X_c (%) (PP-2 system)	43.7	43.1	42.6	43.1	43.3

increases with increasing glass bead content continuously.

CONCLUSIONS

We have compared the tensile properties of PP-1 and PP-2 filled glass bead blends. The results indicate that the influence of the β crystalline phase on the mechanical properties of inorganic particles filled polypropylene is obvious. For PP-1/glass bead blends, the Young's modulus first decreases with increasing glass bead content up to 6 wt %; thereafter, it increases with increasing the glass bead content. However, for PP-2/glass bead blends, the Young's modulus increases with increasing the filler content continuously. It can be concluded that the tensile behavior of PP-1/glass bead blends results from the competing effects between the β -phase and the strengthening of the glass beads. The Young's modulus of the β -crystalline phase is lower than that of the α -crystalline phase. For lower filler content (≤ 6 wt %), the effect of the forming of β crystals is higher than that of the strengthening of the glass beads. With the filler content increasing (≥ 6 wt %), the filling of the glass beads becomes the leading effect and dominates the Young's modulus of the blends.

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