

COMPATIBILIZATION OF RECYCLED HIGH DENSITY POLYETHYLENE (HDPE)/POLYETHYLENE TEREPHTHALATE (PET) BLENDS

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Abstract

Immiscible blends of recycled high density polyethylene (HDPE) and polyethylene terephthalate (PET) were compatibilized with maleic anhydride grafted polyethylene (PE-g-MA). The effect of the compatibilizer content on the mechanical, morphological, rheological, and thermal properties of recycled HDPE/PET blends was investigated. The blends were prepared in a twin screw extruder. Tensile strength, tensile strain at break, and impact strength improved with the addition of the compatibilizer. The compatibilized blends had a smaller size of dispersed phase compared with the uncompatibilized blends. The addition of the compatibilizer increased the melt viscosity of the compatibilized blends. The compatibilizer affected on the crystallinity behavior of the blends.

Keywords: HDPE/PET blend, PE-g-MA, compatibilization, recycling

Introduction

High density polyethylene (HDPE) and polyethylene terephthalate (PET) have been widely used in packaging applications and constitute a large portion of post-consumer wastes. Recycling offers an alternative solution for handling plastic wastes. A mechanical recycling method which involves blending of the plastics is one of the solutions for recycling plastics. However, the immiscibility of HDPE and PET leads to poor interfacial adhesion and mechanical properties. The compatibility of immiscible blends can be improved by reactive and non-reactive compatibilization. The reduction of interfacial tension and improvement of interfacial adhesion and dispersion are

obtained. (Baker *et al.*, 2001)

Several researchers have studied the compatibilization of HDPE/PET blends using compatibilizers. Dagli and Kamdar (1994) discussed the effects of component addition on the reactive compatibilization of HDPE/PET blends. Ethylene glycidyl methacrylate copolymer (EGMA) was very effective in compatibilization of the blends. The different sequences and modes of component addition affected the mechanical and morphological properties of the blends. The best properties were obtained when EGMA was blended first with HDPE and then with PET. Guerrero *et al.* (2001) studied the effect of a copolymer of ethylene and methacrylic

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acid partially neutralized with zinc (Surlyn) on the mechanical properties of HDPE/PET blends. Elongation at break and impact strength of the blends increased due to a high adhesion between the two phases. The olefinic part of Surlyn was compatible with HDPE, whereas the carboxylic end groups formed hydrogen bonds with the carbonyl group of PET. Pietrasanta *et al.* (1999) pointed out that compatibilization of HDPE/PET blends could be obtained in one-step processing. Mechanical properties of the blends prepared by injection molding were better than those of blends prepared by extrusion followed by injection molding. Rate of shearing in the injection molding process was enough to ensure a dispersion of the dispersed phase and a reduction of interfacial tension. Torres *et al.* (2001) found that the statistical copolymer was more effective in compatibilizing HDPE/PET blends than the graft copolymer. Mechanical and morphological properties of the blends were improved with the addition of the copolymers. However, compatibilization with grafted copolymer was an interesting method because the synthesis of the graft copolymer was easier and cheaper than that of the statistical copolymer. Kalfoglou *et al.* (1995) investigated the compatibilizer effectiveness for PET/HDPE blends. Based on the morphological evidence and tensile testing, the best compatibilizing effect was obtained with copolymer containing epoxy functions because they could react with the hydroxyl and carbonyl end groups of PET. Akkapeddi and Van Buskirk (1992) reported that significant improvement in the toughness and heat resistance of PET/HDPE (1.8:1) blends at 10 wt% EGMA was observed.

Pracella *et al.* (2002) found that the effective compatibilization of HDPE/PET systems was determined by the effect of the type and content of the reactive compatibilizer and mixing procedures. Significant improvement of the tensile properties of the blends was obtained by the addition of EGMA lower than 5 wt%. Lusinchi *et al.* (2001) studied the in situ compatibilization of HDPE/PET blends. HDPE-*g*-MA formed first in the molten state and then the anhydride groups reacted with the end group of PET. The one-step processing offered better

results compared with those blends obtained by adding of graft copolymer to the blends. Pawlak *et al.* (2002) reported that the elongation at break and impact strength of recycled HDPE/PET blends increased with the addition of EGMA or maleic anhydride grafted styrene-ethylene butylene-styrene (SEBS-*g*-MA). The best results were obtained for PET/HDPE/EGMA at 75%/25%/4 pph and PET/HDPE/SEBS-*g*-MA at 75%/25%/10 pph. The mechanical properties of the blends were related to the phase dispersion. The increase in the viscosities of the compatibilized blends was observed due to the reaction during blending.

The objective of this study is to evaluate the effect of PE-*g*-MA as a compatibilizer on the mechanical, morphological, rheological, and thermal properties of recycled HDPE/PET blends. The efficiency of the compatibility is determined as a function of the compatibilizer content.

Methods

Recycled PET (drinking water and soft drink bottles) and recycled HDPE (drinking water bottles) were cleaned by water and ground by a mechanical grinder (Retsch). Before blending, the reground HDPE and PET were dried at 105°C and 160°C, respectively. The dried HDPE and PET (75/25 and 25/75 wt%) with and without the PE-*g*-MA (Fusabond® E MB 100D, DuPont) as a compatibilizer (2, 5, 7, 10 phr) were tumble-blended and fed into an intermeshing corotating twin screw extruder (Brabender) at a barrel temperature of 255-260-265 - 270°C. The screw speed was 50 rpm. The specimens for mechanical testing were prepared by injection molding (Chuan Lih Fa, CLF-80T). Tensile properties were studied by using a 5565 model INSTRON with a load cell of 5 kN. Tensile tests were followed the American Society for Testing and Materials (ASTM) D638 at a crosshead speed of 5 mm/min. Impact tests were performed according to notched Izod impact strength (ASTM D256) using Atlas testing machine. Blend morphologies were examined using a scanning electron microscope (SEM, JEOL model JSM 6400). The samples

were fractured in liquid nitrogen and coated with gold. The viscosities were measured at 270°C using a Kayeness Capillary Rheometer. The melting temperature and percent crystallinity of the blends were analyzed by a Perkin Elmer DSC-7 differential scanning calorimeter. The samples were first heated to 280°C, cooled to 40°C, and then re-heated to 280°C under nitrogen atmosphere. The heating and cooling rates were 10°C/min. The crystallinity of blend components is calculated from the ratio of the melting enthalpy (ΔH_m) on the 2nd run and melting enthalpy (ΔH_m^o) of 100% crystalline polymer. $\Delta H_{m, \text{crystalline PET}}$ is 119.8 J/g and $\Delta H_{m, \text{crystalline PE}}$ is 293.0 J/g. (Wunderlich and Dole, 1957).

Results and Discussion

The tensile properties and impact strength of HDPE, PET, and their blends are shown in Table 1. The properties of the uncompatibilized blends depend on the ratio of HDPE and PET. The tensile strength and Young's modulus of the

blends increase with PET concentration while the tensile strain at break and impact strength decrease. For both HDPE-rich blends and PET-rich blends, the tensile strength and tensile strain at break increase with an increase of the compatibilizer content. A large increase of the tensile strain at break is found for both PET-rich blends, from 0.04 to 0.18 mm/mm and HDPE-rich blends, from 0.08 to 0.34 mm/mm with increasing PE-g-MA content. The addition of the compatibilizer to the blends also increases the Izod impact strength. However, the Young's modulus of the compatibilized blends is lower than that of the uncompatibilized blends. This may be due to a toughening effect, leading to a decrease in modulus and an improvement in impact resistance. (Jabarin and Bhakkad, 1995) The result is in agreement with Pietrasanta *et al.* (1999) and Guerrero *et al.* (2001). Kunori and Geil (1980) reported that tensile failure of a polymer blend resulted from the adhesion between the matrix and dispersed phase through a crazing or dewetting effect.

Table 1. Mechanical properties of HDPE, PET, uncompatibilized and compatibilized HDPE/PET blends

Sample	Tensile strength (MPa)	Young's modulus (MPa)	Tensile strain at break (mm/mm)	Izod impact strength (J/m ²)
HDPE	Not broken	751.55	Not broken	19,187.17
PET	58.36	1,770.89	0.05	1,656.99
HDPE/PET 25/75	27.02	1,270.31	0.03	1,623.15
HDPE/PET/PE-g-MA 25/75/2	34.78	1,246.13	0.04	2,277.10
HDPE/PET/PE-g-MA 25/75/5	34.86	1,228.07	0.08	2,571.09
HDPE/PET/PE-g-MA 25/75/7	36.72	1,137.51	0.08	5,135.28
HDPE/PET/PE-g-MA 25/75/10	37.95	1,084.27	0.18	5,496.72
HDPE/PET 75/25	18.95	923.97	0.07	4,736.23
HDPE/PET/PE-g-MA 75/25/2	19.65	919.49	0.08	6,408.18
HDPE/PET/PE-g-MA 75/25/5	21.50	916.68	0.08	6,632.63
HDPE/PET/PE-g-MA 75/25/7	24.05	901.07	0.15	6,644.15
HDPE/PET/PE-g-MA 75/25/10	24.35	900.51	0.34	6,719.05

The morphologies of the HDPE-rich blends and PET-rich blends are shown in Figure 1. In case of the HDPE-rich blend, the dispersion of the dispersed component is better than that of the PET-rich blend. This result may come from that HDPE has higher viscosity than PET during blending. The viscosity of the HDPE and PET are shown in Figure 2. The dispersed phase sizes depend on the compatibilizer

materials. Figure 3 shows the viscosities of HDPE/PET blends without and with 2, 5, 7, 10 phr PE-g-MA. It can be seen that the viscosities of the blends decrease as the HDPE component in the blends decreases. The viscosities of the compatibilized blends are higher than those of the uncompatibilized blends and increase with the amount of the compatibilizer. The increase in the viscosities is due to the interaction

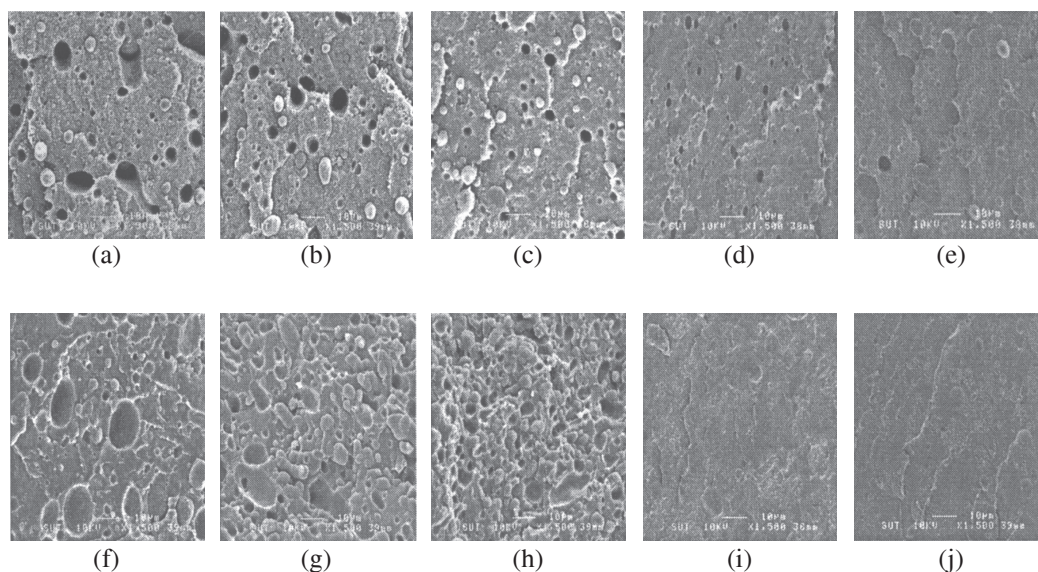


Figure 1. SEM micrographs (a) HDPE/PET 75/25 (b) HDPE/PET/PE-g-MA 75/25/2 (c) HDPE/PET/PE-g-MA 75/25/5 (d) HDPE/PET/PE-g-MA 75/25/7 (e) HDPE/PET/PE-g-MA 75/25/10 (f) HDPE/PET 25/75 (g) HDPE/PET/PE-g-MA 25/75/2 (h) HDPE/PET/PE-g-MA 25/75/5 (i) HDPE/PET/PE-g-MA 25/75/7 (j) HDPE/PET/PE-g-MA 25/75/10 (x1500)

content. Reduction in the size of the dispersed phase with an increase of the compatibilizer content is observed. The compatibilizer controls the morphology of the blends by preventing the coalescence and reduction of interfacial tension. The compatibilizer improves the adhesion between the two phases and leads to an increase in the mechanical properties.

The viscosities versus shear rate of HDPE, PET, and PE-g-MA are shown in Figure 2. HDPE is the most viscous among the three

between the compatibilizer and polymers during blending. (Dagli and Kamdar, 1994; Pawlak *et al.*, 2002; Pracella *et al.*, 2002) The melting point (T_m) and percent crystallinity ($\%X_c$) of HDPE, PET and their blends are listed in Table 2. DSC melting thermograms of the HDPE-rich blends and PET-rich blends are shown in Figure 4. For HDPE, the T_m is detected at 133.03°C and $\%X_c$ is 62.39%. The T_m and $\%X_c$ of PET are found to be 246.77°C and 20.87%, respectively. PE-g-MA affects

the melt behavior and crystallinity of the blend components. With an increasing PE-g-MA content, the % X_c of the HDPE and PET component in the HDPE-rich blends and PET-rich blends reduces. Depression of the % X_c of both the matrix and dispersed phase is due to the effects of the miscibility of the functionalized polyolefins with the HDPE phase and chemical reactions of functional groups with the chain end groups of PET at the interface of the melt. (Pracella *et al.*, 2002) Jabarin and Bhakkad (1995) suggested the decrease in crystallinity of the components is localized around the interfacial area between the two

components. Melting temperatures of the HDPE and PET component in the uncompatibilized and compatibilized blends do not change significantly compared with the HDPE and PET. This behavior is normal for immiscible polymers in the melt state. (Wilfong *et al.*, 1986) The similar results were obtained by Torres *et al.* (2001) and Park *et al.* (1996). Pang *et al.* (2000) studied PP/PET/PP-g-MA (75/20/5) blend and found that the change in melting enthalpy of PP component related to morphology changes of the blend: the finer the dispersed phase, the lower is the melting enthalpy value.

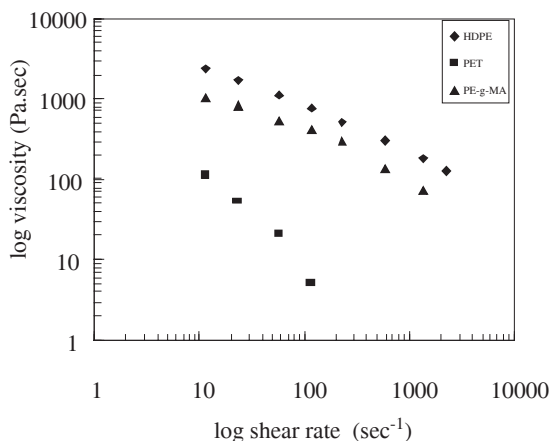


Figure 2. The viscosities versus shear rate of HDPE, PET and PE-g-MA measured at 270°C

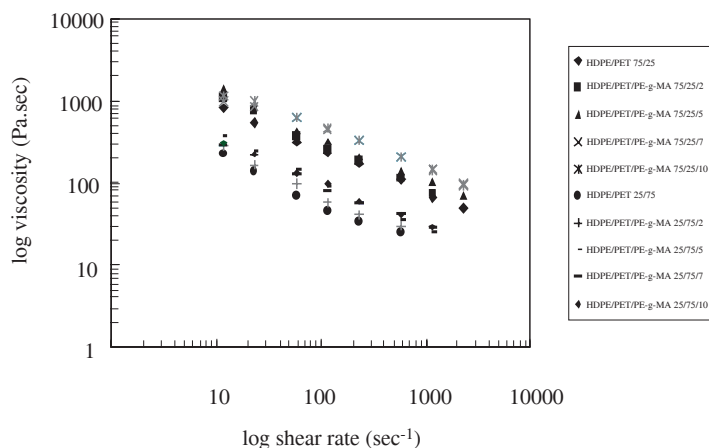
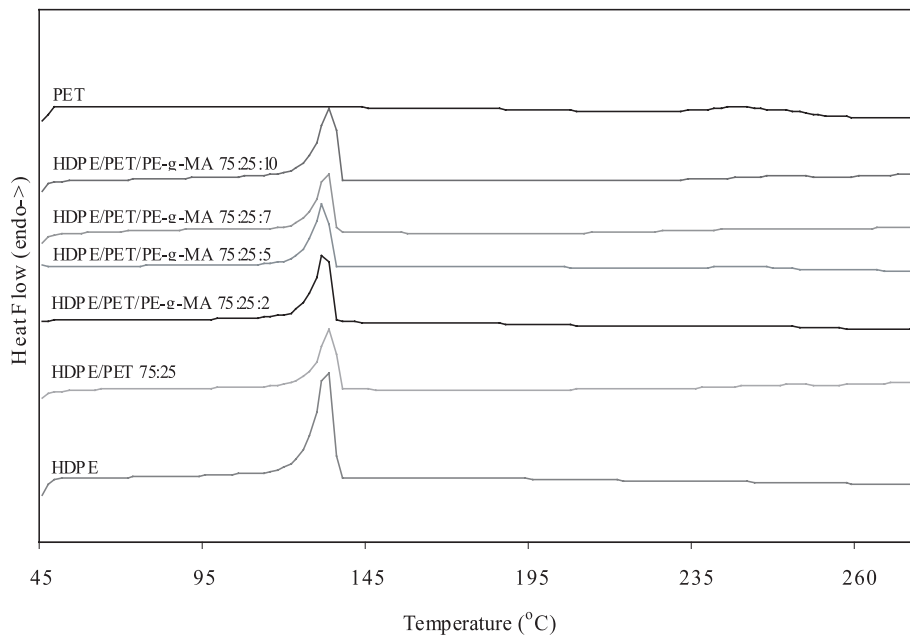
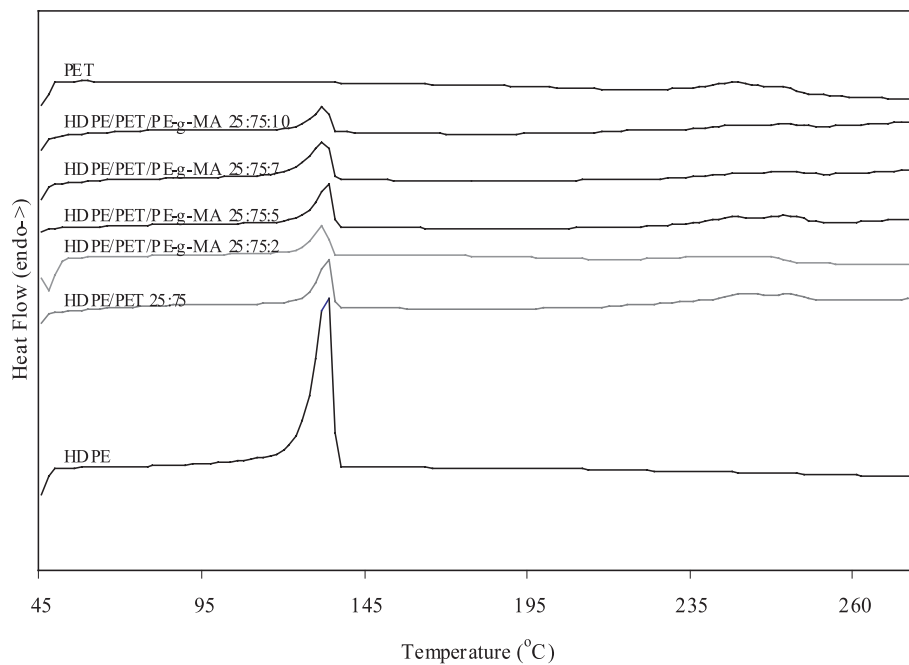


Figure 3. The viscosities versus shear rate of uncompatibilized and compatibilized blends measured at 270°C



(a)



(b)

Figure 4. DSC melting thermograms of HDPE, PET and blends (a) HDPE-rich blends (b) PET-rich blends

Table 2. Melting temperature (T_m) and percent crystallinity ($\%X_c$) of HDPE and PET in uncompatibilized and compatibilized HDPE/PET blends

Sample	HDPE component		PET component	
	T_m (°C)	$\%X_c$	T_m (°C)	$\%X_c$
HDPE	133.03	62.39	-	-
PET	-	-	246.77	21.87
HDPE/PET 25/75	132.90	14.04	248.90	20.69
HDPE/PET/PE-g-MA 25/75/2	132.67	12.18	248.43	18.22
HDPE/PET/PE-g-MA 25/75/5	132.76	13.87	248.91	15.40
HDPE/PET/PE-g-MA 25/75/7	132.44	12.17	248.64	6.60
HDPE/PET/PE-g-MA 25/75/10	131.69	11.02	248.59	5.62
HDPE/PET 75:25	133.11	45.13	248.52	4.04
HDPE/PET/PE-g-MA 75/25/2	132.69	41.78	246.65	2.95
HDPE/PET/PE-g-MA 75/25/5	132.37	40.25	246.10	3.44
HDPE/PET/PE-g-MA 75/25/7	132.61	39.20	248.29	3.30
HDPE/PET/PE-g-MA 75/25/10	133.33	34.18	248.60	3.31

Conclusions

The improvement of the morphology and mechanical properties of the blends can be achieved by adding the compatibilizer. The mechanical properties of the compatibilized blends enhance with an increase in the compatibilizer content. The improvements in blend ductility have been observed. Addition of the compatibilizer to the blends changes the morphology of the blends and decreases the dispersed phase size. This may result from the enhanced interaction between the matrix and dispersed phase. Maleic anhydride (MA) functionality of PE-g-MA may react with the hydroxyl group of PET.

Rheological properties of the blends are composition dependent. The increase in viscosities of the compatibilized blends is due to the interaction between the compatibilizer and polymers.

Thermal properties reveal that HDPE and PET influence each other crystallization processes. For the compatibilized blends, the %

crystallinity of the both components decreases with an increase of the compatibilizer content. This is due to the compatibility between the components.

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