Mechanical Compatibilization of High Density Polyethylene–Poly(ethylene Terephthalate) Blends

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Synopsis

Blends of high density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) exhibit extremely poor mechanical properties owing to the incompatibility of these two polymers. Such blends, however, would result from the reprocessing of certain carbonated beverage bottles. Addition of small amounts of a commercially available triblock copolymer greatly improved the ductility of these incompatible blends, whereas addition of an ethylene–propylene elastomer did not. The results are discussed in terms of phase morphology and interfacial adhesion among the various components.

INTRODUCTION

Mechanical compatibilization of polymer mixtures by the addition of another polymer is conceptually an attractive route for generating alloys with unique property combinations and for recycling mixed polymer scrap or waste.[1-5] Thus, there is a considerable impetus to discover polymers which exhibit such compatibilizing effects and to understand the mechanisms by which they function. The paper deals with the application of this concept to the mixture which would result if certain types of plastic soft-drink bottles were granulated and processed. The bottle type of interest consists of a poly(ethylene terephthalate) (PET) container with a high density polyethylene (HDPE) pedestal, which is needed since the blown bottle has a rounded bottom. It is quite obvious that PET and any polyolefin would be grossly incompatible[6] and that a very effective compatibilizer would be needed to give the blend adequate mechanical properties for any subsequent application.

The study presented below was stimulated by previous observations that certain block copolymers are very effective compatibilizers for a wide range of polymer types.[1-5,7,8] The properties of PET/HDPE blends containing a triblock copolymer compatibilizer are compared with those of blends containing an EPDM-type compatibilizer. Some of the possible mechanisms for explaining the greater efficiency of the triblock copolymer are explored, and some interesting speculations are made.

MATERIALS AND BLEND PREPARATION

Since this research was fundamental and exploratory in nature, only virgin materials were used. The PET was a bottle grade resin, with an intrinsic vis-

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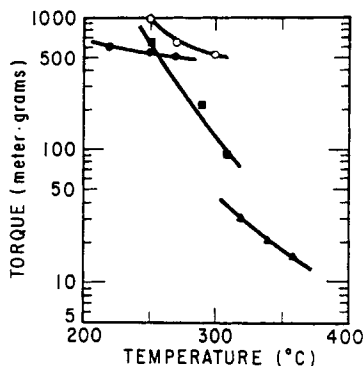* Present address: Dow Chemical Co., Midland, Mich. 48640.

Fig. 1. Brabender torque at 20 rpm vs. temperature for HDPE (●), PET (▲), Kraton G 1652 (■), and Epcar 847 (○).

cosity of 0.74 dL/g, sold by the Celanese Plastics and Specialty Co. under the designation of Petpac 2113. The HDPE had a density of 0.954 g/cm^3 and a melt index of 0.35 g/10 min and is a product of Union Carbide Corp. with designation DEMD-6369.

Two different elastomers were examined for their potential compatibilizing ability. One was a triblock copolymer, Kraton G 1652, produced by the Shell Chemical Co. It had styrene end blocks which comprise about 30% of the mass and a hydrogenated butadiene midblock equivalent to an amorphous copolymer of ethylene and butene-1. The second elastomer was an EPDM with a high ethylene content, resulting in some ethylene crystallinity, sold by B. F. Goodrich Co. under the designation of Epcar 847.

The rheological characteristics of the various polymers mentioned above were determined as a function of temperature using a Brabender Torque Rheometer at a rotor speed of 20 rpm. The results are shown in Figure 1. This information shows that the PET is considerably less viscous than the HDPE, which is relevant to considerations of mixing these two polymers to form a blend. At 300°C, Kraton G 1652 is intermediate to the HDPE and the PET in flow characteristics while the EPDM elastomer is more comparable to HDPE in this regard.

Blends were made by melt mixing in a 0.75-in. laboratory extruder having L/D = 20 and a compression ratio of 3. Prior to this and all other melt processing steps, the feed materials were dried at 100°C for 24 h to reduce the hydrolysis degradation of PET by sorbed moisture during processing. Based on optimization of mechanical properties of blends containing equal parts of PET and HDPE plus 20% Kraton G 1652, which were subsequently injection-molded, 300°C was selected for the temperature setting in both the metering zone of the extruder and the attached die. The latter was either a 0.125-in. rod die on a 6-in. film die depending on the nature of the product sought.

MECHANICAL PROPERTIES OF INJECTION-MOLDED BLENDS

Fabrication and Testing

To prepare these specimens, extruded strand was quenched into cold water and chopped into pellets. This material was dried as before and fed to a Van
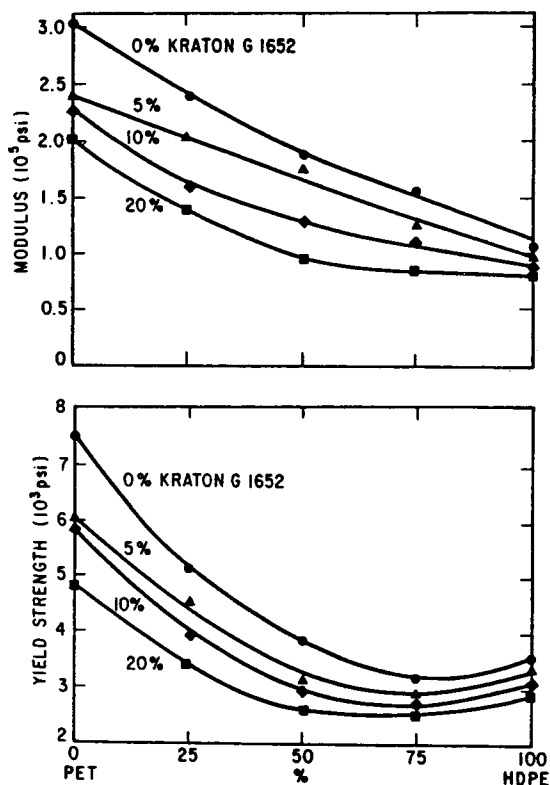
Fig. 2. Modulus and strength of PET–HDPE blends with and without Kraton G 1652 made by injection molding.

Dorn ram injection molding machine fitted with a mold to produce ASTM standard tensile (D638 Type I) and Izod test bars with gating from only one end. The molding conditions were optimized to produce the best mechanical properties for a blend containing equal parts HDPE and PET and 20% Kraton G 1652, and these conditions were used for all other compositions. The optimum barrel temperature was found to be 260°C.

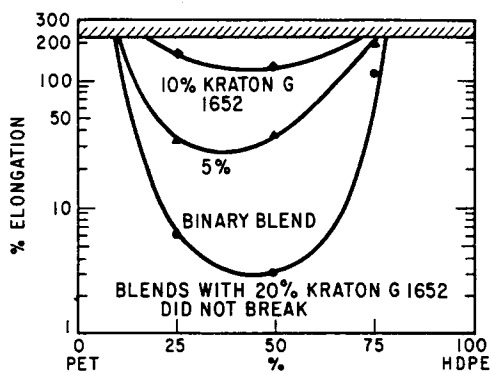Stress–strain diagrams for the tensile bars were obtained using a floor model

Fig. 3. Elongation at break for PET–HDPE blends with and without Kraton G 1652 made by injection molding. Crosshatched region represents full traverse of Instron crosshead.
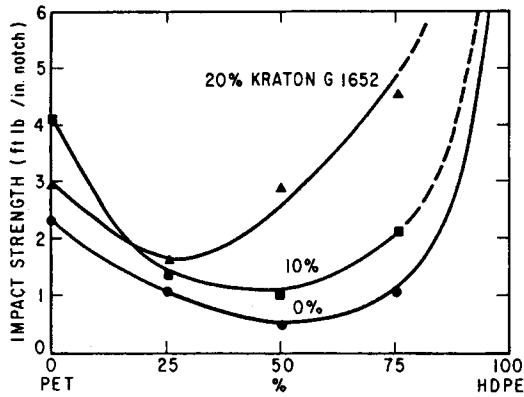
Fig. 4. Notched Izod strength for same materials as in Figures 2 and 3.

Instron. A crosshead speed of 0.2 in./min was used to measure the modulus. After this was done, the extensiometer was removed, and the crosshead speed was increased to 1 in./min until the sample broke or the maximum crosshead traverse was reached. Izod bars were notched and then tested using a Testing Machine, Inc. impact tester.

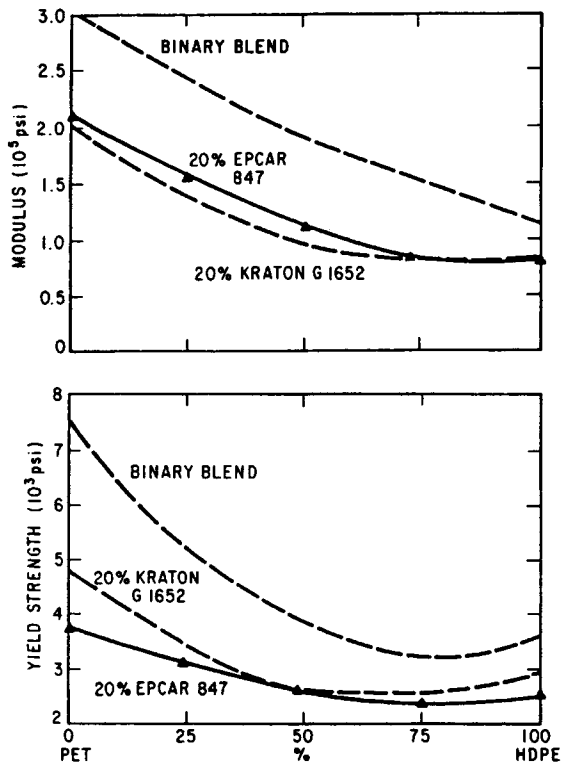The bindary blends of PET and HDPE produced in this fashion showed gross

Fig. 5. Modulus and strength of PET/HDPE/Epcar 847 blends made by injection molding. Dashed curves are data from Figure 2 shown for comparison.
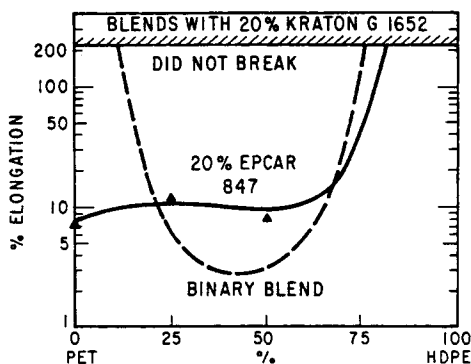
Fig. 6. Elongation at break for same materials as in Figure 5.

mechanical incompatibility as one might expect for this pair. As seen in Figures 2, 3, and 4, strength, elongation at break, and impact strength all show a minimum vs. blend composition. A wide range of incompatible blends have been prepared in this laboratory in the past; however, this system is among the poorest in terms of mechanical properties. Clearly, these properties would have to be improved dramatically to render such blends useful. The following summarize efforts to accomplish this using the elastomers mentioned earlier as blend additives.

Kraton G 1652

The Kraton family of triblock copolymers have been found to produce improvements in the mechanical behavior of a wide range of polymer blends[4,5,8]; hence, they were considered as potentially useful candidates for mechanical compatibilization for the HDPE–PET system. Figures 2, 3, and 4 show the results using Kraton G 1652. This elastomer has flow properties intermediate to HDPE and PET for the mixing conditions employed here. As expected, the modulus and strength are reduced by addition of an elastomer; however, there is a dramatic increase in ductility upon adding modest amounts of this block copolymer as seen in Figure 3. Blends containing 20% of Kraton G 1652 did not break within the available traverse of the Instron crosshead (slightly more than 200%). Blends containing equal parts PET and HDPE can be converted from very brittle materials into quite ductile ones (>100% elongation at break) by adding only 10% of this block copolymer—a very remarkable transformation. Impact strengths are also improved by addition of this block copolymer. The beneficial effects are more dramatic for HDPE rich blends than for those rich in PET as seen in Figure 4; however, the latter did show very high ductility in the slower Instron test.

Epcar 847

The EPDM elastomer, Epcar 847, was found to be an effective compatibilizer for various polyolefin blends[2,7]; hence, it was introduced as an additive in the present blend system to ascertain whether it might play a similar role in this case. It was added at the 20% level only, and its effect on mechanical properties is shown in Figures 5–7 relative to the binary PET–HDPE blends and the ternary
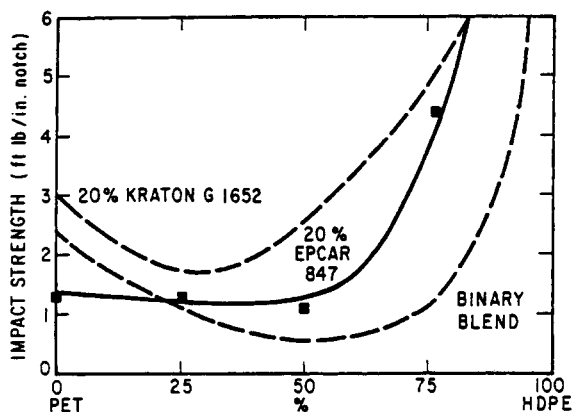
Fig. 7. Notched Izod strength for same materials as in Figures 5 and 6.

blends containing 20% Kraton G 1652. Data for the latter two from previous figures are shown as dashed curves for comparison. Modulus and strength values are slightly, but not significantly, different when either Kraton G 1652 or Epcar 847 is the additive. However, there are remarkable differences in the ductility of the ternary blends for the two different elastomers, as shown in Figure 6.
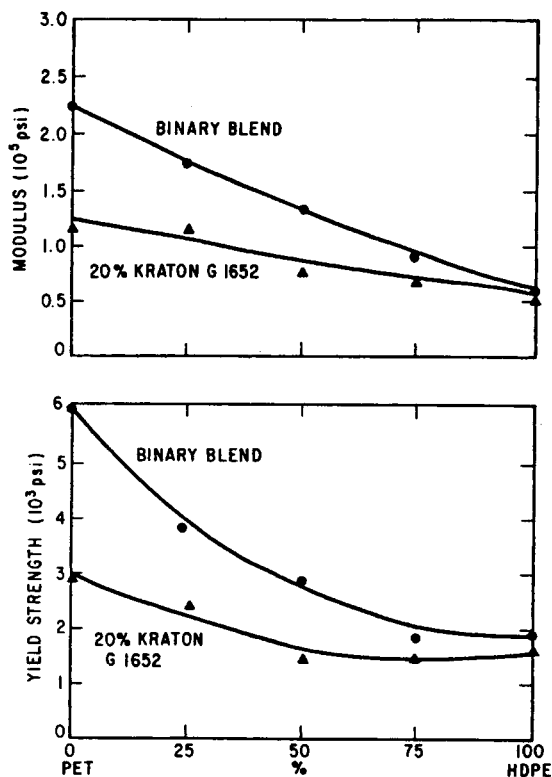

Fig. 8. Modulus and strength of films of PET–HDPE blends with and without Kraton G 1652. Tests were made on 10-in. strips cut in the longitudinal direction.
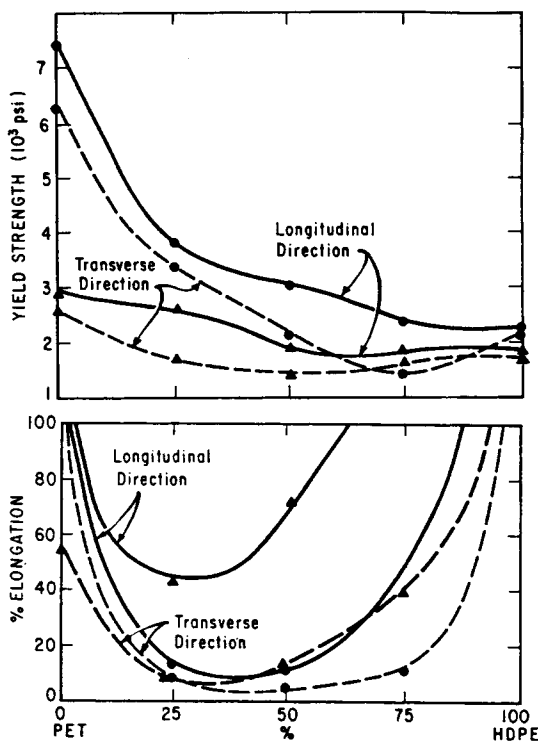
Fig. 9. Longitudinal and transverse properties for 1-in. test samples cut from film with 20% Kraton G 1652 (▲) and without Kraton G 1652 (●).

Epcar 847 causes a significant reduction in the ductility of PET and only slightly improves the behavior of blends containing both PET and HDPE. In contrast, similar blends to which Kraton G 1652 was added exhibited elongations at failure greater than the full traverse of the Instron crosshead travel ($\simeq 200\%$). Similar trends are shown for the impact strength in Figure 7. The pivotal issue in comparing Epcar 847 and Kraton G 1652 seems to be the difference they produce in blends with PET. The block copolymer imparts a modest toughening of PET while the EPDM decreases the toughness of PET, i.e., the EPDM is mechanically incompatible with PET.

The results given here clearly demonstrate the importance of elastomer molecular structure in fulfilling the role of a blend compatibilizer. That is, the ductility improvements shown in Figure 3 stem from other causes than merely adding any elastomeric component to the blends of HDPE and PET. Further comments on this are given later.

MECHANICAL PROPERTIES OF EXTRUDED FILM

Films of the various blends of PET and HDPE and ternary mixtures containing Kraton G 1652 were examined in order to assess the effect of fabrication techniques on mechanical properties. For this case, the extruder was outfitted with a 6-in. film die, and the extrudate was taken up by nip rolls through which cooling water was circulated. All films were made with a draw ratio, defined as
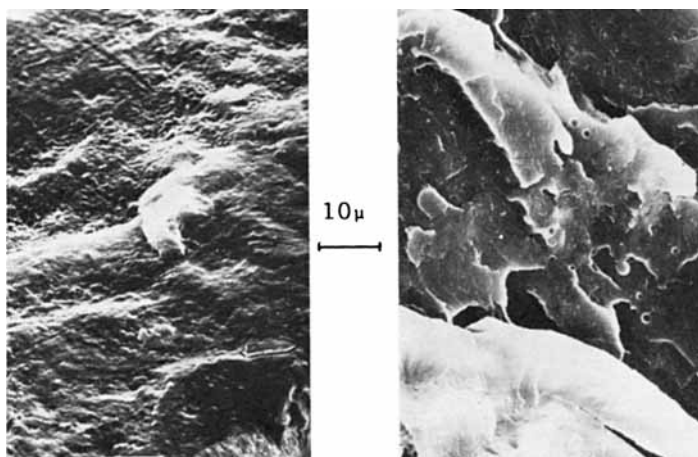
Fig. 10. Scanning electron photomicrographs of HDPE (left) and PET (right) fracture surfaces.

the ratio of the cross-sectional area of the die compared to that of the final film, of 3–4.

For mechanical testing, strips 0.375 in. wide were cut from the extruded film. These were tested by a table model Instron using a crosshead speed of 0.5 in./min. Strips with a gage length of 10 in. were used to obtain the modulus (no extensiometer was used) and strength of the films in the longitudinal direction while a gage length of 1 in. cut either parallel or transverse to the machine direction was used to obtain the elongation at break.

Modulus and strength characteristics obtained for specimens cut parallel to the machine direction and having a gage length of 10 in. are shown in Figure 8. In every case, the film exhibits a lower modulus and a lower strength than observed for the corresponding injection molded specimen. This no doubt stems from a lower degree of molecular orientation in the film than in the bars. Figure 9 shows yield and failure behavior obtained on the 1 inch gage specimens. As expected, strength and ductility are generally poorer in the transverse than the longitudinal directions.[9] Interestingly, in the transverse direction Kraton G 1652 causes a reduction in the elongation at break for PET. These results were developed, in part, to demonstrate what appears to be a general feature of incompatible polymer blends. By virtue of flow during processing, phase orientation (distinct from molecular orientation within a phase) develops, and mechanical behavior in the flow direction improves because of the conversion to a more nearly parallel arrangement of phases. This reduces the reliance on transfer of stress across the phase interfaces when strained in this direction.[9] However, this problem, which we believe to be the major issue in mechanical incompatibility, is exaggerated in the transverse direction as demonstrated by the film results in Figure 9. To a degree, similar behavior exists in injection-molded samples but fails to be detected because molded bars cannot be tested transversely. To this extent, examination only of injection-molded bars for immiscible blends may lead to somewhat misleading conclusions concerning the intrinsic characteristics of the blend.
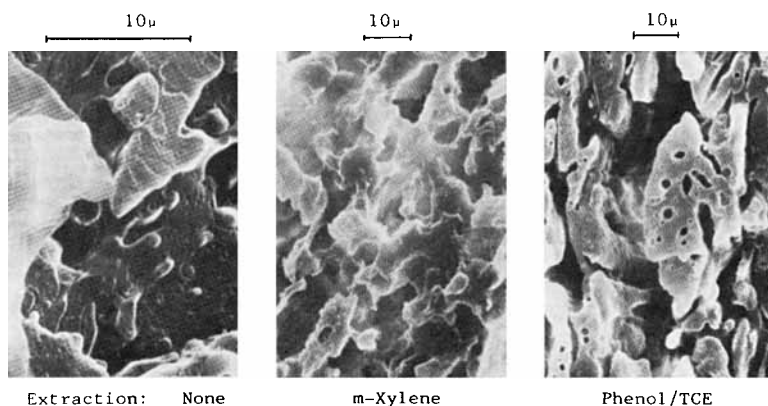
Fig. 11. Scanning electron photomicrographs of fracture surfaces of a 50/50 PET/HDPE blend containing 20% Kraton G 1652 prior to extraction (left), after extraction for hydrocarbons (center), and after extraction for PET (right).

PHASE MORPHOLOGY OF BLENDS

To gain further insight into the remarkable differences in mechanical behavior of PET–HDPE blends using Kraton G 1652 and Epcar 847 as additives, the phase morphology of these systems was examined by scanning electron microscopy. For this, injection-molded bars were fractured after being cooled by immersion in liquid nitrogen. For further comparison, Figure 10 shows SEM photomicrographs of the fracture surfaces of both HDPE and PET which are typical for such polymers. Similar fracture surfaces are shown on the extreme left in Figures 11 and 12 for blends containing equal parts by weight of PET and HDPE plus 20% by weight of Kraton G 1652 and of Epcar 847, respectively. For the latter, clear distinctions between at least two phases are evident, whereas such distinction is not so clear for the former.

To enhance observation of the configuration of the various phases at the fracture surfaces, solvents were used to selectively extract components from the blend. To remove the PET, the fracture surface was immersed in a stirred solution of 60/40 phenol/tetrachloroethane, which is a solvent for this component, at ambient temperature for 48 h. The opposite fracture surface of the same bar was immersed in refluxing m-xylene for 20 h, which should remove both the HDPE and either elastomer. Following these extractions, the bars were rinsed thoroughly with cold acetone and dried under vacuum for 24 h. In all cases, the fractured surfaces were gold-coated and mounted on brass stages prior to viewing with a JEOL JSM 35C scanning electron microscope.

Photomicrographs of the fracture surfaces after each of these extraction procedures are shown in Figures 11 and 12. For the blend containing Kraton G 1652 shown in Figure 11, there appears to be a skeletal phase remaining after extraction with m-xylene, which presumably is composed of PET since both hydrocarbon polymers should have been removed by this procedure. Similarly, another skeletal phase remains after the extraction procedure that should remove only PET. From these observations, it follows that there is cocontinuity of phases, that is, an interpenetrating network of phases, such as that described
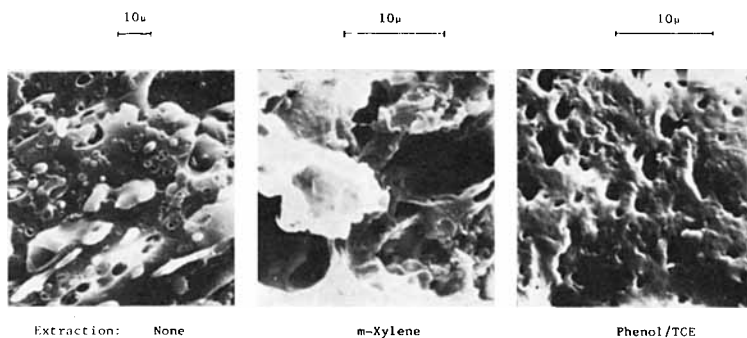
Fig. 12. Scanning electron photomicrogaphs of fracture surfaces of a 50/50 PET/HDPE blend containing 20% Epcar 847 prior to extraction (left), after extraction for hydrocarbons (center), and after extraction for PET (right).

by Gergen and Davison.[8]   A quite different morphology was found for blends containing Epcar 847 as the additives as may be seen in Figure 12.   After extraction with phenol/TCE, there is a distinct matrix phase, which should consist of HDPE plus elastomer, from which a dispersed phase, PET, has been removed. After extraction with m-xylene, the remaining material, PET, appears very indistinct in morphology, which we feel is the result of having removed the continuous phase leaving behind some distorted and collapsed dispersed phase, PET. This interpretation is consistent with the appearance of the unextracted fracture surface shown on the left in Figure 12.   We believe the lighter appearing phase here is PET which when removed leaves the structure shown on the extreme right.   Based on all knowledge of this system, the Epcar 847 is probably well mixed into the HDPE phase but not with the PET nor is it necessarily at the interface between PET and HDPE.   Extraction of the darker phase, presumably the hydrocarbon phase since it occupies the greater area, also removes some PET since it is postulated to be a noncontinuous dispersed phase—the result being the rather irregular structure shown in the center.   The appearance of the unextracted surface in Figure 12 suggests that there is poor adhesion between the darker and lighter phases described above.   In contrast, the unextracted surface on the left in Figure 11 does not reveal such a clear delineation of phases. Higher magnification photomicrographs of this surface (not shown here) suggest that adhesion at phase boundaries was much better than that in Figure 12—this would explain some of the differences in appearance for the two unextracted fracture surfaces.

Extracted and unextracted fracture surfaces for binary blends containing equal mass of PET and HDPE were rather irregular in appearance with no evidence for cocontinuity of phases.   From these observations, we conclude that one of the functions of the block copolymer additive is to reorganize the blend morphology into an interpenetrating network of phases which is beneficial for mechanical properties.   Gergen and Davison[8] came to similar conclusions using such block copolymers as additives for a wide range of other blend systems. Evidently Epcar 847 does not cause the same effect.

ADHESION OBSERVATIONS

We feel that interfacial adhesion in multiphased blends is an important factor
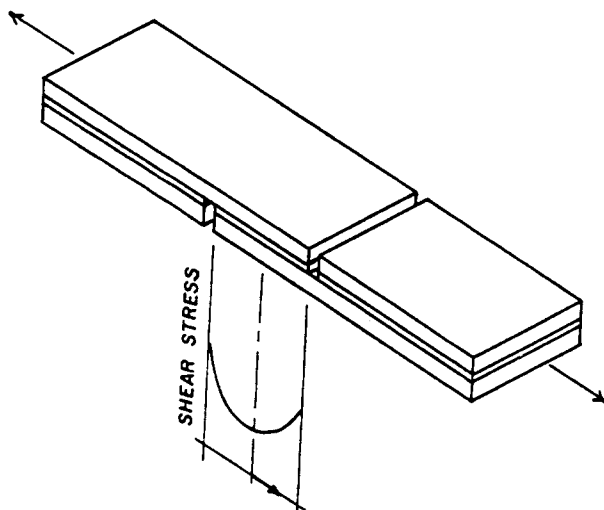
Fig. 13. Schematic of laminate notched to form lap shear specimen. Variation of stress with position is indicated.

in determining their mechanical performance. Consequently, some measure of the propensity for the various components in the present blends to adhere to each other was sought. The approach adopted consisted of making trilaminates which could be converted into a lap shear specimen by appropriate notching, as shown in Figure 13. The laminate consists of a sandwich of one polymer between two identical sheets of another polymer formed by compression molding above the melting or softening temperature of each component in the laminate. When notched as shown in Figure 13, a lap shear joint is formed which can be tested for adhesive strength. As suggested in Figure 13, the actual stress in the joint varies with position and can be calculated by an appropriate analysis[10]; however, for the present purpose we will report only the average shear stress at which a one inch square joint failed. The results are tabulated in Table I. As can be seen, the adhesion of PET to HDPE is quite poor. However, the block copolymer, Kraton G 1652, adheres better to both PET and HDPE than this pair does to each other. The strong adhesion of the block copolymer to HDPE is no doubt a result of the similarity of the polyolefin midblock to polyethylene. The modest adhesion of the block copolymer to PET is somewhat surprising and apparently stems from the aromatic character of the end blocks. In any case, the adhesion of the block copolymer to PET and HDPE suggests that at least part of the beneficial effect of adding Kraton G 1652 to PET/HDPE blends stems from its ability to act as a mutual adhesive for these components, which do not adhere to each other very well.

Experimental difficulties precluded development of similar adhesion data using Epcar 847; however, the behavior was clearly established qualitatively. This elastomer adheres very well to HDPE but very poorly to PET, as might be expected. We believe this is an important factor in the poor compatibilizing effect of Epcar 847 for this system.

While this approach to component adhesion in blends is informative, it does suffer limitations. The interfacial surfaces in blends are nascent ones not subject

TABLE I
Lap Shear Adhesion Results

Laminate	Average shear stress at failure (psi)
PET–HDPE–PET	34
HDPE–K–HDPE[a]	288
PET–K–PET[a]	86

[a] K = Kraton G 1652.

to various forms of contamination and the variables of fabrication which are factors in making these laminates. An ideal way to overcome these issues would be to coextrude the laminates. This approach would better simulate the interfaces found in blends.

SUMMARY

The results presented here show that a styrene/ethylene-co-butene-1/styrene type triblock copolymer is a very effective additive for improving the tensile toughness of PET/HDPE blends which otherwise exhibit very poor mechanical behavior. It is quite clear from the structure of this block copolymer that the mechanism for the "compatibilization" cannot involve the incorporation of its segments into the phases of the two immiscible blend components to form molecular bridges across this interface as the classical, and perhaps simplistic, model for interfacial agents suggests.[1] Yet the compatibilizing effect produced in these blends is specific to the molecular nature of the additive, as demonstrated by the fact that an EPDM elastomer produced essentially no benefit effect—the same EPDM does produce a compatibilizing effect for blends of various polyolefins.[2,7]

Some insight into the mechanism of this effect was established by examining the phase morphology and the nature of the interfaces in these blends. Addition of the block copolymer tends to cause the blends to form an interpenetrating network of phases as suggested by Gergen and Davison.[8] Furthermore, the block copolymer adheres to both PET and HDPE better than these two do to each other. Both facts would contribute to better sharing of applied stresses by the PET and HDPE in a blend and, consequently, to improved mechanical performance. We speculate that the observed adhesive characteristics stem from interfacial energy considerations that also exist in the melt state during mixing. Following this reasoning, phase contacts between block copolymer and HDPE or block copolymer and PET are preferred to phase contacts between PET and HDPE. This being the case, the preferred morphology would be cocontinuous phases of PET and HDPE with a interlayer or interphase of block copolymer between them. Similar morphologies have been proposed for microemulsions.[11]

This suggestion qualitatively explains these observations; however, it is highly speculative and cannot be fully defended by information available to date. The EPDM elastomer does not have the required affinity for both components to fulfill a role similar to that suggested for the block copolymer.

References

1. D. R. Paul, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Vol. II, Chap. 12.

2. E. Nolley, J. W. Barlow, and D. R. Paul, *Polym. Eng. Sci.*, **20**, 364 (1980).

3. C. R. Lindsey, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **26**, 9 (1981).

4. C. R. Lindsey, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **26**, 1 (1981).

5. D. W. Bartlett, D. R. Paul, and J. W. Barlow, *Mod. Plast.*, **58**(12), 60 (1981).

6. A. Rudin, D. A. Loucks, and J. M. Goldwasser, *Polym. Eng. Sci.*, **20**, 741 (1980).

7. D. W. Bartlett, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **27**, 2351 (1982).

8. W. P. Gergen and S. Davison, U.S. Pat. 4,107,130 (1978), assigned to Shell Oil Co.

9. J. W. Stell, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.*, **16**, 496 (1976).

10. T. D. Traugott, M.S. thesis, University of Texas at Austin, 1982.

11. L. E. Scriven, in *Micellization, Solubilization, and Microemulsions*, K. L. Mittal, Ed., Plenum, New York, 1977, Vol. 2, p. 877.