

## Reactive Compatibilization of an Immiscible Polyester/Polyolefin Blend with PP-g-MAH and PMPI Dual Compatibilizers

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**ABSTRACT:** Blends of a polyester hot melt resin and a poly- $\alpha$ -olefin hot melt resin were modified using the reactive compounding technique. The effects of the compatibilizers were evaluated by studying the mechanical properties, the morphology, and the thermal properties of the modified blends. A pronounced compatibilizing effect was obtained with dual compatibilizers composed of maleated polypropylene and poly[methylene (phenylene isocyanate)] (PMPI). The addition of 1 phr of PMPI was sufficient to improve the elongation and tensile strength. From the results, it is anticipated that PMPI can be used as an efficient coupler to enhance the compatibility of immiscible polyester/polyolefin blends. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40232.

**KEYWORDS:** blends; compatibilization; morphology; mechanical properties

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### INTRODUCTION

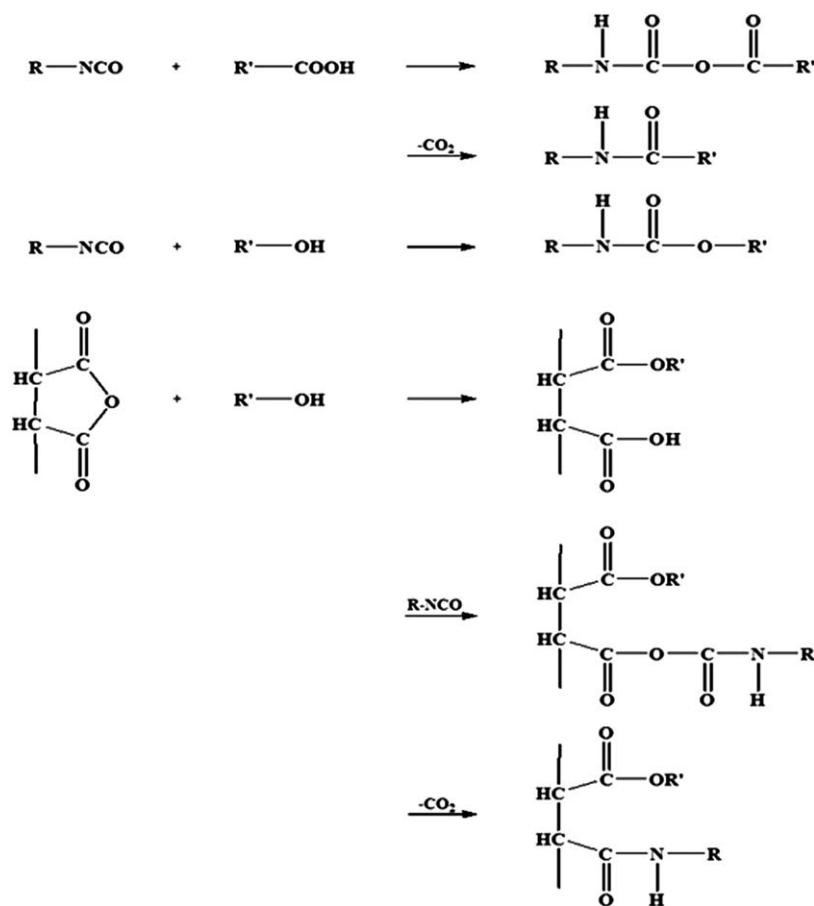
Polymer blending is one of the most attractive methods to develop new materials with a useful property balance.<sup>1–3</sup> However, the rule of mixtures (which predicts that blend properties will be the average of their ingredients) generally does not hold in polymer blends because the blend components are usually immiscible. Hence, the basic requirement for the development of a useful set of properties through blending is compatibilization of the immiscible constituents. By applying a compatibilization method, the interfacial properties of an immiscible polymer blend are suitably modified, such that desired morphologies and properties are obtained. The two methods of compatibilization that have found practical application are (i) incorporation of a separate chemical compatibilizer such as non-reactive graft or block copolymers into an immiscible polymer blend during melt compounding<sup>4</sup> and (ii) reactive compounding to form *in situ* a compatibilizer.<sup>5</sup> The reactive compounding technique utilizes a copolymer containing functional groups that are able to react with one (or more) of the blend components to form graft or block copolymers during melt blending. These *in situ* formed compatibilizers are believed to interact with the component polymers of the blends, reducing the interfacial tension, enhancing the interfacial adhesion, and stabilizing the domain structure.

Blends of thermoplastic polyesters and polyolefins are considered as one of important groups of polymer blends.<sup>6–10</sup> The primary reason for blending polyolefins with polyesters is to combine the high impact strength of the former at low temper-

ature with the solvent resistance and good mechanical properties of the later. Other benefits include good processibility and cost reduction.

It is well known that polyesters and polyolefins are immiscible. As polyolefins do not contain reactive functionality, adding functionalized copolymers that are miscible with polyolefins is an effective approach for reactive compatibilization. Copolymers functionalized with maleic anhydride (MAH) or glycidyl methacrylate (GMA) have often been used as reactive compatibilizers.<sup>2,11–13</sup> In some cases, two kinds of compatibilizers have been used simultaneously. Ju and Chang<sup>14</sup> reported that dual compatibilizers composed of styrene maleic anhydride (SMA) random copolymer and poly[methylene (phenylene isocyanate)] (PMPI) effectively compatibilized the immiscible and incompatible blends of poly(ethylene terephthalate) (PET) and polystyrene (PS). They found that PMPI reacted with PET and SMA to form PET-*co*-PMPI-*co*-SMA copolymers at the interface. These copolymers were able to anchor along the interface and serve as efficient compatibilizers. Consequently, significant improvements in mechanical performance were achieved. They also showed that the crystallization behaviors of the PET component in compatibilized blends were hindered because of the presence of the *in situ* formed copolymer molecules. Lumlong et al.<sup>15</sup> also demonstrated that the combination of a random copolymer with GMA and PMPI provided dual compatibilization and a new approach to improve the mechanical properties of polyester blends.

Polyester hot melt resins are generally considered high performance adhesive in terms of thermal stability, adhesion to nonporous



**Scheme 1.** Possible reactions of PMPI with component polymers.

surface, and oil resistance. Their properties can be tailored by altering monomer ratios in the polymerization batch, where the applicable monomers include terephthalic acid, butanediol, and aliphatic dibasic acids. Poly- $\alpha$ -olefin hot melt resins are based on the chemistry of propylene, ethylene, 1-butene, and 1-hexene. Properties of the poly- $\alpha$ -olefin polymers can be controlled via variation of the monomer composition, molecular weight, and chemical modification. In this study, polypropylene grafted with MAH (PP-*g*-MAH) and PMPI were employed as dual compatibilizers in blends consisting of a polyester hot melt resin and a poly- $\alpha$ -olefin hot melt resin. We report on the specific compatibility and correlation with resultant morphological, thermal and mechanical properties. In particular, we demonstrate that PMPI can be used as an efficient coupler to improve the compatibility of immiscible polyester/polyolefin blends.

## EXPERIMENTAL

### Materials

The materials employed in this study were commercially available saturated polyester and poly- $\alpha$ -olefin hot melt resins. The polyester was SKYBON ES-100, supplied by SK Chemical (Korea) and had a number-average molecular weight  $M_n$  of  $2.6 \times 10^4$  and a softening point of  $140^\circ\text{C}$ . The poly- $\alpha$ -olefin was Vestoplast 828, obtained from Evonik Degussa, and according to the supplier it is a propylene-rich copolymer with  $M_n = 1.32 \times 10^4$ . Hereafter, the polyester and poly- $\alpha$ -olefin resins used in this study are denoted as ES100 and VP828, respectively. The compatibilizer used was

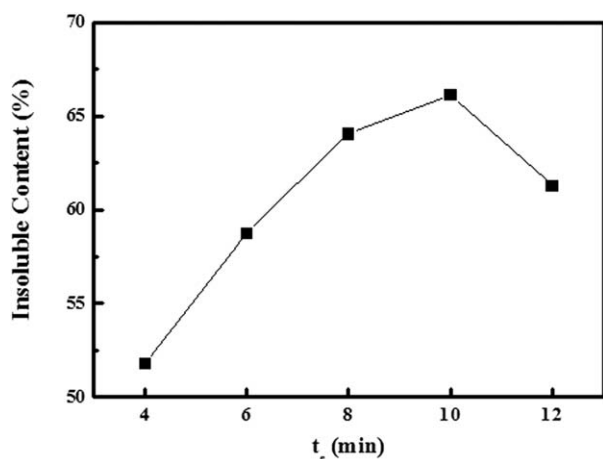
1 wt % MAH grafted PP (Polybond 3200, Chemtura). The reactive coupler, PMPI with 2.7 isocyanate groups per chain, was obtained from BASF Chemical Co.

### Blend Preparation

Resin materials were dried at  $80^\circ\text{C}$  for 24 h prior to melt-mixing. PMPI was dried at  $60^\circ\text{C}$  for 2 h before being used. All blends were prepared in a Brabender Plasticorder internal mixer. The temperature was controlled at  $220^\circ\text{C}$  and the rotational speed was set at 40 rpm. During the mixing, a small amount of mixed melt was picked up by a pincette at appropriate intervals and was quickly quenched in liquid nitrogen to prevent reactions.

### Characterization

The quenched specimen was treated with chloroform. In chloroform, the selective solvent used in this work, ES100 is soluble whereas VP828 is not. Soluble and insoluble fractions in chloroform were separated, dried, and weighed. Tensile specimens were prepared using a hot pressing machine. Tensile tests were carried out with a universal testing machine (H25K-S, Hounsfield) at room temperature with a gauge length of 30 mm and a crosshead speed of 250 mm/min. Results presented are an average of tests of five specimens. The morphology of the blends was studied by scanning electron microscopy (SEM). The compression-molded specimen was fractured in liquid nitrogen. The resulting fracture surface was coated with gold and examined with a JEOL 6400V SEM. A thermal analysis was performed using a Perkin Elmer DSC-7



**Figure 1.** Solubility in chloroform for ES100/VP828/PP-g-MAH/PMPI blend with melt-mixing time,  $t_s$ .

differential scanning calorimeter (DSC). The DSC cooling thermograms were obtained by annealing the samples for 5 min at 230°C and cooling them at a rate of  $-10$  °C/min. The melting thermograms were obtained by heating the samples at a rate of 10 °C/min under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

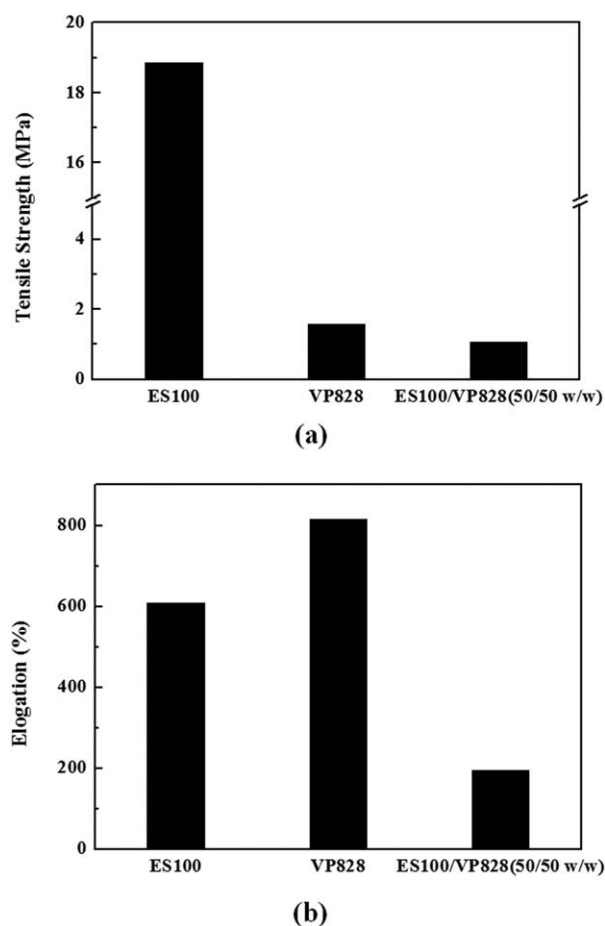
Blends composed of polyesters and functionalized copolymers have been extensively studied.<sup>14,16–19</sup> Several types of copolymers functionalized with MAH, GMA, or oxazoline (OXA) have been introduced as the counterpart of the polyester. In the case of blends involving MAH, contradictory results have been reported in the literature on the reactivity between MAH and the polyester end groups. Ju and Chang<sup>14</sup> and Oyama et al.<sup>17</sup> found that the reaction between the MAH group and the hydroxyl group was unlikely to occur or occurred insignificantly. However, a combination of a copolymer functionalized with MAH and PMPI was demonstrated to induce reactions between the component polymers. The isocyanate group of PMPI is able to react with the MAH group of the copolymers and the terminal groups of the polyester, i.e. both  $-\text{COOH}$  and  $-\text{OH}$ . The possible reactions of PMPI with the component polymers are illustrated in Scheme 1. In ES100/VP828/PP-g-MAH/PMPI blends, the PMPI molecules would act not only as a chain extender of the polyester to form ES100-*co*-PMPI-*co*-ES100 but also as a joint to create ES100-*co*-PMPI-*co*-PP-g-MAH. Here, the desired copolymer, ES100-*co*-PMPI-*co*-PP-g-MAH, is believed to anchor along the interface and serve as an efficient compatibilizer for the ES100/VP828 blends.

The reactivity between PMPI and component polymers was investigated by solubility testing. A blend of ES100/VP828/PP-g-MAH/PMPI at a weight ratio of 50/50/3/1 was prepared by mixing at 220°C for the test. Figure 1 shows the change in the soluble weight fraction with melt-mixing time,  $t_s$ . In the absence of any reactions, the soluble weight fraction for the blend may remain constant at about 50 wt %. On the other hand, when reactions take place, a progressive shift toward larger amounts of soluble or insoluble fraction is expected because copolymers such as ES100-*co*-PMPI-*co*-ES100 and ES100-PMPI-*co*-PP-g-

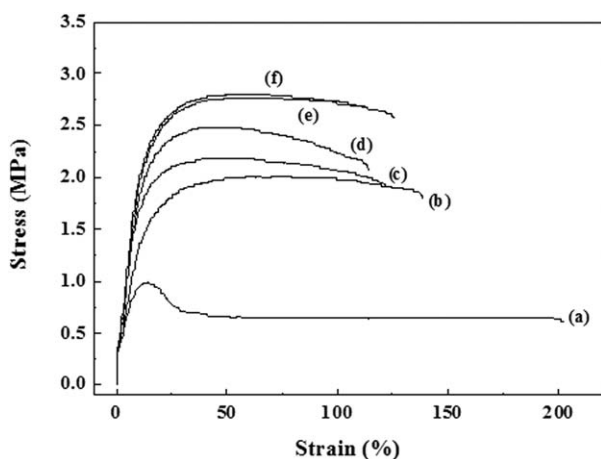
MAH formed by the reactions have different solubility. The increase in the insoluble fraction implies that the reactions occur in the presence of PMPI, leading to the formation of desirable copolymers. The decrease in the insoluble fraction for  $t_s > 10$  min can be attributed to shortening of the chain length due to thermal degradation during melt-mixing.

The tensile properties of the ES100/VP828 (50/50 wt/wt) blend and the pure component polymers are compared in Figure 2. The blend without compatibilizing agent shows poor elongation and strength on account of the incompatibility between ES100 and VP828. The results indicate that compatibilization may be required to obtain improved mechanical properties in the ES100/VP828 blend system.

Figure 3 shows stress–strain curves for uncompatibilized blend and compatibilized blend with various amounts of PP-g-MAH. The tensile strength of the compatibilized blends is enhanced progressively with an increase of PP-g-MAH content. Such an increase in tensile strength indicates that PP-g-MAH has compatibilizing effect. However, the compatibilized blends exhibit a large decrease in tensile elongation. Generally, strain at break has been used to evaluate the degree of compatibility in polymer blends, as it is sensitive to adhesion strength between blend components.<sup>20–24</sup> Therefore, the large decrease in tensile



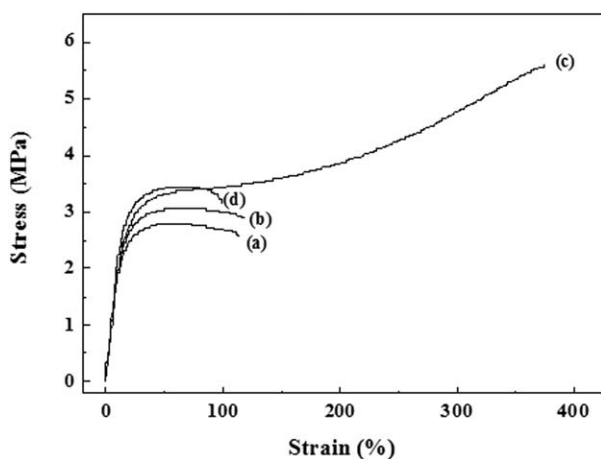
**Figure 2.** Tensile properties of ES100/VP828 (50/50 wt/wt) blend and pure component polymers: (a) tensile strength, (b) elongation.



**Figure 3.** Stress–strain curves for ES100/VP828 (50/50 wt/wt) blends compatibilized with various amounts of PP-g-MAH. Amount of PP-g-MAH: (a) 0 phr, (b) 1 phr, (c) 2 phr, (d) 3 phr, (e) 4 phr, (f) 5 phr.

elongation for the compatibilized blends with PP-g-MAH suggests that PP-g-MAH is not an effective compatibilizer for the blends of ES100 and VP828. The results also confirm a finding reported by other researchers,<sup>20,24</sup> that is, reaction between the anhydride group and the end-groups of polyester is unlikely to occur or occurred insignificantly.

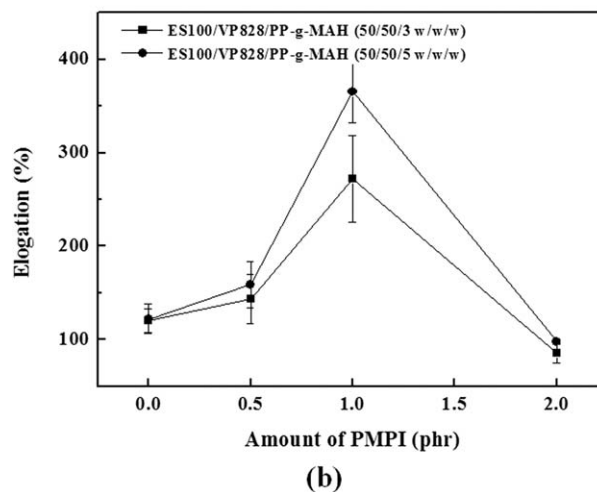
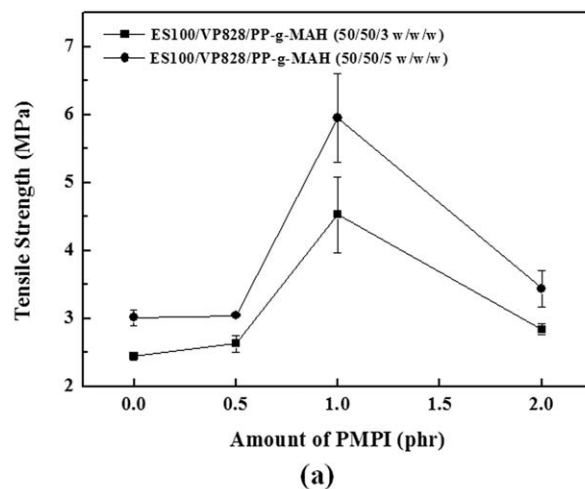
PMPI can react with the end-groups of ES-100 and the anhydride group in PP-g-MAH. Therefore, it is expected that copolymerization between ES100 and PP-g-MAH would be assisted by addition of the PMPI. The copolymer formation can bring about improved interfacial adhesion strength, leading to enhanced mechanical properties. Tensile tests were carried out for PMPI added ES100/VP828/PP-g-MAH (50/50/5 wt/wt/wt) blends. Samples containing PMPI were prepared by mixing at 220°C for 10 min. When the amount of added PMPI is 1 phr, the blend behaves in a ductile manner, as shown in Figure 4, whereas other samples exhibit no substantial improvement in tensile properties. The ductile behavior indicates that the desired copolymer formation by adding PMPI plays an impor-



**Figure 4.** Stress–strain curves for ES100/VP828/PP-g-MAH (50/50/5 wt/wt/wt) blends compatibilized with various amounts of PMPI. Amount of PMPI: (a) 0 phr; (b) 0.5 phr; (c) 1 phr; (d) 2 phr.

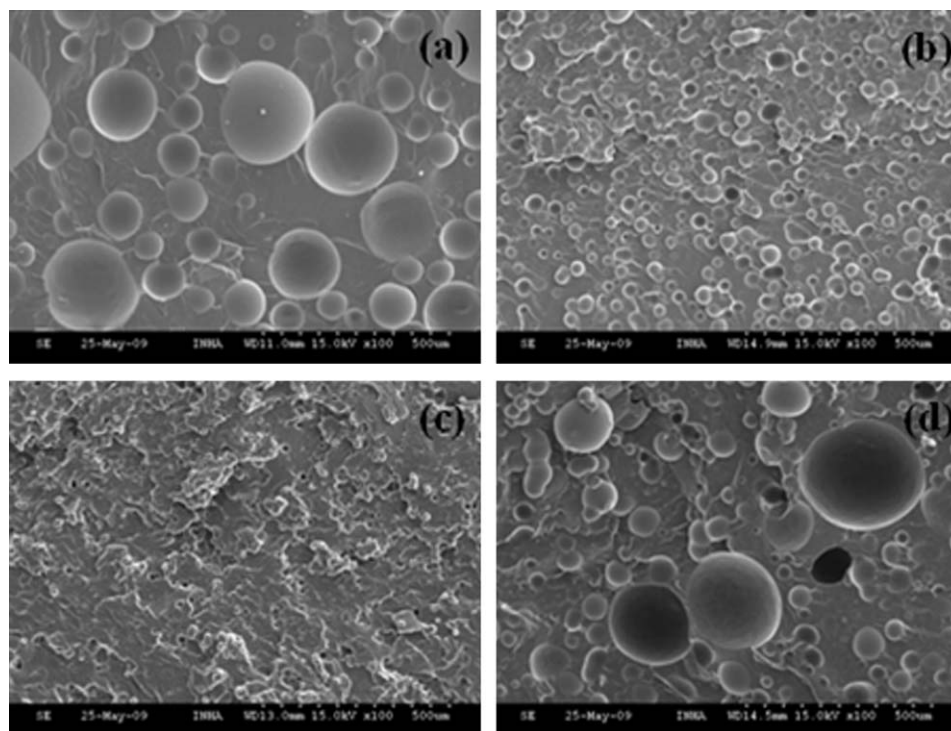
tant role in the improved interfacial adhesion strength of the blend system. Figure 5 shows the tensile properties of ES100/VP828 blends with different contents of PP-g-MAH as a function of the amount of PMPI. One interesting feature here is that the sample with a PMPI content of 2.0 phr shows very low tensile properties, having a similar value to the sample without PMPI. It is likely that the molecular weight of ES100 may increase as the amount of added PMPI is increased, because the reactions of PMPI with ES100 would cause chain extension and/or branching of the ES100 molecules. In general, an increase in the molecular weight of the component polymers deteriorates the blend compatibility.<sup>25–27</sup> Therefore, the negative effect of increasing the molecular weight on compatibility counterbalances the positive effect of increasing the amount of *in situ* formed ES100-co-PMPI-co-PP-g-MAH copolymers. As a result, it is considered that the maximum tensile properties are obtained for the sample with a PMPI content of 1.0 phr.

As is well known, SEM micrographs of fractured surfaces of blends and observation of their morphology, particle sizes, and degree of dispersion often provide useful information to elucidate the



**Figure 5.** Tensile properties of ES100/VP828 blends with different contents of PP-g-MAH as a function of amount of PMPI: (a) tensile strength, (b) elongation.



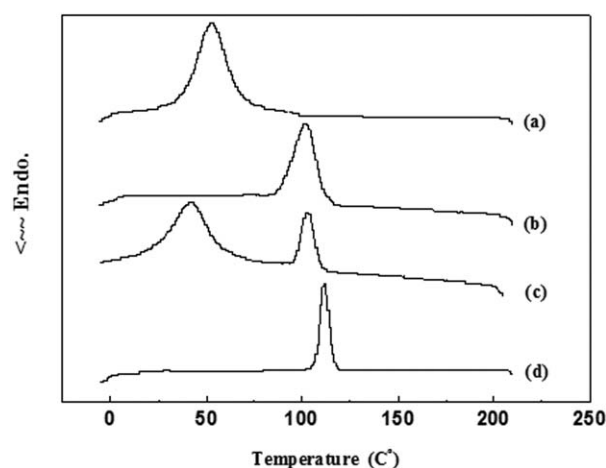


**Figure 6.** Typical SEM micrographs for blend samples: (a) ES100/VP828 (50/50 wt/wt), (b) ES100/VP828/PP-g-MAH (50/50/5 wt/wt/wt), (c) ES100/VP828/PP-g-MAH/PMPI (50/50/5/1.05 wt/wt/wt/wt), (d) ES100/VP828/PP-g-MAH/PMPI (50/50/5/2.1 wt/wt/wt/wt).

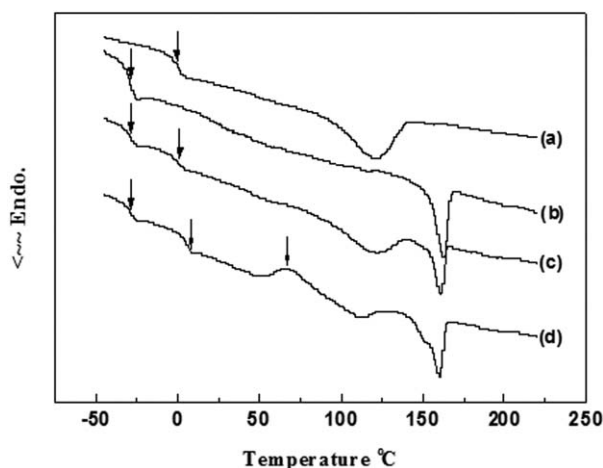
compatibility between the blend components or to evaluate the effectiveness of a compatibilizer.<sup>11,23,28,29</sup> Typical SEM micrographs for the blend samples are shown in Figure 6. Phase-separated domain morphology can be clearly observed in the ES100/VP828 blend due to the incompatibility of these two polymers [Figure 6(a)]. In Figure 6, ES100 exhibits a dispersed phase and VP828 forms a continuous phase, which was confirmed by a solvent extraction technique. With the presence of PP-g-MAH, the domain size of the ES100 dispersed particles substantially decreases [Figure 6(b)]. This illustrates that PP-g-MAH can reduce the interfacial tension between two immiscible polymers, thereby permitting a fine dispersion during melt-mixing. The formation of the desired ES100-co-PMPI-co-PP-g-MAH copolymers by introducing PMPI leads to lower interfacial tension and phase stabilization. Therefore, few spherical ES100 particles remain and a corded dispersed phase is mainly formed [Figure 6(c)]. As noted previously, a large amount of PMPI appears to be less efficient for compatibilization. As a result, the sample with a PMPI content of 2.0 phr shows a coarse morphology [Figure 6(d)]. Good agreement between the mechanical properties and the morphological structures further confirms that PP-g-MAH alone has some compatibilizing effect, but a combination of PP-g-MAH and PMPI is certainly better to improve the compatibility of the polyester/polyolefin blend system.

Figures 7 and 8 show the DSC cooling and heating thermograms for the pure polymers and blends, respectively. It is found that crystallization of the ES100 component in the PMPI added blend is significantly delayed, resulting in no observation of the crystallization peak during the cooling step. On the other hand, an exothermic peak due to the cold crystallization of ES100 appears during the heating step, as shown in Figure 8(d).

This reduction of the crystallization rate for the ES100 component in the PMPI added blend is attributed to the formation of copolymers. The ES100-co-PMPI-co-PP-g-MAH copolymer molecules anchored along the interface might hinder crystallization of the ES100 component. Decreased chain mobility due to an increase of molecular weight by chain extension and/or branching may also cause a further reduction of the crystallization rate for the ES100 component. The melting peak temperature of the ES100 component in the PMPI added blend is lower than that of the other samples. This result indicates that the copolymer molecules prohibit crystal formation and lead to less perfect



**Figure 7.** DSC cooling thermograms for pure polymers and blends : (a) ES100, (b) VP828, (c) ES100/VP828 (50/50 wt/wt), (d) ES100/VP828/PP-g-MAH/PMPI (50/50/5/1.05 wt/wt/wt/wt).



**Figure 8.** DSC heating thermograms for pure polymers and blends: (a) ES100, (b) VP828, (c) ES100/VP828 (50/50 wt/wt), (d) ES100/VP828/PP-g-MAH/PMPI (50/50/5/1.05 wt/wt/wt/wt).

crystals. It is worth noting that the PMPI added blend exhibits a much sharper crystallization exotherm of the VP828 component in comparison with the pure VP828. The reason for the higher crystallization peak temperature and narrow crystallization temperature range is somewhat unclear. One cause may be that the addition of PMPI induces reactions that serve to create highly branched points and/or crosslinks that are able to hold several molecules together and thus increase the probability of nucleation occurring in the VP828 phase. Figure 8 demonstrates that ES100 possesses a glass transition temperature of about  $3.9^{\circ}\text{C}$  ( $T_{g2}$ ). VP828 is a semicrystalline polymer with a glass transition temperature of  $-33.5^{\circ}\text{C}$  ( $T_{g1}$ ). In all blends, uncompatibilized and compatibilized, the corresponding  $T_{g1}$  does not shift. The constant value of  $T_{g1}$  suggests that mutual dissolution of ES100 and VP828 is negligible even after compatibilization. One interesting behavior is that the corresponding  $T_{g2}$  of the PMPI added blend shifts to higher temperature. This implies that the change in the molecular architecture due to copolymerization, branching, and/or crosslinking may cause restricted molecular motion of the ES100 component.

## CONCLUSION

PP-g-MAH alone was not an adequate compatibilizer in blends of ES100 and VP828 due to low reactivity between the functional groups. However, the combination of PP-g-MAH and PMPI provided effective dual compatibilizers for ES100/VP828 blends. Copolymers such as ES100-co-PMPI-co-PP-g-MAH *in situ* formed by adding PMPI showed lower interfacial tension and resulted in substantial changes of the phase morphology. Consequently, significant improvements in mechanical performance were achieved. From the results, it was found that PMPI could be used as an efficient coupler to enhance the compatibility of immiscible polyester/polyolefin blends.

## ACKNOWLEDGMENTS

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