

In Situ Compatibilization of Polystyrene/Polyethylene Blends using Amino-Methacrylate-Grafted Polyethylene

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SYNOPSIS

Blends of a styrene–maleic anhydride copolymer (SMA) with polyethylene (PE) or polyethylene melt grafted with tertiary (PE-g-DMAEMA) or secondary (PE-g-tBAEMA) amino methacrylate were prepared by blending in a batch melt mixer. The morphology of these blends at various compositions was examined with a scanning electron microscope (SEM) and related to their tensile and impact properties. The SMA/PE blends are found to have the typical coarse morphology of incompatible blends and poor mechanical properties, while their reactive counterparts, SMA/PE-g-DMAEMA or SMA/PE-g-tBAEMA blends, show finer morphology and modestly improved tensile and impact strength. This was attributed to chemical interaction of the acidic anhydride and the basic amino groups. The greater improvement in morphology for SMA/PE-g-tBAEMA than for SMA/PE-g-DMAEMA suggests a stronger interaction between the secondary amino groups and the anhydride groups, possibly with the formation of SMA-g-tBAEMA-g-PE graft polymer through amide covalent bonds. The amide formation appears to occur at the interfacial region in the blends and is too little to be detected by Fourier transform infrared (FTIR) spectra. However, differential scanning calorimeters (DSC) and the viscosity measurements indicate crystallinity and molecular weight changes for the SMA/PE-g-tBAEMA blends, supporting an argument for the formation of SMA-g-tBAEMA-g-PE grafts at the phase interface.

INTRODUCTION

Polymer melt blending has provided an economically viable and versatile way to produce new materials with a wide range of properties. In pursuing this opportunity, however, it is found that most polymer pairs are immiscible at the molecular level because of the very low entropy and enthalpy of mixing of macromolecules. The dispersed phase in immiscible polymer blends tends to form undesirably large domains that, furthermore, can coalesce during the postcompounding steps. Compatibilization of immiscible polymer blends is therefore very important to promote a finer and more stable dispersed phase, which, when optimized, can improve mechanical properties. A common method of compatibilization is the introduction of a third component, known as

compatibilizer, to the blend. The compatibilizer, usually a block or graft copolymer, comprises blocks chemically identical to or physically miscible with the respective components of the blend.

Compatibilization can also be achieved by melt blending two polymers containing functional groups that can react with each other. In such a case, a graft copolymer can form *in situ* during the melt blending, likely locating at the phase interface and enhancing compatibilization. This latter technique has received much attention recently because it eliminates the separate preparation of block or graft copolymers. Examples of *in situ* reactive compatibilization include the many studies on blending nylons with polymers containing acid-functional groups. Polymers grafted with maleic anhydride, such as ethylene–propylene rubber,^{1–3} HIPS,² ABS,² polypropylene,⁴ and ethylene–vinyl acetate copolymer,³ as well as polypropylene grafted with acrylic acid,⁴ partially neutralized poly(ethylene-co-methacrylic acid),⁵ and partially hydrolyzed styrene–

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methyl methacrylate diblock copolymer,⁶ have been used. The primary amino end groups in nylon molecules react with the acidic groups of the other polymer blend component to form block or graft copolymers *in situ* during the melt blending that serve as a compatibilizer for the blend. Blends of polystyrene containing oxazoline groups (OPS) with acidic polymers, such as an ethylene-acrylic acid copolymer⁷⁻⁹ and a terpolymer of acrylonitrile-butadiene acrylic acid,¹⁰ have also been the subject of investigation. The hydroxyl and carboxyl end groups in polyesters are potential reactive groups for *in situ* compatibilization blending. Thus, toughening polybutyleneterephthalate and polyethyleneterephthalate with copolymers of ethylene-ethylacrylate containing maleic anhydride or glycidyl methacrylate has been reported through reactive extrusion.¹¹

In studies on reactive blending of polymers, it became clear that, although there are several commercially available polymers containing acidic functionalities, few commodity or engineering polymers with basic functionalities are available. Attempts to make nucleophilic or basic functionalized polymers have successfully resulted in polyolefins grafted with a tertiary¹²⁻¹⁵ amine, 2-dimethylamino ethyl methacrylate (DMAEMA), or a secondary¹⁶ amine, *t*-butylamino ethylmethacrylate (*t*-BAEMA). A model study showed that secondary amino groups can form both ionic and covalent bonds, while tertiary amino groups can only form ionic bonds or polar interaction with polymers containing carboxylic acid or maleic anhydride groups.¹⁷ Preliminary studies on the potential interpolymer melt reaction between these basic graft polymers and acidic polymers have also been reported.^{16,18} The secondary amine in the *t*-BAEMA grafted linear low-density polyethylene (LLDPE) is capable of reacting with carboxylic acid in an ethylene-acrylic acid copolymer to form graft copolymer through amide linkages.¹⁶ However, chemical reaction between these amine-grafted polyethylenes and a styrene-maleic anhydride copolymer (SMA) appears to be limited.^{16,18} Nevertheless, the blend of the DMAEMA-grafted polyethylene with SMA was found to have a finer morphology, suggesting improved compatibility through polar interaction.¹⁸

In this article, a more extensive study on the blends of *t*-BAEMA- and DMAEMA-grafted polyethylene with SMA is reported. The objective is to evaluate and compare the compatibilization effect of these two reactive polymer pairs through measurement of morphology and mechanical and thermal properties of these blends.

EXPERIMENTAL

Materials

The reactive polystyrene used is a copolymer of styrene-maleic anhydride containing 6 wt % of maleic anhydride (SMA) with a weight average molecular weight (\overline{M}_w) of about 245,000 and polydispersity of $\overline{M}_w/\overline{M}_n = 1.2$ supplied by the Arco Company (Dylark 132). The polyethylene phase is composed of a linear low-density polyethylene either in its natural ungrafted form or in one of its grafted forms. The LLDPE supplied by ESSO Chemical Canada is an ethylene-butene copolymer with a density of 922 kg/m³, a \overline{M}_w of about 85,000, and a $\overline{M}_w/\overline{M}_n$ of about 4. The LLDPE was grafted with DMAEMA or *t*-BAEMA in a twin-screw extruder as described in previous papers.^{15,16} The grafting procedure resulted in some homopolymer of the amino methacrylate monomer intermingled in the polyethylene product. The grafted products were extracted with boiling water for 4 h to get rid of monomer residue and some homopolymer and then dried in a vacuum oven to give materials identified as PESC for *t*-BAEMA- and PETC for DMAEMA-grafted LLDPEs. Some grafted products were more thoroughly purified to remove all amino methacrylate homopolymer. The purification involves dissolving the grafted product in refluxing toluene and then precipitating with methanol as described in previous papers.^{15,16} Such purified materials were designated as PESD for *t*-BAEMA- and PETD for DMAEMA-grafted LLDPEs. The LLDPE was processed without any monomer or peroxide in the twin screw extruder at the same conditions as for the grafting process to give a control polyethylene material designated as PE. The properties of the polyethylene phase materials are summarized in Table I. Irganox 1010, a high-molecular-weight-hindered phenol antioxidant (AO), was used in the blend to prevent any possible degradation.

Procedures

All blends were melt blended in a Haake-Buchler Rheomix mixer, Model 600, with roller blades. The mixing variables were controlled through the System 40 control module. Before the preparation of the blends, torque measurements were made on each individual polymer in the mixer to assess their relative viscosity characteristics at the blending conditions used in this study following the technique developed by Favis and Chalifoux.¹⁹ The torque ra-

Table I Polyethylene Phase Materials

Material Code	Grafted Monomer	Degree of Graft, wt % (mol/kg)	Homopolymer Content, wt %	MFI ^a (dg/min)	Torque ^b Ratio
PE	no	0 (0)	0.0	4.7	1.05
PESC	t-BAEMA	1.62 (.088)	6.7	2.9	1.11
PESD	t-BAEMA	1.62 (.088)	0.0	2.1	1.15
PETC	DMAEMA	1.30 (.083)	7.2	4.7	0.72
PETD	DMAEMA	1.30 (.083)	0.0	4.6	0.97

^a ASTM D1238 Condition E: 190°C, 2,160 g.

^b Torque of PE phase/torque of SMA.

tios of the polyethylenes to the polystyrene are close to unity as shown in the last column of Table I.

A quantity of 60 g of the required polymers in the desired proportions and 0.1 wt % antioxidant were premixed in a beaker and then charged into the mixer, which was operated at 100 rpm and 220°C. All blends were processed for 20 min. Five series of blends were prepared from the five different polyethylene materials (Table I) by blending with the SMA in proportions ranging from 0 to 100% as listed in Table II.

The morphology of the blends was examined with a JEOL Model JSM 840 scanning electron microscope (SEM). The melt-blended samples were frozen directly in liquid nitrogen and fractured. The fractured surfaces of the samples were coated with gold to prevent charging.

Tensile testing was performed using an Instron tensile tester. Dumbbell-shaped specimens of 3 × 3.5 × 60 mm with a neck section of 20 mm in length were injection molded at 180°C. The samples were tested at room temperature. An initial gauge length of 20 mm and a constant cross-head speed of 12.7 cm/min were used. Impact testing was performed

with an instrumented Rheometrics drop-weight impact tester (RDT-5000) at room temperature using an impactor speed of 7.62 m/s. Round specimens of 38 mm diameter and about 2.3 mm thickness were injection molded at 180°C. The impact energies obtained from the instrumented impact test were normalized for the exact specimen thickness and reported as the relative impact energy (J/m). At least five specimens of each sample were used for the tensile or impact testing and average values of tensile strength, elongation at break, and impact energy were obtained. The results are summarized in Table III.

Thermal properties of the blends and the components were measured with a Mettler TA3000 thermal analysis system equipped with a DSC30 cell. The sample weight used was about 10 mg. To ensure similar thermal history for all the samples to be compared, a heating scan was first run at 20°C/min from 0 to 160°C for each sample. The sample was then quenched at a cooling rate of about 130°C/min to room temperature. A second heating scan, run at 10°C/min, was then performed and the differential scanning calorimetry (DSC) thermogram

Table II Compositions of the Blends

Blend Series ^a	Polymer Components					
	PE	PESD	PESC	PETD	PETC	SMA
EB x	10x	—	—	—	—	100 - 10x
SD x	—	10x	—	—	—	100 - 10x
SC x	—	—	10x	—	—	100 - 10x
TD x	—	—	—	10x	—	100 - 10x
TC x	—	—	—	—	10x	100 - 10x

^a x, the number in the series, is also the weight percent of polyethylene phase divided by 10.

Table III Tensile Strength (σ_b , MPa), Elongation at Break (ϵ , %), Relative Impact Energy (U, J/m), and Standard Deviation for σ_b (SD_{σ_b} , MPa) and U (SD_U , J/m) for various EB, SD, SC, TD, and TC blends

Series	Number in Series									
	1	2	3	4	5	6	7	8	9	10
EB										
σ_b	15.0	16.6	15.5	17.0	22.0	16.9	14.5	8.5	11.0	13.4
ϵ	9.1	9.1	9.3	9.4	9.8	12.8	39.5	100	332	399
U	5.4	75.9	65.4	104	99.7	251	650	3322	4321	5222
SD_{σ_b}	3.3	0.8	2.5	2.3	1.3	0.5	0.3	0.6	0.5	0.4
SD_U	0.26	9.1	7.6	13	5.0	23	91	456	244	138
SD										
σ_b	16.2	17.3	17.8	19.0	20.7	19.3	17.4	9.0	11.7	13.5
ϵ	9.4	9.1	9.1	9.3	10.1	11.1	38.1	117	349	429
U	11.7	84.2	105	104	184	320	761	1617	3941	2226
SD_{σ_b}	0.8	0.5	1.6	1.3	1.6	0.8	1.0	0.2	0.8	1.1
SD_U	0.56	12	21	16	29	44	187	537	130	451
SC										
σ_b	16.2	18.2	18.5	17.1	19.5	18.2	19.8	9.0	10.0	11.6
ϵ	9.1	8.9	9.4	9.4	10.3	11.3	30.8	73.4	290	562
U	5.2	94.0	105	142	183	211	609	3460	3550	5005
SD_{σ_b}	1.9	0.5	1.5	0.5	2.2	2.3	1.2	0.4	0.2	1.6
SD_U	0.54	6.2	14	13	37	27	105	221	368	571
TD										
σ_b	18.1	18.8	17.0	19.0	16.7	17.4	14.4	8.3	9.2	10.1
ϵ	9.0	9.8	9.4	9.3	10.4	11.5	29.4	83.0	302	445
U	5.4	122	98.0	125	254	272	836	2652	3608	3150
SD_{σ_b}	1.9	0.8	3.1	0.6	0.7	0.3	0.2	0.3	0.3	0.9
SD_U	0.45	23	19	8.8	15	40	115	474	761	1025
TC										
σ_b	16.9	18.2	18.1	21.4	19.7	15.3	17.0	7.8	8.7	8.6
ϵ	9.4	9.2	9.1	9.8	10.5	10.6	27.5	82.0	199	575
U	5.2	113	127	122	189	312	244	1777	3160	2258
SD_{σ_b}	2.2	1.1	1.7	1.0	1.3	0.7	0.4	0.2	0.2	1.3
SD_U	0.29	9.0	18	11	19	52	36	375	420	609

obtained was used for comparison. Crystallinity was calculated using a theoretical heat of fusion for crystalline polyethylene of 290 J/g.

Films, compression molded at 170°C and 14 MPa, were analyzed with a Bruker IFS85 spectrometer to obtain Fourier transform infrared (FTIR) spectra. The melt flow index (MFI) of the blends were measured with a Tinius Olsen Extrusion plastometer under a load of 5,000 g at 200°C (ASTM D1238 condition G).

RESULTS AND DISCUSSION

The five different polyethylenes, whose properties are listed in Table I, were blended with the SMA to obtain the five series of blends shown in Table II.

Series EB indicates the nonreactive blends involving ungrafted polyethylene. Series SD and TD are reactive blends in which the polyethylene phase contains either grafted secondary (in SD) or tertiary (in TD) amino functional groups that can react with the maleic anhydride groups in SMA. As shown in Table I, the PESD and PETD used for the polyethylene phase in blends SD and TD contain the same level of secondary (as t-BAEMA) and tertiary (as DMAEMA) amino functional groups, respectively. This allows a comparison of effectiveness of secondary and tertiary amino groups in the *in situ* reactive compatibilization with SMA. The grafting reaction products from the extruder contain not only grafts onto the PE backbone but also significant amounts of homopolymer of t-BAEMA (as in PESC) or DMAEMA (as in PETC).^{15,16} In the

blending process, it may be desirable, from an ultimate process standpoint, to use the grafted reaction products as they come directly from the grafting extruder since the purification to remove the homopolymer could be a costly process. Thus, series SC and TC blends were also prepared with unpurified, grafted PE phase for comparison with their purified counterparts, SD and TD blends, to determine the influence of homopolymer.

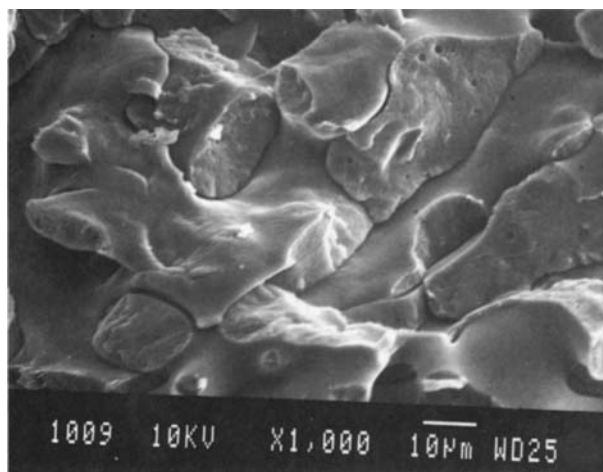
SMA/PE blends (EB) are incompatible in the whole composition range. A significant improvement in compatibility is achieved when the polyethylene phase was grafted with only a small amount of amino methacrylate (about 0.08 mol/kg). This is well demonstrated by the finer morphology for blends TD3, TC3, SD3, and SC3, which contain 30 wt % PE phase as shown in Figure 1. In the blend containing the nonreactive polyethylene (EB3), a wide size distribution of phase-separated polyethylene regions, most of them over 10 μm in diameter, is observed [Fig. 1(a)]. When the polyethylene was grafted with the tertiary amino groups (TD3), the particle size was reduced somewhat [Fig. 1(b)]. An even more significant reduction in the particle size and narrower size distribution can be observed when the polyethylene was grafted with the secondary amino group (SD3). Blend SD3 gave a much more uniform polyethylene dispersion with an average particle diameter of about 2.5 μm as shown in Figure 1(d). This is expected since the secondary amino groups are more reactive than the tertiary amino groups toward the maleic anhydride groups of the polystyrene (SMA) phase.¹⁷ The possibility of the secondary amino groups in the t-BAEMA grafts forming amide covalent bonds¹⁷ in addition to acid/base polar interactions with maleic anhydride may be responsible for the greater compatibility of the PESD with SMA. Mere acid/base polar interactions can be obtained between the tertiary amino groups in PETD and maleic anhydride in the SMA. Moreover, the tertiary amine of DMAEMA in PETD has a lower basicity than the secondary amine of t-BAEMA in PESD.^{20,21} The overall interaction of PETD with SMA is therefore lower than that of PESD, resulting in less improvement in compatibility with SMA as indicated by the larger particle sizes in blend TD3 [Fig. 1(b)].

Similar morphology observations were obtained for blends SC3 and TC3 containing the unpurified, grafted polyethylene phases as can be seen by comparing Figures 1(c) and 1(e). This suggests that the homopolymer contained in PESD (6.7 wt %) and PETC (7.2 wt %) has little influence on the morphology of the blends obtained and the com-

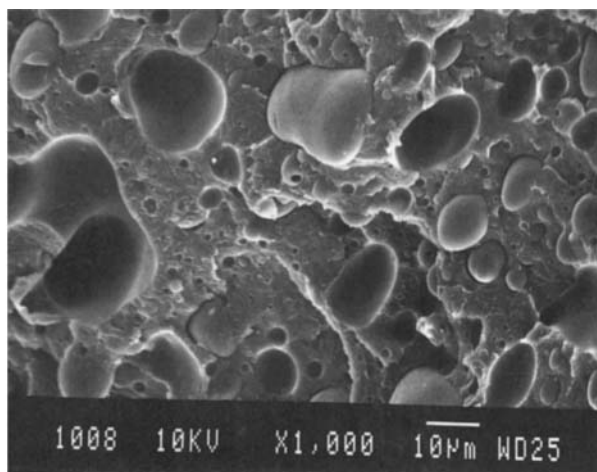
patibilization was achieved mainly through the interaction of the bound amino methacrylate in the polyethylene phase and the maleic anhydride in the polystyrene phase. The degree of grafting is essential for the *in situ* compatibilization. This is further demonstrated by blend SC3A25, containing 70/22.5/7.5 SMA/PE/PESC. Little improvement in compatibility was obtained for SC3A25 as can be seen by comparing the morphology of SC3A25 [Fig. 1(f)] and EB3 [Fig. 1(a)]. Only 25 wt % of the total polyethylene phase in SC3A25 is PESC. This gives the polyethylene phase about 2 wt % t-BAEMA-functional groups, which is higher than in SD3. However, only 0.4 wt % of the t-BAEMA-functional groups in SC3A25, compared to 1.6 wt % in SD3, are chemically grafted onto the polyethylene backbone. The negligible improvement in morphology of SC3A25 blend also suggests that there is a minimum degree of grafting greater than 0.4 wt % for the polyethylene phase necessary for *in situ* reactive compatibilization with this SMA.

Figure 2 shows the morphology of the blends containing 50 wt % of polyethylene phase. A co-continuous and laminated two-phase morphology is observed for the nonreactive EB5 blend [Fig. 2(a)]. The reactive SD5 blend, however, shows a polyethylene-dispersed morphology with a wide size distribution and large dispersed phase domains [Fig. 2(b)]. When the weight of the polyethylene phase increased above 60 wt %, the polyethylene becomes the continuous phase and the SMA the dispersed phase. Figure 3 shows the morphology of the blends containing 80 wt % polyethylene phase. Again, finer morphology is observed for the reactive SD8 blend [Fig. 3(b)] compared to the morphology of its nonreactive counterpart EB8 blend [Fig. 3(a)]. However, the improvement in morphology is not as marked as in the case when polyethylene is the dispersed phase (Fig. 1).

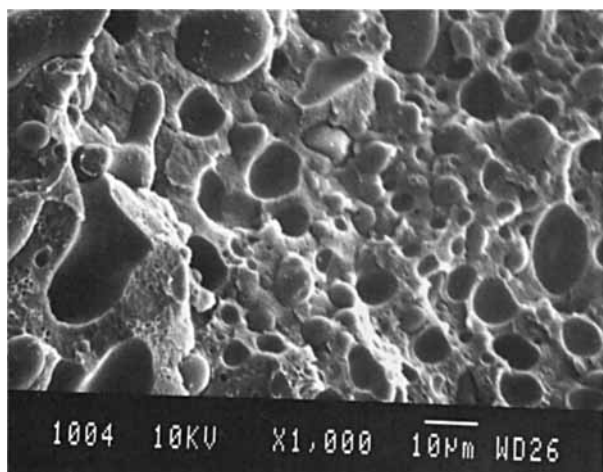
A change in morphology toward smaller domains of a dispersed low-modulus polymer is expected to give rise to an improvement in some mechanical properties. The mechanical properties of the polymer blends prepared in this study are summarized in Table III. Ultimate tensile properties of the two sets of EB and SD blends are compared in Figures 4 and 5. An overall trend shows that reactive blends (SD) have higher tensile strengths but comparable elongations at break when compared to the unreactive blends (EB). However, the improvement in the tensile strength is only moderate. Similar moderate improvement in tensile strength has also been reported for blends of reactive polystyrene containing oxazoline groups (OPS) and reactive polyethylene



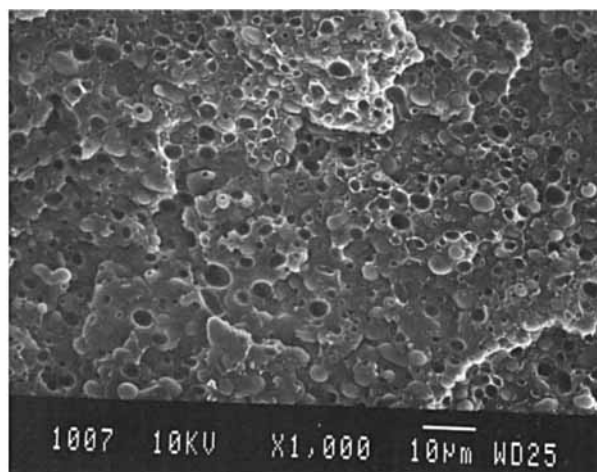
A



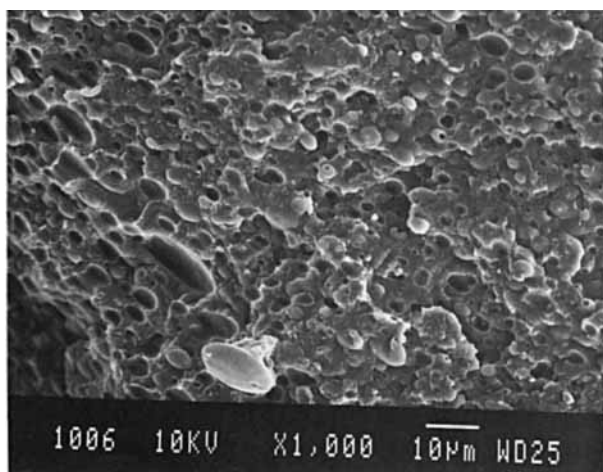
B



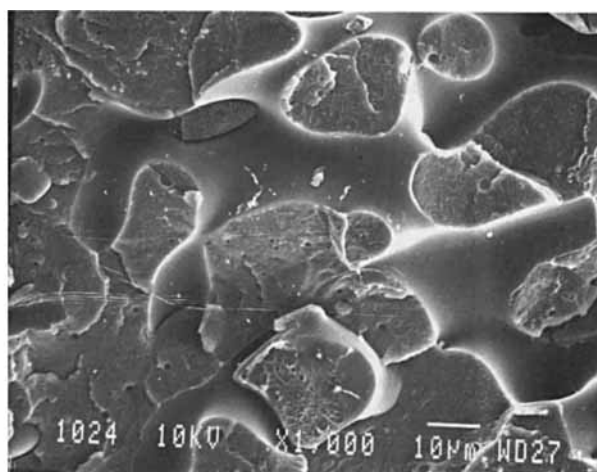
C



D



E



F

Figure 1 Scanning electron micrographs of the blends with 30 wt % polyethylene phase. A, EB3; B, TD3; C, TC3; D, SD3; E, SC3; F, SC3A25.

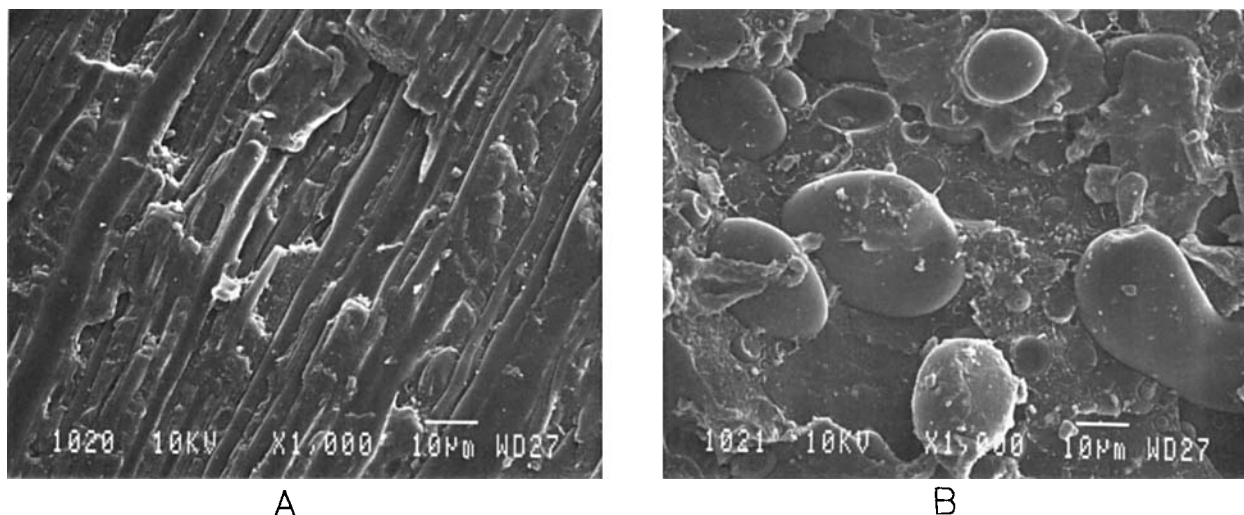


Figure 2 Scanning electron micrographs of the blends with 50 wt % polyethylene phase. A, EB5; B, SD5.

containing carboxylic acid groups (CPE).⁹ Although the formation of a graft copolymer at the interface might be expected to change the stress transfer in tension, it is unlikely that higher tensile strength should be observed in the high polystyrene fraction systems since the polyethylene has a lower tensile strength. However, the dispersion of polyethylene in the polystyrene matrix does increase the impact strength of the blends as shown in Figure 6. The impact strength of the blends increases with increasing polyethylene weight percent. In general, the blends with the amino-methacrylate-grafted poly-

ethylenes give higher impact strength than their unreactive counterparts, the EB blends. Although there are increases in impact of as much as 100% for some of the reactive blends, it is difficult to see trends among the different reactive systems. The domain sizes in the SMA/PE-g-tBAEMA (SD) and SMA/PE-g-DMAEMA (TD) blends are smaller than for the nonreactive systems but greater than the optimum particle size for rubber-toughening HIPS.²³ It is likely that the graft polymer formation at the domain/matrix interface does, in this case, contribute somewhat to the toughening mechanism.

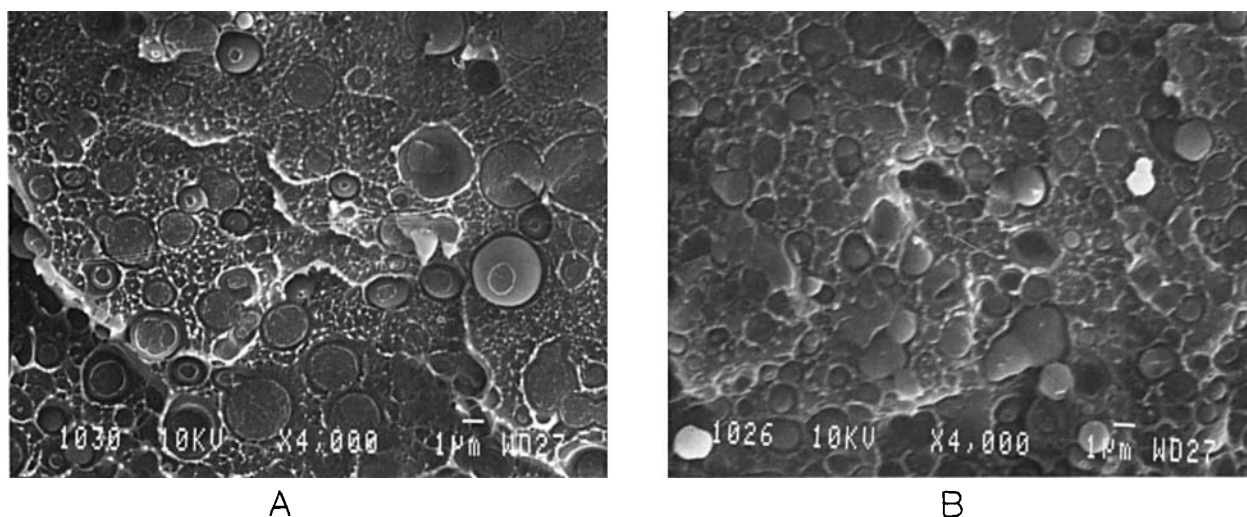


Figure 3 Scanning electron micrographs of the blends with 80 wt % polyethylene phase. A, EB8; B, SD8.

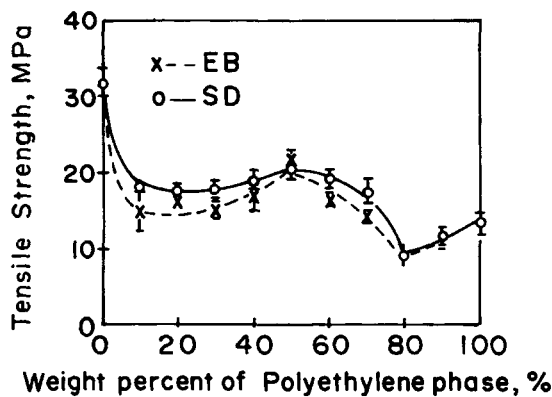


Figure 4 Variation of the tensile strength with weight percent of polyethylene phase for EB and SD blends.

It is also possible that the grafted polyethylenes have lower crystallinity, which leads to lower modulus domains.

The MFI of the blends were measured to indicate changes in the melt viscosity for the reactive blends of SMA with amino-methacrylate-grafted polyethylene. A decrease in MFI suggests an increase in the melt viscosity and molecular weight. Figure 7 shows the variation of the MFI with weight percent of polyethylene phase for EB, SD, and TD blends. In general, the reactive SD and TD blends have lower MFI values than their nonreactive counterparts, the EB blends. The decrease in the MFI compared to that of nonreactive EB blends is greater for the SD blends containing secondary amino groups than for the TD blends containing tertiary amino groups.

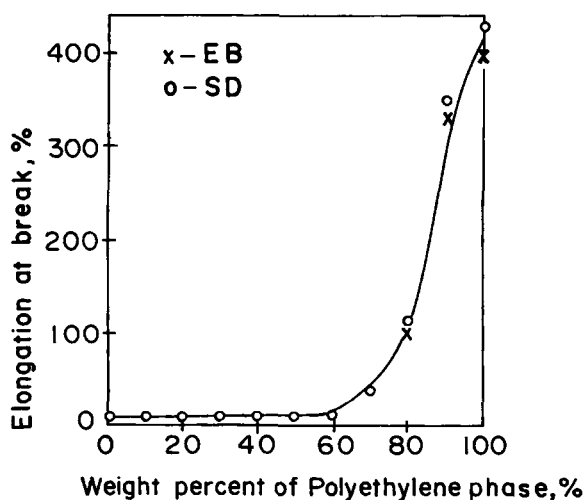


Figure 5 Variation of the tensile elongation at break with weight percent of polyethylene phase for EB and SD blends.

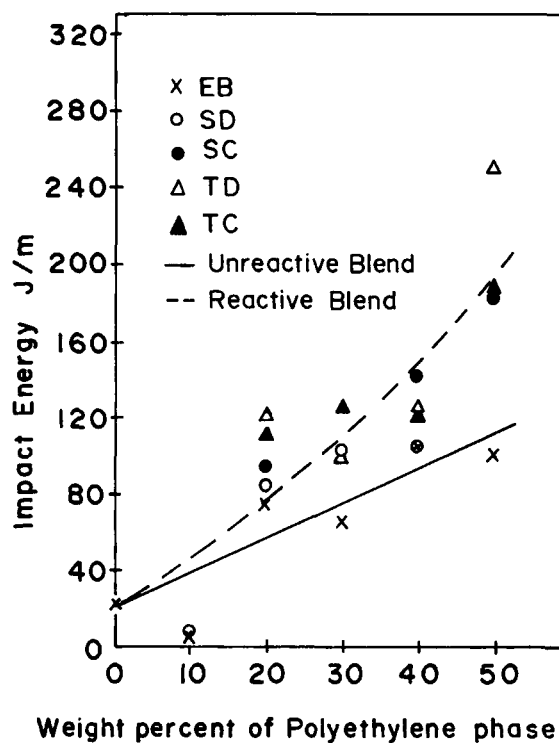


Figure 6 Variation of the impact strength with weight percent of polyethylene phase for EB, SD, SC, TD, and TC blends.

Although it is recognized that PESD alone has a higher viscosity than PETD, it is unlikely that this explains the higher viscosity of the SD blends, at least in the lower PE content blends. Rather, this increase in the melt viscosity is likely a result of the chemical interactions between the basic amino

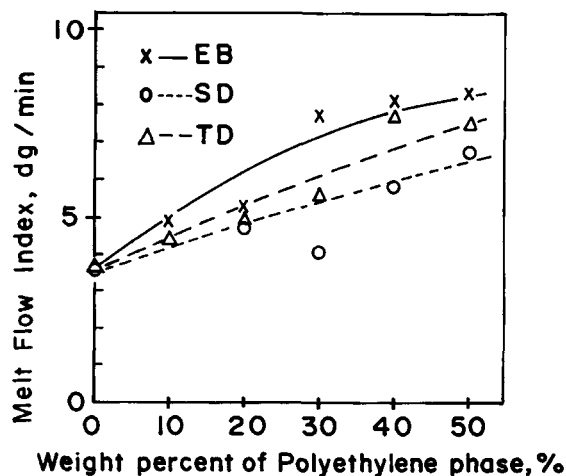


Figure 7 Variation of the MFI with weight percent of polyethylene phase for EB, SD, and TD blends.

groups of PESD or PETD and the acidic anhydride groups of SMA.

In a previous study using low-molecular-weight diamines,¹⁷ it was shown that tertiary amino groups participate only in polar interaction with the anhydride groups of the SMA while the secondary amino groups not only show polar interactions with the SMA but also react with the anhydride groups of the SMA to form amidic acid. The polar interaction between the amino groups and the anhydride groups was indicated by a weak new absorption band at about 1740 cm^{-1} in the FTIR spectra. The formation of amidic acid with the secondary amino groups was evident from a strong new absorption band at 1700 cm^{-1} in the FTIR spectrum due to the carbonyl stretching of the carboxylic acid formed, though the carbonyl stretching vibration of the amide formed, which usually occurs at around 1620 cm^{-1} , could not be observed because of the strong absorption from the benzene ring vibration that also occurs in this region (1601 cm^{-1}).

FTIR spectra were obtained for the reactive SD and TD polymer blends with 40, 50, and 60 wt % polyethylene phase. However, both the absorption at $1,740\text{ cm}^{-1}$ due to amine-anhydride polar interaction and the absorption at $1,700\text{ cm}^{-1}$ due to the amidic acid formation could not be identified (Fig. 8), at least in part because of the strong ester carbonyl stretching of the methacrylates at 1734 cm^{-1} in the FTIR spectra. The amino-methacrylate-grafted polyethylene contains equivalent numbers of the amino groups and the methacrylate ester

groups. If all the secondary amino groups had reacted with the anhydride groups of SMA to form amidic acid, the SD blend would have had an equivalent number of carboxylic acid groups and methacrylate ester groups. In that case, the absorption band at 1700 cm^{-1} for the carboxylic acid groups formed would be roughly comparable to that at 1734 cm^{-1} for the methacrylate ester groups and should be identifiable in the FTIR spectra. The FTIR spectrum in Figure 8, in fact, suggests that the amount of the SMA-g-tBAEMA-g-PE graft polymer formed, if any, is much smaller than that possible from the total amount of amino groups available in the SD blend. Nevertheless, the chemical interactions revealed by the model study¹⁷ are consistent with the improvement in morphology and the increase in the melt viscosity of the reactive SD and TD blends reported here. The more significant improvement in morphology (Fig. 1) and the greater increase in the melt viscosity (Fig. 7) for the SD blends compared to the TD blends may further suggest the possibility of formation of amidic acid with the secondary amino groups in the SD blends. The SMA-g-tBAEMA-g-PE graft polymer formed through amide covalent bonds is probably localized at the phase interface, which leads to the *in situ* compatibilization and thus the finer morphology. This grafting onto the SMA may increase the molecular weight somewhat and be responsible for the greater decrease in the MFI for the SD blends shown in Figure 7.

DSC normally provides useful insights into improved miscibility in polymer blends. Unfortunately, the DSC thermograms showed that the SMA has a glass transition temperature, T_g , at around 117°C , which is close to the melting point of the polyethylene at 124°C . The T_g of the SMA is thus hidden by the strong melting endotherm of the polyethylene for both reactive and nonreactive blends, and any change in T_g cannot be detected from the DSC thermograms. However, useful information can be drawn from the melting endotherm of the polyethylene related to changes in the crystallinity of the PE phase in the blends.

If PESD is grafted to SMA at the interface, its molecular mobility will be reduced and a reduction in crystallinity is expected. The melting points (T_m) and the % crystallinity obtained from the DSC measurements are listed in Table IV for the blends as well as for the pure PE blend components—PE (EB10), PESD (SD10), or PETD (TD10)—which were also processed under the same conditions as were the blends. There is little difference in the melting temperatures of the reactive SD (or TD) blends and the nonreactive blends. The measured

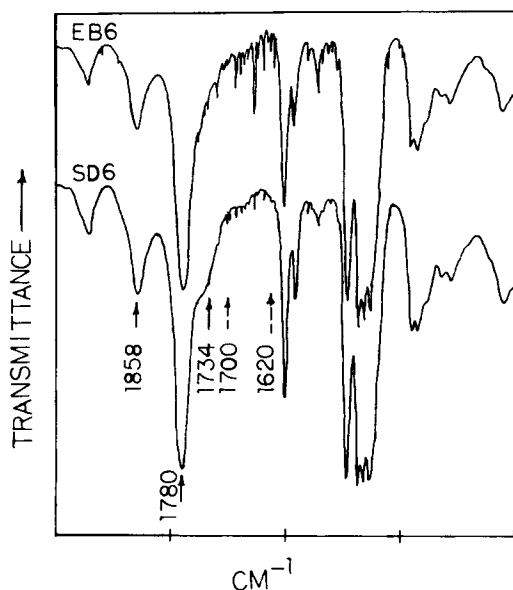


Figure 8 FTIR spectra of EB6 and SD6 blends.

crystallinity of a blend obtained directly from the DSC thermogram was normalized by the weight fraction of the PE phase in the blend and is listed in the last column of Table IV. The normalized crystallinity of the blends with low PE contents (e.g., EB1, SD1, and TD1) are much higher than that of their corresponding pure polyethylene materials (EB10, SD10, and TD10) simply because of the significant contribution from the glass transition at 117°C of the SMA phase to the PE melting endothermal peaks from which the crystallinity was calculated. For the blends with high PE contents (e.g., EB5 and EB7), the contribution of the glass transition from the SMA phase becomes negligible and the normalized crystallinity is similar to that of the pure PE (EB10). However, it is the difference in the crystallinity between the reactive SD (or TD) and the nonreactive EB blends at the same level of PE content that is interesting. As can be seen from Table IV, the difference in the normalized crystallinity between the TD blends and EB blends is small taking into account the considerable difference between the two separate PE materials, TD10 and EB10. However, there is a significant reduction in the normalized crystallinity for the reactive SD1 blend of 10 wt % PE content (36%) compared to that of the nonreactive EB1 blend (48%). The ex-

Table IV Crystallinity and Melting Points (T_m) of the Blends

Sample	T_m , °C	Crystallinity, %	
		Measured	Normalized
Blends			
EB1	122.1	4.8	48
SD1	122.2	3.6	36
TD1	122.2	3.9	39
EB3	123.3	11.0	36.7
SD3	122.6	8.9	29.7
TD3	123.3	9.8	32.7
EB5	123.8	15.3	30.6
SD5	123.1	14.5	29.0
TD5	123.7	15.3	30.6
EB7	122.9	21.0	30.0
SD7	122.8	20.7	29.6
TD7	122.9	20.4	29.1
Polyethylene Components			
EB10	124.0	32.8	32.8
SD10	124.1	30.4	30.4
TD10	122.8	28.0	28.0

Table V Number Average Particle Diameter (d) and the Specific Surface Area (A_s) for SD1, SD3, and SD5 Blends

Blend ID	d , μm	$A_s \times 10^{-6}$, m^2/m^3
SD1	0.8	7.5
SD3	3	2.0
SD5	10	0.6

tent of the reduction in the crystallinity for the SD blends decreases as the weight percent of the PE phase is increased. Almost no reduction in the crystallinity can be observed when the weight percent of the PE phase is increased to 50% or greater (SD5 and SD7).

It is assumed that the reduction in the crystallinity of the SD blends results primarily from grafting the amorphous SMA onto the PESD through the reaction between the secondary amino groups and the anhydride groups. Therefore, the extent of reduction in the crystallinity depends on the relative amount of PE grafted with SMA based on the total amount of the PE phase or the percentage of the amino groups reacted. The relative amount of the PE grafted with SMA is likely to be proportional to the specific surface area of the dispersed PE phase since the anhydride groups can only be accessed by the amino groups at the phase boundary. The specific surface area of the PE-dispersed phase depends on its particle size and can be calculated to be $6/d$ assuming the particles are uniform spheres with diameter d . Table V shows the number average particle diameters obtained from the SEM pictures by counting about 50 particles and hence the specific surface areas of the PE disperse phase calculated from these diameters for SD1, SD3, and SD5 blends. It can be seen that the specific surface area of the PE phase for SD1 ($7.5 \times 10^6 \text{ m}^2/\text{m}^3$) is much greater than that for SD5 ($6 \times 10^5 \text{ m}^2/\text{m}^3$). This may explain why the reduction in the crystallinity of the PE phase measured from the DSC is negligible for SD5 but significant for SD1 even though SD5 has a PE phase five times in weight greater than SD1.

CONCLUSIONS

Melt blends of SMA with the amino-methacrylate-grafted polyethylene display finer morphology and somewhat improved mechanical properties compared to the blends of SMA with the same polyethylene unmodified. Blends with the secondary

amino-methacrylate-grafted polyethylene show finer morphology than blends with tertiary amino-methacrylate-grafted polyethylene. The improvement in compatibility indicated by this finer morphology is believed to result from the chemical interaction between the amino and anhydride groups. The possible chemical reaction of the secondary amino groups with the anhydride groups to form SMA-g-tBAEMA-g-PE graft copolymer at the phase interface is likely responsible for the greater compatibilizing effect of PE-g-tBAEMA with the SMA than that of PE-g-DMAEMA. The amount of the graft copolymer formed *in situ* during melt blending appears to be small since it could not be detected by FTIR spectra. However, measurements of the crystallinity with DSC and the melt viscosity of the blends support an argument for *in situ* compatibilization by the formation of a graft copolymer at the interface.

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