

EFFECT OF INTERFACIAL ADHESION ON CRYSTALLIZATION AND MECHANICAL PROPERTIES OF POLY (ETHYLENE TEREPHTHALATE)/GLASS BEAD COMPOSITES

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ABSTRACT

The interfacial adhesion between poly (ethylene terephthalate) (PET) and glass bead was investigated by scanning electron microscope and parallel-plate rheometer. Effect of interfacial adhesion on the crystallization and mechanical properties of PET/glass bead composites was also studied by differential scanning calorimeter and mechanical testers. The results obtained indicate that the glass bead has a heterogeneous nucleation effect on the PET crystallization. Although better interfacial adhesion is advantageous to the increase of the tensile strength of the composite, yet it is unfavorable to the crystallization of PET. It should be pointed out that the crystallization rate of filled PET is always higher than that of pure PET, regardless of the state of interfacial adhesion.

INTRODUCTION

Poly (ethylene terephthalate) (PET) is especially useful for manufacturing fibre and film due to its excellent wear-, heat- and chemical-resistance properties, and has been widely used in various production areas^[1,2]. But its low crystallization rate and impact strength restrict its application as engineering plastics to some extent, and therefore, many researches are directed towards how to increase its crystallization rate and impact strength^[3-5]. Reinforcement of PET with glass fibre undoubtedly becomes one of the research topics of PET modification. In order to improve the mechanical properties of the composite, it is necessary to surface-treat the glass fibre so as to improve the interfacial adhesion between glass fibre and PET matrix. But, on the other hand, it is still not quite certain whether the improvement of interfacial

adhesion has any effect on the crystallization behavior of PET and, if so, to what degree.

A series of PET/glass bead composites with different interfacial adhesion strengths were designed as model materials in the present paper. The effects of glass bead itself and its interfacial adhesion with PET on the crystallization behavior and mechanical properties of PET were studied by SEM, DSC and rheometer, in order to obtain a deeper understanding of the heterogeneous nucleation ability of glass bead and the effect of interfacial adhesion on this ability.

EXPERIMENTAL

1. *Materials*

PET resin, $[\eta] = 0.62$, was obtained from Yanshan Petro-Chemical Plant. It was dried at 135°C under high vacuum for 12 hrs before compounding with glass bead.

Glass bead, 250—400 mesh, was obtained from Shanghai Glass Factory.

γ -Aminopropyltriethoxysilane KH550, used as surface-treating reagent, was purchased from Liaoning Gai County Chemical Factory.

Epoxy resin with terminal double epoxy groups (BY-94), used as interfacial modifier, was prepared in our laboratory.

2. *Surface treatment*

Glass bead was surface-treated with a water solution of KH550 (the amount of KH550 was about 1 wt% of that of the filler), magnetically stirred for 30 mins, dried at 120°C and ready for use.

3 *Composite preparation*

According to the weight ratios listed in Table 1, after the PET, untreated or treated filler and interfacial modifier were dry-mixed in high-speed mixer, they were extruded and pelleted in Brabender Twin Screw Extruder at a screw speed of 50rpm. The barrel temperatures of the first to the fifth zones were 260, 275, 280, 260 and 280°C, respectively.

The pellets were injection-molded into standard tensile, flexural and impact specimens on an injection-molding machine SZ-160/80NB from Ningbo Plastics Machine Factory.

4. *Mechanical property testing*

The tensile and flexural experiments were carried out on an Instron 1122 Universal Tensile Tester according to National Standard Testing Methods GB 1040-79 and GB 1042-79 respectively. The tensile strength and elongation at break were measured at a crosshead speed of 50 mm/min. The flexural modulus was determined at a crosshead speed of 2 mm/min.

Table 1 Compositions of PET filled with untreated or treated glass beads

Exp. No.	PET	Glass bead	KH550 Glass bead ^(a)	BY-94 ^(b) (%)
1	100			
2	85	15		
3	85		15	
4	85	15		1.3
5	85		15	1.3
6	85		15	3.3

Notes: (a) KH550 glass bead=KH550 treated glass bead;

(b) Based on filler content

The impact experiment was conducted on an Impact Tester XJ-40 from Wuzhong Material Tester Factory following GB 1843-80.

5. SEM observation

The impact-fractured surface of the specimen was gold-plated and then examined under a Hitachi S-450 Scanning Electron Microscope.

6. Rheological property testing

The specimen was placed between two rotating parallel plates of RMS-605 Parallel-plate Rheometer. The dynamic viscosity of the composite was measured at 280°C under the protection of N₂ atmosphere. The diameter of the parallel plates was 25 mm and the distance of two plates was 1.4 mm.

7. Thermal analysis

An equal-speed nonisothermal scanning was carried out on a Perkin-Elmer DSC-7 Differential Thermal Analyzer at a heating or cooling rate of 10°C/min in the temperature range of 30–280°C. Before the thermal analysis of pure PET and its composite, they were vacuum-dried at 100°C for 6 hrs. The whole thermal analysis was conducted under the protection of N₂ atmosphere.

RESULTS AND DISCUSSION

1. The state of interfacial adhesion

Figs. 1 (a) and (b) show the impact fractographs of PET composites filled with untreated glass bead. It can be seen that the surfaces of glass bead and PET matrix are smooth, the interface is clear, and the interfacial destroying mode appears to be brittle. After surface-treating with γ -aminopropyltriethoxysilane (KH550), the interfacial adhesion between glass bead and matrix is scarcely improved, as shown in Figs. 1 (c) and (d). This indicates that the reactivity of terminal amino group with KH550 and PET is low and therefore, the filler/matrix interfacial adhesion cannot be

improved. If an 1.3 wt% interfacial modifier (BY-94) is first coated on the surface of KH550 treated glass bead prior to the compounding with PET, the surface of glass bead becomes rough, the interface is obscure, indicating that the interfacial adhesion has been improved, as shown in Figs. 2 (e) and (f). This may be attributed to the fact that during the melt processing one of the terminal epoxy group of BY-94 reacts with the amino group of KH550, while another terminal epoxy group reacts with the hydroxy or carboxy group of the PET molecular chain. Therefore, the interfacial adhesion is improved, especially, when the amount of BY-94 attached to the surface of KH550 treated glass bead is increased to 3.3%, more BY-94 will couple with the filler/matrix interface and, further enhances the interfacial adhesion effect (as shown in Figs. 2 (g) and (h)).



Fig. 1 Impact fractographs of (a) and (b), PET/untreated glass bead (85/15); (c) and (d), PET/KH550 treated glass bead (85/15)

From Figs. (2) (e) and (g), it can also be seen that the fractured surface of the system with BY-94 is very rough. This is due to the following facts: during the melt extrusion, BY-94, which is pre-adsorbed onto the surface of KH550 treated glass bead during dry-mixing process, undergoes interfacial coupling reaction with glass bead and PET matrix, and part of it diffuses into PET matrix and acts as chain extender. This conjecture is further supported by Figs. (2) (i) and (j), which are

the impact fractographs of KH550 untreated glass bead filled PET, with the glass bead physically coated with 1.3% BY-94. It can be seen that the surface of glass bead is smooth. This suggests that BY-94 does not couple the PET molecular chain onto filler surface. BY-94 can only diffuse into the PET matrix and act as chain extender, leading to the roughness of PET matrix surface.

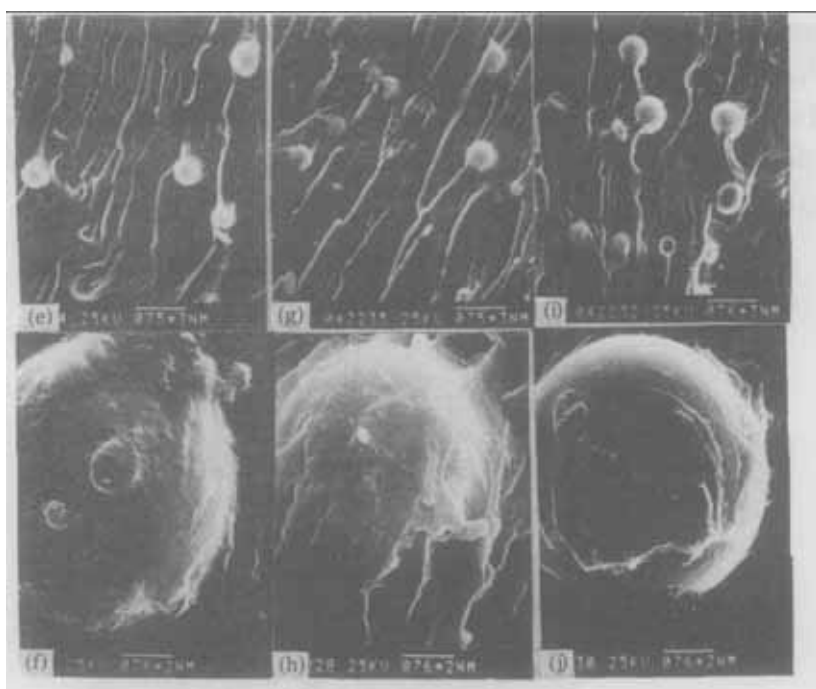


Fig. 2 Impact fractographs of (e) and (f), PET/BY-94/KH550 glass bead (85/1.3%/15); (g) and (h), PET/BY-94/KH550 glass bead (85/3.3%/15); (i) and (j), PET/BY-94/untreated glass bead (85/1.3%/15). * Based on the content of glass beads

2. Rheological behavior

The effect of KH550 and BY-94 on the state of interfacial adhesion of PET/glass bead composite is also reflected in its rheological behavior^[6]. Fig.3 is the melt viscosity curves of PET/glass bead composites with different states of interfacial adhesion (280°C). It can be seen that after surface-treating the glass bead with KH550, the viscosity of composite does not increase, but decreases slightly. This is also due to the facts that KH550 does not improve the filler/PET interfacial adhesion and that the amino group of KH550 has a certain degree of catalytic degradation effect on PET. After coating the glass bead, which is not treated with KH550, with 1.3% BY-94, the melt viscosity of filled PET increases significantly. Combined

with the results of SEM observation it can be concluded that the increase of melt viscosity is not due to the interfacial factors but due to the chain extending effect of BY-94 on PET matrix. Only after the filler was first surface-treated with KH550 and then coated with 1.3% BY-94, a part of BY-94 undergoes coupling reaction at the interface of PET/KH550 treated glass bead, and another part of BY-94 plays the role of chain extender in the PET matrix, and thus significantly increases the viscosity of PET/BY-94/KH550 treated glass bead composite. The increase of viscosity is more pronounced when the amount of BY-94 in the composite is increased to 3.3%.

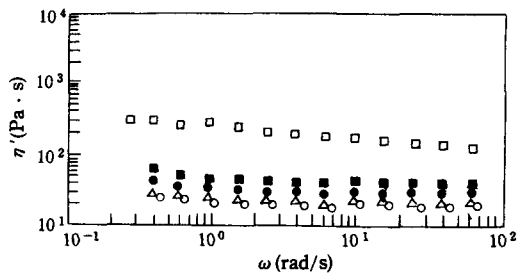


Fig. 3 Dynamic viscosity vs. frequency at 280° for glass beads filled PET composites
Δ No.2; (○) No.3; (●) No.4; (■) No.5; (□) No.6

3. *Effect of glass bead and its surface-treatment on the PET crystallization behavior*
(1) Thermal behavior of pure PET

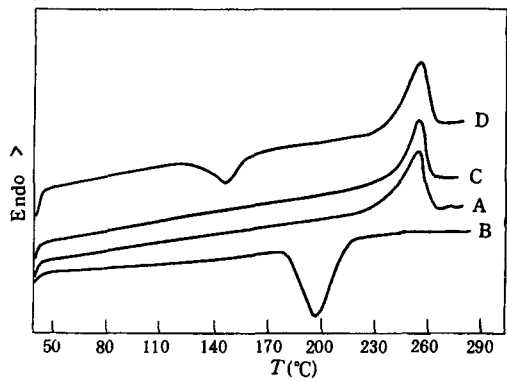


Fig. 4 DSC scans of pure PET. Curve A: heating at a rate of 10°C/min; Curve B: cooling at a rate of 10°C/min; Curve C: reheating at a rate of 10°C/min; Curve D: reheating at 10°C/min after quenching at a rate of 200°C/min

Fig. 4 shows the DSC scanning curve of pure PET. Curves A, B, C and D represent heating, cooling, reheating and reheating after quenching scanning modes respectively. Because the pure PET sample was dried at 100°C before testing, the

exothermic cold crystallization peak did not appear on the heating curve A^[7], but a melting peak appears at 254°C instead. Then, after cooling at a rate of 10°C/min (curve B), a heating scan was carried out at a heating rate of 10°C/min, but the exothermic cold crystallization peak still did not appear (see curve C). However, when a 10°C/min heating scan was carried out after a 200°C/min cooling, as can be seen from curve D, a PET exothermic cold crystallization peak appears at about 146°C. This demonstrates that a 200°C/min cooling rate can partly inhibits the PET crystallization.

(2) Promoting effect of glass bead on PET crystallization

Fig. 5 is the DSC scanning curve of 15% untreated glass bead filled PET sample. Different from pure PET, even after such a -200°C/min fast cooling treatment, the exothermic cold crystallization peak still does not appear on curve D. This suggests that the addition of glass bead affects the crystallization of PET even at such a fast cooling rate it can still cause the complete crystallization of PET^[7].

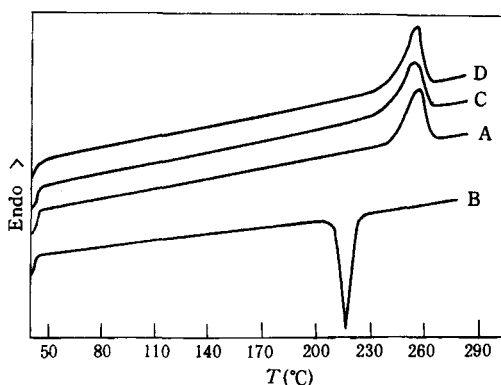


Fig. 5 DSC scans of PET/untreated glass bead (85/15). Curve A: heating at a rate of 10°C/min; Curve B: cooling at a rate of 10°C/min; Curve C: reheating at a rate of 10°C/min; Curve D: reheating at a rate of 10°C/min after quenching at a rate of 200°C/min

(3) Effect of surface treatment on the crystallization behavior of PET/glass bead composite

The DSC scanning curves of glass bead filled PET with different surface treatments at a uniformly heating and reheating rates of 10°C/min are shown in Fig. 6. The various parameters of crystallization behavior are listed in Table 2. Because the samples were all heat treated under vacuum at 100°C prior to thermal analysis, the effect of glass bead and its surface treatment on the PET melting peak can hardly be seen on the first heating scanning curves. When the second heating scan was

carried out after a rate of 10°C/min cooling, the presence of glass bead leads to the appearance of double-peak on the PET melting peak. For the three composites of PET/glass bead, PET/KH550 treated glass bead and PET/BY-94/glass bead with weak interfacial adhesion, their major peaks appear at about 250°C. On the other

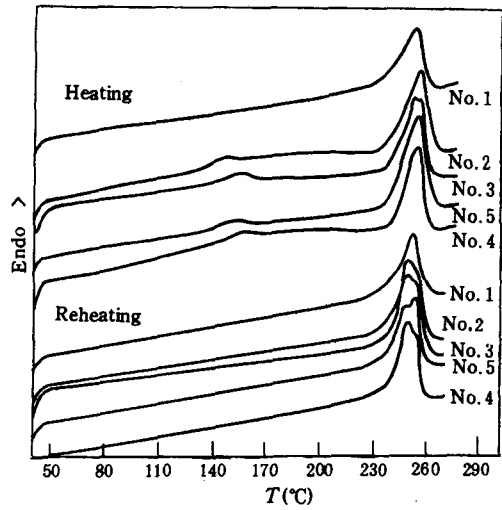


Fig. 6 DSC scans of PET filled with untreated or treated glass beads at a heating rate of 10°C/min; The upper curves represent heating of the original samples; the lower curves represent reheating of the samples after cooling at a rate of 10°C/min

hand, for the PET/BY-94/KH550 treated glass bead composite, its major peak appears at 254.6°C. From Table 2, it can also be seen that the crystallinity of filled systems is always lower than that of pure PET during the first heating scan, while the crystallinity of filled systems is higher than that of pure PET during the second heating scan. Similar phenomenon was also observed in the PET/PMMA blend system by Nadkarni et al.^[7].

Table 2 Thermal properties of PET filled with untreated or treated glass bead

Exp. No.	Heating scan			Reheating scan		
	T_{onset}	T_m	X_c^*	T_{onset}	T_m	X_c^*
	(°C)	(°C)	(%)	(°C)	(°C)	(%)
1	237.7	254.0	40.0	241.0	253.5	36.4
2	243.0	255.1	32.2	240.7	250.6	49.4
3	243.7	254.6	34.9	240.2	249.6	48.1
4	243.6	255.9	32.0	241.3	250.7	43.0
5	243.0	254.4	34.2	239.2	254.6	32.7

* Heat of fusion of pure PET crystal is 32.5 cal/g^[8]

The effect of glass bead and its interfacial adhesion with PET on the PET crystallization behavior is shown in Table 3 in which various parameters of crystallization peak of the PET/glass bead composite system with the same rate of cooling ($10^{\circ}\text{C}/\text{min}$) are listed. The crystallization peak can be analyzed from the following several aspects^[8-10]: the temperature of onset of crystallization T_{onset} ; the peak temperature of the crystallization exotherm T_p ; the half-peak width of the crystallization peak ΔW ; the initial slope of the exotherm S_i and the crystallization enthalpy ΔH_c . T_p , T_{onset} and S_i can well illustrate the nonisothermal dynamical process of the system. T_p is a function of the cooling rate and is a measure of the supercooling degree of the system. In general, for the crystallizing polymer system with the presence of heterogeneous nucleating agent, T_p shifts towards the higher temperature, which indicates that the system's supercooling degree of nonisothermal crystallization decreases; S_i is indicative of the nucleation rate of the polymer crystallization; ΔW may reflect the distribution of crystallite size; ΔH_c is directly related with the crystallinity and is a measure of the system's crystallinity.

Table 3 Values of various crystallization parameters of PET components in PET/glass bead composites from cooling scans ($10^{\circ}\text{C}/\text{min}$)

Exp. No.	T_c ($^{\circ}\text{C}$)	T_{onset} ($^{\circ}\text{C}$)	S_i	ΔW arbitrary units	ΔH_c (kJ/kg)	ΔT^* ($^{\circ}\text{C}$)
1	197.2	212.8	3.3	1	45.6	56.3
2	216.9	221.4	19.7	0.7	50.1	33.7
3	216.9	221.4	22.9	0.7	50.5	32.7
4	215.4	219.8	16.3	0.7	48.1	35.3
5	211.8	217.5	14.3	0.9	48.7	42.8

$$* \Delta T = T_m - T_c$$

Moreover, according to the principle of polymer crystallization, the difference of melting endothermic peak temperature T_m in the heating scan and crystallization exothermic peak temperature T_c in the cooling scan, ΔT , can be used to evaluate the crystallization rate of the polymer during the nonisothermal process. The smaller the ΔT , the easier the nucleus of crystal can be formed in the melt during the cooling procedure, that is, the easier the melt can crystallize^[11]. The ΔT value of glass bead filled PET is also listed in Table 3. It can be seen that incorporation of the glass bead significantly decreases the supercooling degree of the equal-speed cooling crystallization of PET and renders T_p of the PET crystallization peak shift towards the higher temperature. This indicates that the glass bead has a heteroge-

neous nucleation effect during the PET crystallization. The decrease of S_i value also indicates that the presence of glass bead indeed increases the nucleation efficiency of PET. As a result, the crystallization speed and crystallinity of PET is significantly increased and the distribution of crystallite size becomes more even, which is reflected in the decrease of $(T_m - T_c)$, ΔH_c and the decrease of ΔW . Surface modification of glass bead with KH550 has only slight effect on the PET crystallization behavior. But when the glass bead surface is coated with BY-94, a great change is observed in the PET crystallization behavior, as reflected in the increase of system's supercooling degree and the decrease of nucleation efficiency, crystallization rate and crystallinity. This is partly attributed to the decrease of nucleation rate of filled PET system containing BY-94 (evidenced by the decrease of S_i). But the more important reason is that BY-94 plays the role of chain extender in the PET matrix, weakens the relative mobility of PET molecular chain segment and leads to the decrease of crystal growth rate. Particularly when BY-94 is used in the PET/KH550 treated glass bead system, BY-94 affects the PET crystallization rate not only by chain-extending PET but also by undergoing interfacial coupling reaction with the PET and KH550 treated glass bead, leading to the further increase of supercooling degree of PET and further decrease of the crystallization rate. And the distribution of crystallite size broadens accordingly. From this, it can be concluded that an improvement in interfacial adhesion is unfavorable to the PET crystallization. It should be pointed out that the crystallization rate of filled PET is invariably higher than that of the pure PET, no matter whether the glass bead surface is treated or not and whether the interfacial adhesion is strong or weak.

4. *Effect of interfacial adhesion on the mechanical properties of PET/glass bead composite*

Table 4 lists the results of mechanical properties of the glass bead filled PET composites. It can be seen that when the glass bead is treated with KH550, σ_b and ε_b of the filled PET all decrease. When the glass bead is coated with BY-94, σ_b , S_I and ε_b of the filled PET changes only slightly, because at this time almost all of the BY-94 diffuses into the PET matrix and reacts with PET molecules, therefore the PET crystallinity is decreased and E_f is decreased accordingly. When KH550 treated glass bead is coated with 1.3% BY-94, due to the improvement of interfacial adhesion, σ_b is increased appreciably, but its effect on S_I , E_f and ε_b is insignificant. Especially, when BY-94 is increased to 3.3%, more BY-94 is used in improving the matrix/filler interfacial adhesion and extending the molecular chain of PET matrix. Therefore, E_f and ε_b of the filled PET is significantly increased and

its overall properties are all distinctly better than those of other filled systems.

Table 4 Mechanical properties of glass bead
filled PET composites

Exp. No.	σ_b (MPa)	S_I (J/m)	E_f (GPa)	ε_b (%)
2	63.7	10.1	2.5	20
3	58.5	12.7	2.5	14
4	64.5	9.1	2.2	17
5	75.1	10.0	2.2	17
6	75.8	12.5	2.4	31

Notes: σ_b : Tensile strength; S_I : Izod impact strength;
 E_f : Flexural modulus; ε_b : Elongation at break

Keywords:

Poly(ethylene terephthalate); Glass bead; Interface; Crystallization; Mechanical properties

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