Influence of High Density Polyethylene-*g*-Maleic Anhydride on Compatibility and Properties of Poly(butylene terephthalate)/High Density Polyethylene Blends

Rongrong Qi,[1] Jinghui Nie,[1] Chixing Zhou,[1] Dalian Mao,[2] Bian Zhang[2]

[1]*School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*
[2]*Nantong Xingchen Synthetic Material Corporation Limited, Nantong 226006, China*

ABSTRACT: Poly(butylene terephthalate)/high density polyethylene (PBT/HDPE) blends and PBT/HDPE-grafted maleic anhydride (PBT/HDPE-*g*-MAH) blends were prepared by the reactive extrusion approach, and the effect of blend compositions on the morphologies and properties of PBT/HDPE blends and PBT/HDPE-*g*-MAH blends was studied in detail. The results showed that flexural strength, tensile strength, and notched impact strength of PBT/HDPE blends decreased with the addition of HDPE, and flexural strength and tensile strength of PBT/HDPE-*g*-MAH blends decreased, while the notched impact strength of PBT/HDPE-*g*-MAH increased with the addition of HDPE-*g*-MAH. Compared with PBT/HDPE blends, the dimension of the dispersed phase particles in PBT/HDPE-*g*-MAH blends was decreased and the interfacial adhesion was increased. On the other hand, the effects of HDPE and HDPE-*g*-MAH contents on the crystalline and the rheological properties of the blends were also investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 6081–6087, 2006

Key words: PBT; HDPE; HDPE-*g*-MAH; blend

INTRODUCTION

Poly(butylene terephthalate) (PBT) is a conventional engineering plastic with high degree of crystallinity and high crystallization rate, good processability, good solvent resistance property, and good thermal stability. Blends of PBT with polyethylene (PE) are of significant practical interest largely due to the good toughness at low temperatures, the low absorption of humidity, and the low cost of PE.[1–10] However, because of the poor compatibility between both polymers,[1,2] simple melt blending results in morphologically unstable and brittle products. One efficient method of improving compatibility is to add an appropriate compatibilizer. Block or graft copolymers are well-known compatibilizers that locate themselves preferentially at the interface of the blending components. Kang et al.,[3] Pesneau et al.,[4] Kim et al.,[5] Favis et al.,[6] Yang et al.,[7,8] and Anttila et al.[9] suggested that the addition of ethylene-*co*-vinyl acetate (EVA), ethylene-*co*-vinyl acetate grafted with maleic anhydride (EVA-*g*-MAH), linear low-density polyethylene-grafted acrylic acid (LLDPE-*g*-AA), and oxazoline as a compatibilizer to PBT/ LLDPE or PBT/HDPE blending systems considerably improved the impact strength without significantly sacrificing the tensile and flexural strength and decreased the size of dispersion phase.

In this work, the blends of PBT with HDPE were prepared. For improving compatibility, HDPE functionalized with maleic anhydride by a novel method was adopted in place of plain HDPE. The effects of the compatibilization on the mechanical properties, morphology, rheological properties, and crystal behavior of the PBT/HDPE and PBT/HDPE-*g*-MAH blends were investigated systematically.

EXPERIMENTAL

Materials

The materials investigated in this study are blends of a PBT, chosen as the main component, with HDPE or HDPE-*g*-MAH. The PBT, obtained from Nantong Xingchen Synthetic Material (097), is a semicrystalline polymer. The HDPE is a product of Yanbet in Saudi Arabia with a melt index of 8 g/10 min (HDPE 80064). Finally, the HDPE-*g*-MAH (made by School of Chemistry and Chemical Engineering in Shanghai Jiao Tong University) contains 1.2% MAH by weight and has a melt index of 2.5 g/10 min (ASTM D1238). Grafting reaction was carried out in the molten state with a TSE-35 corotating twin-screw extruder (Ruiya Group,

Nanjing, China) at 180°C. HDPE (80064), MAH, initiators, solvent, and comonomers were simultaneously introduced into the twin-screw extruder after dry blending, which was similar to the preparation of ABS-*g*-MAH.[11]

Blend preparation

The blends were prepared in a TSE-35 corotating twin-screw extruder (Ruiya Group, Nanjing, China). The diameter of the screws was 35 mm, and the ratio of the length to the diameter (*L/D*) was 44. The extrusion temperature was set at 210–250°C from the feeder to the die, and the die temperature was set at 235°C. The screw speed was 150 rpm. The PBT/HDPE or PBT/HDPE-*g*-MAH mixtures were added through a feeder. Extrudates were cooled with water and pelletized. Prior to blending, the PBT pellets were dried at 80°C for 15 h.

Preparations of the specimens for mechanical testing

Pure PBT, PBT/HDPE blends, and PBT/HDPE-*g*-MAH blends for mechanical testing were prepared with a HTB110X/1 injector by Haitian Group (Ningbo, China), at 250°C. Before being inject-molded, PBT and all blend pellets were dried at 120°C for 12 h.

Scanning electron microscopy

Morphological analyses were carried out on impact fracture surfaces. The corresponding cross sections were examined by scanning electron microscopy, using S-2150 (Hitachi, Japan). The surfaces of samples were dried under vacuum and then gold was evaporated before SEM analysis.

Mechanical testing

The tensile strength of blends was studied by an Instron machine under 50% humidity and 23°C according to the ASTM D 882 testing method (testing rate: 50 mm/min). Several specimens (an average at least five) of each sample were tested to determine the mechanical parameters.

The Izod notch impact strength was measured by Izod instrument (Ray-Ran). All materials were inject-molded in 100 mm × 40 mm × 2 mm specimen according to ASTM D 256. The notch was cut by a notch instrument (Ray-Ran).

Rheological measurements

The rheological properties of the blends were measured with a rotational rheometer (Gemini 200HR Rheometer, Bohlin Instruments, UK) fitted with a parallel

plate geometry. The plate diameter was 25 mm and the gap between two plates was set to 2.0 mm. The tests were carried out by varying the frequency from 0.01 to 100 rad/s at 240°C under a nitrogen atmosphere to prevent oxidation.

Thermal analysis

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin–Elmer PYRIS-1 differential scanning calorimeter. Transition temperatures were calibrated using indium and zinc standards. Samples were heated from the room temperature to 240°C at a rate of 10°C/min and held for 3 min to destroy any residual nuclei before cooling at 10°C/min to the room temperature, and reheated through the melting range in the same conditions. All DSC measurements were performed under a nitrogen atmosphere at a heating rate of 10°C/min, and samples of about 5 mg were cut.

X-ray diffraction measurements

XRD patterns were obtained using a Philips PW1710 X-ray diffractometer equipped with a Ni-filtered Cu Kα source. The voltage and the current of the X-ray tubes were 40 kV and 100 mA, respectively.

RESULTS AND DISCUSSION

Mechanical Properties

In general, the mechanical properties of the material could roughly be classified into two categories: strength and toughness. Tensile strength and flexural strength could be considered the material strength, while Izod impact strength was the material toughness. To inves-
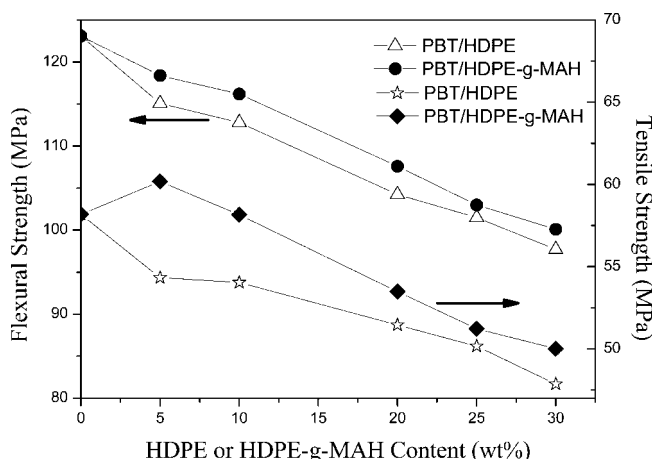

Figure 1 Flexural strength and tensile strength of PBT/HDPE and PBT/HDPE-*g*-MAH blends with various contents of HDPE and HDPE-*g*-MAH.
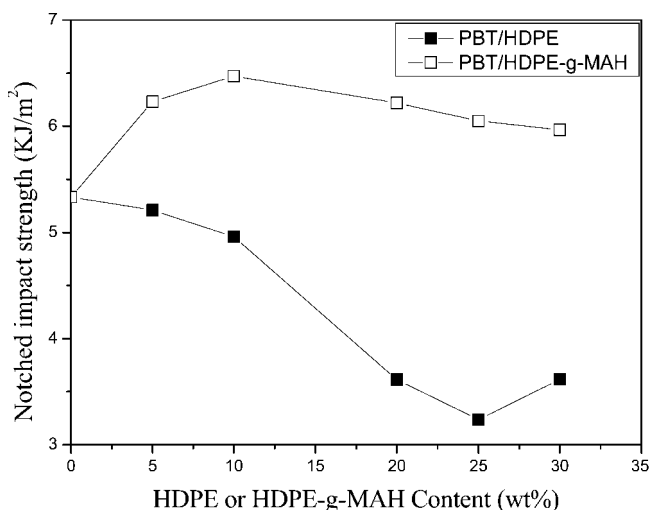
Figure 2 Notched impact strength of PBT/HDPE and PBT/HDPE-*g*-MAH blends with various contents of HDPE and HDPE-*g*-MAH.

tigate of the effect of the addition of HDPE-*g*-MAH on the mechanical properties of HDPE/EVOH blends, tensile strength, flexural strength and notched Izod

impact strength were measured using universal testing machine according to the standard methods.

Figure 1 showed the tensile strength and flexural strength of the blends with HDPE or HDPE-*g*-MAH content. As shown in Figure 1, it was found that the tensile strength and flexural strength of the blends decreased with an increase in HDPE or HDPE-*g*-MAH, while the tensile strength and the flexural strength of PBT/HDPE-*g*-MAH blends were higher than those of PBT/HDPE blends at the same composition, which indicated that the binary PBT–HDPE was incompatible, while HDPE-*g*-MAH acted as an effective compatibilizer. It was likely that the addition of HDPE-*g*-MAH yields a finer dispersion of the dispersed HDPE phase and stronger adhesion between PBT and HDPE phases, contributing to the improvement of the tensile and flexural properties of the compatibilized blends.

Figure 2 showed the notched impact strength of the blends with HDPE or HDPE-*g*-MAH content. It was shown from Figure 2 that the notched impact strength of the PBT/HDPE blend decreased with increase of HDPE, and the PBT/HDPE-*g*-MAH blend increased with increase of HDPE-*g*-MAH up to 10 wt %, while
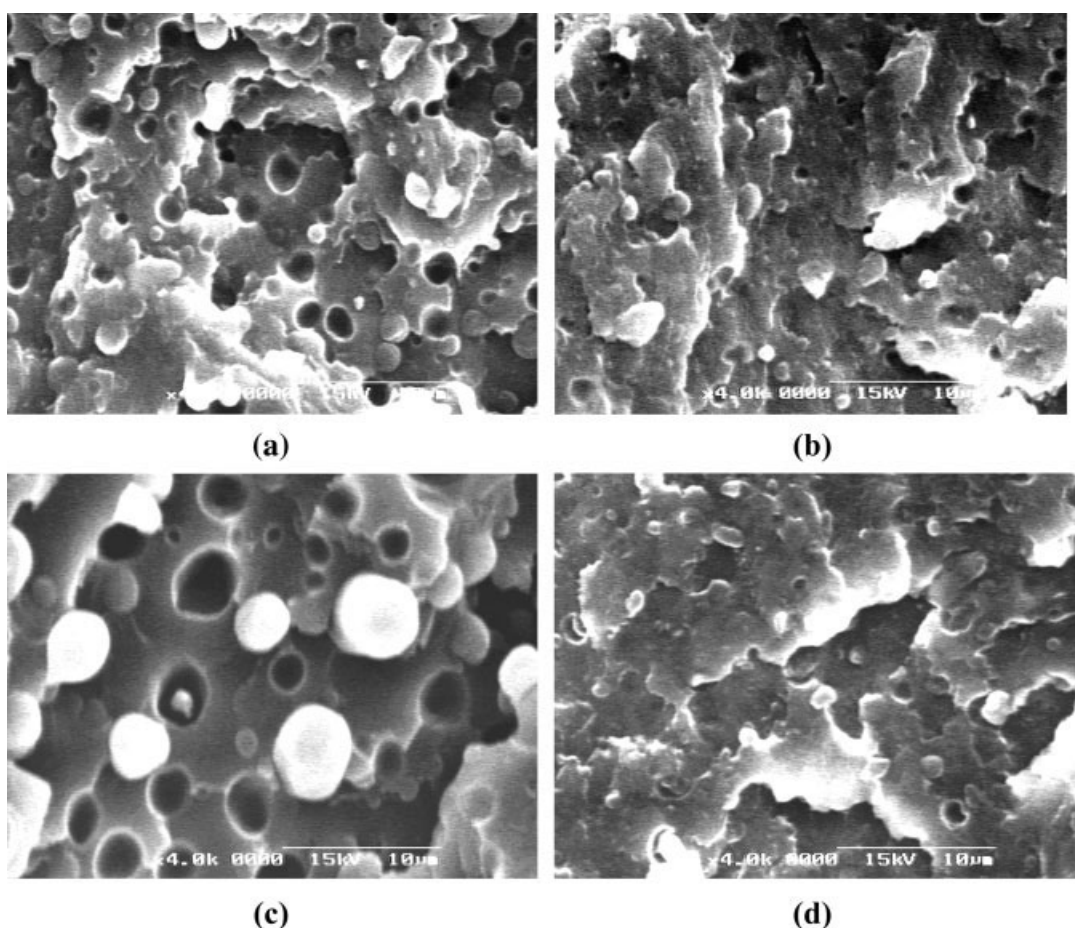

Figure 3 SEM micrographs showing the fractured surfaces of impact specimens of PBT/HDPE and PBT/HDPE-*g*-MAH blends. (a) PBT/HDPE = 90/10; (b) PBT/HDPE-*g*-MAH = 90/10; (c) PBT/HDPE = 80/20; (d) PBT/HDPE-*g*-MAH = 80/20.
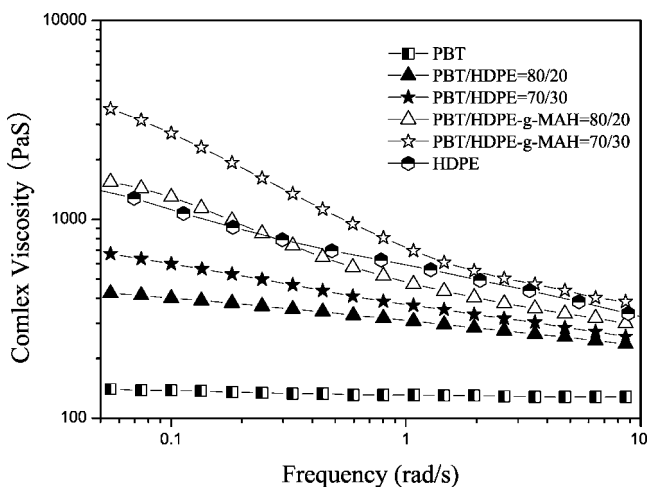
Figure 4 Complex viscosity versus shear rate for PBT, HDPE, PBT/HDPE, and PBT/HDPE-*g*-MAH blends.

notched impact strength of the blend in which HDPE-*g*-MAH content was higher than 10 wt % decreased with increase of HDPE-*g*-MAH content. It could also be found that the notched impact strength of the PBT/HDPE-*g*-MAH blends was much higher than those of the PBT/HDPE blends at the same composition. It seemed that the size of the dispersed domains and the adhesive properties were very important for high toughness in a polymer blend. It was likely that the improvement in the compatibility of the polymer blends would lead to smaller domain sizes and low interfacial tension. There was an interaction between the carboxylic groups of the HDPE-*g*-MAH copolymer and the side functional groups or the end groups of PBT (carboxyl or hydroxyl). Therefore, the compatibility of PBT with HDPE-*g*-MAH should be much better than that with the PBT/HDPE blends, which resulted in the enhancement of the toughness of the PBT/HDPE-*g*-MAH blends. However, the reaction rate of the carboxyl groups of HDPE-*g*-MAH and hydroxyl end groups of PBT for forming an ester were very low,[12] which might be one of the reasons that the notched Izod impact strength of the related blending system was not improved so dramatically.

Morphology

The morphology of the PBT/HDPE blends and the PBT/HDPE-*g*-MAH blends was studied using scanning electron microscopy. It is well known that the volume ratio of the blending components plays a predominant role in determining which of the two blending components forms the disperse phase and the matrix phase. From Figure 3, it could be seen that PBT acted as the continuous phase, while HDPE or HDPE-*g*-MAH served as the dispersed phase because the content of PBT was larger than 70 wt % and the vis-

cosity of HDPE is much higher than that of PBT. Furthermore, the domains for PBT/HDPE-*g*-MAH blends were smaller and more uniform than that for PBT/HDPE blends, and gaps between dispersed domains and matrix in PBT/HDPE could be clearly seen, while the interface between the domains and the matrix in the micrographs of PBT/HDPE-*g*-MAH was not so clear. It could be explained that the compatibilization induced by the interaction of grafted MAH and the side functional groups or the end groups of PBT was the main effect influencing the morphology of PBT/HDPE-*g*-MAH blends, because it reduced the interfacial tension and increased the interfacial adhesion.

Rheology

Figure 4 showed the complex viscosity of PBT, HDPE, PBT/HDPE blends, and PBT/HDPE-*g*-MAH blends, respectively. In Figure 4, the shear thinning behavior (the complex viscosity decreased with an increase of the shear rate), which was the typical behavior of non-Newtonian fluid, was observed in the pure HDPE, the 70/30, 80/20 PBT/HDPE blends or PBT/HDPE-*g*-MAH blends except for the pure PBT. From Figure 4, it was seen that the complex viscosity increased with increase of HDPE or HDPE-*g*-MAH content, and the complex viscosity of the PBT/HDPE-*g*-MAH blends was observed to be higher than that of the PBT/HDPE blends. This behavior could be explained by the observation of the SEM micrographs shown in Figure 3. From Figure 3, the dispersed domains size of the PBT/HDPE-*g*-MAH blends was smaller than that of
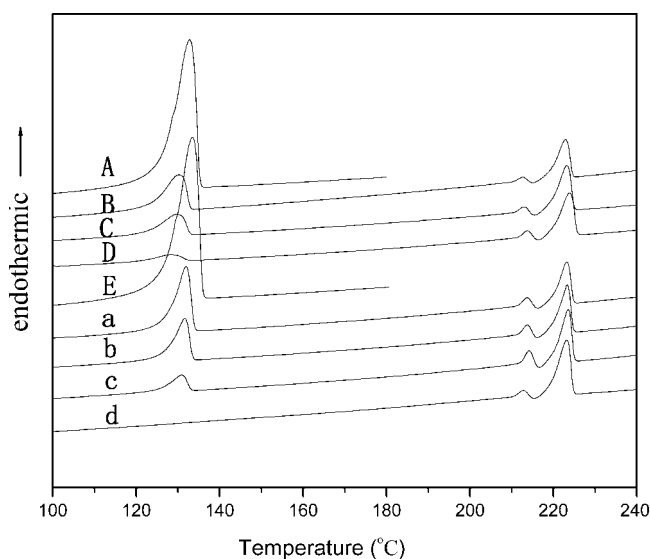

Figure 5 Melting behavior of PBT/HDPE and PBT/HDPE-*g*-MAH blends. (A) HDPE-*g*-MAH; (B) PBT/HDPE-*g*-MAH = 70/30; (C) PBT/HDPE-*g*-MAH = 80/20; (D) PBT/HDPE-*g*-MAH = 90/10; (E) HDPE; (a) PBT/HDPE = 70/30; (b) PBT/HDPE = 80/20; (c) PBT/HDPE = 90/10; (d) PBT.
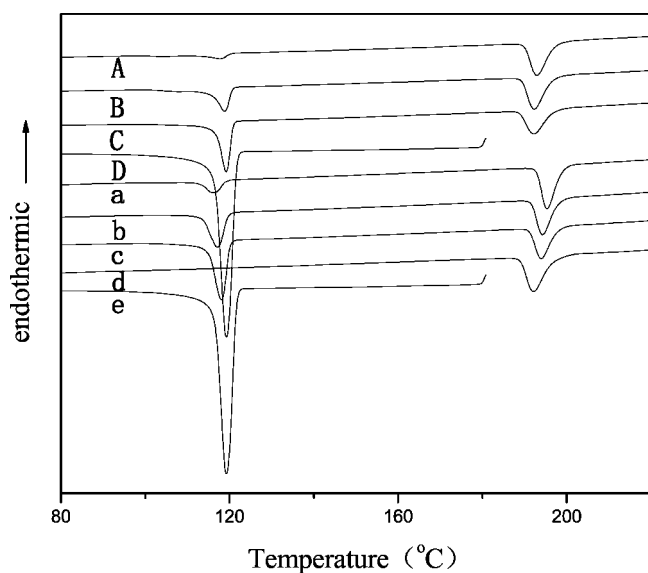
Figure 6 Crystallization behavior of PBT/HDPE and PBT/HDPE-*g*-MAH blends. (A) PBT/HDPE-*g*-MAH = 70/30; (B) PBT/HDPE-*g*-MAH = 80/20; (C) PBT/HDPE-*g*-MAH = 90/10; (D) HDPE-*g*-MAH; (a) PBT/HDPE = 70/30; (b) PBT/HDPE = 80/20; (c) PBT/HDPE = 90/10; (d) PBT; (e) HDPE.

PBT/HDPE blends, which suggested that the compatibility in the PBT/HDPE-*g*-MAH blends was improved. Also, as mentioned in morphology section, it was suggested that finer morphology of the PBT/HDPE-*g*-MAH blends compared with the PBT/HDPE blends might be caused by the interaction of grafted MAH and the side functional groups or the end groups of PBT and this morphology of the PBT/HDPE-*g*-MAH blend affected the rheological properties of the blend. Therefore, increase in the viscosity of the PBT/HDPE-*g*-MAH blends in Figure 4 was probably due to the interaction of grafted MAH and end groups of PBT. The effect of the compatibilizer on the viscosity of the blends is very complicated in reactive blend system because there were several variables such as composition, viscosity ratio, functionality,

compatibilizer quantity, and plasticization. Molecular weight increases through *in situ* reaction are mainly responsible for such viscosity increase after compatibilization.[13]

Crystallization behavior

The effect of blend composition on the melt temperature (T_m) and crystallization temperature (T_c) of the PBT/HDPE blends and the PBT/HDPE-*g*-MAH blends was shown in Figures 5 and 6, respectively. Two melting peaks for PBT appeared. Some research suggested that PBT could have two kinds of spherulites depending on the cooling and processing conditions.[13] The usual type of spherulite had a dark Maltesee cross 45° to the polarizer caused by an inclined position of the crystalline lamella cross parallel to the polarizer, whereas the unusual type of spherulite had a Maltese (planes of polarization) with respect to the spherulite radius. From the DSC parameters of PBT/HDPE and PBT/HDPE-*g*-MAH (listed in Table I and shown in Fig. 5), we could see that the melting peaks of PBT in the blends slightly improved when HDPE or HDPE-*g*-MAH was added, and the melting peaks of HDPE in PBT/HDPE or PBT/HDPE-*g*-MAH blends decreased with an increase of PBT content. As shown in Figure 6, the crystallization temperature of PBT in the PBT/HDPE or PBT/HDPE-*g*-MAH blends was 10–13°C higher than that in pure PBT, and the crystallization temperature of HDPE in the blends changes little with the addition of PBT. However, the crystallization temperature of HDPE in PBT/HDPE blends was lower than that in PBT/HDPE-*g*-MAH blends. On the other hand, the degree of crystallinity (X_c) of PBT in the blends slightly decreased compared with that of pure PBT. Furthermore, the degree of crystallinity of HDPE in either PBT/HDPE blend or PBT/HDPE-*g*-MAH was lower than that in pure HDPE. It could be interpreted as a mutual nucleating agent to enhance or hinder the crystallization on the other component.[14–16] Moreover, the crystallization temperature and the degree of crystallinity of PBT in the PBT/HDPE

TABLE I
DSC Parameters of PBT/HDPE and PBT/HDPE-*g*-MAH Blends

| Samples	PBT				HDPE			
	T_m (°C)	T_c (°C)	$-\Delta H_c$ (J/g)	X_c (%)	T_m (°C)	T_c (°C)	$-\Delta H_c$ (J/g)	X_c (%)
PBT	212.7/223.1	182.0	48.6	33.6				
PBT/HDPE 90/10	213.9/223.0	195.3	42.5	32.3	131.0	116.6	11.1	38.7
PBT/HDPE 80/20	213.9/223.3	194.3	37.1	32.1	131.6	117.3	33	57.2
PBT/HDPE 70/30	213.8/223.3	194.0	33.8	33.4	132.3	118.1	50.8	58.0
HDPE					133.3	116.8	212.1	73.8
PBT/HDPE-*g*-MAH 90/10	214.1/223.9	193.0	39.1	30.1	128.6	118.1	2.8	9.8
PBT/HDPE-*g*-MAH 80/20	213.1/223.3	192.3	36.8	31.8	130.0	118.9	14.5	25.2
PBT/HDPE-*g*-MAH 70/30	212.9/222.8	192.2	31.6	31.2	130.5	119.2	34.1	39.5
HDPE-*g*-MAH					132.7	119.3	169.5	59.0
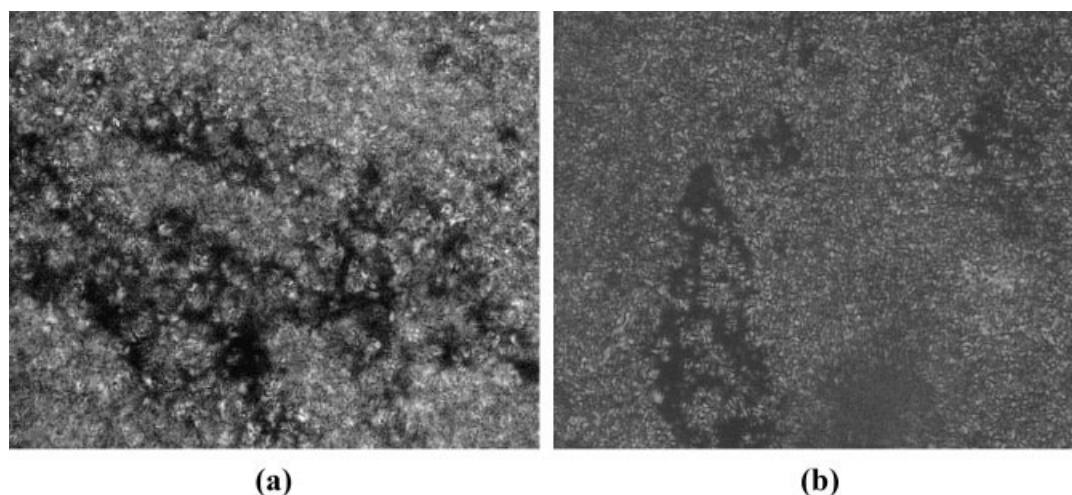
Figure 7 Polarized optical micrographs of quenched films of PBT blends at 180°C (×200). The crystallization of PBT molecular chains in the (a) PBT/HDPE and (b) PBT/HDPE-*g*-MAH.

blends was higher than that of PBT in the PBT/HDPE-*g*-MAH under the same conditions, which indicated that the nucleating effect of HDPE on PBT was more effective than that of HDPE-*g*-MAH. All these features suggested that the crystallization of PBT molecular chains was prohibited, and the perfection of PBT crystals decreased because of the addition of HDPE-*g*-MAH and the interaction between grafted MAH and the side functional groups or the end groups of PBT. These results were similar to the work of Yang et al.[7] The results of polarized optical micrographs of PBT blends also indicated that the crystallization of PBT molecular chains in the PBT/HDPE-*g*-MAH was smaller and faultier than that of PBT in the

PBT/HDPE blend (in Fig. 7). From X-ray spectra results (in Fig. 8), it could be found that the type of spherulite of PBT or HDPE was unchanged although the melt temperature (T_m) and crystallization temperature (T_c) of PBT or HDPE are affected by the other component.

CONCLUSIONS

PBT/HDPE blends and PBT/HDPE-*g*-MAH blends are prepared with a reactive extrusion method. The mechanical, morphological, and rheological properties and crystalline behavior were investigated in details. The important results are summarized as follows:

1. The mechanical tests showed that the impact strength, tensile strength, and flexural strength of the PBT/HDPE-*g*-MAH were higher than those of the PBT/HDPE blends.
2. The domains for the PBT/HDPE-*g*-MAH blends were smaller and more uniform than that for the PBT/HDPE blends.
3. The complex viscosity of the PBT/HDPE-*g*-MAH blends is observed to be higher than that of the PBT/HDPE at the same components.
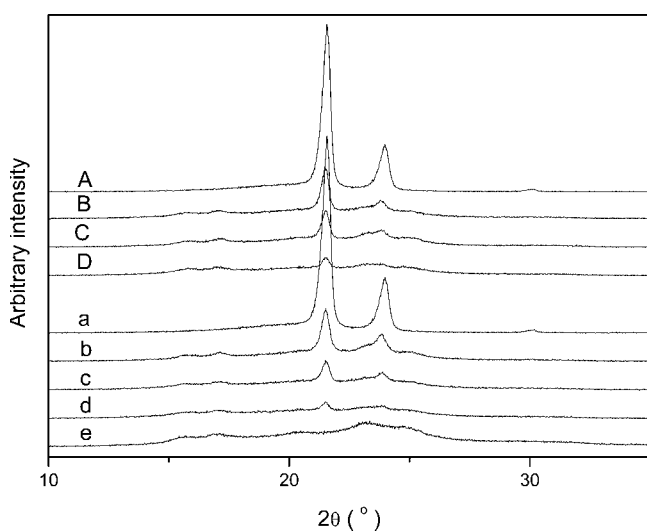4. The crystallization of PBT molecular chains was prohibited, and the perfection of PBT crystals decreased.

Figure 8 Wide-angle X-ray spectra for various blends. (A) HDPE-*g*-MAH; (B) PBT/HDPE-*g*-MAH = 70/30; (C) PBT/HDPE-*g*-MAH = 80/20; (D) PBT/HDPE-*g*-MAH = 90/10; (a) HDPE; (b) PBT/HDPE = 70/30; (c) PBT/HDPE = 80/20; (d) PBT/HDPE = 90/10; (e) PBT.

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