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PET/LDPE REACTIVE COMPATIBILIZATION THROUGH THE CARBAMATE FUNCTIONALIZED EPM

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ABSTRACT

To investigate the effect of reactive compatibilization in the immiscible poly(ethylene terephthalate) (PET)/low-density polyethylene (LDPE) blend, ethylene-propylene copolymer-*g*-methacryloyl carbamate (MEPM) was prepared and used as a reactive compatibilizer. The interfacial reaction of carbamate group in MEPM with OH/COOH in PET was confirmed by measuring the interfacial tension between the PET and LDPE using the breaking thread method. The two-step blending process strongly influenced the blend morphology at high concentration of the dispersed phase in the blend. The MEPM showed a discrepancy in the reactive compatibilization ability with a blend sequence in the blends of different dispersed phase concentration.

Key Words: Reactive compatibilization; PET/LDPE blends; Carbamate; Interfacial reaction; Blend sequence

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INTRODUCTION

Polymer blends give an efficient method for improving their end-use properties. However, most polymers are thermodynamically incompatible and phase separate on blending. The satisfactory performance in immiscible polymer blends is usually attained by the compatibilization that minimizes an interfacial tension and improves an interfacial adhesion between the polymers.[1–3] Reactive melt blending methods that graft or block copolymers as compatibilizer and formed in situ by a reaction between complementary groups of the blend components in the blends are among many compatibilization techniques and have been widely investigated.[4–7] This reactive compatibilization has been demonstrated to be an effective and cost-efficient route in controlling the properties of various immiscible blend systems.[8–10]

In particular, reactive copolymers containing epoxy or oxazoline functional groups have been widely investigated due to their high reactivity to the low nucleophilic active hydrogen such as carboxyl, hydroxyl and anhydride groups.[11,12] Dagli et al.[13] and Liu et al.[14] reported that ethylene-glycidyl methacrylate copolymers and polypropylene (PP)-*g*-oxazoline copolymers were an effective compatibilizer in the blends of high-density polyethylene with polyethylene terephthalate (PET) and PP/acrylonitrile-*co*-butadiene-*co*-acrylic acid rubber (NBR) blends. Their investigations showed that the reaction between epoxy (or oxazoline) of ethylene (or PP) and carboxyl and hydroxyl of PET (or NBR) produced the in situ generation of copolymers and resulted in significant refinement of the blend morphology. Other than the above strongly electrophilic functional groups, the isocyanate (NCO) group was suggested in our previous works.[15–19]

The morphology of a polymer blend is determined by material parameters such as interfacial tension and viscosities of the components and by the processing parameters including blend sequence and temperature.[20] Favis et al.[21] and Kim et al.[22] showed the distinct role by interfacial tension and by coalescence on the morphology of polymer blend using a compatibilizer. The in situ copolymers reduced interfacial tension and suppressed the coalescence, which significantly affect the dispersed phase size. Also, the effects of blend sequence with a compatibilizer on the blend morphology were studied in immiscible blends.[23,24] However, until now, no research has been studied on the effects of blend sequence with a concentration of disperse phase in the blend morphology.

In this study, functional monomer, methacryloyl carbamate (MAC) having carbamate group as masked NCO functionality was synthesized and used in the synthesis of reactive polymer. Ethylene-propylene copolymer (EPM) functionalized with MAC (MEPM), reactive compatibilizer, was prepared by the solution grafting method and used to emulsify the blends of PET and low-density polyethylene (LDPE). We first present the Rayleigh stability of PET/LDPE blend in the presence of MEPM to examine the effect

of MEPM on the interfacial reaction between PET and LDPE. Then, we shall present a change of morphology of PET/LDPE blends with the concentration of MEPM to demonstrate the formation of in situ copolymer (EPM-*g*-PET) at the interfaces. Also, we shall represent the effect of blend sequence on the morphology in PET/LDPE blends.

EXPERIMENTAL

Materials

EPM (Kumho Polychem, ethylene content = ca. 69 wt%, $M_w = 1.11 \times 10^5$ g·mol^{-1}) was used as received. MAC was synthesized from a reaction of methacryl amide (Aldrich Chemical) with ethyl chloroformate (Junsei Chemical) as previously described in the literature.[17,19] Dicumyl peroxide (DCP, Aldrich Chemical) was used as a radical initiator. LDPE (Hanwha Chemicals, $M_w = 2.38 \times 10^5$ g·mol^{-1}), used as received and a bottle grade PET (SK Chemical Co., $M_w = 5.2 \times 10^4$ g·mol^{-1}), having end group concentrations of 42.3 mol/1000 kg OH and 29.2 mol/1000 kg COOH, was used after drying for 48 h under vacuum at 100°C.

Functionalization

The functionalization of the EPM was carried out in four neck round-bottom bottle equipped with overhead stirrer, condenser, thermometer, and a nitrogen gas inlet. The EPM (20 g) was dissolved in xylene (160 g) at 100°C under a nitrogen gas stream. DCP (0.2 g) and MAC (10 g) were added to this homogeneous solution and the reaction was continued for 2 h. The reaction mixture was then poured into the acetone under vigorous stirring. The precipitated graft copolymer was isolated and washed several times with acetone to eliminate unreacted monomer, initiator and homopolymers of MAC that could possibly be formed during the grafting reaction. Finally, the products were dried in a vacuum oven at 40°C for 24 h. The extent of grafting (0.3 wt%) was determined from ^{1}H-NMR spectroscopy.[17–19]

Blends

Blends of PET/LDPE containing MEPM copolymer were prepared with one-step and two-step by melt blending. For two-step blending, premixing virgin LDPE with MEPM was carried out prior to blend with PET. Then, molded LDPE/MEPM mixing samples were granulated and dry blended with the PET, using an internal mixer (Haake, Rheomix 900) at

270°C, 50 rpm for 5 min. Homopolymers were vacuum dried for 48 h at 70°C and the MEPM were dried for 1 week at 40°C under vacuum.

Measurements

The morphology of blend was observed by scanning electron microscopy (SEM, JSM-35CF, JEOL) from a cryogenically fractured (in liquid nitrogen) surface. A breaking thread method was used to measure the interfacial tension as follows. PET thread with the diameter of $50 \sim 70\,\mu m$ were melt spun from the capillary rheometer. To make a sandwich, a thread of 10 mm length is placed between two LDPE (or premixed LDPE with MEPM) sheets of $10 \times 10 \times 0.5$ mm dimension, and this composite was enclosed between two glass slides and placed on hot stage (Mettler, FP-82 HT) linked with optical microscope and heated up to 265°C. At the desired temperature, the distortion of the thread was photographed at regular intervals of time. The interfacial tension was calculated from Tomotika's equation.[25]

$$\sigma = \frac{\eta_m D_0 q}{\Omega(p, \lambda)} \tag{1}$$

where σ is the interfacial tension, η_m is the zero shear viscosity of the matrix, D_0 is the initial thread radius, q is the growth rate of thread distortion, and Ω is a function of wave length λ and viscosity ratio p. The growth rate q is determined from the plot of thread distortion amplitude vs. time, as obtained by analyzing the series of regularly taken photographs. Zero-shear viscosity of molten component was obtained by measuring the viscosity at different shear stress (Rheometric Scientific, ARES) and by extrapolating a Newtonian plateau value. The initial thread diameter was measured from an enlarged photograph. The $\Omega(p, \lambda)$ function was tabulated by Tomotika and was presented graphically by Elmendorp.[26]

RESULTS AND DISCUSSION

In Situ Compatibilization Effect of MEPM

According to our previous experimental results, the carbamate groups of MEPM can be activated above 140°C and form a chemical bonding with the end groups such as carboxyl or hydroxyl groups of PET. The reaction of carbamate with active hydrogen compounds may be a S_N 2 type reaction.[17] To confirm the presence of the in situ copolymers at the interface, the Rayleigh stability was observed for a PET thread embedded in a matrix of LDPE (or MEPM/LDPE mixture) using a breaking thread method. Figure 1 shows the distortion and its evolution with time for PET/LDPE and

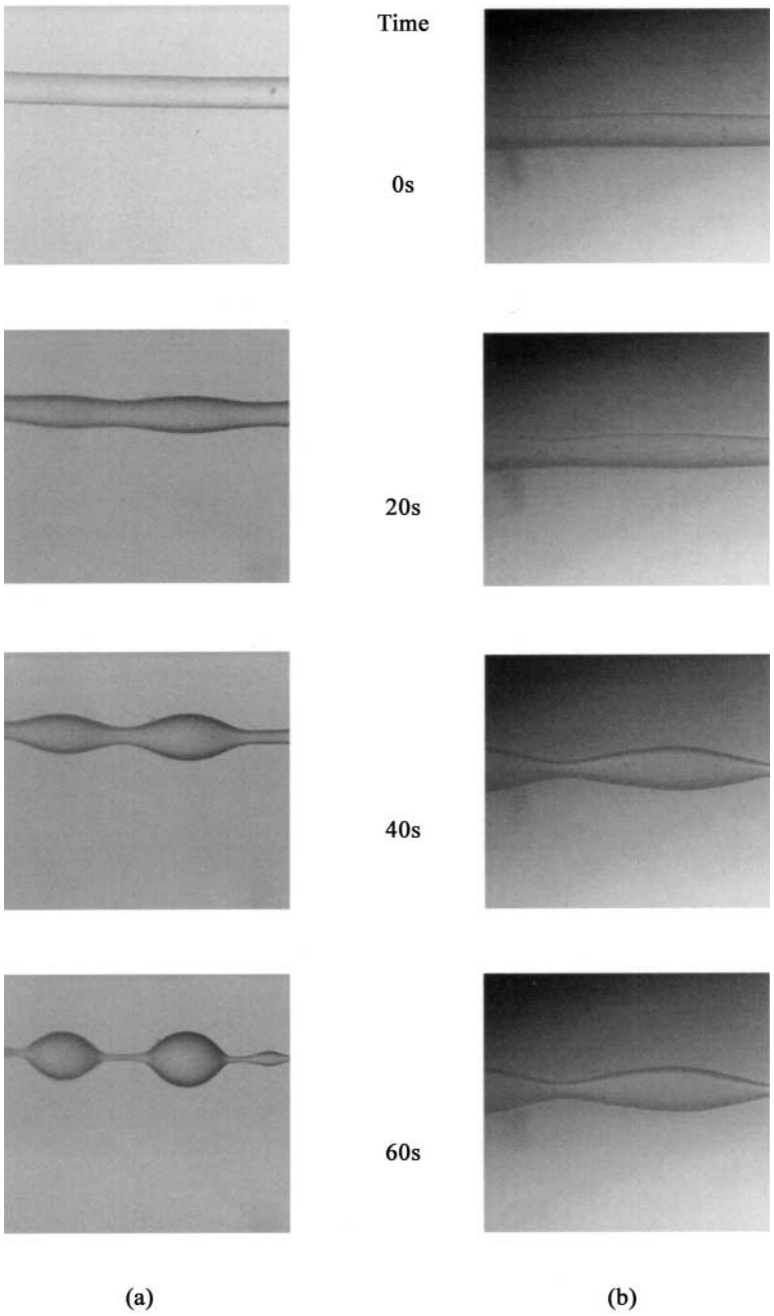

Figure 1. Typical examples of sinusoidal distortion (temperature 270°C): (a) PET thread/LDPE matrix; (b) PET thread/(LDPE/MEPM) matrix.

PET/(MEPM/LDPE mixture) system. The distortions of PET thread between the pure LDPE matrixes are rapidly developed, while the distortions corresponding to PET thread and LDPE/MEPM matrixes become suppressed.

Cho et al.[27] observed the interfacial reaction in a system of sulfonated PS and nylon 6. They suggested that the decrease of interfacial tension was induced by formation of a block copolymer at the interface, eventually leading to decreasing a distortion of thread. Viewed in this light, it is shown that during annealing time, chemical reactions between PET thread and MEPM/LDPE matrix produce the in situ copolymer, resulting in suppressing the distortion of PET thread.

The interfacial tensions for the different compositions are given in Fig. 2 as a function of the contents of MEPM present in the LDPE matrix. It is evident that the addition of MEPM to LDPE decreases the interfacial tension between PET and LDPE, indicating that MEPM act as interfacial active agent. This can be interpreted as a result of the chemical bond with

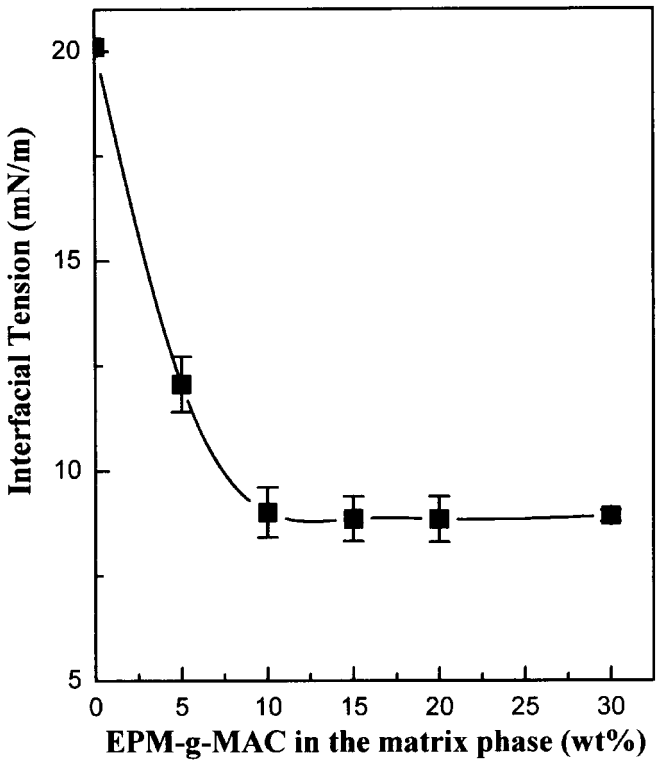

Figure 2. Dependence of the interfacial tension between LDPE (matrix) and PET (thread) as a function of the percentage of MEPM in the matrix.

the PET by reacting with the end groups of PET, causing the chemical reactions between carbamate groups of the MEPM and end groups of PET, as a consequence, in situ copolymers are formed at the interface of PET/LDPE.

Effect of Blend Sequence on the Morphology

The variations of the dispersed phase size upon the addition of compatibilizer are mainly caused by the interfacial tension, coalescence of the dispersed phase particles and blend sequence. In order to verify the relationship among these phenomena, morphology and emulsification curves of the 10/90 and 30/70 PET/LDPE blends with a blend sequence (one-step and two-step blend) were compared.

Figure 3 shows the cryogenically fractured surface of the PET/LDPE (10/90, 30/70) blends prepared without using MEPM. The size of the dispersed phase, PET particles, is significantly larger for the 30/70 PET/LDPE blend than for the 10/90 PET/LDPE. Several researchers[22,28] have reported that increasing the concentration of the dispersed phase led to the formation of the large dispersed phase particle due to the increased coalescence. So, the larger particle size for 30/70 PET/LDPE can be explained by the fact that coalescence of PET particles strongly occurs in the 30/70 PET/LDPE blends. Namely, at high concentration of dispersed phase in the blends, the size of dispersed phase was seriously larger than a low concentration of dispersed phase in the blends due to the extension of coalescence after immiscible blending.

A change in the size of the dispersed phase with the concentration of MEPM in PET/LDPE (10/90, 30/70) blend is illustrated in Fig. 4. The size of the dispersed phase decreases with an increase of MEPM concentration in all blend compositions. Unlike 10/90 PET/LDPE blends exhibiting a slight decrease in the size of the dispersed phase, 30/70 PET/LDPE blends shows a greater decrease in the size of the dispersed phase with an increase of MEPM concentration in blend compositions. This result indicates MEPM is more effective as reactive polymer at higher concentration of dispersed phase (PET). According to the above results, role of in situ copolymers was focused on reduction of interfacial tension and suppression of coalescence at high concentration of dispersed phase in the blends and concentrated on reduction of interfacial tension at low concentration of dispersed phase in the blends.

Cimmino et al.[29] observed a much-reduced dispersed phase size when the blends were prepared by the two-step in comparison to the one-step blend. They suggested that the mode of the added compatibilizer was found to be an important parameter determining the resultant morphology. So, we examined the size of dispersed PET particles in blend prepared with two

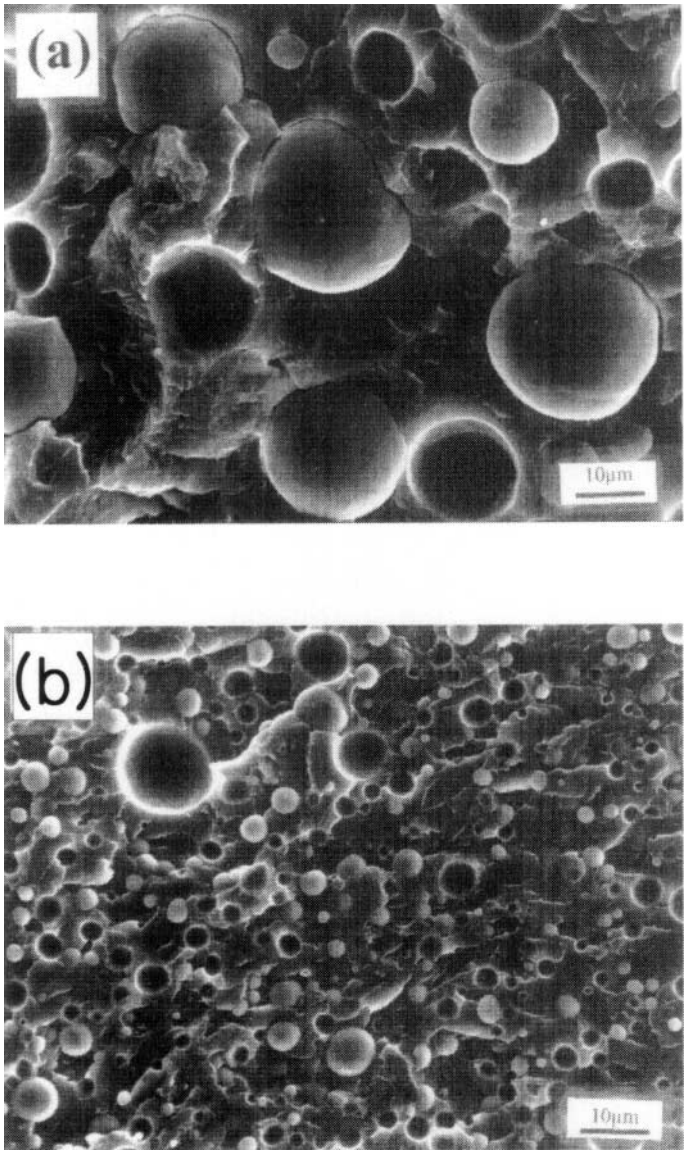

Figure 3. Morphologies of fractured surfaces for 30/70, 10/90 (wt/wt) PET/LDPE blends without compatibilizer: (a) PET/LDPE (30/70); (b) PET/LDPE (10/90).

different blend modes using SEM, which is illustrated in Fig. 5. At the same concentration of MEPM, PET/LDPE blends prepared with two-step blending showed a smaller size of dispersed PET particles than one-step blends.

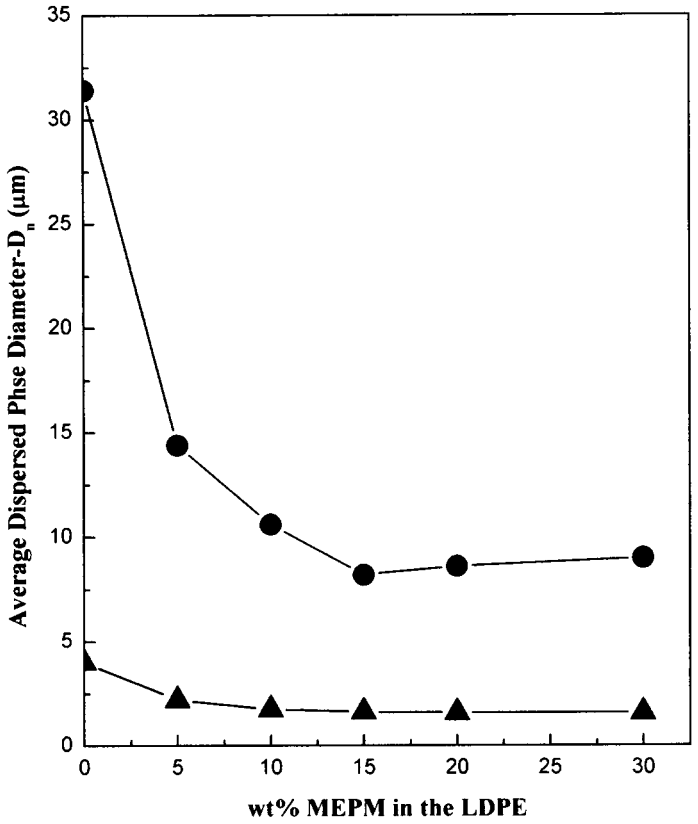

Figure 4. Plot of the average dispersed phase diameter (D_n) vs. the 30/70 and 10/90 (wt/wt) PET/LDPE blends as a function of MEPM content in LDPE: (●) 30/70 PET/LDPE blend, (▲) 10/90 PET/LDPE blend.

Figures 6 and 7 present a change of size of PET particles in the blends with MEPM content in LDPE prepared with blend sequence, respectively. The size of dispersed PET particles decreased as the concentration of MEPM increased. Two-step blends exhibited a larger decrease in the size of PET particles than one-step blends. In addition, the reduction extent of PET particles size increased by the two-step blends at high concentration of dispersed phase in the blends more than at the low concentration of dispersed phase in the blends. So, this smaller size of dispersed PET particles for two-step blends can be interpreted as being due to the formation of a larger amount of in situ copolymers through two-step blends. Also, effective compatibilization was achieved by the two-step blends at high concentration of dispersed phase in the blend. That is, larger amount of in situ copolymer are formed through the two-step blends and coalescence of dispersed phase

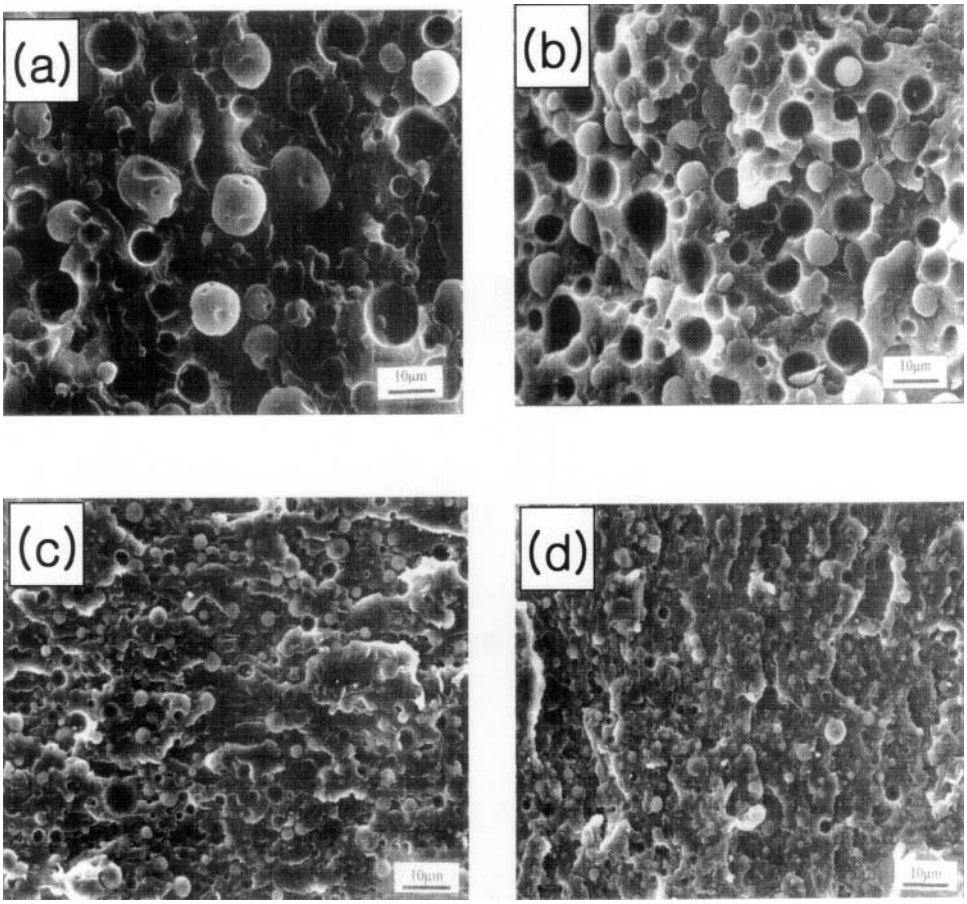

Figure 5. Morphologies of fractured surfaces for 30/70, 10/90 (wt/wt) PET/LDPE blends with the blend sequence as a function of dispersed phase concentration. 15 wt% MEPM concentration based on the LDPE weight: (a) PET/(MEPM/LDPE) (30/70) by the one step blend; (b) PET/(MEPM/LDPE) (30/70) by the two step blend; (c) PET/(MEPM/LDPE) (10/90) by the one step blend, (d) PET/(MEPM/LDPE) (10/90) by the two step blend.

particles are strong suppressed by the two-step blends at a high concentration of dispersed phase.

In order to establish a relationship among the interfacial tension, blend sequence and morphology, the average diameters (D_n) of the PET/LDPE blend without compatibilizer and at saturation are compared with their respective interfacial tension in Table 1. It can be seen that the D_n (initial)/D_n (critical) value for the 10/90 PET/LDPE blend is similar for the initial interfacial tension/critical interfacial tension. This indicates that there is a direct relationship between the interfacial tension and the morphology

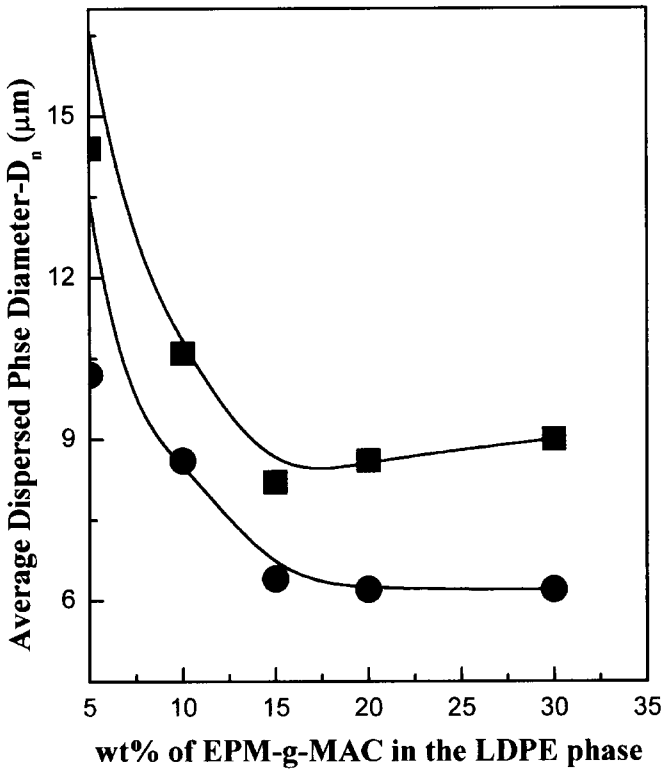

Figure 6. Plot of the average dispersed phase diameter (D_n) vs. the 30/70 (wt/wt) PET/LDPE blends with the blend sequence as a function of MEPM contents in LDPE: (■) one-step blend, (●) two-step blend.

under suppressed coalescence. Also, it was shown that the D_1/D_2 values were compared to the low concentration of dispersed phase blend with a high concentration of dispersed phase blend. The values have been increased at the high concentration of dispersed phase blends. From the above results, we concluded that the blend morphology was significantly affected with a blend sequence at the high concentration of dispersed phase in the blend.

CONCLUSION

The reactive compatibilizer, MEPM, having masked isocyanate groups was synthesized by a solution copolymerization of EPM with MAC. MAC containing EPM chains facilitated in situ formation of EPM-g-PET copo-

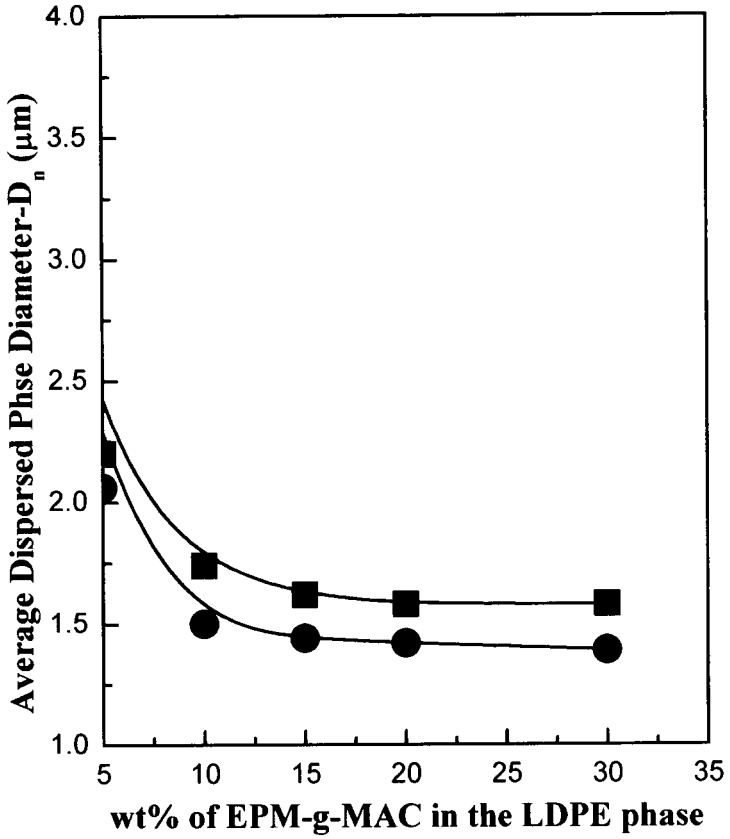

Figure 7. Plot of the average dispersed phase diameter (D_n) vs. the 10/90 (wt/wt) PET/LDPE blends with the blend sequence as a function of MEPM contents in LDPE: (■) one-step blend, (●) two-step blend.

lymers by a reaction between carbamate groups of EPM and end groups of PET, which was confirmed by the decrease of distortions of PET thread and interfacial tension between the PET and LDPE. Each PET/LDPE blend prepared with two different ratio of (30/70 and 10/90) PET/LDPE blend exhibited a size decrease of dispersed PET particles in matrix with an increase of the concentration of MEPM in blend composition. However, a greater concentration of PET (30 wt%) in PET/LDPE blends having greater coalescence cause a larger decrease in the size of PET particles with the MEPM concentration increase compared to 10/90 PET/LDPE blends. Also, at the same concentration of PET and MEPM in the blend compositions, the size of PET particles in LDPE matrix was largely changed with the blend sequence.

Table 1. Dispersed Phase Size (D_n) for (10/90, 30/70) PET/LDPE Blends with Blend Sequence and Interfacial Tension Between PET and LDPE Without MEPM and Saturation

	Without EPM-g-MAC	Critical[a]	Initial/Critical[b]	D_1/D_2[c]
D_1 (30/70 PET/LDPE) (μm)	31.46	8.19[a]	3.84[b]	
D_2 (30/70 PET/LDPE) (μm)	31.46	6.13[a]	5.13[b]	1.34
D_1 (10/90 PET/LDPE) (μm)	4.21	1.74[a]	2.42[b]	
D_2 (10/90 PET/LDPE) (μm)	4.21	1.62[a]	2.60[b]	1.07
Interfacial tension (mN/m)	20.11	9.31[d]	2.16[e]	

D_1; dispersed phase size by one-step blend D_2; dispersed phase size by two-step blend
[a]15 wt% MEPM concentration based on the LDPE weight;
[b]The dispersed phase size at 0 wt% MEPM concentration are divided dispersed phase size at critical concentration of MEPM;
[c]The dispersed phase sizes at critical concentration of MEPM by the one-step blend are divided dispersed phase sizes at critical concentration of MEPM by the two-step blend;
[d]15 wt% MEPM concentration based on the LDPE weight;
[e]The interfacial tension at 0 wt% MEPM concentration are divided interfacial tension at critical concentration of MEPM.

That is, the blend morphology was significantly affected with a blend sequence at a high concentration of dispersed phase in the blend.

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