

Morphology of HDPE / (PEC / PS) Blends Modified with SEBS Copolymers

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Synopsis

In this study, immiscible blends of HDPE and an amorphous glassy polymer were compatibilized with styrene-hydrogenated butadiene block copolymers. The glassy phase consisted of either pure PS or a miscible blend of PS and polyether copolymer (PEC); PEC is similar to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The morphology of these two-phase mixtures depended on physical characteristics of the components and the method of fabrication. Suitable copolymers increased the degree of dispersion and minimized heterogeneities resulting from the inherent incompatibility of the individual phases. Further reduction in the phase size and increased adhesion between the components of modified blends were achieved by increasing the composition of PEC in the glassy phase. It was concluded that favorable exothermic mixing between PEC and PS endblocks of the copolymers provided an additional driving force for compatibilization. Results from dynamic mechanical thermal analysis suggests that penetration by the copolymers into the homopolymer phases is not complete.

INTRODUCTION

The concept of physically combining different polymers to fabricate a new material having some of the desired properties of each component is becoming an important approach for the development of new specialty products. One obstacle to the use of multicomponent polymer systems for many commercial applications is poor properties due to the inherent incompatibility of most polymer combinations. Gross segregation of the blend components into a distinctly heterogeneous structure and the lack of interfacial adhesion result in an inability to transfer imposed stresses between these phases. Control of the morphology and ultimately the mechanical properties of incompatible polymers is possible only to a limited extent by the fabrication process.¹⁻³

Addition of a compatibilizer to reduce the interfacial tension between immiscible polymers may effectively stabilize the morphology during compounding, extrusion, or molding process.^{3,4} Suitably chosen block or graft copolymers may form an interphase, at the interface between the immiscible blend components⁵⁻⁷ so that imposed stresses can be transferred between the phases via the covalent bonds along the copolymer backbone. In addition to this improved adhesion, such copolymers generally reduce the phase sizes and increase the interfacial area; all of which act to improve the mechanical properties of the material. Characteristics of the copolymer that govern its ability to emulsify the mixture generally depend on the structure and the molecular weight of all components involved.

Optimization of immiscible high density polyethylene (HDPE)/polystyrene (PS) blends, both commodity materials that comprise a large fraction of the polymers in use, has been successfully accomplished through the use of styrene-butadiene-based block copolymers.⁸ The present work is an attempt to further improve the morphology and properties of such materials and to increase their useful temperature range by using an additional polymer, polyether copolymer (PEC). PEC is structurally similar to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) except for the random incorporation of approximately 5% of trimethyl phenol into the backbone. PEC has virtually the same properties as PPO, including complete miscibility with PS over the full range of compositions.⁹ In blends with HDPE, PEC/PS blends form a single glassy phase having a glass transition temperature governed by the relative properties of PEC and PS. In these blends, the HDPE exists, of course, as a separate phase with a melting point of approximately 145°C.

Several different block copolymers based on styrene and butadiene have been evaluated as compatibilizers for this blend system. These block copolymers are envisioned to locate at the interface, since their styrene endblocks are expected to penetrate the PS homopolymer phase to some degree and the olefin midblocks are expected to have some affinity for the HDPE. An additional and potentially beneficial factor is invoked when the glassy phase of the blend also contains PEC. Any mixing of styrene endblocks and PS homopolymer can only be driven by entropic forces since the mixing process is athermal. On the other hand, the miscibility of PS with PPO¹⁰ and PEC⁹ is based on an exothermic heat of mixing.¹¹ This provides an additional driving force for styrene endblocks to mix with a phase containing PEC. As a result, the compatibilizing effect of such copolymers may be better when PEC is present in the glassy phase of these blends rather than pure PS.

This paper describes the morphology and some properties of HDPE/(PEC/PS) blends resulting from different fabrication procedures and copolymers added to improve the blend properties. Subsequent papers will explore more fully the mechanical behavior and deformation mechanisms of these blends.

EXPERIMENTAL

Materials

Table I summarizes the materials and their abbreviations used here. Both high density polyethylenes (HDPE) used in this study were supplied by Union Carbide Corporation. HDPE-1 was used in HDPE/compatibilizer blends and all blends with PS made by injection molding; whereas, HDPE-2 was used in all of the remaining blends. For identical molding procedures, virtually no difference was detected in the bulk properties of HDPE-1 and HDPE-2. The polystyrene, Cosden 550 PS, was an extrusion grade supplied by Cosden Oil and Chemical Company.

The polyether copolymer was supplied specifically for this study by Borg-Warner Chemicals, Inc. in the form of preblends with Cosden 550 PS contain-

TABLE I
Materials Used in This Study

Polymer	Abbreviation	Source	Characteristics ^{a, b, c}
High density polyethylene	HDPE-1	Union Carbide Corp. (DMDJ 7904)	$\rho = 0.951$ Melt flow = 3.95
	HDPE-2	Union Carbide Corp. (DEMD 8907)	$\rho = 0.954$ Melt flow = 7.0
Polystyrene	PS	Cosden Oil & Chemical Co. (550)	$\rho = 1.05$ Melt flow = 2.3 $M_n = 100,000$ $M_w = 350,000$
Polyether ^d copolymer	PEC	Borg-Warner Chemical Co.	$\rho = 1.07$
	PEC80	Borg-Warner Chemical Co.	Miscible blend of PEC containing 20% PS $T_g = 181^\circ\text{C}$
	PEC60	Borg-Warner Chemical, Inc.	Miscible blend of PEC containing 40% PS $T_g = 155^\circ\text{C}$
Triblock copolymer	SEBS-L	Shell Chemical Co. (Kraton G 1652)	PS blocks $M_n = 7,000$ EB block $M_n = 37,500$ $\rho = 0.91$
Triblock ^e copolymer	SEBS-H	Shell Chemical Co. (Kraton G 1651)	PS blocks $M_n = 29,000$ EB block $M_n = 116,000$ $\rho = 0.91$
Diblock ^e copolymer	SEB	Shell Chemical Co. (TRW1601)	PS endblock $M_n = 8,700$ EB endblock $M_n = 16,000$
Ethylene propylene rubber	EPDM	B. F. Goodrich Chemical Co. (Epcar 847)	$\rho = 0.86$

^a Density in g/cm^3 .

^b Melt flow index in $\text{g}/10$ min.

^c The glass transition temperatures (T_g) were determined by DSC at $20^\circ\text{C}/\text{min}$.

^d PEC is similar to poly(2,6-dimethyl-1,4-phenylene oxide) except for the random incorporation of approximately 5% of the trimethyl phenol as a comonomer.

^e All block copolymers are based on styrene-butadiene; however, the butadiene blocks have been hydrogenated and are similar to an ethylene/butene copolymer.

ing 80% PEC/20% PS (PEC80) and 60% PEC/40% PS (PEC60). Each of these mixtures exhibited a single glass transition temperature.

Table I also summarizes the compatibilizers used in this study. SEBS-L and SEBS-H are triblock copolymers where the molecular weight of each segment of SEBS-H is approximately 3–4 times that of SEBS-L (see Table I). SEB is the diblock that would be obtained if SEBS-L were cut in half through the EB midblock. All of the block copolymers, supplied by Shell Chemical Co., are based on styrene-butadiene; however, the polybutadiene midblocks with both 1,4- and 1,2-diene units were hydrogenated to be structurally similar to an ethylene-(butene-1) random copolymer.

If PS blocks were not present in the copolymer, the effectiveness of these elastomers as compatibilizers would be limited. This is demonstrated using an

ethylene-propylene-diene terpolymer rubber (EPDM) supplied by B. F. Goodrich Chemical Co. instead of the block copolymers in selected blends.

Processing Procedures

Processing and rheological variables determine in part the morphology and final properties of multiphase blends.¹²⁻²⁴ A brief review of the literature on this subject will help understand the choices made here and the resulting observations. Stresses imposed during processing operations may cause the dispersed phase to become elongated into rods or fibrils oriented in the flow direction.¹²⁻¹⁵ If the imposed forces overcome the retractive forces of the dispersed phase, the latter may break into smaller particles.^{3,12} Eventually, the forces are in equilibrium, and further reduction in size of the dispersed phase is not possible. By equating the viscous shear forces and the interfacial forces, Taylor developed a theoretical relationship between the imposed shear stresses and the radius of an isolated sphere dispersed in a matrix.¹⁶ Heikens and Barensten confirmed qualitatively that Taylor's model describes the size of dispersed particles for LDPE/PS blends mixed in a Brabender.³ These results also indicate that the dispersed phase size increases with the composition of the minor component until semicontinuous microphases are formed between 30–60% PS.

In general, when the blend components are present in equal amounts, the lower viscosity polymer migrates around the higher viscosity polymer. This type of encapsulation increases as the viscosity ratio becomes greater.¹⁷⁻²¹ Starita found that the finest dispersion in PE/PS blends resulted when the viscosities of both components were equal.²³ Likewise, studies with rubbers have shown that as the difference between viscosities of the components increases, the degree of dispersion becomes poorer²² and more intensive milling does little to increase the degree of dispersion.²

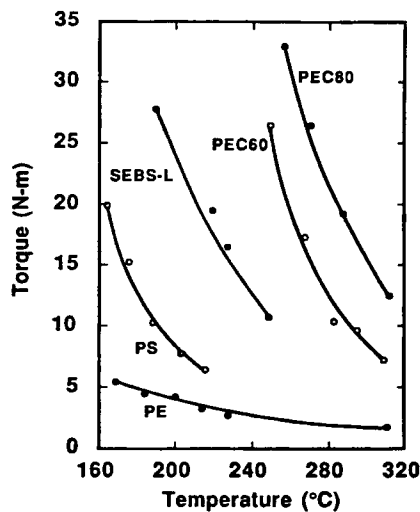


Fig. 1. Brabender torque at 60 rpm versus temperature for polymers used in this study.

Several studies have found that the domain size of the dispersed phase is reduced when the viscosity of the matrix exceeds the viscosity of the dispersed phase^{14, 15, 23} in accordance with Taylor's prediction. A coarser dispersion results when the viscosities are reversed so that the dispersed phase viscosity is greater than that of the matrix. Thus, one method for improving the degree of dispersion is by processing at temperatures where the major phase has a higher viscosity.^{14, 15}

In an attempt to utilize these principles for the fabrication of HDPE/(PEC/PS) blends, the torque-temperature relationship was determined for the individual components. Figure 1 shows the data obtained in a Brabender mixer at 60 rpm where the torque is proportional to the melt viscosity at the corresponding effective shear rate. Regardless of the temperature, the viscosity of the glassy polymers always exceeds that of HDPE for the materials used here. Processing and molding at temperatures where the viscosities are equal is seen to be impossible without degradation of the components. Processing at temperatures that were too low resulted in poor dispersions. Figure 2 shows the extrusion and injection-molding temperatures selected for this work as a function of the blend composition. Compression molding was carried out at slightly lower temperatures for blends with PEC/PS phases. In blends containing PEC, the temperature was lowered as the amount of HDPE increased.

The blend components were dried at least 6 hours in an air oven at 60°C before blending and molding. Extrusion was carried out in two passes through a Killion Extruder at 60 rpm using a shear mixing screw and the extrudate was pelletized. In an attempt to prevent thermal degradation of HDPE, PEC and the compatibilizers, about 0.1% of an antioxidant mixture containing Irganox B 225 and Irganox 1035, supplied by Ciba-Geigy Corporation, were mixed with the pellets prior to blending. High temperatures were not required to process HDPE/PS blends so the antioxidant was not added to these blends.

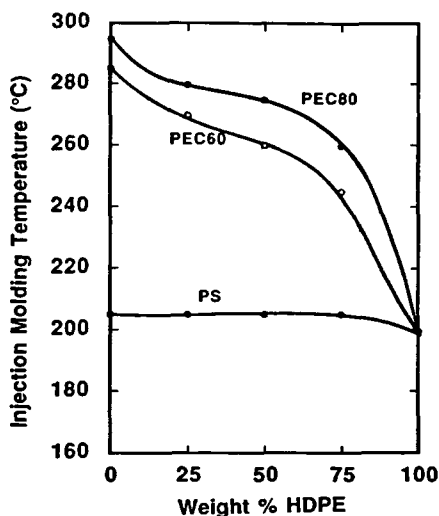


Fig. 2. Temperatures used in this study for injection molding HDPE/(PEC/PS) blends.

Injection molding of tensile and impact samples was carried out in an Arburg injection molder. Compression-molded sheets of each blend were made from extruded pellets in a compression press. After removal from the mold, the polymer sheets were held for at least 24 h before cutting into tensile and impact specimens using a Tensilkut router.

Testing Procedures

Mechanical properties of the specimens were determined by ASTM D638 using a floor model 1137 Instron Testing Machine. A test speed of 0.2 in./min was used in all cases. Notched Izod impact values were determined according to ASTM D256. Notching and subsequent measurements were carried out using Testing Machines, Inc. equipment.

A Jeol 35C scanning electron microscope (SEM) operating at 25 kV was used to evaluate the morphology and mode of deformation of the blends. Prior to viewing in the electron microscope, all mounted samples were coated with gold or gold-palladium in a Pelco sputter coater.

Dynamic mechanical properties of the molded specimens were measured using a Polymer Laboratories dynamic mechanical thermal analyser (DMTA). Runs were carried out at a frequency of 1 Hz in the single scan mode at a ramp rate of 4°C/min.

The heat distortion temperature (HDT) of selected blends was determined using a Custom Scientific Instruments, Inc. heat distortion/vicat softening point instrument according to ASTM D648. Values were recorded at 264 psi using 0.5×0.125 in. injection-molded samples.

RESULTS

The morphology of injection-molded and compression-molded blends of HDPE with PS, PEC60, and PEC80 were examined over the full range of compositions. In most cases, the resulting morphology depended on the HDPE content, regardless of the composition of the glassy phase (PEC/PS). Figure 3 and 4 show typical surfaces of compression and injection-molded, respectively, HDPE/PEC80 blends fractured at liquid nitrogen temperatures. Phase inversion occurs between 40 to 50 wt% HDPE for all of these blends.

Even though higher temperatures were required to prepare HDPE/PEC80 blends compared to HDPE/PS, the resulting morphology for the compression-molded samples of both blends are comparable to the trends presented by Heikens for LDPE/PS blends.³ Based on examination of many photomicrographs, the distribution of sizes is greater in blends containing 75% HDPE than 25% HDPE, as the results shown illustrate. The photomicrograph of 25 HDPE/75 PEC80 reveals holes in most of the larger dispersed HDPE particles. Similar holes were detected in the HDPE phase of compression-molded 25 HDPE/75 PEC60 blends. The origin of these holes is unknown. Blends containing 50% HDPE fall in the cocontinuous region where no really distinct matrix phase is detectable.

Subjecting the same materials to greater stresses encountered in injection molding changes the morphology and reduces the size of the dispersed phase (see Fig. 4). No distinct continuous phase is detectable for the injection-molded 25 HDPE/75 PEC80 blend. Although the cross-section is perpendicular to the

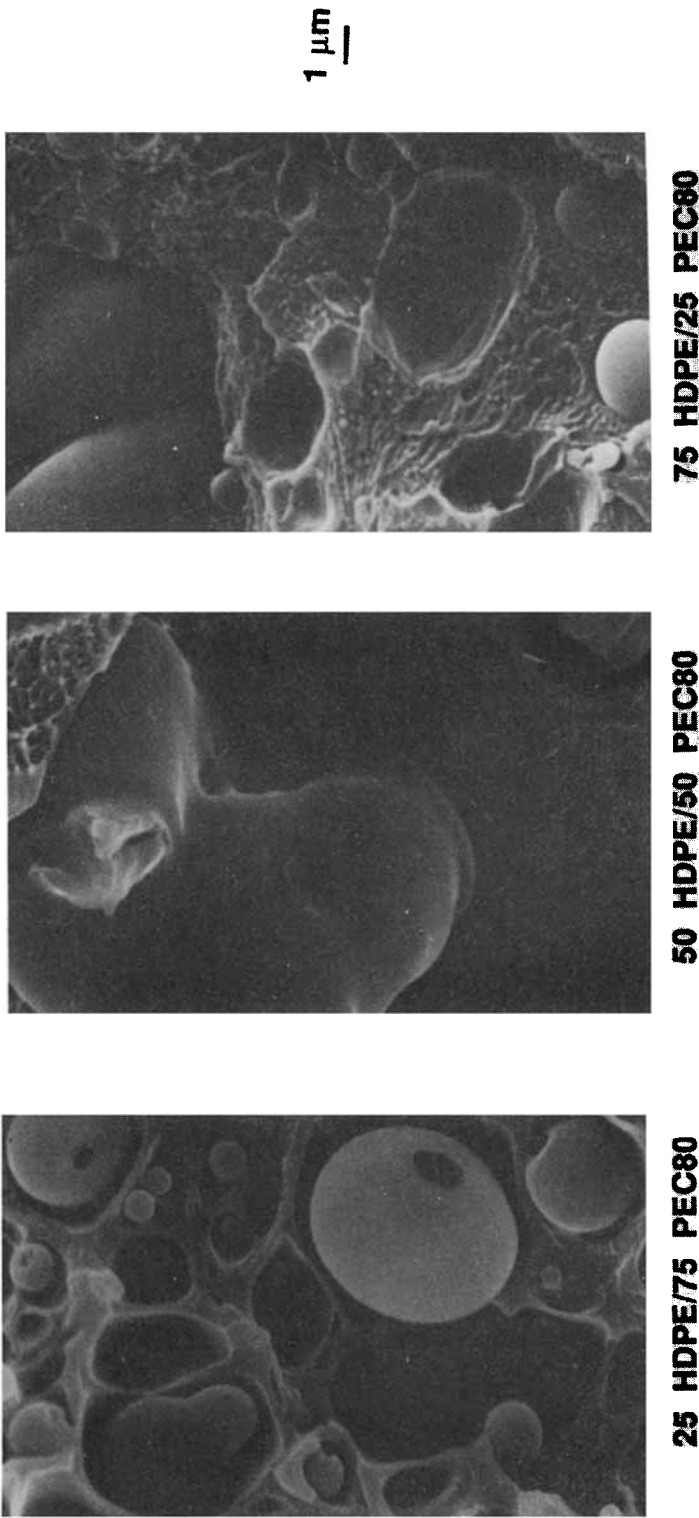


Fig. 3. Scanning electron photomicrographs of fracture surfaces of compression-molded HDPE/PEC80 blends. These samples were prepared by fracturing at liquid nitrogen temperatures.

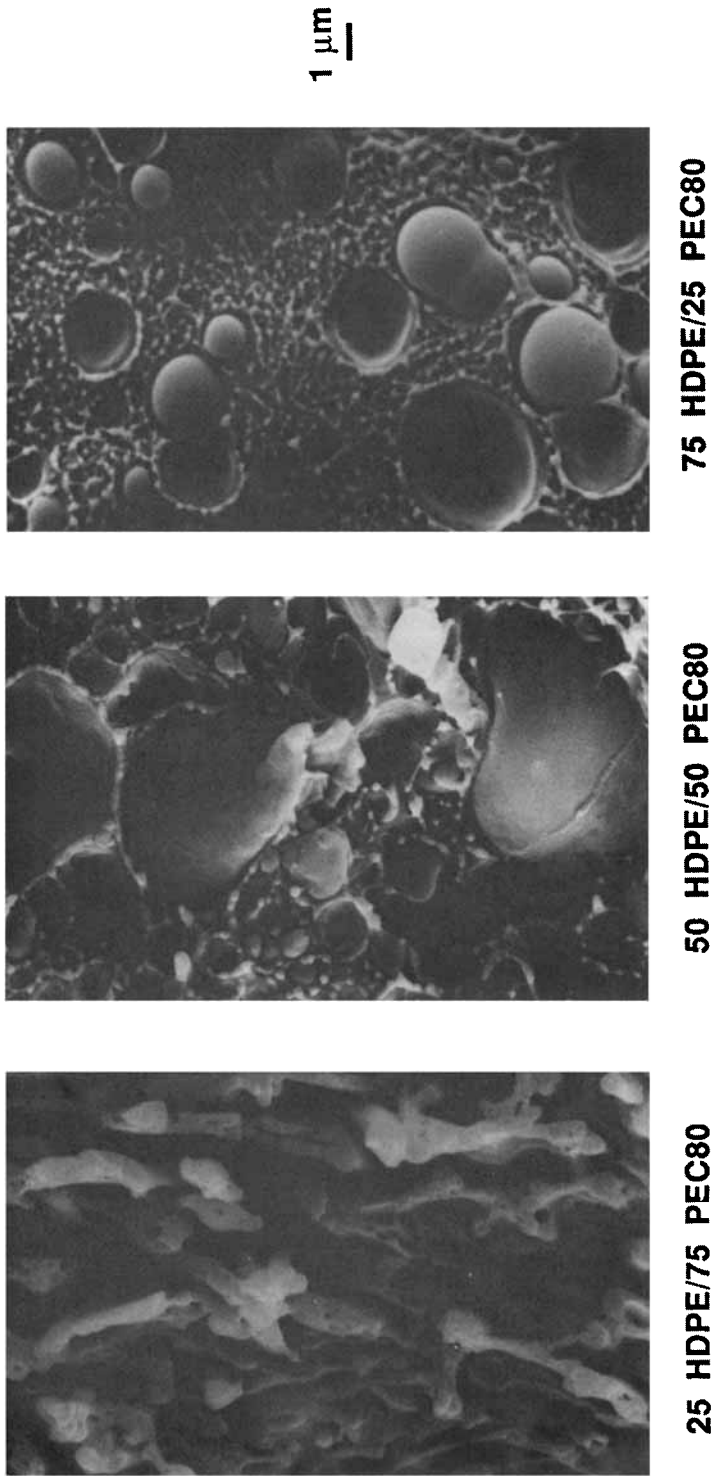


Fig. 4. Cryofracture surfaces of injection-molded HDPE/PEC80 blends.

direction of flow, the stratification seen is probably promoted by stresses parallel to the side wall of the mold. Center regions of the sample show less orientation since the stresses are lower there. Longer cooling times for the interior of the sample also permit greater relaxation and coalescence of the incompatible phases hence reduced phase orientation.¹²

Blends containing 50 and 75% HDPE are affected less by the imposed shear stresses during processing. Instead of exhibiting the residual stratification of injection molding, the dispersed phase is nearly spherical across the entire cross-section of the sample. Since the HDPE matrix is less viscous than PEC80 at the processing temperatures, the relative phase size of PEC80 in the HDPE matrix is slightly larger than those for HDPE in the PEC80 matrix.

In all cases, larger particle sizes in the compression-molded samples are the result of coalescence during molding of smaller dispersed phase particles formed by high stress extrusion blending.^{3,4} Figure 5 compares injection- and compression-molded 50 HDPE/50 PEC80 blends in which PEC80 was removed with toluene to facilitate viewing the phase sizes. At low magnifications, the finer dispersion of the injection-molded sample is evident. A cocontinuous morphology and distinctly larger phase sizes are clearly visible in the compression-molded blends.

Further investigations necessary to fully understand the temperature and composition dependence of the morphology are beyond the scope of this research.

Effect of Compatibilizer

It is known in the literature that addition of suitable block or graft copolymers will eliminate the macroscopic inhomogeneities²⁵⁻³² and increase stability of the morphology for immiscible polymer blends during processing.^{3,4} These compounds reduce the interfacial tension and subsequently decrease the dispersed phase size as expected from Taylor's model. The beneficial effects resulting from the addition of such a copolymer to immiscible polymer blends is qualitatively evident by improvements in the mechanical properties compared to the unmodified materials.^{25-29,31-41} However, the degree of improvement largely depends on the characteristics of the copolymer selected for the particular blend system. Several studies have explored the influence of physical structure on the compatibilizing ability of different copolymers.^{26-28,31,32,39-41}

In light of these previous investigations, the influence of molecular weight on emulsifying ability of triblock copolymers (SEBS-L and SEBS-H) was explored and compared to blends containing a diblock copolymer (SEB) and an ethylene-propylene-diene terpolymer rubber (EPDM). All materials are listed in Table I. Based on morphology and mechanical properties, the most effective compatibilizer for mixtures of HDPE with PEC/PS blends was selected for use in subsequent studies. Using identical mixing and molding conditions, 5 parts per hundred (pph) of each compatibilizer was added to 75 HDPE/25 PS and 75 HDPE/25 PEC80 blends while 5 and 20 pph of each was blended with PS.

Table II summarizes the mechanical property results for all blends and PS containing each of the compatibilizers. The progressive decrease in modulus

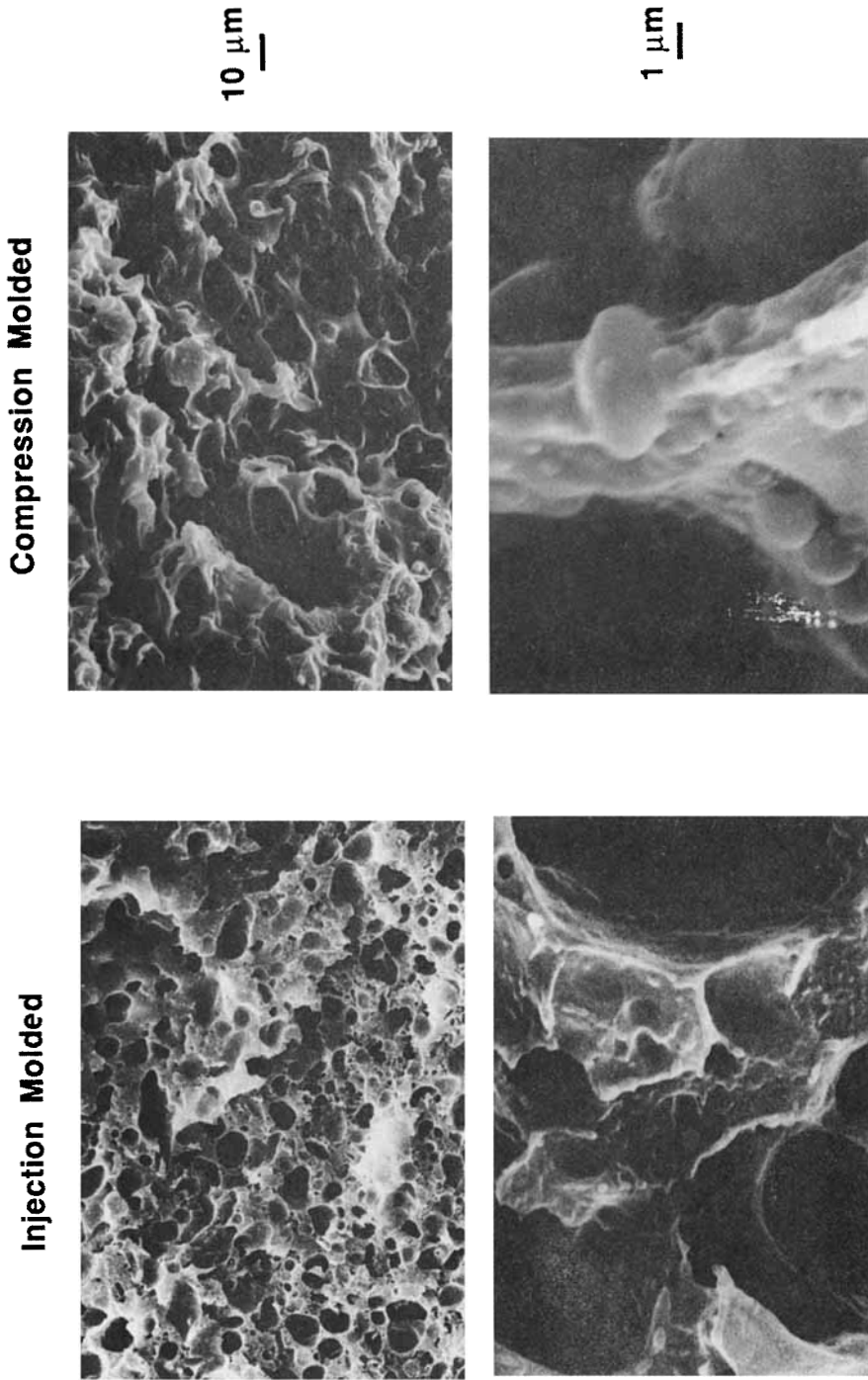


Fig. 5. Cryofracture surfaces of injection- (left) and compression- (right) molded 50 HDPE/50 PEC80 blends shown at two different magnifications. Surfaces etched with toluene.

TABLE II
Properties of Injection-Molded Blends Containing Compatibilizers Used in This Study

Blend composition	Compatibilizer	Compatibilizer content (pph) ^a	Yield stress (peak) (10^{-3}) psi	Modulus of elasticity (10^{-3}) psi	Strain at break %	Notched Izod impact strength ft-lb/in.
75PE/25PEC80		0	2.5	187	7	0.27
	SEBS-L	5	2.5	129	42	2.2
	SEBS-H	5	2.6	158	35	0.57
	SEB	5	2.6	142	11	0.54
	EPDM	5	2.4	140	22	0.38
75PE/25PS		0	2.5	166	25	0.48
	SEBS-L	5	2.6	150	76	0.54
	SEBS-H	5	2.7	159	12	0.35
	SEB	5	2.5	149	17	0.37
	EPDM	5	2.6	148	41	0.40
Polystyrene		0	8.4	460	2.9	0.65
	SEBS-L	5	7.5	430	2.9	0.66
	SEBS-H	5	7.2	443	4.3	1.1
	EPDM	5	7.9	439	3.7	1.1
	SEBS-L	20	6.0	357	7.6	2.1
	SEBS-H	20	5.6	340	14	4.5
	EPDM	20	6.3	361	3.6	1.5

^a Parts per 100 parts of material.

and yield (or peak) stress with the addition of the compatibilizers reflects the contribution of the low modulus material to the bulk properties. In general, the modulus and yield stress are equivalent regardless of the type of compatibilizer, as long as the same amount is used. Increases in the notched Izod impact strength, or the elongation at break, and decreases in the relative size of the dispersed phase are expected. The extent of these changes are the criterion used to evaluate the compatibilizers.

Figure 6 shows the morphology of 75 HDPE/25 PEC80 blends with 5 pph of each compatibilizer. These specimens were fractured at liquid nitrogen temperatures and solvent etched with toluene to facilitate observation of the individual phase sizes. Only the HDPE/PEC80 series is shown; however, the trends and conclusion regarding the effectiveness of each compatibilizer are identical for the HDPE/PS series. The nodular structure visible in several photomicrographs is HDPE that deformed by drawing and is not related to the degree of dispersion.

By comparing photomicrographs for the 75 HDPE/25 PEC80 blends, it is clear that addition of either SEBS-L, SEBS-H, or SEB improves the dispersion. Virtually no difference in the morphology is readily detectable between blends with SEBS-L and SEBS-H. However, the notched Izod impact strength increased nearly tenfold on addition of SEBS-L (from 0.27 to 2.2 ft-lb/in.) while the impact strength only doubled (0.27 to 0.54 ft-lb/in.) by addition of SEBS-H. The strain at break was also larger for blends with SEBS-L. Similarly, the improvements in strain at break and notched Izod impact strength were greater for HDPE/PS blends modified with SEBS-L. One possible explanation for the lower effectiveness of SEBS-H is its much higher viscosity so that efficient mixing is reduced.

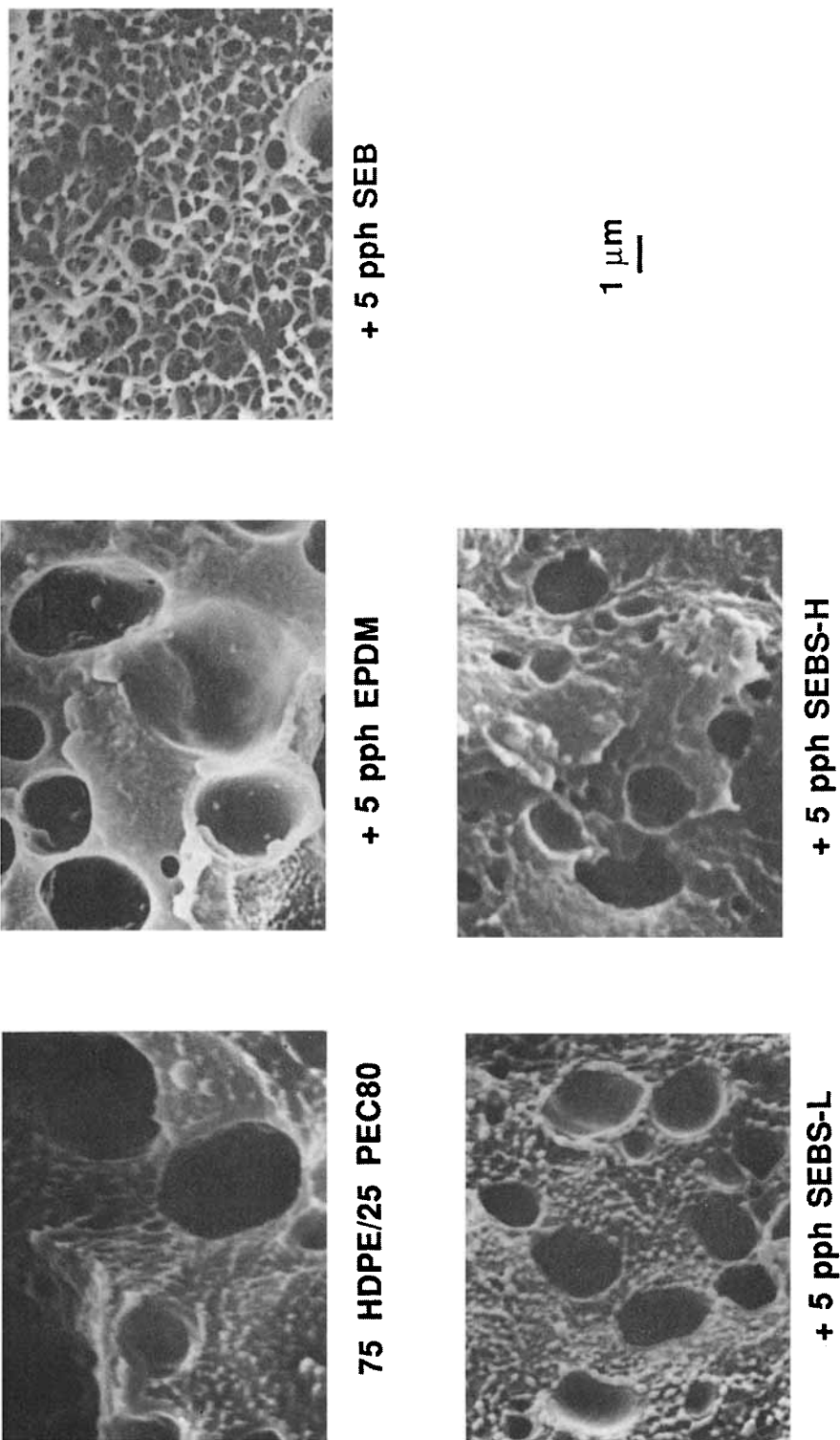


Fig. 6. Cryofracture surfaces of 75 HDPE/25 PEC80 blends containing 0 and 5 ppb of the indicated compatibilizer. Surfaces etched with toluene.

The diblock copolymer SEB, which is exactly half the SEBS-L molecule, was used in 75 HDPE/25 PEC80 and 75 HDPE/25 PS blends. A comparison of blend morphologies in Figure 6 shows that the dispersion in blends containing SEB are finer than those using either triblock copolymer or EPDM. In contrast, the properties of HDPE/PEC80 and HDPE/PS blends containing SEB are only slightly better than the unmodified blends. In this case, greater reduction in phase size does not necessarily lead to better mechanical properties. A possible reason may be that the shorter length of the olefin block fails to provide good mechanical coupling to the HDPE phase. Fayt et al. observed superiority of a larger, but similar, pure diblock copolymer compared to SEBS-H in LDPE/PS blends.²⁷ However, the emulsifying process is complex and clearly related to the fabrication process employed as well as the molecular weight of the copolymers.

EPDM was blended with the materials to demonstrate the necessity of the PS endblocks for compatibilization. The 75 HDPE/25 PEC80 and 75 HDPE/25 PS blends containing EPDM showed little improvement over the unmodified materials. While EPDM has relatively good affinity for HDPE, it will have very little for the glassy phase; consequently the degree dispersion is approximately the same for unmodified blends and there is no interfacial adhesion.

SEBS-L, SEBS-H, and EPDM were also blended with pure PS and each increases toughness to varying degrees, as seen in Table II. SEBS-H is the most effective toughening agent for PS. Visually, the molded samples containing SEBS-H appear to be more homogeneous than other blends.

Fracture surfaces for PS blends with SEBS-L and SEBS-H are compared with the fracture surface of pure PS in Figure 7. The samples were strained at room temperature then fractured at liquid nitrogen temperatures in order to preserve intermediate deformations.⁴² For pure PS, the surface resembles the patchwork pattern for materials that deform by crazing. Small holes and rubber particles can be seen in the fracture surface for blends with SEBS-L; however, the fracture surface otherwise remains relatively unchanged and the toughness of the characteristics are only marginally improved. No particles are easily detected on the fracture surface for PS/SEBS-H blends, but improvements in Izod impact strength and strain at break were considerable. Several studies⁴³⁻⁴⁷ have shown that polystyrene can be toughened by block copolymers of the types SBS, SB, or SEBS; however, copolymers with higher molecular weights are usually more effective.

Small increases in impact strength and elongation at break were observed by adding of 5 pph EPDM to PS; however, greater quantities (20 pph) resulted in no significant increase in toughness. Comparison with PS/triblock copolymer blends in Figure 7 reveals a poorer dispersion and void formation at the interface between the PS matrix and dispersed EPDM. Since EPDM does not have a block segment compatible with PS, it is not able to adhere to the PS phase. The resulting lack of adhesion limits stress transfer; hence, under load, the PS matrix deforms and creates voids around the unstressed EPDM.

Although SEBS-H was the most effective toughening agent for PS, SEBS-L was superior as a compatibilizer for immiscible HDPE/(PEC/PS) blends. Therefore, SEBS-L was selected for subsequent studies. Reduction of the phase size in HDPE/PEC80 blends after compatibilization with SEBS-L is shown by comparing Figures 4 and 8 for injection-molded blends. Twenty pph

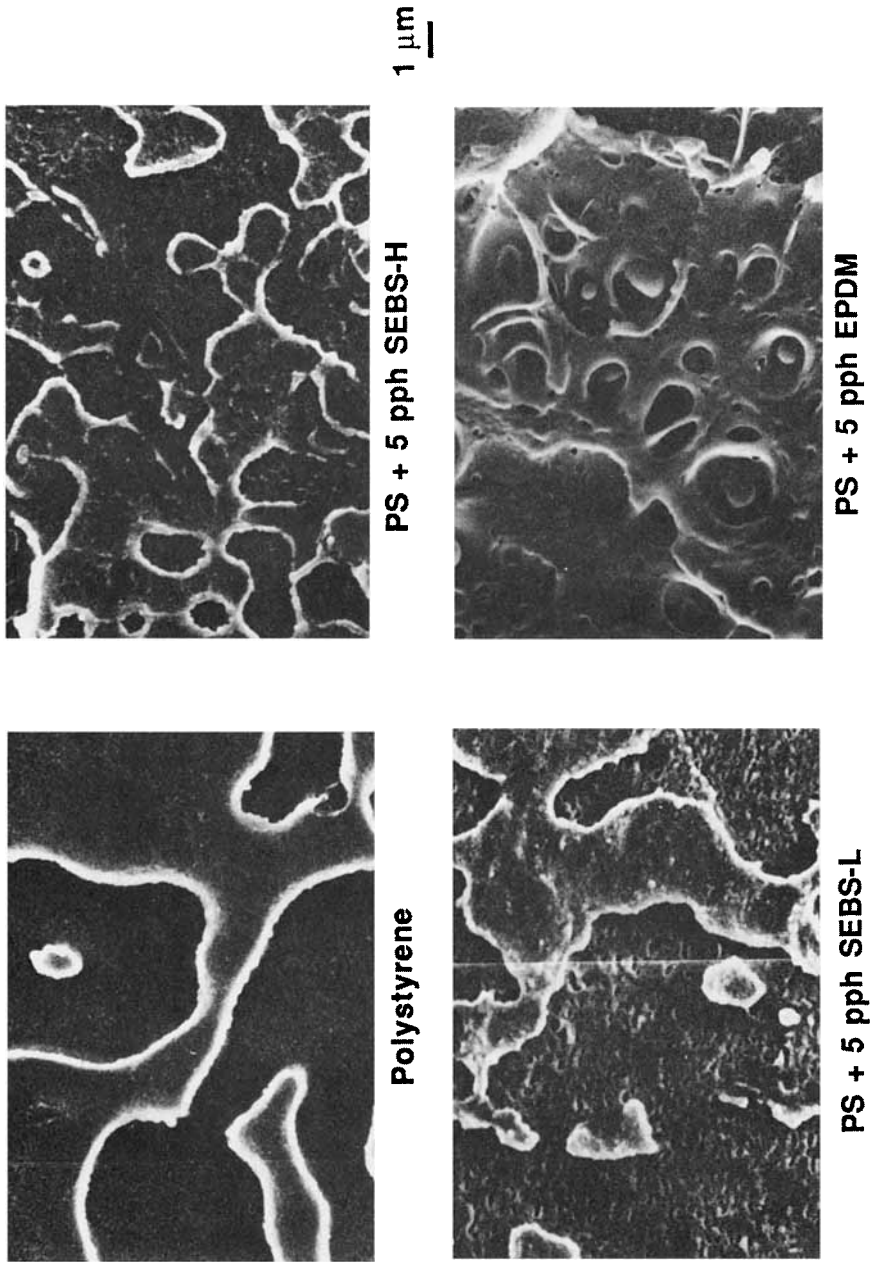
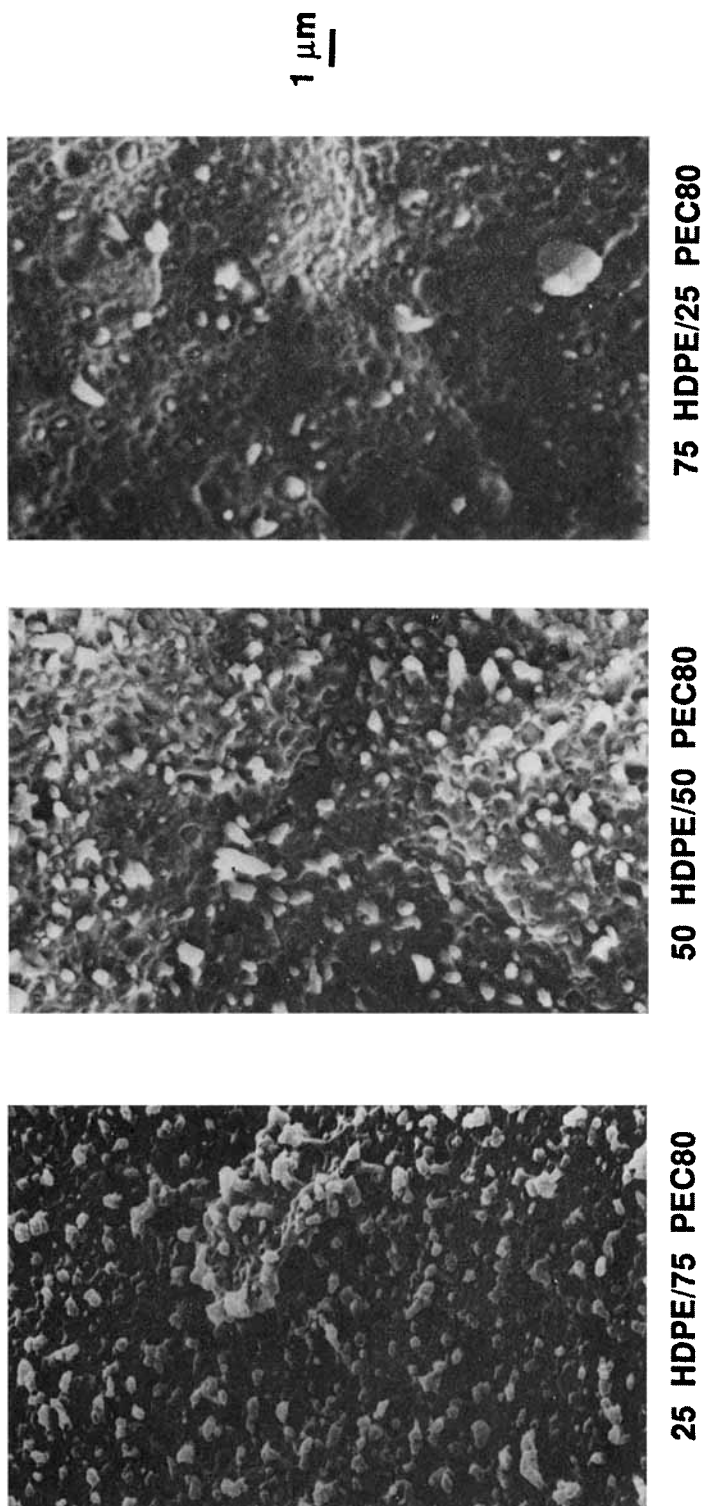


Fig. 7. Cryofracture surfaces of PS containing 0 and 5 pph of the indicated compatibilizer. All surfaces were prepared by uniaxial straining followed by cooling to liquid nitrogen temperatures and then fracturing. No extraction.



All Blends Contain 20 pph SEBS-L

Fig. 8. Cryofracture surfaces of HDPE/PEC80 blends containing 20 pph SEBS-L. No extraction.

SEBS-L stabilizes HDPE/PEC/PS blends and reduces the tendency for phase segregation. Unlike blends prepared without a block copolymer, the relative sizes of the dispersed phase in the blends with 20 pph SEBS-L are constant at about 0.5–1 μm over the full range of HDPE contents.

Figure 9 compares compression- and injection-molded blends of 50 HDPE/50 PEC80 with 5 pph SEBS-L. The surfaces were solvent etched to facilitate viewing of the phase sizes. The size of the dispersed phase is reduced by the copolymer (see Fig. 5 for comparison) for both fabrication methods. In addition, the degree of coalescence during compression molding is reduced by the compatibilizer; hence, the morphology more closely resembles that seen for injection-molded samples. Blends containing 50% HDPE exhibit large differences in morphology between injection- and compression-molded samples.

Effect of PEC / PS Ratio

Verification that the size of the dispersed phase in HDPE/(PEC/PS) blends is not a strong function of the viscosity of the minor component was accomplished by changing the PEC/PS ratio in blends with a constant HDPE content. Fracture surfaces prepared at liquid nitrogen temperatures (Fig. 10) reveal the morphology and phase sizes for injection-molded blends containing 75% HDPE. Increasing the proportion of PEC in the dispersed glassy phase from 0 (PS) to 80% (PEC80), raises the viscosity of this phase but the effect on the size of this phase and overall blend viscosity is relatively small. In all cases the dispersed phase size is 1–10 μm . The viscosity/temperature relationships are given in Figure 1.

Addition of SEBS-L to HDPE/PS blends decreases the interfacial tension to achieve a better dispersion; however, the reduction in the dispersed phase size for blends containing PEC is even greater which may be due to the additional thermodynamic driving force for the styrene segments of the block copolymer to mix with the glassy phase when PEC is present.⁴⁸ By comparing the SEM photomicrographs of fractured and solvent-etched compression-molded samples in Figure 11, it is clear that the dispersion becomes finer as the amount of PEC in the dispersed glassy phase increases. A similar trend occurred for all compositions, regardless of the molding method and quantity of SEBS-L used to emulsify the system.

A closer look at the interaction occurring between the phases during deformation provides further evidence of greater compatibilization in blends containing PEC. The SEM photomicrographs in Figure 12 show samples containing 50% HDPE that were strained prior to fracturing at liquid nitrogen temperatures. For HDPE/PS, the fracture propagated along the interface between the two phases, exposing relatively smooth surfaces of dispersed PS particles and leaving smooth holes in the HDPE matrix. In some cases, the fracture propagated through the dispersed PS phase, indicating interfacial adhesion caused by the addition of the compatibilizer. As the amount of PEC in the blends increased, small fibrils anchoring the largest dispersed particles in the HDPE matrix become visible. Fibrils that held a PEC60 particle in place are exposed on the interior surface of the hole remaining in HDPE/PEC60 after the force of the fracture ripped the particle from the

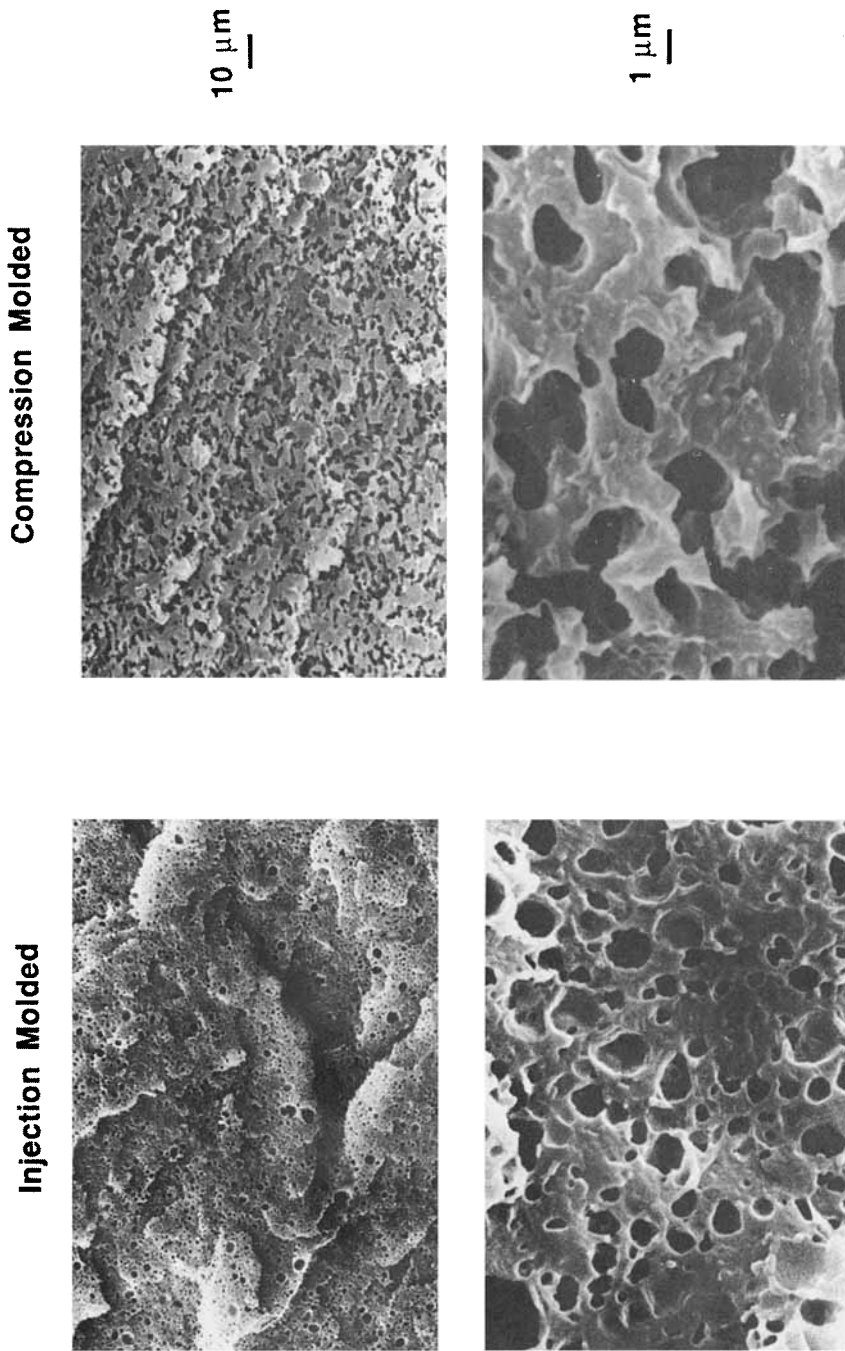
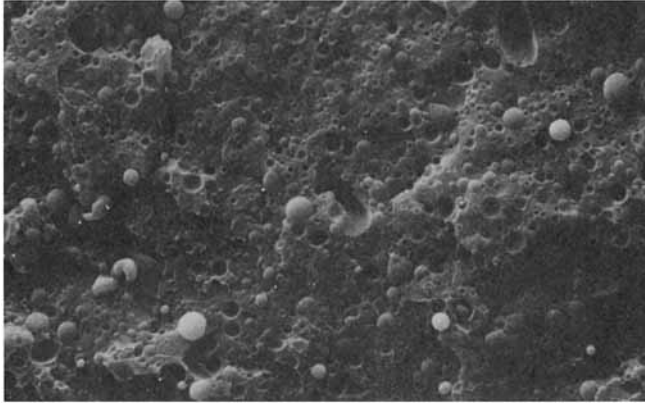
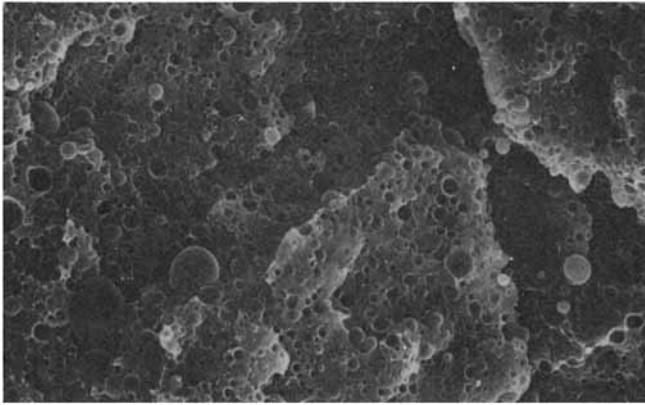


Fig. 9. Cryofracture surfaces of injection- (left) and compression- (right) molded 50 HDPE/50 PEC80 blends containing 5 phh SEBS-L shown at two different magnifications. Surfaces etched with toluene.

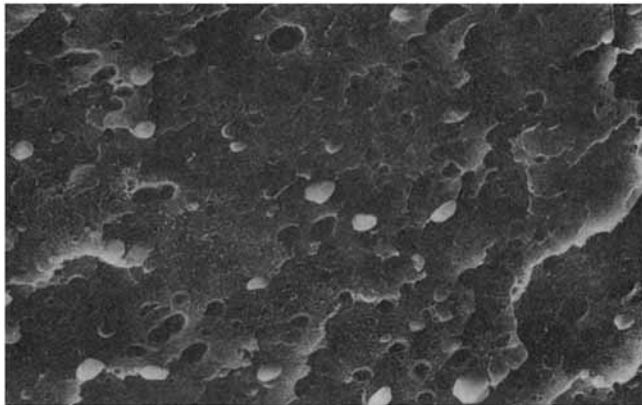
10 μm



75 HDPE/25 PEC80



75 HDPE/25 PEC60



75 HDPE/25 PS

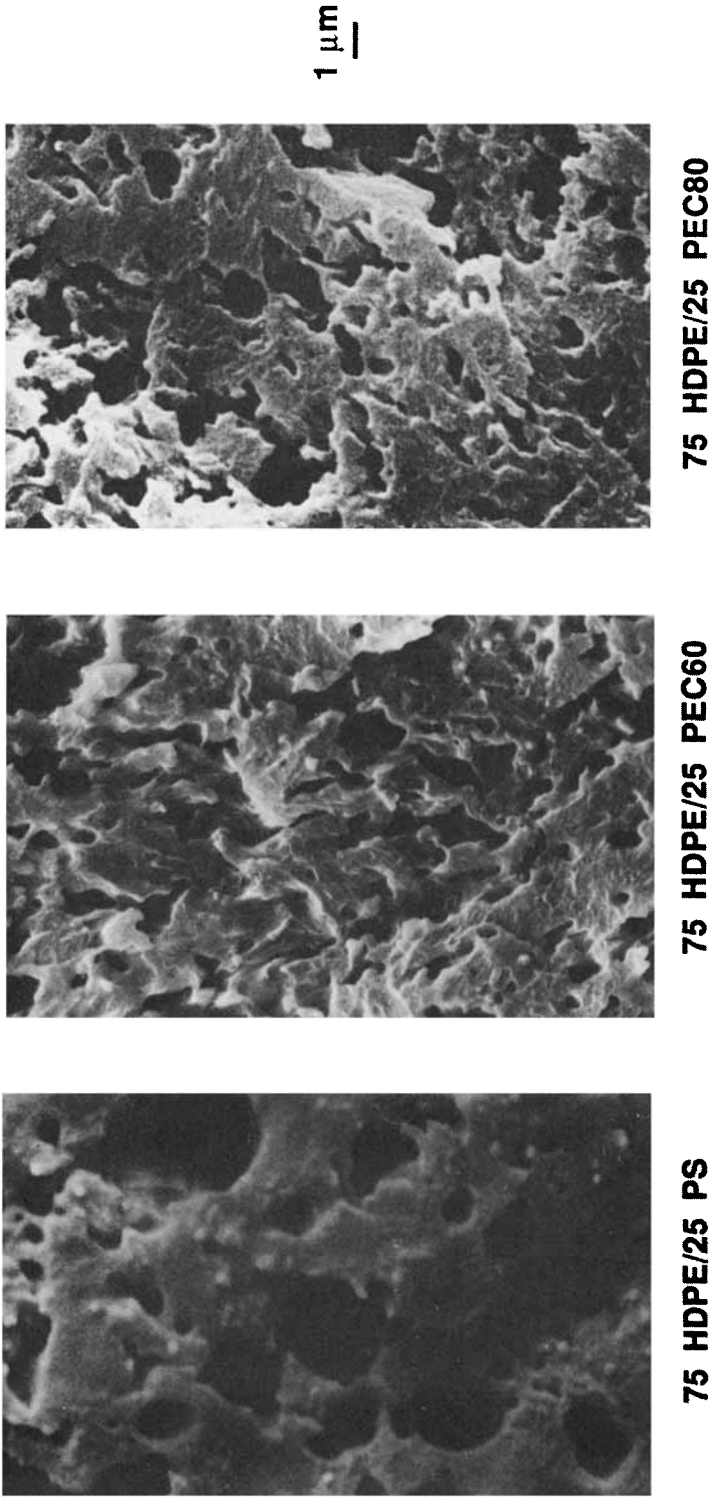


Fig. 11. Cryofracture surfaces of 75 HDPE/25 (PEC/PS) blends containing 20 pph SEBS. Surfaces etched with toluene.

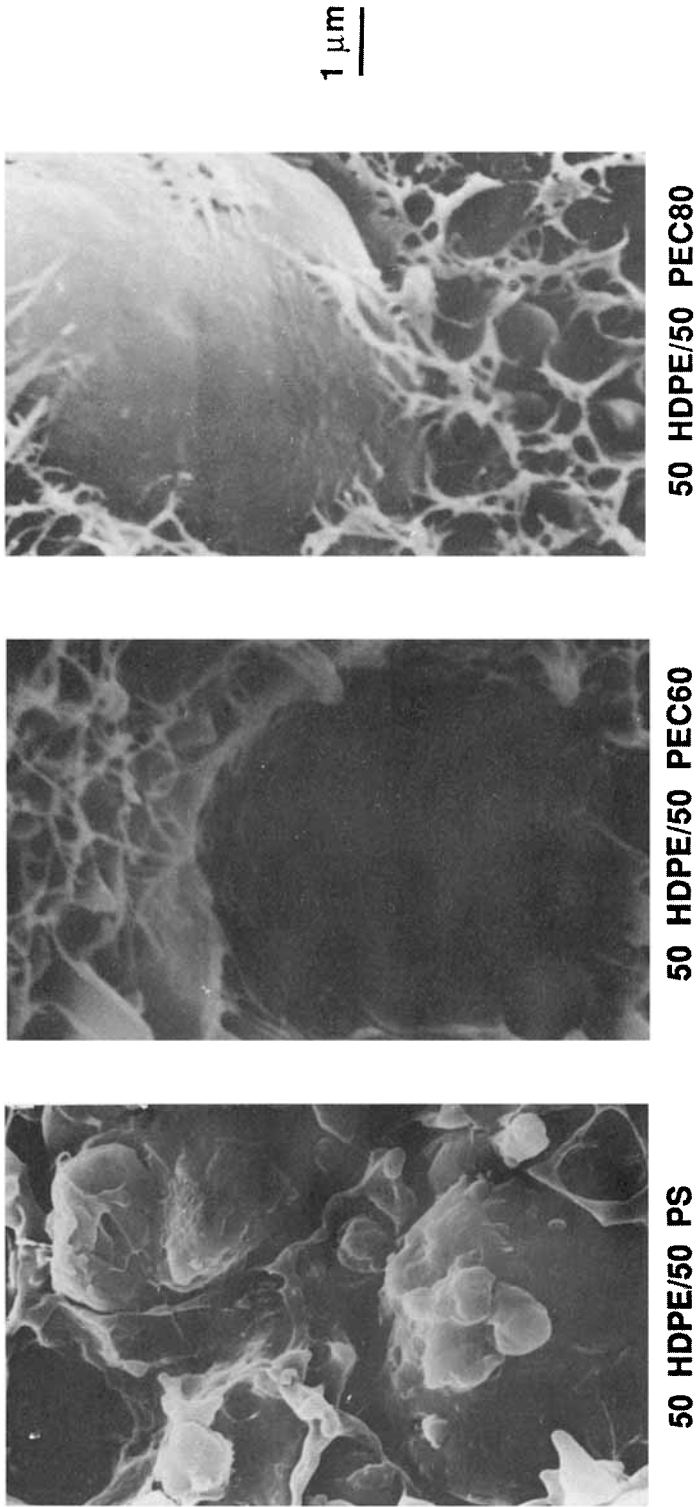


Fig. 12. Cryofracture surfaces of 50 HDPE/50 (PEC/PS) blends containing 5 pph SEBS. Samples were strained uniaxially before fracturing at liquid nitrogen temperatures.

matrix. Similar fibrils holding a PEC80 particle in the HDPE phase are evidence of increased penetration of the styrene blocks into the glassy phase. The rough texture of the surface of the PEC80 particle, compared to the surface of the PS particles, is another indication of greater adhesion.^{26, 35, 44}

Reduction in phase sizes and the fibrils securing the dispersed particles in place, as mentioned above, provide distinct evidence of the greater compatibilizing effect in blends containing PEC. This phenomenon may be explained by the extra thermodynamic driving force provided by the negative heat of mixing between the PS endblocks of the copolymer and the PEC rich phases of the blend which acts in addition to the entropic gain associated with mixing. Mixing of PS endblocks and homopolymer PS is athermal, therefore, combinatorial entropy of mixing is the only thermodynamic driving force for penetration. Exothermic mixing of PEC with the PS endblocks of SEBS-L thus promotes compatibilization in blends with HDPE. Using this approach to compatibilization, it may be feasible to achieve a better dispersion with smaller quantities of a block copolymer having a segment that is thermodynamically miscible with, but not the same as, one of the blend components.

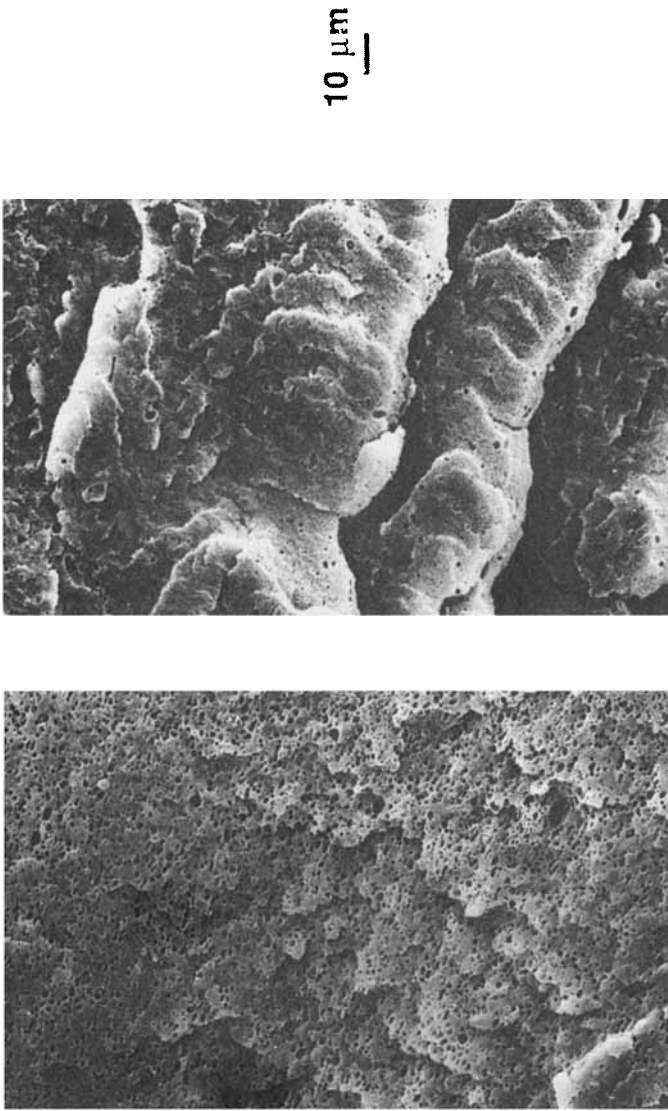
Similar trends in the reduction of the phase sizes also occurred in the blends with SEBS-H and SEB. As shown in Figure 13 for 75 HDPE/25 PEC80 and 75 HDPE/25 PS blends to which SEB was added, the reduction in the dispersed phase size was greater for blends containing PEC compared to blends with only PS. Fibrils between the phases, which are an indication of good adhesion, were not detected in the strained blends containing SEB or SEBS-H. This absence of fibrils, supports the previous conclusion that SEBS-L is superior for compatibilization of PEC/PS blends with HDPE.

Location of Compatibilizer

Ideally, compatibilizers locate at the interface between the immiscible components of the blend with their block segments completely penetrating the respective compatible phases. Alternatively, a compatibilizer interphase may be formed between the immiscible phases of the blend.⁴⁹

Direct observation of the interphase in melt-processed LDPE/PS blends was accomplished by Fayt et al. using a styrene-hydrogenated butadiene block copolymer with a polyisoprene central block.⁵⁰ They observed a continuous dark layer of fairly regular thickness surrounding the dispersed phase using transmission electron microscopy. They also found evidence that the copolymer forms stable microdomains in the LDPE phase in addition to dispersing at the interface. Similar conclusions were made by Heikens et al. from analysis of mechanical modulus results for modified LDPE/PS blends.³¹

Evidence for the formation of a compatibilizer interphase in HDPE/PEC80 blends was investigated using dynamic mechanical thermal analysis (DMTA). $\tan \delta$ and modulus results obtained for 75 HDPE/25 PEC80, SEBS-L, and blends of these materials with 5 and 20 pph SEBS-L are shown in Figure 14. The low temperature $\tan \delta$ peak for SEBS-L at -30°C arises from the glass transition of the ethylene-butene (EB) midblock.^{51, 52} The rapid decrease in modulus at temperatures above -40°C is a result of this transition. Further



Both Blends Contain 5 pph SEB

Fig. 13. Cryofracture surfaces of 75 HDPE/25 (PEC/PS) blends containing 5 pph SEB after toluene extraction.

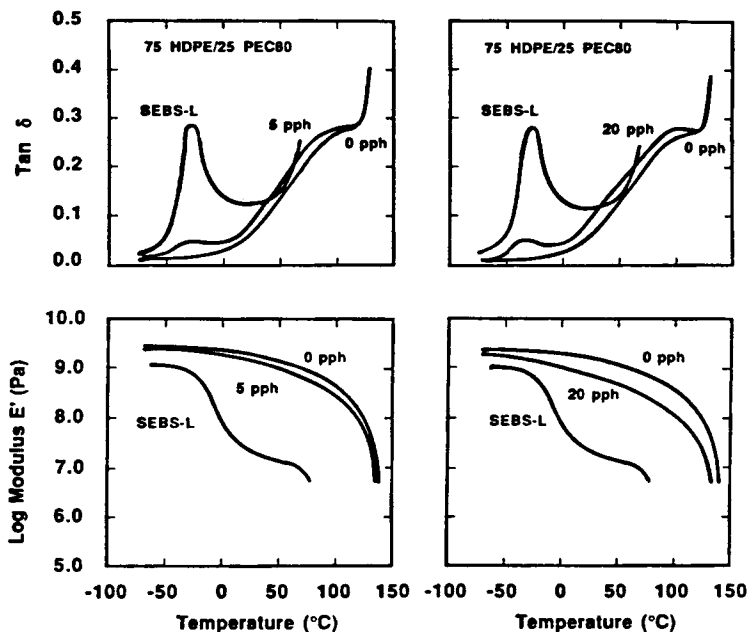


Fig. 14. $\tan \delta$ and modulus for SEBS-L and 75 HDPE/25 PEC80 containing 0, 5 (left) and 0, 20 (right) pph SEBS-L obtained by dynamic mechanical thermal analysis.

softening occurs as the T_g of the PS endblocks is approached. Blends of HDPE/PEC80 exhibit no low temperature relaxation in this region.

Upon addition of 5 pph SEBS-L to HDPE/PEC80, a low temperature $\tan \delta$ peak becomes evident at -30°C , corresponding to the EB transition. The $\tan \delta$ shoulder develops into a peak at $50\text{--}100^\circ\text{C}$ with increasing SEBS-L content. We attribute this peak to the glass transition of the PS segments of SEBS-L. Both the high and low temperature $\tan \delta$ peaks of SEBS-L become more distinct with increasing SEBS-L content in the blends. The modulus also decreases above -50°C in proportion to the amount of SEBS-L in the blend.

Observation of distinct T_g for both segments of SEBS-L in blends with HDPE and PEC80 suggests that the compatibilizer exists primarily as a separate phase, presumably at the interface, and that interpenetration of the block segments with the olefin and glassy phases of the blend are by no means complete. Similar results obtained by others using dynamic mechanical properties support this conclusion.^{53,54}

Heat Distortion Temperature

One of the reasons for adding PEC to HDPE/PS blends is to increase the useful temperature range of products fabricated from these materials. To assess this anticipated benefit, the heat distortion temperatures of HDPE/PS and HDPE/PEC80 blends were measured over the full range of compositions and are shown in Figure 15.

Blends of HDPE and PS are limited by the low glass transition temperature (100°C) of the PS phase and the softening of the HDPE phase with premelt-

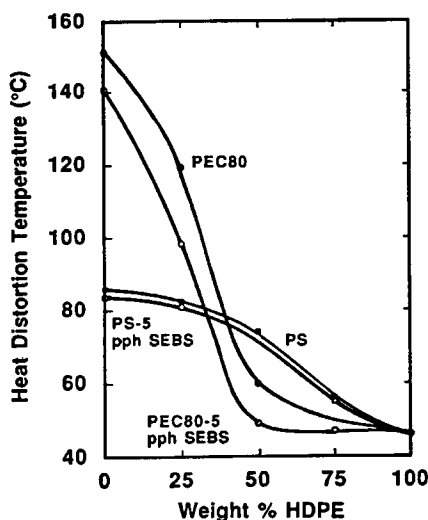


Fig. 15. Heat distortion temperature of HDPE/PEC80 blends containing 0 and 5 pph SEBS-L and HDPE/PS blends containing 0 and 5 pph SEBS-L.

ing. As expected, the HDT of HDPE/PS blends decreases with increasing HDPE content and is proportionately lower for compositions containing SEBS-L. Blends with PEC80 have a higher HDT than HDPE/PS blends for the same HDPE content when PEC80 forms the matrix phase. For HDPE contents greater than 40–50% phase inversion occurs, and the continuous phase is HDPE. At these compositions the HDT for PEC80-based blends is actually less than that for PS-based blends at the same HDPE content. SEBS-L further decreases the HDT. The modulus is also lower when the dispersed phase is PEC80 than when the dispersed phase is PS, which may account for the lower HDT in these blends. These topics will be discussed in a following paper dealing with mechanical properties.

DISCUSSION

The morphology of multiphase HDPE/(PEC/PS) blends as revealed by fracture surfaces depends on blend composition, the physical characteristics of the components, and the processing procedures used to prepare the samples. The present observations on morphology bear close similarity with other reports in the literature for blends of a polyolefin and an amorphous glassy polymer.

For these blends, the size of the dispersed phase can be reduced at least by a factor of two with the addition of 5 pph of an SEBS block copolymer; further size reductions result when larger amounts of copolymer are added. Eventually, the differences in morphology caused by fabrication techniques are minimized. Even larger reductions in the size of the dispersed phase were produced by the addition of an SEB diblock copolymer; however, this does not translate into significant improvements in mechanical properties. This points out the importance of using physical properties rather than morphology alone as a basis for the selection of a compatibilizer.

For all block copolymers used, the largest reductions in the dispersed phase size were observed for blends containing some PEC rather than pure PS. The PS endblocks of the copolymer and the PEC-rich phases of the blend are expected to mix exothermically, which is an additional thermodynamic driving force for the PS endblocks to penetrate the glassy phase of the blend when it contains PEC rather than just PS. This, in effect, promotes better bonding between HDPE and the amorphous glassy phase. SEM observations of the interfaces provide evidence of this. Fracture surfaces of prestrained HDPE/(PEC/PS) specimens containing block copolymers reveal fibrils which secure the dispersed PEC-rich particles to the HDPE matrix. This phenomenon was not observed when the glassy phase was pure PS. These results suggest greater penetration of the PS endblocks into the glassy phase and improved adhesion.

Evidence from dynamic mechanical analysis suggests that the block copolymer probably exists primarily as an interphase between the components of HDPE/(PEC/PS) blends. The transitions corresponding to both phases of the block copolymer were detected in blends at essentially the same temperatures at which these transitions occur for the pure block copolymer.

As a measure of the potential maximum use temperature of these blends, the heat distortion temperature was examined. The heat distortion temperature is substantially higher for blends containing a larger proportion of PEC rather than pure PS when the glassy phase is the matrix of the blend. However, after phase inversion so that the glassy phase is dispersed, around 45% HDPE, the heat distortion temperature is lower for blends containing PEC. The lower modulus exhibited by these blends may contribute to the lower heat distortion temperature observed.

Subsequent papers will report on thorough investigations of the mechanical properties of the HDPE/(PEC/PS) blends modified by the SEBS-L copolymer and information about the deformation mechanisms of the blends.

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