Effect of the Compatibilization of Linear Low-Density Polyethylene-*g*-Acrylic Acid on the Morphology and Mechanical Properties of Poly(butylene terephthalate)/Linear Low-Density Polyethylene Blends

JINGHUI YANG, DEAN SHI, ZHANHAI YAO, ZHIRONG XIN, JINGHUA YIN

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

ABSTRACT: A poly(butylene terephthalate) (PBT)/linear low-density polyethylene (LLDPE) alloy was prepared with a reactive extrusion method. For improved compatibility of the blending system, LLDPE grafted with acrylic acid (LLDPE-*g*-AA) by radiation was adopted in place of plain LLDPE. The toughness and extensibility of the PBT/LLDPE-*g*-AA blends, as characterized by the impact strengths and elongations at break, were much improved in comparison with the toughness and extensibility of the PBT/LLDPE blends at the same compositions. However, there was not much difference in their tensile (or flexural) strengths and moduli. Scanning electron microscopy photographs showed that the domains of PBT/LLDPE-*g*-AA were much smaller and their dispersions were more homogeneous than the domains and dispersions of the PBT/LLDPE blends. Compared with the related values of the PBT/LLDPE blends, the contents and melting temperatures of the usual spherulites of PBT in PBT/LLDPE-*g*-AA decreased. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1059–1066, 2002; DOI 10.1002/app.10399

Key words: poly(butylene terephthalate); linear low-density polyethylene; compatibilization; reactive extrusion

INTRODUCTION

Blending two or more polymers to obtain polymer alloys has become one of the main methods for tailoring mechanical properties and other properties of polymeric materials. Because of thermodynamic immiscibility, polymer blends often represent a two-phase morphology that depends on the process parameters, intrinsic properties, and interfacial properties of the component polymers. For a fine and stable morphology for immiscible polymer blends, compatibilization is usually needed. Block or graft copolymers are well-known compatibilizers that locate themselves preferentially at the interface of the blending components. As a result, they tend to reduce interfacial tension, facilitate dispersion, stabilize morphology, and enhance adhesion between the phases in the solid states. Reactive compatibilization, which is designed to enhance interactions between the matrices and domains, could be employed to generate *in situ* the desired quantities of either block or graft copolymers. For this process, the block or

graft copolymers are generated during the process of extrusion.[1]

Poly(butylene terephthalate) (PBT) is a conventional engineering plastic that has a high degree of crystallinity and a high crystallization rate, good chemical resistance, good thermal stability, and excellent processing properties. Blends of PBT with polyethylene are of significant practical interest, largely because of their toughness at low temperatures, low absorption of humidity, and good electrical resistance and the low cost of polyethylene.[2–4] However, because of their incompatibility, simple melt blending leads to morphologically unstable and brittle products. An efficient method of compatibilization is required for improved mechanical properties and the final morphology of the blends. Kang et al.[5] suggested that the addition of ethylene-co-vinyl acetate (EVA) or ethylene-co-vinyl acetate grafted maleic anhydride (EVA-*g*-MAH) as a compatibilizer to PBT/LLDPE blending systems considerably improved the impact strength without significantly sacrificing the tensile and flexural strength. Saheb and Jog[6] reported that an ethylene-based compatibilizer resulted in significant improvements in the mechanical properties of blends of PBT and very low-density polyethylene through the modification of the phase morphology and interfacial adhesion.

In this work, blends of PBT and linear low-density polyethylene (LLDPE) were prepared. For improved compatibility, LLDPE functionalized with acrylic acid (LLDPE-*g*-AA) by a novel method was adopted in place of plain LLDPE. The effects of the compatibilization on the mechanical properties, morphology, and thermal behavior of the PBT/LLDPE and PBT/LLDPE-*g*-AA blends were investigated systematically.

EXPERIMENTAL

Materials

The PBT used in this work, Arnite thermoplastic polyester (T04 200), was provided by DSM (Emmen, The Netherlands). The intrinsic viscosity of this PBT(in *m*-cresol) was about 1.85 dL/g, and the content of the carboxylic end groups was about 45 mequiv/kg. LLDPE was supplied by Daqing Petrochemical Co. (Daqing, China). Its density was 0.918 g/cm^3, and the melt flow rate was 2 g/10 min (ASTM Standard D 1238). Two LLDPE-*g*-AA samples were pre-

pared in this laboratory. The common method for modifying polyolefins is melt grafting during extrusion with the addition of peroxide and monomers containing functional groups, such as anhydride, epoxy, and so forth. However, side reactions, such as crosslinking in polyethylene and degradation in polypropylene, occur that diminish their processability and mechanical properties. We developed a novel method for preparing functionalized LLDPE.[7] This method involved the preirradiation of LLDPE with γ-radiation in the presence of oxygen. The dose of irradiation was selected to be lower than 10 kGy so that the crosslinking of LLDPE would be avoided. Then, the irradiated LLDPE was coextruded with ethylene monomer containing functional groups such as maleic anhydride, AA, and so forth. By this method, we obtained a high degree of grafting of polyethylene with a lower gel content. The grafted LLDPE was first resolved in xylene, and then the solution was poured into acetone with stirring. The precipitate was filtered *in vacuo*, washed with acetone, and dried in a vacuum oven. The degree of grafting was determined with the same procedure mentioned in a previous article of ours.[8]

Preparation of the PBT/LLDPE-*g*-AA and PBT/LLDPE Blends

PBT and LLDPE and PBT and LLDPE-*g*-AA were predried at 120 and 60°C, respectively, for 8 h and then were premixed immediately in the fixed compositions shown in Table I. The preparations of both the PBT/LLDPE-*g*-AA and PBT/LLDPE blends were carried out with a SHJ-30 corotating twin-screw extruder (Fengyang Group, Beijing, China). The diameter of the screws was 30 mm, and the ratio of the length to the diameter (L/D) was 44. L/D was 24 for the reactive zone and 16 for the melting zone. The extrusion temperature was set at 200–260°C from the feeder to the die, and the die temperature was set at 230°C. The screw speed was 150 rpm, and the feeder screw speed was 27 rpm. Under these conditions, the residence time of the blends in the extruder was about 100 s. The premixed PBT/LLDPE and PBT/LLDPE-*g*-AA mixtures were added through a feeder. Extrudates were cooled with water and pelletized. Mechanical tests indicated that PBT did not undergo considerable degradation under these processing conditions.

Table I   Composition Range of PBT/LLDPE and PBT/LLDPE/LLDPE-*g*-AA Blends

PBT/LLDPE (by Weight)		PBT/LLDPE-*g*-AA (by Weight)			
		Graft Degree = 0.6%		Graft Degree = 1%	
Code	Composition	Code	Composition	Code	Composition
900	90/10	901	90/10	902	90/10
700	70/30	701	70/30	702	70/30
500	50/50	501	50/30	502	50/50
300	30/70	301	30/70	302	30/70

Preparations of the Specimens for Mechanical Testing

Specimens for mechanical testing were prepared with a JSW J17SA injector made by Japan Steel Works, Ltd. (Hiroshima, Japan), at 240°C. Before injection molding, PBT and all blend pellets were dried at 120 and 60°C, respectively, for 8 h.

Testing and Characterization

Tensile tests were carried out with an Instron 1121 tester (High Wycombe, UK) according to ASTM Standard D638. The Izod impact and non-notched impact strengths were measured with an XJ-40A impacter (Wuzhong, China) according to ASTM Standard D256. The maximum pendulum energy was 5 J for non-notched impact tests and 1 J for Izod tests for all samples.

Morphological observations of Izod impact fracture surfaces of two blending systems were performed with a JEOL JXA-840 scanning electron microscope. Micrographs were taken at a 20-kV acceleration voltage. Before the scanning electron microscopy (SEM) observations, the fracture surfaces of the blends were coated with a thin layer of gold to avoid electrical charging during the examination.

The thermal behaviors of the two blending systems were studied with a PerkinElmer DSC-7 differential scanning calorimeter (Norwalk, CT). A heating scan up to 250°C was followed by cooling to 50°C at a scanning rate of 10°C/min. Five minutes was allowed between the heating and cooling scans. Both heating and cooling procedures were carried out under an atmosphere of N_2.

RESULTS AND DISCUSSION

Mechanical Properties

Values of the impact strengths of non-notched specimens of PBT/LLDPE and PBT/LLDPE-*g*-AA

blends and their Izod impact strengths with different compositions are shown in Table II. The impact strengths of non-notched specimens of PBT/LLDPE-*g*-AA blends were much higher than the values of PBT/LLDPE blends at the same composition. For example, non-notched specimens of PBT/LLDPE-*g*-AA were not broken in the investigated composition range, but all samples of the PBT/LLDPE blending system were broken at very low impact strengths. For the Izod impact strengths of the two blending systems, the values of PBT/LLDPE-*g*-AA were also higher than those of PBT/LLDPE, but the difference was not so obvious. The improvement of the impact strength with the PBT/LLDPE-*g*-AA blending system could be attributed to the interaction between grafted AA and hydroxyl end groups of PBT, which led to some degree of compatibilization.

As for the difference in the extent of the improvement in the impact strength for non-notched and notched specimens, a tentative explanation is as follows. The notched impact strength was re-

Table II   Impact Strength of PBT/LLDPE and PBT/LLDPE-*g*-AA Blends

Code	Nonnotched Impact Strength (J/m^2)	Izod Impact Strength (J/m)
900	35.5	23
901	No break	25
902	No break	30
700	13.6	16
701	42.1	17
702	No break	19
500	13.1	12
501	25.9	12
502	No break	18
300	42.0 (Partial break)	58
301	No break	84
302	No break	155

lated to the crack propagation energy, whereas the non-notched impact strength was related to both the crack initiation energy and the crack propagation energy. In this case, the improved compatibility for the PBT/LLDPE-*g*-AA system mainly increased the crack initiation energy and had a smaller affect on the crack propagation energy.

Toughening mechanisms for polymeric materials have been proposed by many researchers, including critical matrix ligament thickness for rubber-toughening nylon, suggested by Wu,[9,10] and a cold-drawing mechanism, proposed by Kurauchi and Ohta.[11] It seems that the size of the dispersed domains and the adhesive properties are very important for high toughness in a polymer blend. The improvement in the compatibility of the polymer blends will lead to smaller domain sizes and low interfacial tension. There is an interaction between the carboxylic groups of the LLDPE-*g*-AA copolymer and the end groups of PBT (carboxyl or hydroxyl). Therefore, the compatibility of PBT with LLDPE-*g*-AA should be much better than that for the PBT/LLDPE blending system, which results in the enhancement of the toughness or extensibility of the PBT/LLDPE-*g*-AA system. However, the reaction rate of the carboxyl groups of LLDPE-*g*-AA and hydroxyl end groups of PBT for forming an ester were very low,[12] which might be one of the reasons that the Izod impact strength of the related blending system was not improved so dramatically, as shown in Table II. This speculation was supported by the fact that with an increasing grafting degree of LLDPE-*g*-AA, the Izod impact strength and other mechanical properties of the related PBT/LLDPE blending samples increased somewhat.

As shown in Table III, there was not much difference between the tensile or flexural strengths and moduli of PBT/LLDPE-*g*-AA and PBT/LLDPE blends at the same composition. However, the elongation at break for the PBT/LLDPE-*g*-AA blend was higher than the value for the PBT/LLDPE blend at the same composition. For an incompatible polymer blend, one of the following possibilities may occur, improving the mechanical properties after compatibilization: (1) the strength and modulus are improved, whereas the toughness or extensibility (impact strength or elongation at break) change little; (2) the strength and modulus are kept constant, but the toughness or extensibility is improved; and (3) the strength, modulus, and toughness or extensibility are improved. Me-

Table III   Tensile Strength, Young's Modulus, and Elongation at Break of PBT/LLDPE and PBT/LLDPE-*g*-AA Blends

Code	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
900	49	26	830
901	51	33	796
902	50	37	892
700	37	11	820
701	35	18	785
702	38	38	860
500	25	6	652
501	28	23	663
502	31	29	768
300	22	164	503
301	22	104	527
302	22	80	512

chanical properties obtained from the PBT/LLDPE-*g*-AA blending system suggested that the second possibility could apply.

The aforementioned features could be tentatively explained as follows. As is well known, the tensile or flexural strength and modulus of polyethylene are lower but the toughness and extensibility are much higher than the values for plain PBT. There are two general modes of failure: brittle fracture and ductile fracture. Brittle fracture is frequently a result of highly localized crazing confined to a very small volume of the material. Ductile fracture, however, may be broken down into either multiple crazing, in which crazes are initiated in a comparatively large volume of the polymer, or shear yielding, that is, plastic flow without crazing. Generally, ductility imparts greater impact resistance to most materials.[13] When PBT was the continuous phase and LLDPE was the dispersed phase, the addition of LLDPE-*g*-AA to PBT changed the failure of PBT from brittle fracture to ductile fracture. When a sample of the PBT/LLDPE blends was under tensile stress, the interlayer slip between the matrix and dispersed phase of the blend hindered the cold drawing of the matrix, resulting in premature rupture of the material because the interface adhesion was very poor. However, for PBT/LLDPE-*g*-AA blends, because of enhanced interface adhesion, the dispersed-phase polyethylene was stretched. Therefore, greater elongation was obtained.
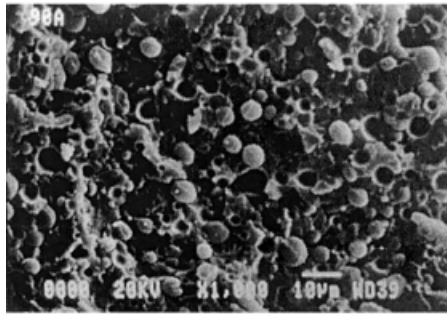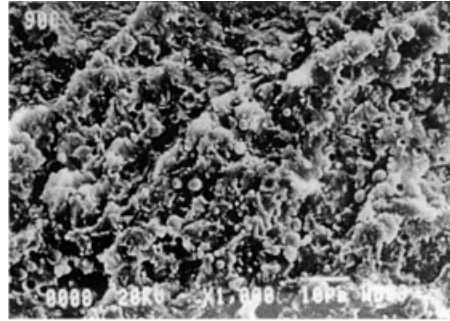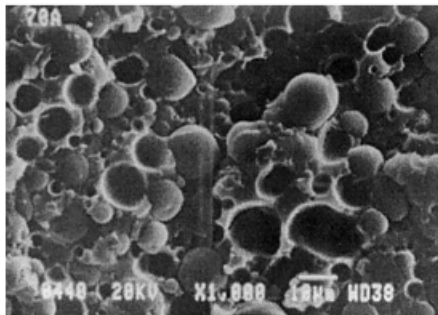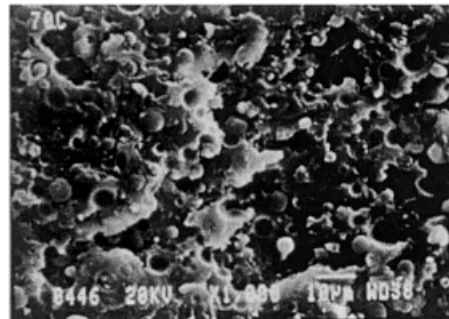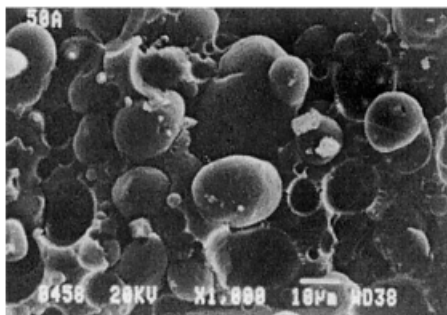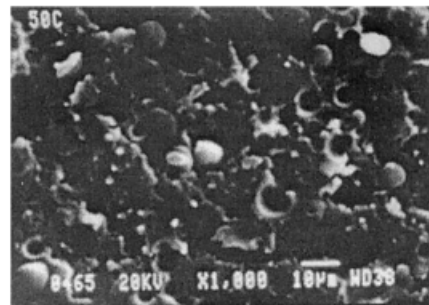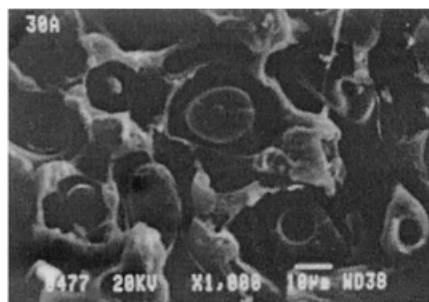
Figure 1   SEM micrographs of PBT/LLDPE and PBT/LLDPE-*g*-AA blends (grafting degree of LLDPE-*g*-AA = 1.0 wt %).
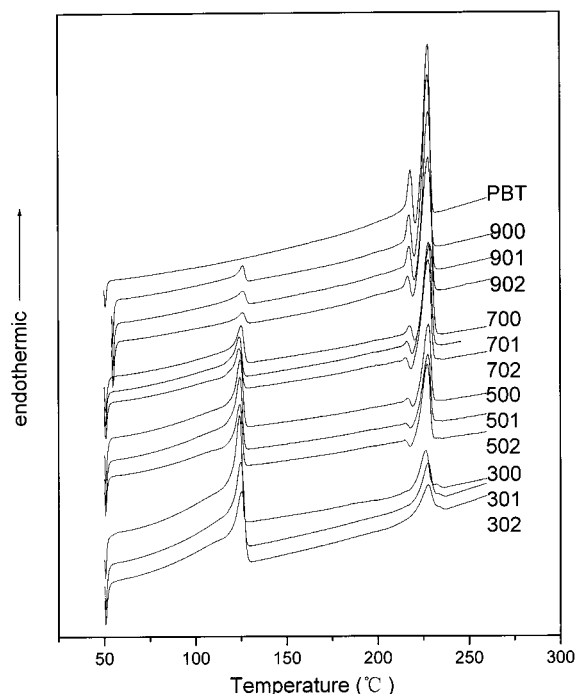
Figure 2 DSC heating thermograms for PBT/LLDPE-*g*-AA and PBT/LLDPE blends.

Morphology Observations

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 dispersed phase and the matrix phase. In Figure 1, it can be seen that, when the content of PBT was larger than 50% (by weight), PBT was the continuous phase and LLDPE or LLDPE-*g*-AA was the dispersed phase. Otherwise, when the content of PBT was 30% (by weight) or less, PBT was the dispersed phase and LLDPE or LLDPE-*g*-AA was the continuous phase.

Moreover, the domains for PBT/LLDPE-*g*-AA blends were smaller and more uniform than the domains of PBT/LLDPE blends. The size and dispersion of the dispersed phase of the polymer blends were mainly dependent on the compatibility and ratio of the viscosity of the blending components. It can be speculated that the compatibilization induced by the interaction of grafted AA and end groups of PBT was the main effect influencing the morphology of PBT/LLDPE-*g*-AA blends because it reduced the interfacial tension and increased the interfacial adhesion. This assumption is supported by Figure 1. Particles of the dispersed phase or holes left by the particles

are very smooth and open. Gaps between dispersed domains and matrix can be clearly seen. However, the interface between the domains and the matrix in the micrographs of PBT/LLDPE-*g*-AA is not so clear, and some kind of interconnection can be found in the fracture section of the impact specimens.

Crystallization Behavior

Differential scanning calorimetry (DSC) thermograms of PBT/LLDPE-*g*-AA and PBT/LLDPE blends are given in Figure 2. Two melting peaks for PBT (PBT, 900–902, 700–702, 500–502 in Figure 2) appeared. Some research suggests that PBT could have two kinds of spherulites depending on the cooling and processing conditions.[14] The usual type of spherulite has a dark Maltese cross parallel to the polarizer, whereas the unusual type of spherulite has a Maltese cross 45° to the polarizer caused by an inclined position of the crystalline lamellae (planes of polarization) with respect to the spherulite radius. The melting temperature (T_{m1}) and enthalpy (ΔH_{m1}) of the usual type of spherulite, the melting temperature (T_{m2}) and melting enthalpy (ΔH_{m2}) of the unusual type of spherulite, the total melting enthalpy ($\Delta H_{m1} + \Delta H_{m2}$), and the crystallization temperature (T_c)
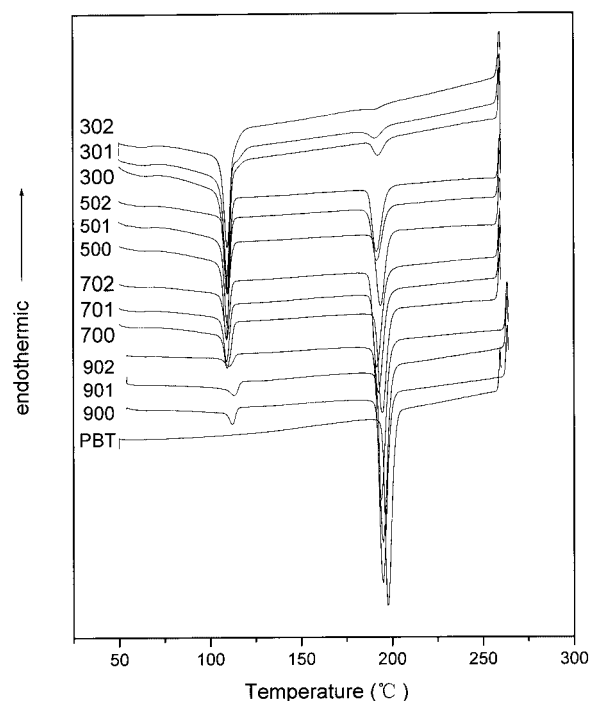

Figure 3 DSC cooling thermograms for PBT/LLDPE-*g*-AA and PBT/LLDPE blends.

Table IV   Melting Temperatures (T_{m1} and T_{m2}), and Enthalpy (ΔH_{m1} and ΔH_{m2}) Crystallization Temperature (T_c) and Enthalpy (ΔH_c), and Total Melting Enthalpy ($\Delta H_{m1} + \Delta H_{m2}$) of PBT in Both PBT/LLDPE and PBT/LLDPE-*g*-AA Blends

Sample Code	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)	ΔH_c (J/g)	$\Delta H_{m1} + \Delta H_{m2}$
PBT	218.0	227.8	197.7	18.6	32.7	−44.1	51.3
900	217.3	227.6	195.0	16.6	37.8	−53.8	54.4
901	217.3	227.8	195.0	14.0	40.0	−53.3	54.0
902	216.5	227.7	194.9	11.6	42.0	−53.9	53.6
700	217.5	228.6	194.6	10.8	35.4	−43.1	46.2
701	215.9	227.9	192.5	8.6	37.1	−43.3	45.7
702	215.2	227.8	191.7	7.1	37.9	−42.9	45.0
500	216.3	227.8	193.7	10.6	35.0	−45.2	45.6
501	215.1	227.5	191.7	7.0	37.6	−45.2	44.6
502	215.2	227.4	191.7	5.8	38.0	−43.4	43.8
300		226.3	192.4		43.0	−15.7	
301		227.6	191.3		43.7	−16.7	
302		227.5	190.7		45.0	−7.0	

and enthalpy (ΔH_c) of PBT in both blending systems are summarized in Table IV.

As shown in Figure 2 and Table IV, with the addition of LLDPE and LLDPE-*g*-AA, the melting peaks of the usual type of spherulite of PBT became smaller and smaller. At the same compositions, the content of the usual type of spherulite of PBT in PBT/LLDPE-*g*-AA blends was always less than that in PBT/LLDPE blends. With an increasing grafting degree of LLDPE-*g*-AA, the content of PBT spherulites decreased. When the content of LLDPE or LLDPE-*g*-AA was 70%, the usual type of PBT spherulite disappeared. T_{m1} and T_c of PBT in PBT/LLDPE-*g*-AA blends were always smaller than the values of pure PBT. Except for 90/10 PBT/LDPE and PBT/LLDPE-*g*-AA compositions, $\Delta H_{m1} + \Delta H_{m2}$ for PBT in the two blending systems was smaller than that of plain PBT, and the value of PBT in PBT/LLDPE-*g*-AA blends was a little lower than that in PBT/LLDPE blends for the same composition. All these features suggest that the crystallization of PBT molecular chains was prohibited, and the perfection and crystallinity of PBT crystals decreased because of the addition of LLDPE-*g*-AA and the interaction between grafted AA and end groups of PBT.

CONCLUSIONS

1. The mechanical tests showed that the impact strengths and elongations at break of PBT/LLDPE-*g*-AA blends were higher than those of PBT/LLDPE blends, but there was not much difference between PBT/LLDPE and PBT/LLDPE-*g*-AA blends in their tensile or flexural strengths and moduli. The compatibilization induced by the interaction of grafted AA of LLDPE-*g*-AA and end groups of PBT was mainly shown to improve toughness and extensibility, not strength and modulus; this might be caused by the limited compatibility effect and low strength and modulus of LLDPE.

2. Because of the morphology of the two blending systems, the domains of PBT/LLDPE-*g*-AA blends were always smaller and more uniform than those of PBT/LLDPE blends. This suggests that the improvement of compatibility between PBT and LLDPE-*g*-AA could reduce the interfacial tension and increase the interfacial adhesion.

3. Results obtained from DSC tests indicated that, at the same compositions, the content of the usual type of spherulite of PBT in PBT/LLDPE-*g*-AA blends was always less than that in PBT/LLDPE blends. With an increasing grafting degree of LLDPE-*g*-AA, the content of the unusual type of spherulite of PBT decreased. T_{m1} and T_c of PBT in PBT/LLDPE-*g*-AA blends were always smaller than values of pure PBT. These

features could be tentatively explained by the fact that the crystallization of PBT molecular chains was prohibited, and the perfection of PBT crystals decreased because of the addition of LLDPE-*g*-AA and the interaction between grafted AA and end groups of PBT.

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