Properties of Uncompatibilized and Compatibilized Poly(butylene terephthalate)–LLDPE Blends

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ABSTRACT: In this work, blends of poly(butylene terephthalate) (PBT) and linear low-density polyethylene (LLDPE) were prepared. LLDPE was used as an impact modifier. Since the system was found to be incompatible, compatibilization was sought for by the addition of the following two types of functionalized polyethylene: ethylene vinylacetate copolymer (EVA) and maleic anhydride-grafted EVA copolymer (EVA-*g*-MAH). The effects of the compatibilizers on the rheological and mechanical properties of the blends have been also quantitatively investigated. The impact strength of the PBT–LLDPE binary blends slightly increased at a lower concentration of LLDPE but increased remarkably above a concentration of 60 wt % of LLDPE. The morphology of the blends showed that the LLDPE particles had dispersed in the PBT matrix below 40 wt % of LLDPE, while, at 60 wt % of LLDPE, a co-continuous morphology was obtained, which could explain the increase of the impact strength of the blend. Generally, the mechanical strength was decreased by adding LLDPE to PBT. Addition of EVA or EVA-*g*-MAH as a compatibilizer to PBT–LLDPE (70/30) blend considerably improved the impact strength of the blend without significantly sacrificing the tensile and the flexural strength. More improvement in those mechanical properties was observed in the case of the EVA-*g*-MAH system than for the EVA system. A larger viscosity increase was also observed in the case of the EVA-*g*-MAH than EVA. This may be due to interaction of the EVA-*g*-MAH with PBT. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 989–997, 1999

Key words: poly(butylene terephthalate); LLDPE; blend; compatibilization; EVA

INTRODUCTION

Poly(butylene terephthalate) (PBT) is a conventional semicrystalline engineering polymer having high degree and rate of crystallization, good chemical resistance, thermal stability, and excellent flow properties. PBT was introduced in 1970 and grew rapidly as it found utility in various high-volume automotive, electrical, and other engineering applications since it possesses good tensile strength, flexural modulus, and dimensional stability, especially in water, and high resistance to hydrocarbons.[1–3] PBT suffers from low impact strength, and there have been many experimental studies on improvement of this property by blending a rubber-like polymer with PBT.

Bier and Rempel[4] showed that the blending of polyacrylate graft rubber with PBT improved both the impact strength and hardness of PBT. Yates[5] reported that nitrile rubber blended with

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PBT improved impact strength. Wefer[6] claimed that the impact strength of PBT is greatly enhanced by blending with styrene–acrylonitrile (SAN) grafted ethylene propylene diene rubber (EPDM-*g*-SAN). Polycarbonate (PC) can also be used as the compatibilizer in the PBT–EPDM-*g*-SAN system. He showed that addition of about 10% PC and about 20% EPDM-*g*-SAN in the PBT gave a ten-fold improvement in the impact strength. Laurienzo et al.[7,8] reported that the impact strength of PBT is improved by blending with functionalized ethylene propylene rubber (EPR). The EPR was functionalized by alcoholic or ester groups. Pratt et al.[9] showed that glycidyl methacrylate grafted on EPDM acts as a good compatibilizer for PBT–EPDM blends for impact modification. Dekkers and Moffett[10] reported that the impact strength of PBT can be improved by blending with EPDM, which has been functionalized by an epoxy monomer. Parikh et al.[3] reported that, in the PBT–EPR blend, the impact strength was improved without significantly affecting heat deflecting temperature and flexural modulus, by functionalizing EPR with maleic anhydride. Akkapeddi et al.[11] showed that reactive toughening and compatibilization techniques have been found to be particularly useful in achieving high-thermal embrittlement resistance in the blends of recycled poly(ethylene terephthalate), functionalized ethylene copolymers, and polycarbonate. That is, dispersing a small amount of low modulus polymer into PBT can lead to improvement in impact strength.

In this work, blends of PBT and linear low density polyethylene (LLDPE) were prepared. LLDPE was used as an impact modifier. Since the system was found to be incompatible, compatibilization was sought for by the addition of functionalized polyethylene. The effects of the compatibilizer on the rheological and mechanical properties of the blends have been also quantitatively investigated.

EXPERIMENTAL

PBT, LLDPE, and functionalized polyolefins were all commercially available grades. The characteristics of the materials are given in Table I. The PBT contained at its chain ends 0.075 eq/kg of hydroxyl group and 0.045 eq/kg of carboxylic group. All of the resins except LLDPE were dried at 100°C for 12 h *in vacuo* before use. LLDPE was used as received. Blending was carried

Table I   The Characteristics of Materials
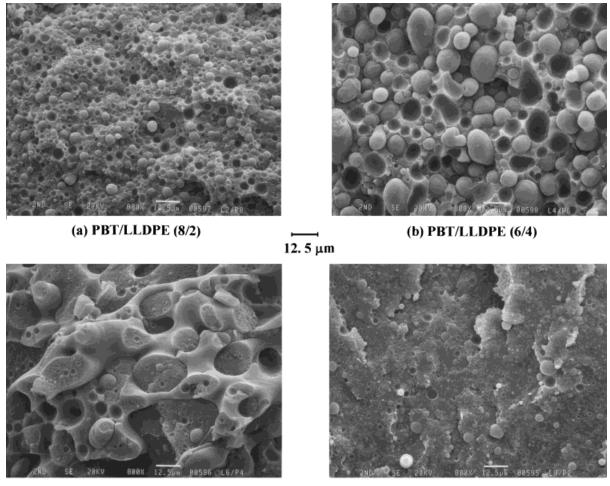
Polymer	M_w	Viscosity (poise)[a]	Source
PBT	71,280	725.5	Kolon Co. KP 210
LLDPE	100,600	950.5	Yukong Co. FT 810
EVA[b]	203,735	2,052	Dupont Elvax 470
EVA-*g*-MAH[c]	108,334	2,550	synthesized

[a] Shear rate: 1,000 s^{-1} at 240°C.
[b] Vinyl acetate content: 18%.
[c] Comonomer content: 20%. MAH content: 0.796 wt %.

out in a counter-rotating twin-screw extruder (Temperature, Z1/Z2/Z3 = 140/260/260°C; average residence time = 2 to 3 min; Brabender Plasticorder PLE-331). Blended samples were injection-molded using an injection-molding machine (Kum Sung Co.) for further testing and measurements. To prevent the thermal aging of blended polymers during melt mixing, 0.1 phr of tri(2,4-di-*t*-butylphenyl) phosphate (Miwon Commercial Co., Ltd., Mianto P-650) was added as an antioxidant. Thermal analyses were performed under nitrogen, with a heating rate of 10°C/min using Perkin–Elmer differential scanning calorimeter (DSC7); blend samples were initially heated from 50 to 280°C at a heating rate of 10°C/min, and then the heated samples were cooled to room temperature at a cooling rate of 10°C/min; the second heating was done as for the first scan step. Tensile property measurements were done on an universal test machine (Instron model 4202) at room temperature following the procedure described in ASTM D638. A crosshead speed of 500 mm/min was used in measurements. The notched Izod impact strength was measured using a Testing Machines Inc. (TMI) impact testing machine at room temperature. The specimens for the Izod impact strength measurements had the dimensions of 63 × 12.5 × 3.1 mm with a notch 3 mm in radius. The glass transition temperature (T_g) was measured at 1 Hz using a rheometric mechanical spectrometer (RMS) (Rheomatrics RMS 7700) in a torsion rectangular dynamic mode. The samples were injection-molded specimen with 3.13 mm thickness, 12.54 mm width, and 45.37 mm length. Strain was maintained at 0.1% for all of the samples. The rheological properties of the blends were measured using a capillary rheometer (Toyoseiki Capiro Graph 1B) at 250°C. The length and diam-

(a) PBT/LLDPE (8/2)

(b) PBT/LLDPE (6/4)

12. 5 μm

(c) PBT/LLDPE (4/6)

(d) PBT/LLDPE (2/8)

Figure 1   SEM micrographs of PBT–LLDPE blends.

eter of the capillary were 10 and 1 mm, respectively. The morphology of blend samples was observed with a scanning electron microscope (JEOL JSM-35CF). Samples were cryogenically fractured in liquid nitrogen. The fractured surface of the specimens was directly observed by gold coating.

RESULTS AND DISCUSSION

Effect of Blend Composition on Morphology and Mechanical Properties

Morphology is a major factor determining the mechanical properties of immiscible blends. The main factors that determine the final morphology of the blends are the component ratio, their melt viscosities, and the rate of shear. Nielsen[12] has

shown that the morphology of the blends, prepared by melt mixing, changes as a function of composition. In Figure 1, it is clear that the LLDPE particles were dispersed in the PBT matrix below 40 wt % of LLDPE. However, at 60 wt % of LLDPE, a co-continuous morphology was obtained. When the concentration of LLDPE was above 50 wt %, phase inversion took place. Of interest is the size of the dispersed particles. The blend having 2/8 composition exhibits a much finer domain morphology than that of 8/2 composition. When the components have different melt viscosity, the morphology of the blends depends on whether the minor component has a lower viscosity or a higher viscosity. If the minor component has a lower viscosity than that of the major one, the minor component will be finely dispersed; the reverse is also true. Danesi and
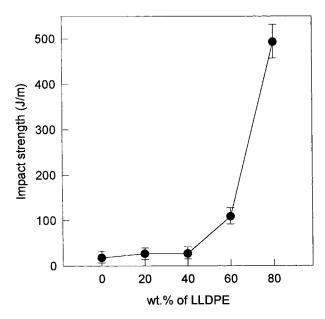
Figure 2 Impact strength of PBT–LLDPE blends.

Figure 3 Tensile strength of PBT–LLDPE blends.

Porter have shown that, for the same composition ratios, melt viscosity differences of the components determine the morphology.[13] Thus, the difference in morphology depending on the composition in Figure 1 can be easily explained, considering the molecular weight and viscosity data list in Table I.

The Izod impact strength of the PBT–LLDPE blends is shown in Figure 2. The impact strength of PBT homopolymer was 18.23 J/m. The impact strength of the blends slightly increased with increasing LLDPE compositions at a lower concentration of LLDPE but was remarkably increased with increasing LLDPE compositions above a concentration of 60 wt % of LLDPE. The rapid increase of impact strength is due to the presence of LLDPE but can be easily inferred from the phase change morphology, as already shown in Figure 1. Although LLDPE acts as the toughening material for PBT also at lower concentrations of LLDPE, the larger LLDPE particles dispersed in PBT cannot act as a good toughening material due to immiscibility with PBT, which causes weak interfacial adhesion in between. But after phase inversion occurred, the impact strength of the blends might be governed by the LLDPE matrix. Figures 3 and 4 show the tensile strength and the flexural strength of the PBT–LLDPE blends, respectively. In general, the tensile strength and the flexural strength decreased with the added LLDPE contents. The reduction in tensile strength and flexural strength should be expected as a result of the
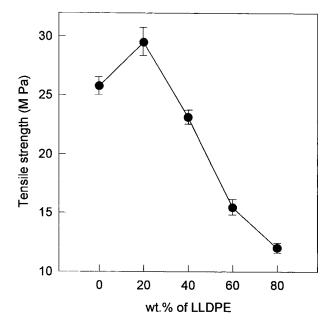
inherently weaker strength of the LLDPE in comparison with PBT. The initial increase of the tensile strength of PBT when 20% of LLDPE was incorporated is reminiscent of the polypropylene (PP)–high-density polyethylene (HDPE) blend of 80/20 composition by weight percent. This kind of increase in the tensile strength of immiscible semicrystalline polymer blends has been reported in the literature as due to the role of small
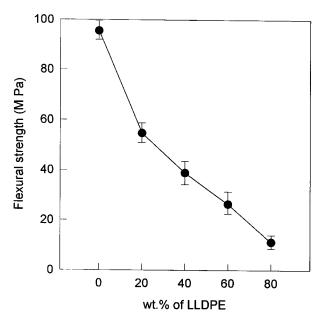

Figure 4 Flexural strength of PBT–LLDPE blends.

Table II   Thermal Properties of PBT–LLDPE Blends

Components	PBT (H)[a]		PBT (L)[a]		LLDPE	
	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)
PBT	223.4	49.88	204.4	9.88	—	—
PBT–LLDPE (8/2)	222.1	42.0	204.0	10.27	125.4	8.45
PBT–LLDPE (6/4)	221.3	32.38	202.9	10.78	125.3	27.38
PBT–LLDPE (4/6)	221.8	19.81	204.1	2.86	125.5	44.97
PBT–LLDPE (2/8)	221.1	9.06	—	—	125.3	63.56

[a] The H and L in parenthesis denote the higher-melting crystal and the lower-melting crystal, respectively. For example, T_m(H) means the melting point of higher melting crystal of PBT.

amounts of a minor semicrystalline component as a nucleating agent.[14]

Thermal Properties

When LLDPE is added to PBT, the change of melting temperature of PBT and LLDPEs is shown in Table II. The PBT homopolymer shows a first endotherm around 223°C on the DSC thermogram and a second endotherm at a temperature below that of the first endotherm. It has been reported that the second lower-melting endotherm peak of PBT is often displayed in a subsequent scanning thermal analysis at a temperature below that of the original endotherm when PBT is annealed. To explain the multiple peaks of PBT, Kim et al. noted that the crystallization of originally amorphous material is of two types: that coupled to preexisting crystals, and that not. The coupled amorphous material cannot crystallize without molecular rearrangements within the crystalline material to which it is coupled.[15–17] The amorphous material that can crystallize only at higher annealing temperature is likely to be coupled to preexisting crystals. Thus, the lower-melting peak on DSC thermogram was said to occur apparently at the expense of a higher-melting peak because of annealing during the second heating scan with no chemical change. Kim et al. proposed that the apparent transformation of high temperature to low temperature-melting material during annealing of PBT arises mainly from the coupled crystallization–recrystallization of amorphous and preexisting crystalline material.

Both higher and lower melting temperatures of PBT in the blends did not appreciably change, suggesting that the addition of LLDPE didn't af-fect the coupling of crystallization–recrystallization of amorphous and preexisting crystalline material in PBT at all. Also, the melting temperature of LLDPE was not appreciably changed. The result may be due to the fact that PBT is immiscible with LLDPE over all the blend concentrations.

Figure 5 shows tan δ behaviors of the PBT–LLDPE blends with various blend concentrations. The numbers in the figure denote the wt % of PBT in the blends. The T_gs, taken from the peak positions of the tan δ curves, with the standard deviation of 2.1°C, assigned to PBT and LLDPE in the blends are shown in Figure 6. This figure shows that the T_g of LLDPE decreases as the amount of
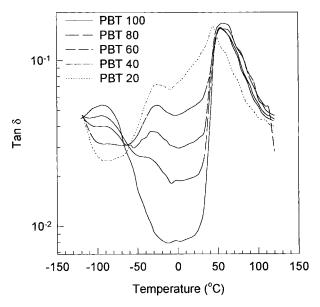

Figure 5   Tan δ behaviors of PBT–LLDPE blends. The numbers in the figure denote the wt % of PBT in the blends.
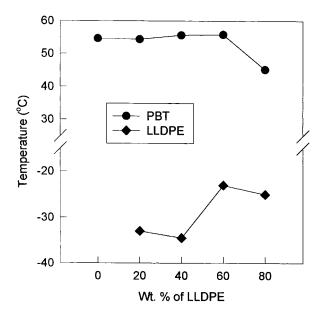
Figure 6 T_g changes of PBT–LLDPE blends.

PBT is increased, while T_g of PBT is not changed with the addition of LLDPE, except at high concentrations of LLDPE. Bohn[18,19] and Moribitzer et al.[20] found that in acrylonitrile–butadiene–styrene terpolymer (ABS), the T_g of the rubber (PB) domains in the hard matrix of poly(styrene-*co*-acrylonitrile) (PSAN) decreased with increasing amount of hard matrix. Bohn explained that with decreasing amounts of rubber phase, the difference in the thermal expansion coefficients between the rubber phase and the rigid matrix becomes larger and causes the thermal stress (that is, negative hydrostatic pressure) to increase around the rubber phase. Because this increased thermal stress makes the volume of the rubber domain dilate, the T_g of the latter decreases as the amount of rubber phase in the system is decreased. Moribitzer et al. found further that when the thermal stress resulting from the difference in thermal expansion coefficients overcame the adhesion between the rubber domain and the rigid matrix, the T_g of the rubber phase then increased with increasing rubber content. These authors concluded the following. In addition to the thermal stress resulting from differences in the thermal expansion coefficients, the adhesion between the rubber phase and the rigid matrix also plays an important role in determining the T_g of the rubber phase as a function of the rubber content in these ABS systems. Tucker and coworkers[21] have observed similar observations in styrene–butylene–styrene block copolymer (SBS)/polyphe-

nyleneether (PPE) blends. Han et al.[22] reported that the T_g of the PB block in a neat SBS block copolymer was higher than that measured for its blend with poly(α-methylstyrene) (PαMS) when the molecular weight of the latter was relatively high. In addition, Kim et al.[23] reported that the T_g of the ethylene–butylene (EB) block decreased as the amount of PPE was increased in SEBS–PPE mixtures. It should be noted that the blends reported by Paul and coworkers and Han et al. had no macrophase-separated regions, while the blends reported by Kim et al. had macrophase-separated regions.

Effects of Compatibilizers on Mechanical Properties and Rheology

Most of binary polymer blends are immiscible, which leads to poor adhesion between the two phases, causing very weak and brittle mechanical behavior in blends. This problem can be overcome by use of compatibilizers. A properly chosen third component should preferentially locate at the interface between the two phases. Thus, a compatibilizer improves the interfacial condition of an immiscible blend. Usually, as a third component, a block, or graft copolymer is used as a compatibilizer. PBT–LLDPE blends are immiscible due to the difference in polarity between the two polymers and, hence, have poor impact properties at lower concentration of LLDPE. In the present work, EVA and EVA-*g*-MAH were tested as compatibilizers to determine whether either of the functionalized polyethylenes could improve the mechanical strength of the immiscible PBT–LLDPE (70/30) blend systems.

The effects of compatibilizer concentration on mechanical strength of PBT–LLDPE (70/30) blends are shown in Figures 7–9. In Figures 7 and 8, the tensile strength and the flexural strength show maxima at contents around 1–3 wt % of EVA or EVA-*g*-MAH and decrease with further increasing of the contents of EVA or EVA-*g*-MAH. In particular, the maxima in tensile and flexural strength for the blends containing about 1–3 wt % of EVA-*g*-MAH should be noted. The synergistic effect of those mechanical properties could be due to the compatibilizing effect of EVA-*g*-MAH for the PBT–LLDPE blend. It should be also noted that the impact strength of the blend remarkably increased with an increase in the copolymer contents (Fig. 9). A much more significant improvement was observed in the case of the EVA-*g*-MAH system than for the EVA system. This may be due
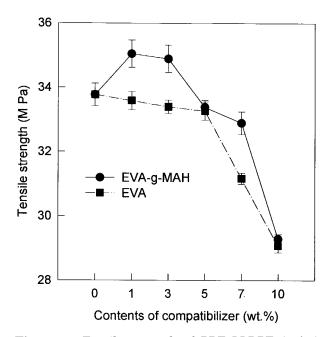
Figure 7 Tensile strength of PBT–LLDPE (70/30) blends with various compatibilizers.

Figure 9 Impact strength of PBT–LLDPE (70/30) blends with various compatibilizers.

to the compatibilizing effect of EVA-*g*-MAH for the PBT–LLDPE blend.

The addition of compatibilizers usually increases the melt viscosity of immiscible blends due to the increasing interaction between components in the sense of rheology. Typical results can
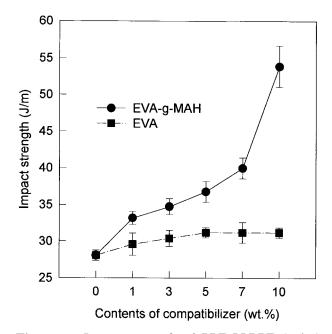
be shown in case of the EVA-*g*-MAH added blends. Figure 10 shows the effect of EVA-*g*-MAH contents on the melt viscosity of the PBT–LLDPE blend. One can easily see that the melt viscosity increases with increasing EVA-*g*-MAH contents. It may be thought that the increase of the viscos-
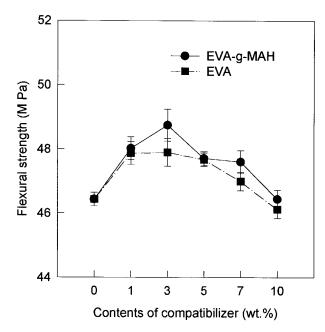

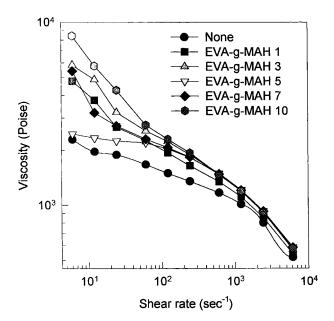**Figure 8** Flexural strength of PBT–LLDPE (70/30) blends with various compatibilizers.

Figure 10 Viscosity changes of PBT–LLDPE (70/30) blends compatibilized with different contents of EVA-*g*-MAH.
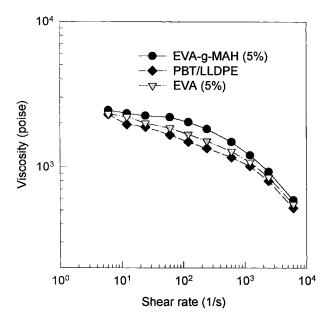
Figure 11 Melt viscosity of PBT–LLDPE (70/30) blends with different compatibilizers (the wt % of a compatibilizer was fixed at 5%).

ity may be related to the expected grafting reaction and the increased interfacial interaction of the compatibilizers locating at the interface. A higher compatibilizer content is expected to cause more graft reaction. The viscosity increase is larger in the case of the EVA-*g*-MAH than EVA. Figure 11 shows the effect of different compatibilizers on the melt viscosity of the blend. In this figure, the content of the compatibilizer is 5 wt %. The rheological and mechanical results suggest that EVA-*g*-MAH exhibits a better compatibilizing effect for 70/30 PBT–LLDPE blend than EVA. The enhanced compatibility of the MAH-modified EVA in comparison with EVA may be expected because of the intermolecular dipole-dipole interaction between the carbonyl oxygen (δ^-) in maleic anhydride (MAH) of the EVA-*g*-MAH and the hydrogen in the hydroxyl group (δ^+) of PBT. The enhanced compatibility may be also due to the potential reactivity of MAH with the hydroxyl ends of PBT to form a graft copolymer, PBT-*g*-EVA, at the interface between PBT and LLDPE.

CONCLUSIONS

The impact strength of the PBT–LLDPE binary blends slightly increased at lower concentrations of LLDPE but remarkably increased above a concentration of 60 wt % of LLDPE. The morphology of the blends showed that the LLDPE particles were dispersed in the PBT matrix below 40 wt % of LLDPE, while, at 60 wt % of LLDPE, a co-continuous morphology was obtained, which could explain the increase of the impact strength of the blend. Generally, the mechanical strength was decreased by adding LLDPE to PBT.

Addition of EVA-*g*-MAH as a compatibilizer to PBT–LLDPE (70/30) blend considerably improved the impact strength of the blend, even though tensile strength and flexural strength slightly decreased with small amounts of the compatibilizers. The tensile strength and the flexural strength, however, showed maxima at contents around 1–3 wt % of EVA or EVA-*g*-MAH, due to their compatibilizing effect for the PBT–LLDPE blend. A more distinct improvement in those mechanical properties is observed in the case of the EVA-*g*-MAH system than for the EVA system. This may be due to interaction between maleic anhydride functional groups in EVA-*g*-MAH with the hydroxyl ends of PBT.

The increase of the viscosity may be related to the expected grafting reaction and the increased interfacial interaction of the compatibilizers locating at the interface. A higher compatibilizer content is expected to cause more graft reaction. A larger viscosity increase was also observed in the case of the EVA-*g*-MAH than EVA.

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