Deformation Behavior of HDPE / (PEC / PS) / SEBS Blends

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Synopsis

Immiscible blends of high density polyethylene (HDPE) and an amorphous glassy phase consisting of either pure polystyrene (PS) or a miscible blend of PS and a polyether copolymer (PEC) were compatibilized with various amounts of a styrene-hydrogenated butadiene block copolymer (SEBS). PEC is structurally similar to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Using a liquid displacement stress dilatometer, the volume change of samples during uniaxial mechanical straining was determined and related to the various modes of deformation. Blends were fabricated by both injection and compression molding. Miscible PEC and PS blends were found to undergo a craze to shear yielding transition between 40 and 60% PS, which occurred at higher PS concentrations as SEBS was added. Blends with a HDPE matrix and a dispersed glassy phase showed reduced volume dilatation on adding SEBS, indicating better interfacial adhesion between the incompatible blend components. Increases in the sample volume were substantially less in blends with a PEC/PS glassy phase instead of pure PS, suggesting more effective compatibilization by the SEBS copolymer in blends with PEC. This trend is presumed to stem from an exothermic heat of mixing between the PS endblocks of SEBS and the PEC-rich phases in the blend. Microscopic evidence of the improved adhesion and modes of deformation agrees with the results obtained by dilatometry. The volume dilatation of compression-molded materials do not seem to be similarly affected by the composition of the glassy phase which may reflect morphological differences between injection- and compression-molded blends.

INTRODUCTION

Macroscopic changes in the volume of a polymer specimen that accompany imposed uniaxial strains reflect the microscopic mechanisms by which the material deforms. Bucknall and Clayton[1,2] introduced this approach as a quantitative adjunct to creep experiments and demonstrated its usefulness as a means to study craze formation in rubber-modified plastics. A variety of techniques have been used to measure changes in sample volume for such purposes as examining the effect of stress level[1-4] and strain rate[5-7] on the microcavitation or crazing process. Volume strain can be a useful indicator of the various processes which may occur during the course of the usual stress-strain experiment. Prior to yielding there is a primarily elastic volume dilatation normally expressed as the Poison ratio. After yielding, the volume behavior reflects the relative extent of nondilatational (shear deformation) or cavitational (crazing, microvoiding, etc.) processes which may occur.

This technique has been extended to multiphase systems as a method for assessing the interfacial bonding of the phases to each other.[8-14] Using a liquid displacement dilatometer, Coumans and Heikens[9,10] showed that

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changes in the Poisson ratio of blends of low density polyethylene and polystyrene (PS) could be used effectively to demonstrate the improvement in interfacial adhesion that resulted when a compatibilizer, a styrene-butadiene-based block copolymer, was added. Results of the volume dilatation indicated that crazing in PS-rich blends is controlled by adhesion at the interface between the blend components which dominates the mode of postyield deformation. Other investigators have used postyield volume changes to study particulate filled composites.[13,14] Dewetting or void formation at the interface between the matrix and dispersed particles resulting from poor interfacial adhesion is manifested as volume dilatation which decreases as interfacial adhesion is improved.

This is the third paper in a series on the effectiveness of a styrene-hydrogenated butadiene triblock copolymer (SEBS) as a compatibilizer for immiscible blends of high density polyethylene (HDPE) and an amorphous phase consisting of either pure PS or a miscible mixture of PS and various quantities of a polyether copolymer (PEC) added to enhance mechanical and thermal properties of this phase. 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 as a comonomer into the backbone. PEC is miscible with PS over the full composition range just as is PPO.[15] In HDPE/(PEC/PS) blends the PEC/PS mixture forms one phase and HDPE forms another. SEBS is presumed to form a phase at the interface between HDPE and the glassy material. Earlier results showed that SEBS improved the mechanical properties and provided stability during processing of these materials.[16,17] Even larger reductions in the dispersed phase size and more evidence of interfacial adhesion were found when the amorphous phase contained PEC in addition to PS.[16] Impact strength and ductility were also enhanced under similar conditions.[17] These effects are presumed to stem from a possible exothermic driving force for mixing between the PS endblocks of SEBS with PEC phases of the blend.[16] This paper will use the postyield volume changes measured by a liquid displacement stress dilatometer during uniaxial straining of these blends to understand the modes of deformation involved and to assess the adhesion between phases.

EXPERIMENTAL

Materials

The materials used are described in greater detail in the first paper of this series.[16] Injection-molding grades of high density polyethylene were supplied by Union Carbide Corporation. An extrusion grade of polystyrene (Cosden 550 PS) was supplied by Cosden Oil and Chemical Company.

Polyether copolymer (PEC) was supplied specifically for this study by Borg-Warner Chemicals, Inc. in the form of preblends with Cosden 550 PS containing 80% PEC (PEC80) and 60% PEC (PEC60). Other compositions were prepared from these by extrusion blending with additional PS. The glass transition temperatures of the PEC/PS blends were found to be comparable to those for PPO/PS blends of the same composition.[17]

The triblock copolymer (SEBS) selected for this study (designated SEBS-L in the first paper) was supplied by Shell Chemical Co. as Kraton G 1652. SEBS is based on styrene–butadiene; however, the polybutadiene midblock (MW = 37,500) with both 1,4- and 1,2-diene structures was hydrogenated to be structurally similar to an ethylene/(butene-1) random copolymer. The PS endblocks have a molecular weight of about 7,000.

Blend Fabrication

Compounding and processing temperatures used to fabricate these blends varied with their composition as described earlier.[16] Extrusion mixing was carried out in two passes through a Killion extruder using a shear mixing screw. Tensile and Izod impact specimens were prepared in an Arburg injection molder. Compression-molded sheets were fabricated from extruded pellets of each composition in a compression press. Tensile and impact specimens were cut from these sheets using a Tensilkut router.

Stress Dilatometry

Figure 1 is a schematic of the water-filled stress dilatometer used to detect volume changes in tensile samples as they undergo uniaxial elongation. It is quite similar to the design used by Coumans and Heikens.[8] The acrylic plastic tube is secured in place by brass end plates and is removable to facilitate mounting of the sample in the grips. The shaft attached to the upper grip continuously moves out of the enclosed vessel through an O-ring seal as the entire assembly moves downward with the lower crosshead of the Instron machine to which it is attached. A compensating mechanism having a piston of the same diameter as the shaft attached to the grip pumps an equal amount of water back into the chamber so that the only net change in volume is that of the sample itself. Blank runs without a sample installed gave a negligible volume change which confirms that exact compensation was achieved.

Changes in the sample volume were continuously measured by shifts in the water level in the graduated capillary connected to the sample chamber as shown. A differential pressure transducer was used to sense changes in the liquid head of the graduated capillary with respect the stationary liquid head in a reference capillary. The liquid pressure differential, which is directly proportional to the volume change of the sample, was monitored by a strip chart recorder. The stress-strain response was also recorded simultaneously with the volumetric dilatation. Test were made at room temperature on a minimum of 2 samples of each composition with a cross-sectional area of approximately 0.5 in. × 0.125 in. using a crosshead speed of 0.2 in/min. Several problems associated with the start-up of each test (e.g., vibrations, O-ring displacement, etc.) prevented accurate measurement of the initial slope of the volume-strain curve. Consequently, Poisson ratios are not reported here. These problems, however, did not affect results in the postyield region which are the focus of the present work. Commercially available biaxial extensometers are more convenient for measurement of the Poisson ratio,[18]

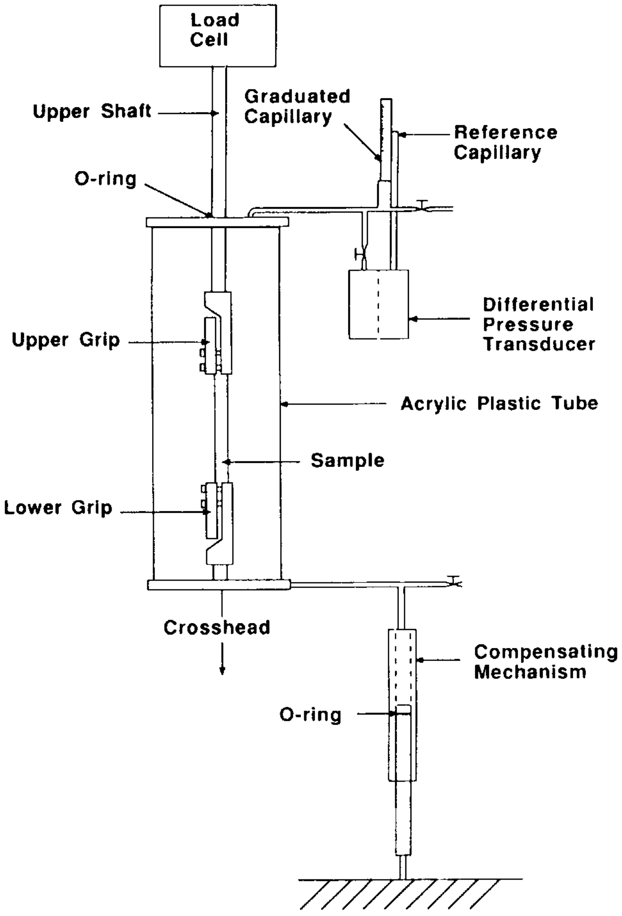


Fig. 1. Schematic of stress dilatometer.

but this approach cannot readily be used for the postyield region because of the large and frequently nonhomogeneous nature of the axial strain.

The definition of several parameters are necessary to fully understand the results presented here. The axial strain (ϵ) was determined from the crosshead travel (ΔL) normalized by the effective axial gauge length (L_{eff}), that is, $\epsilon = \Delta L / L_{\text{eff}}$. The latter quantity was computed from the initial slope of the load versus crosshead travel from

$$L_{\text{eff}} = E \frac{\Delta L}{\sigma} \tag{1}$$

where E is the modulus for the same sample determined in a separate test using a strain gauge extensometer and σ is the stress determined by dividing the load by the original cross-sectional area (A_0). The volume change (ΔV) taken directly from the dilatometer response was normalized by the volume of the gauge section, V_0, which is the product of A_0 and L_{eff}. This ratio, $\Delta V/V_0$, is termed the volume strain. Another quantity of interest here is the rate at which the volume changes with axial strain in the postyield region.

$$\frac{1}{V_0}\frac{d\,\Delta V}{d\epsilon} = \text{Slope} \tag{2}$$

This quantity is referred to later as the slope of the volume strain curve.

As a test of these procedures, multiple tests were made for materials whose response is well-known. For high impact polystyrene (HIPS), whose postyield deformation occurs by crazing,[1,2] the slope of the volume strain curve was found to be 1, or

$$\frac{1}{V_0}\frac{d\,\Delta V}{d\epsilon} = 1 \tag{3}$$

as reported in the literature[2,8]

On the other hand, polycarbonate yields entirely by nondilatational shear deformation, and it was found that

$$\frac{1}{V_0}\frac{d\,\Delta V}{d\epsilon} = 0 \tag{4}$$

as reported in the literature.[7] For mixed modes of deformation involving some shear and some dilatational component (crazing or void formation, delamination) values in between these limits can be expected.[3,4]

A more complete description of this stress dilatometer, its operation, and data reduction is available elsewhere.[19]

Microscopy

A Jeol 35C scanning electron microscope (SEM) operated at 25 kV was used to evaluate the phase morphology of these materials and their modes of deformation. Prior to viewing in the electron microscope, mounted samples were coated with gold or gold-palladium in a Pelco sputter coater. Most fracture surfaces in this study were prepared by prestraining samples uniaxially in an Instron to 5–10% strain followed by immersion in liquid nitrogen for several hours before fracturing the material. Brittle samples were strained to fracture and the prestrained fracture surface was made by cryofracturing the larger section of the broken sample. This method[20] preserves intermediate uniaxial deformation features for observation that would not otherwise be visible using conventional fracture surface preparation techniques.

RESULTS AND DISCUSSION

As mentioned in the Introduction, the focus of this paper is the use of the volume dilatation to investigate the microscopic deformation modes which occur during uniaxially loading of HDPE/(PEC/PS) blends containing various quantities of SEBS. In this complex blend system, HDPE forms one phase while the other phase contains either pure PS or miscible PEC/PS mixtures of different compositions. SEBS is presumed to form an interphase between the polyolefin and glassy components to provide interfacial adhesion and stability during processing.

Complete diagrams of the stress and volume strain responses which were recorded simultaneously as a function of elongational strain are shown for selected injection-molded compositions. The slope of the postyield volume dilatation versus elongational strain curve is reported for all compositions, since this quantity conveys the essential information. Stress–strain properties were described in an earlier paper.[17] Results are first presented for the miscible blends of PEC and PS to which varying amounts of SEBS was added, then blends also containing HDPE are considered. Finally, to illustrate how processing techniques affect the volume dilatation for blends having a HDPE matrix phase, specimens fabricated by compression molding are compared to injection-molded samples of the same composition.

PEC / PS Blends

Figure 2 is an example of stress and volume strain curves for PS containing various amounts of SEBS. In pure PS, an array of visible crazes develop

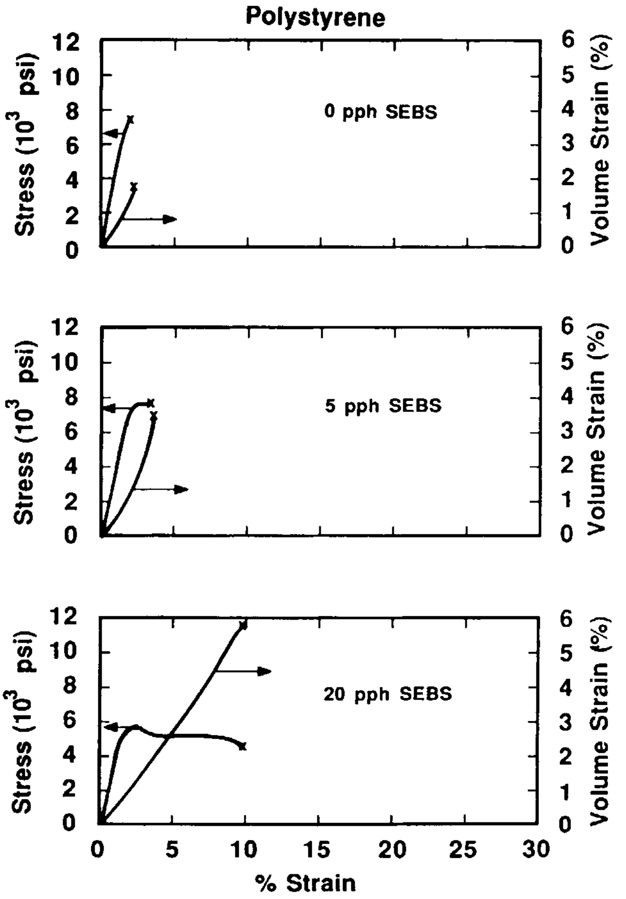


Fig. 2. Simultaneous stress (left axis) and volume strain (right axis) curves for PS containing the indicated amounts of SEBS.

normal to the applied tensile load and the material fails in a brittle mode without yielding. The strain at break increases slightly from about 2 to 4% on adding 5 pph SEBS, but the sample remains brittle. Blends with 20 pph SEBS attain greater elongations and show a distinct yield point. The slope of the postyield volume strain curve reaches a constant value of 0.68. Assuming good adhesion between the blend components, this value indicates that shear yielding contributes 32% to the mode of postyield deformation. Similarly, Coumans et al. reported 32% shear yielding for uniaxially strained samples consisting of 79% PS with 29% of a tapered diblock copolymer.[9]

Figure 3 shows the fracture surface of samples containing PS and SEBS prepared by prestraining and fracturing at liquid nitrogen temperatures as described earlier. Residual craze islands (or patchs) in pure PS formed as the crack propagated through the sample by severing material along the interface between the crazed and uncrazed bulk polymer. Similar residual craze structures have been described previously for PS fracture surfaces.[21-24] Stress whitening during straining of opaque blends containing 5 and 20 pph SEBS indicates that crazes probably form in these materials. The fracture surface of these blends resembles the patch structure of the crazed PS surface, except for the presence of SEBS particles or holes, which are larger in blends containing 20 pph SEBS (about 0.5 μm). Beneficial effects, such as greater elongation at break, are realized by adding SEBS even though the particle size is smaller than the critical rubber particle size for toughening PS (1 μm).[25] The lower postyield slope of the volume strain curve of 0.68 for this blend (relative to the presumed value of 1.0 that PS would show if it yielded) suggests that adding SEBS alters the mode of deformation even though the morphology shows little change.

The stress curves and volume strain curves for PEC20 (20% PEC/80% PS) containing SEBS are shown in Figure 4. PEC20 blends containing either 0 or 5 pph SEBS failed in a brittle manner; however, both of these blends reach greater elongations and show more gradual volumetric dilatation than similar compositions based on PS. On adding 20 pph SEBS, the elongation increases to over 25% while this blend no longer exhibits a distinct yield point like that of PS containing 20 pph SEBS. The slope of the volume strain curve decreased steadily until reaching zero at approximately 20% elongational strain. This trend represents a gradual transition from crazing to a shear mode of deformation. The presence of PEC promoted a reduction in the rate of the volume dilatation compared to pure PS blends of the same composition (20 pph SEBS).

Figure 5 shows structures on the prestrained fracture surface of PEC20 containing 0 and 5 pph SEBS that look like residual craze islands. Clear PEC20 samples visibly craze under stress; however, fewer crazes were seen in comparison to pure PS. The fracture surface of PEC20 appears to have several raised internal structures within the craze islands. For the blend containing 5 pph SEBS, small particles and holes approximately the same size as those in the comparable PS-based sample are noticeable on the fracture surface. The presence of craze-like structures similar to those found in PS blends with SEBS suggest that crazing contributed to the deformation of PEC20 with 5 pph SEBS. On adding 20 pph SEBS, the prestrained fracture surface (Fig. 5) more closely resembles the surface of materials that experience no craze

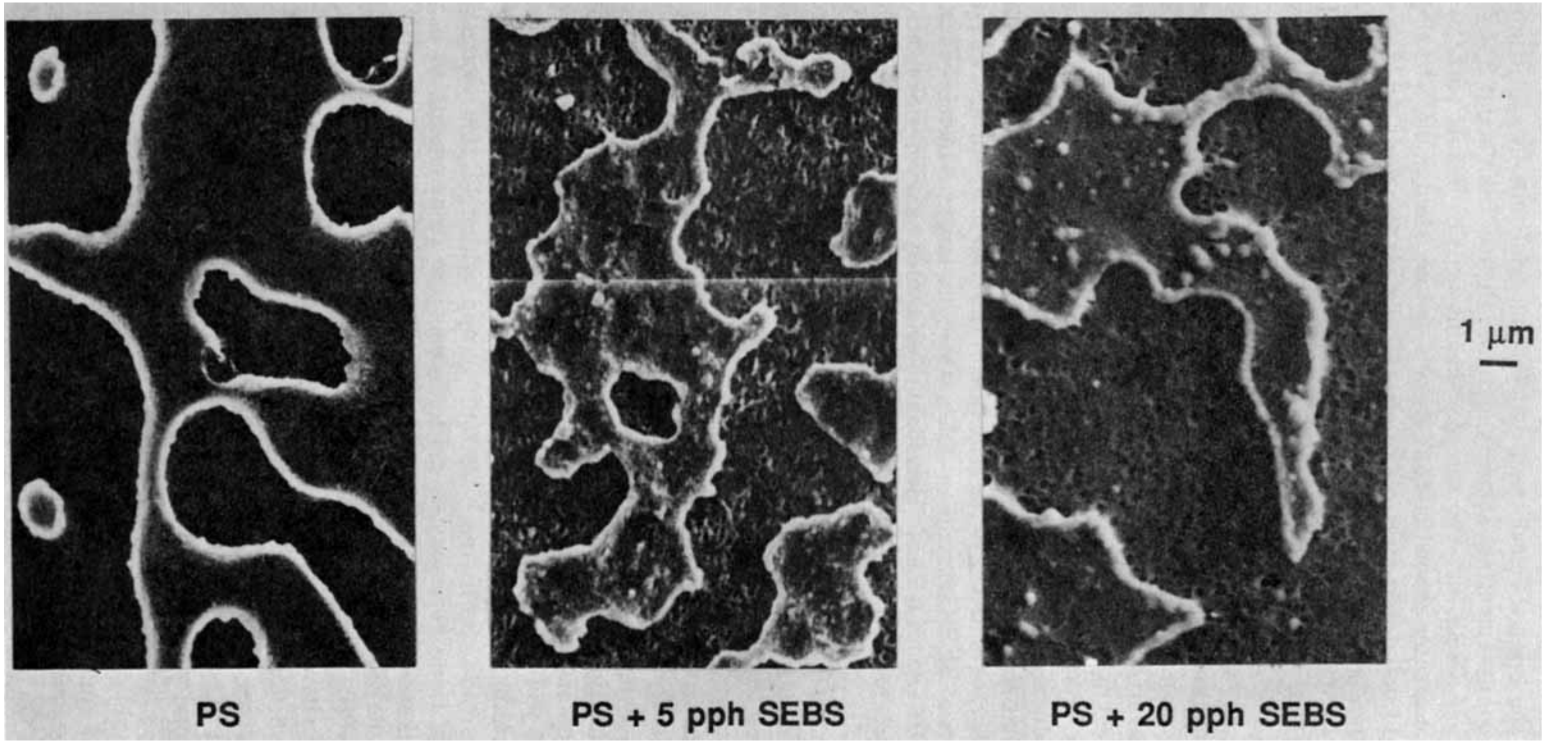


Fig. 3. Scanning electron photomicrographs of fracture surfaces of PS containing SEBS. All surfaces were prepared by uniaxial straining followed by cooling to liquid nitrogen temperatures and then fracturing.

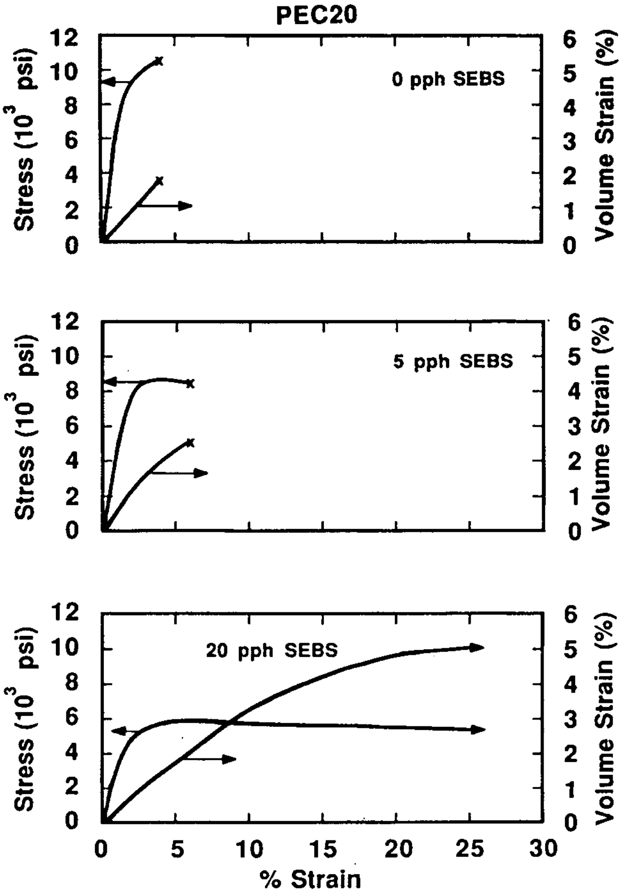
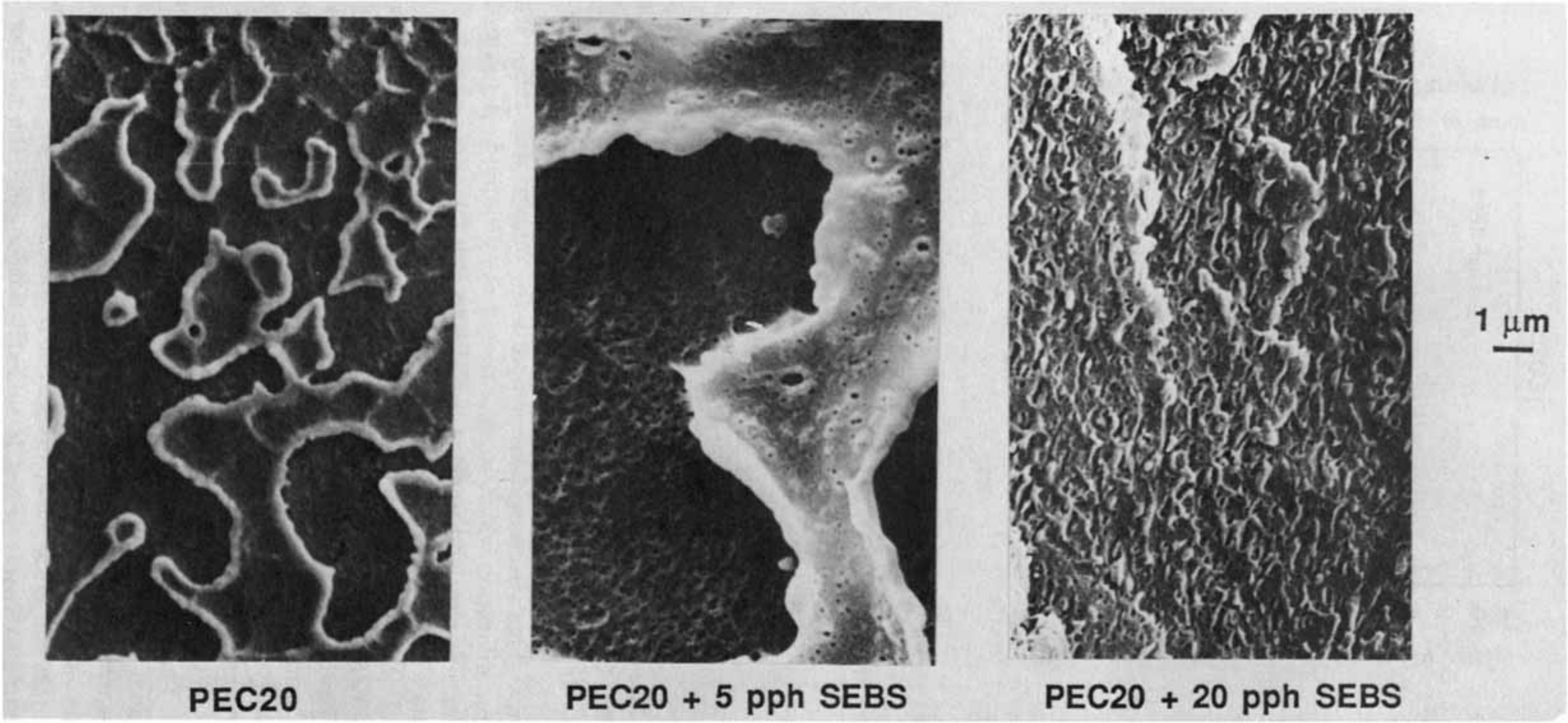


Fig. 4. Stress (left axis) and volume strain (right axis) curves for PEC20 containing the indicated amounts of SEBS.

formation.[21] This visual evidence supports the quantitative measurements of the volume dilatation which suggest that shear yielding is the primary mode of deformation after adding 20 pph SEBS to PEC20.

The stress and volume strain curves for PEC40 containing SEBS in Figure 6 show that this miscible blend is also brittle before adding SEBS. Incorporation of only 5 pph SEBS into PEC40 substantially improves ductility increasing the strain at break from about 4% to over 25%. A distinct yield point becomes evident in the stress curve near 5% strain, after which the sample necks locally. The postyield slope of the volume strain curve decreases to zero, suggesting a craze to shear transition as this material is strained. As the neck propagates throughout the gauge section, the deformation is entirely shear yielding. The peak yield stress is suppressed by adding 20 pph SEBS to PEC40 and the maximum volume dilatation is reduced to only 2% as this blend deforms by shear yielding.

The cryofracture surface of prestrained PEC40, shown in Figure 7, resembles the residual craze islands observed in PEC20 and PS. PEC40 is a clear blend that also visibly crazes in uniaxial tension, but the number of devel-



PEC20 PEC20 + 5 pph SEBS PEC20 + 20 pph SEBS

Fig. 5. Cryofracture surfaces of PEC20 containing SEBS. Samples were strained uniaxially before fracturing at liquid nitrogen temperatures.

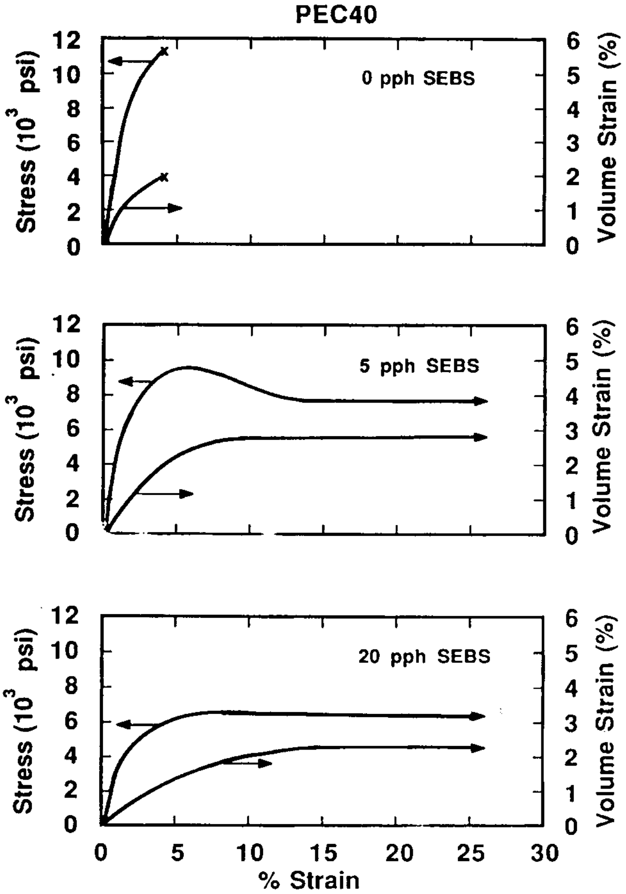


Fig. 6. Stress (left axis) and volume strain (right axis) curves for PEC40 containing the indicated amounts of SEBS.

oping crazes is substantially less than those in either PS or PEC20. After adding 5 pph SEBS, the fracture surface reveals no evidence of crazing as the mode of deformation. Visual evidence supports results from dilatometry, indicating that this blend deforms by shear yielding.

The volume dilatation responses of PEC60 and PEC80, shown in Figure 8, are nearly identical for blends containing equivalent amounts of SEBS. Both PEC60 and PEC80 deform by local necking at a distinct yield point and the neck propagates throughout the gauge section of the sample before final failure. The volume dilatation also peaks at the yield stress but decreases after yielding as a result of reduced load on the sample. As a consequence of necking, no appreciable volume increase is detected after yielding. Adding 5 pph SEBS to either pure component suppresses and broadens the yield point, while the deformation remains entirely shear yielding. In PEC60 and PEC80 blends containing 20 pph SEBS, deformation occurs uninformly throughout the gauge length instead of exhibiting a yield point and necking. Increased volume dilatation as more SEBS is added may be caused by microscopic voiding between the homopolymer and dispersed SEBS phases. For example,

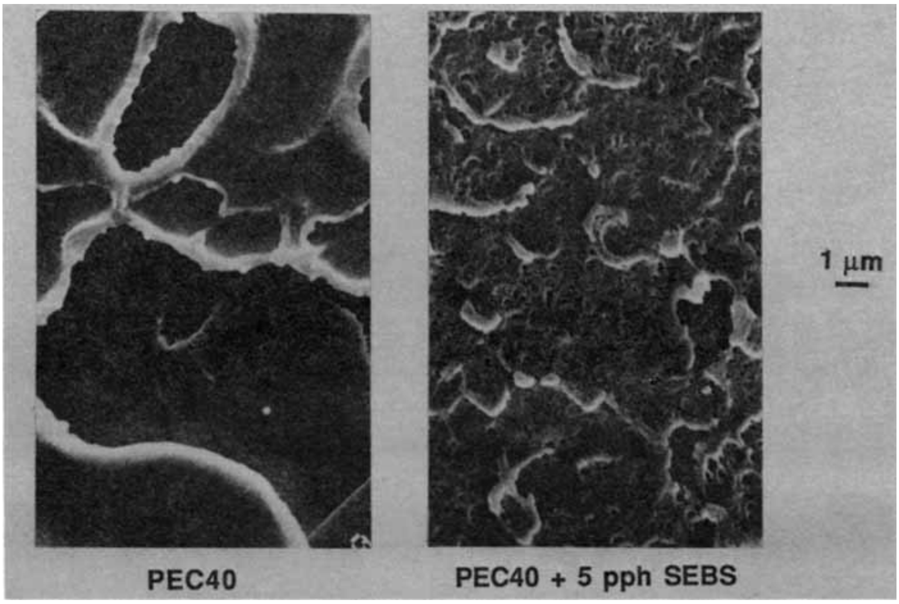


Fig. 7. Cryofracture surfaces of PEC40 containing SEBS. Samples were strained uniaxially before fracturing at liquid nitrogen temperatures.

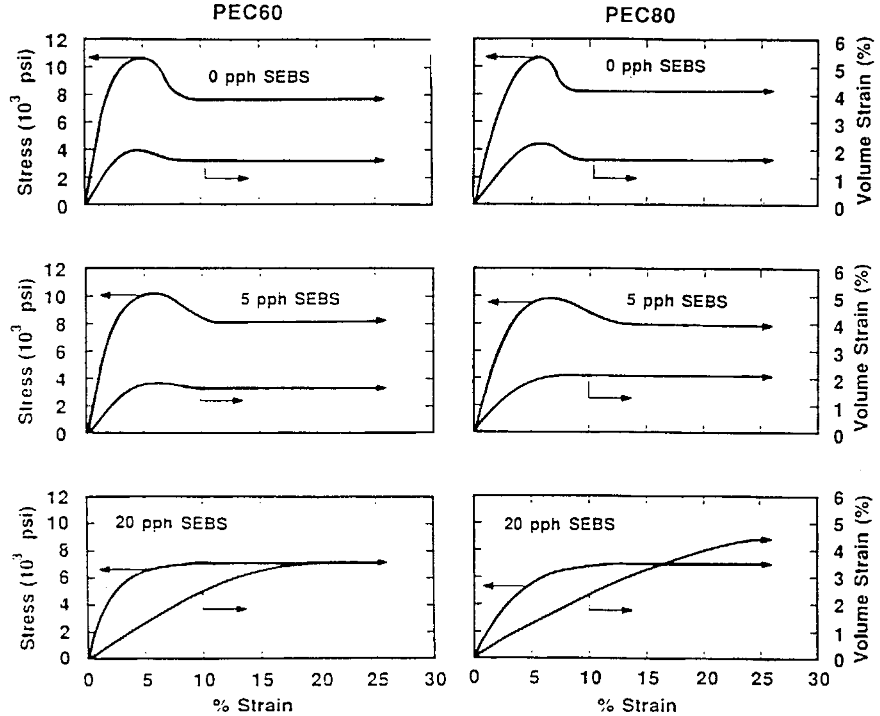


Fig. 8. Stress (left axis) and volume strain (right axis) curves for PEC60 (left graph) and PEC80 (right graph) containing the indicated amounts of SEBS.

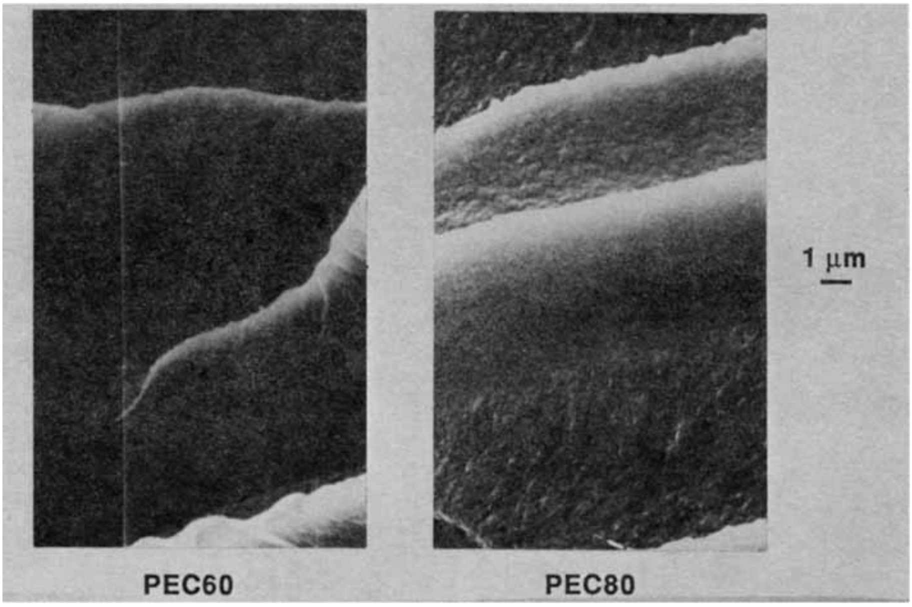


Fig. 9. Cryofracture surfaces of PEC60 and PEC80. Samples were strained uniaxially before fracturing at liquid nitrogen temperatures.

the postyield volume strain of PEC80 reaches a constant value of 1.7% which increases to 2.1% and eventually to 4.3% after adding 5 and 20 pph SEBS, respectively. Ridges on the fracture surface of strained PEC60 and PEC80 in Figure 9 are an artifact of the ductile fracture.[21]

Table I summarizes the values of the slope of the volume strain curve after yielding and the presumed mode of deformation for PEC/PS blends containing SEBS. In general, The relative extent of crazing decreases while shear yielding increases as the PEC content in miscible PEC/PS blends is increased. A craze to shear yielding transition occurs between 40 and 60% PEC. Wellinghoff and Baer[26] reported that a transition from crazing to shear banding occurs in thin films of PPO/PS between 20 and 30% PPO at room temperature. The difference in these two results may, in part, reflect the thickness of the samples used and the method of sample preparation rather than any inherent difference between PEC and PPO.

Addition of SEBS suppresses craze formation in PS, PEC20, and PEC40. Smaller amounts of SEBS are required to change the deformation mode the higher the PEC content of the glassy phase. For example, PEC20 containing 5 pph SEBS is brittle while PEC40 containing the same amount of SEBS reached elongations greater than 25% and deformed by shear yielding. However, in PS, PEC20, and PEC40 blends containing equivalent amounts of SEBS, the size of the dispersed particles remain of the same order of magnitude. In a similar study with rubber toughened PS/PPO blends, Bucknall et al.[3] concluded that the particle size is less important for toughening blends when crazing is accompanied by shear yielding, or in other words, increasing PPO content. Shear bands limit craze growth by terminating them before cracks form. Improvements in the mechanical properties, specifically ductility and impact strength, coincide with transitions from crazing to shear

TABLE I
Postyield Slope of the Volume Strain Curve and Mode of Deformation for PEC/PS Blends with SEBS

Base material	0 pph SEBS		5 pph SEBS		20 pph SEBS	
	$\frac{1}{V_0}\frac{dV}{d\epsilon}$	Mode of deformation	$\frac{1}{V_0}\frac{dV}{d\epsilon}$	Mode of deformation	$\frac{1}{V_0}\frac{dV}{d\epsilon}$	Mode of deformation
Polystyrene	[a]	Crazing	[a]	Crazing & shear yielding	0.67	Crazing & shear yielding
PEC20	[a]	Crazing & shear yielding	0.28	Crazing & shear yielding	0.0[b]	Shear yielding
PEC40	[a]	Crazing & shear yielding	0.0[b]	Shear yielding	0.0	Shear yielding
PEC60	0.0	Shear yielding	0.0	Shear yielding	0.0	Shear yielding
PEC80	0.0	Shear yielding	0.0	Shear yielding	0.0	Shear yielding

[a] Fractured before yielding.

[b] Slope changed continuously but, approached zero at high strains.

yielding with increasing SEBS and PEC contents. For example, PS containing 20 pph SEBS has an impact strength of approximately 2 ft-lb/in., whereas both PEC60 and PEC80 blends containing 20 pph SEBS did not fracture in the Izod impact test.

HDPE / (PEC / PS) Blends

In this section, results for blends that also contain HDPE will be examined. Since the stress and volume strain responses for PEC60 and PEC80 as well as blends containing equivalent amounts of either of these components were virtually identical, only results for blends containing PEC80 are presented in detail while those for PEC60 are given in tables.

In multiphase immiscible blend systems the matrix may become the primary load-bearing phase as a consequence of limited stress transfer between the components when the interfacial adhesion is poor or when the dispersed phase has a much lower modulus. Amorphous PS, PEC60, or PEC80 form the continuous phase in HDPE/(PEC/PS) blends containing less than about 50% HDPE; hence, the mode of deformation for blends in this composition range is determined primarily by the characteristics of the glassy component phase. The simultaneously recorded stress and volume strain curves for blends containing 25% HDPE and 75% of either PS or PEC80 are shown in Figure 10 as a function of the amount of SEBS added. Table II summarizes values for the postyield slope of the volume strain curve for blends containing 25%

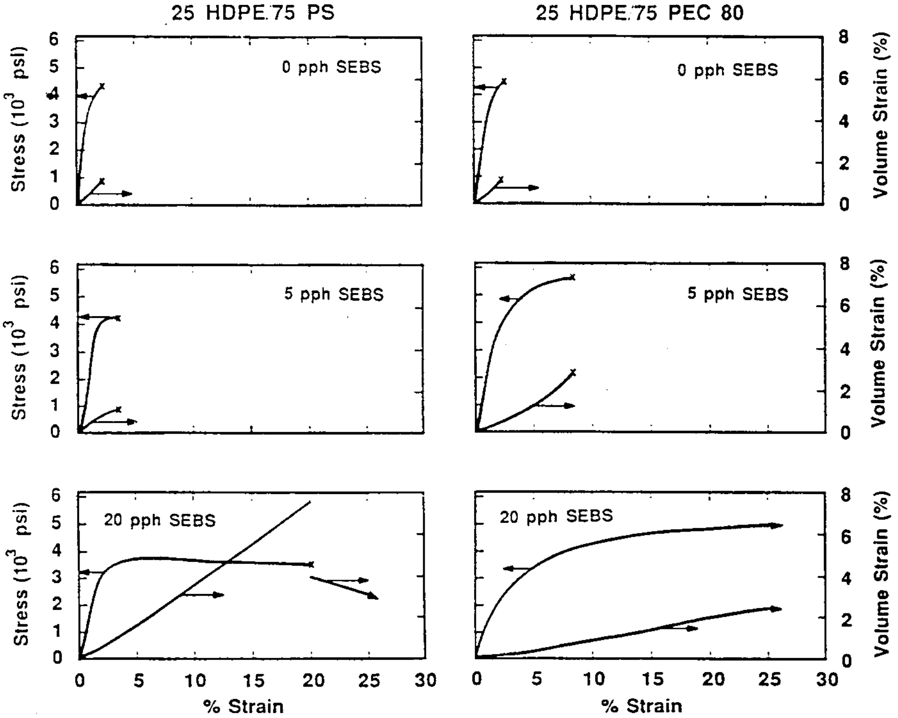


Fig. 10. Stress (left axis) and volume strain (right axis) curves for 25 HDPE/75 PS (left graph) and 25 HDPE/75 PEC80 (right graph) containing the indicated amounts of SEBS.

TABLE II
Postyield Slope of the Volume Strain Curve for 25 HDPE/(PEC/PS) Blends

SEBS pph[a]	25 HDPE/75 PS	25 HDPE/75 PEC60	25 HDPE/75 PEC80
0	[b]	[b]	[b]
5	[b]	0.21	0.32
20	0.39	0.12	0.13

[a] Parts per 100 of base blend.
[b] Fractured before yielding.

HDPE with varying amounts of PEC in the glassy phase and with different levels of SEBS. HDPE/PS blends containing no SEBS or 5 pph SEBS do not yield, as expected. On adding 20 pph SEBS, yielding occurs and beyond the yield point the volume strain increases with a constant slope of 0.39, indicating that shearing contributes at least 61% to the yield deformation. The origin of this dilatation is probably a combination of crazing and interfacial voiding, but it is not possible to quantify the relative contribution of each. This value of the slope is lower than that calculated assuming additivity from the blend components (HDPE, PS, and SEBS) and the value obtained for blends of PS and 20 pph SEBS. This suggests that the extent of crazing is further decreased by adding HDPE to PS/SEBS mixtures. Similar studies on blends of low density polyethylene and PS also showed that increased interfacial adhesion due to the presence of a compatibilizer reduces the number of crazes that can form in the PS phase. Immediately after fracturing, the volume strain drops from a maximum of about 8% to 4%. Further decreases in the volume dilatation occur with time after fracture, but the sample never fully recovers to the original volume. This sudden drop and subsequent gradual decrease in the volume is probably due to relaxation of crazes in the PS phase and closing of voids between the phases when the load was released.

Blends of 25% HDPE and 75% PEC80 without SEBS are also brittle (see Fig. 10). It is clear that adding 5 pph SEBS increases ductility and strength in this blend since the sample begins to yield instead of failing in a brittle manner. Blends containing 20 pph SEBS yield and the volume dilatation proceeds with a slope of 0.13, which is lower than the value obtained for blends of the same composition based on PS instead of PEC80. PEC80 deforms entirely by shear yielding, as shown earlier; therefore, all increases in the volume of these materials is due to interfacial voiding. Two dilatational modes of deformation (interfacial voiding and crazing) induce volume changes in blends with a continuous PS phase which leads to greater volume dilatation compared to blends containing continuous PEC-rich phases. The decrease in the volume dilatation with further addition of SEBS to 25 HDPE/75 PEC80 apparently reflects improvements in adhesion of these phases caused by this compatibilizer. Blends of the same composition containing PEC60 instead of PEC80 exhibit similar trends as may be seen by comparing values in Table II.

Tables III and IV give the postyield slope of the volume strain curves for 50 and 75% HDPE blends, respectively, containing either PS, PEC60, or PEC80 and various amounts of SEBS. In all of these blends HDPE forms the matrix phase which deforms by nondilatational shear yielding. Consequently, the

TABLE III
Postyield Slope of the Volume Strain Curve for 50 HDPE/(PEC/PS) Blends

SEBS pph[a]	50 HDPE/50 PS	50 HDPE/50 PEC60	50 HDPE/50 PEC80
0	[b]	[b]	[b]
5	[b]	0.22	0.21
20	0.19	0.02	0.09

[a] Parts per 100 of material.
[b] Fractured before yielding.

volume dilatation observed is due to interfacial voiding since it is unlikely that the glassy dispersed phase will craze. The trends for each of these materials are the same; therefore, discussion will be limited to selected blend compositions. Figure 11 presents stress and volume strain curves for 75 HDPE/25 PS and 75 HDPE/25 PEC80 compositions containing varying amounts of SEBS.

The binary 75 HDPE/25 PS blend yields at about 5% strain after which the volume dilatation increases with a slope of 0.48 until reaching a maximum at approximately 20% elongational strain. At this point, the sample begins to tear and further elongation continues at substantially reduced loads. It is interesting to note that the volume strain also begins to decrease at this point which reflects various recovery processes (elastic strain and interfacial void closure) as the stress is reduced. Decreases in the volume may also be due to water seeping into exposed voids on the fracture surface. Addition of 5 and 20 pph SEBS reduces the slope to 0.37 and 0.13, respectively. Reduced volume dilatation reflects better interfacial adhesion promoted by the presence of SEBS.

Binary 75 HDPE/25 PEC80 blends are brittle; however, the addition of SEBS dramatically improves ductility as shown in Figure 11. On adding only 5 pph SEBS the elongation increases beyond 25% and the postyield slope of the volume strain curve is reduced to 0.05. At 20 pph SEBS, the slope is further reduces to 0.02. The slopes of the volume strain curves are much lower for blends containing PEC80 instead of pure PS with the same HDPE and SEBS compositions. For example, by changing the dispersed phase from PS to PEC80 in blends containing 75% HDPE with 5 pph SEBS, the slope is reduced from 0.37 to 0.06, indicating better interfacial adhesion. These results agree with previous conclusions that adhesion is enhanced by the presence of

TABLE IV
Postyield Slope of the Volume Strain Curve for 75 HDPE/(PEC/PS) Blends

SEBS pph[a]	75 HDPE/25 PS	75 HDPE/25 PEC60	75 HDPE/25 PEC80
0	0.48	0.63	[b]
5	0.37	0.03	0.06
20	0.09	0.03	0.02

[a] Parts per 100 of material.
[b] Fractured before yielding.

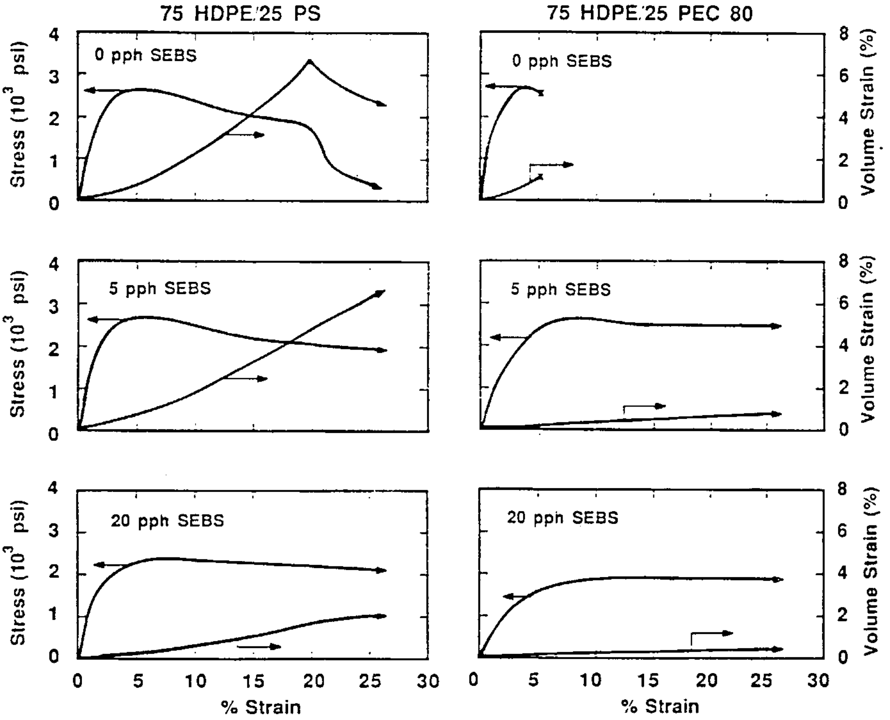


Fig. 11. Stress (left axis) and volume strain (right axis) curves for 75 HDPE/25 PS (left graph) and 75 HDPE/25 PEC80 (right graph) containing the indicated amounts of SEBS.

PEC due to the additional thermodynamic driving force for compatibilization by the copolymer when there is a PEC-rich phase in the blend.

Visual evidence for better interfacial adhesion in blends containing SEBS was obtained by inspecting prestrained fracture surfaces of these materials. Figure 12 shows fracture surfaces for selected compositions, viz. 75 HDPE/25 PS and 75 HDPE/25 PEC80 containing either 0 and 5 pph SEBS. Without SEBS, the photomicrographs show smooth PS or PEC80 balls dispersed in a highly distorted matrix of HDPE. The dispersed PS or PEC80 phases appear to be relatively unaffected by the applied load. The volume dilatation recorded for these materials can be attributed to the formation of large voids between the phases which are clearly visible in Figure 12.

Adding 5 pph SEBS to these blends reduced the size of the interfacial voids formed as revealed by the lower volume dilatation measured. One visual indication of the interfacial interactions in the HDPE/PS blends is the rough and textured surface of the dispersed PS particles. In addition, after the PS particles were flung out of the matrix during fracturing, the interior surfaces of the holes remaining in the HDPE matrix are not smooth. Both indicate greater interfacial interaction between the blend components. Better adhesion stemming from these interactions caused by the addition of SEBS ultimately reduces the volumetric dilatation during elongation. The improvements observed in the mechanical properties can be attributed to these effects.[16]

The photomicrograph for 75 HDPE/25 PEC80 containing 5 pph SEBS shows numerous fibrils connecting the phases. A closer examination for 75

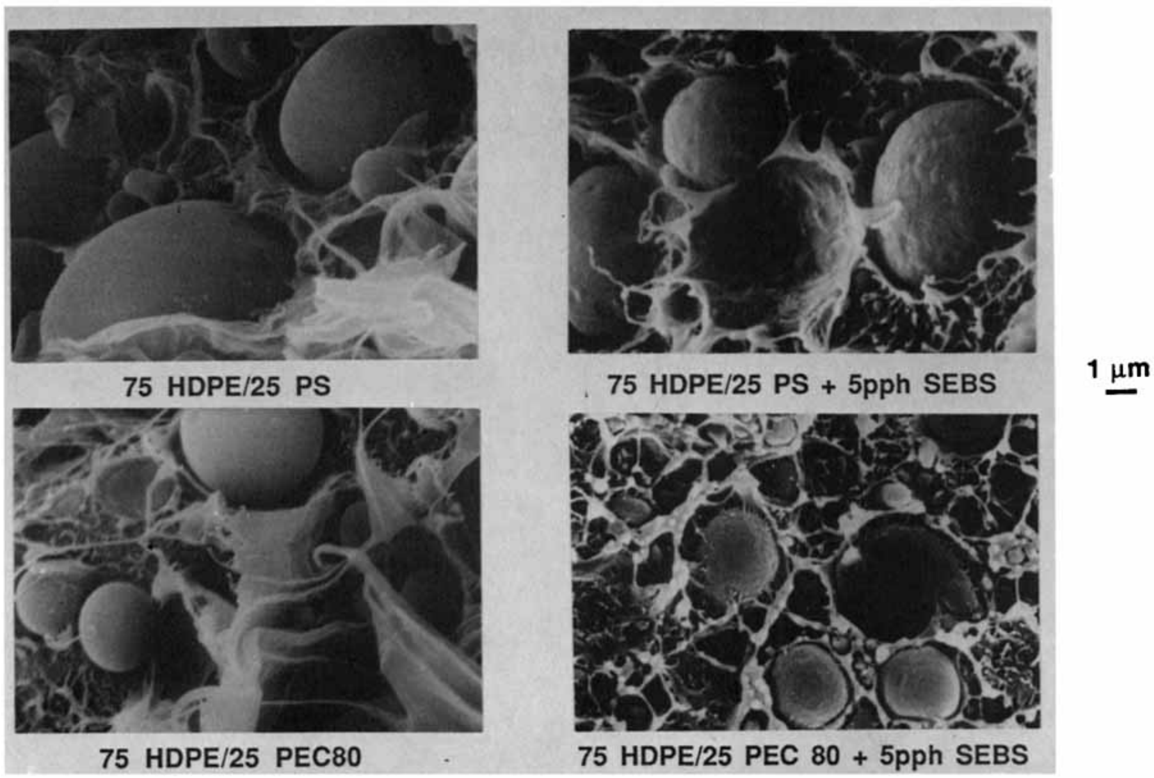
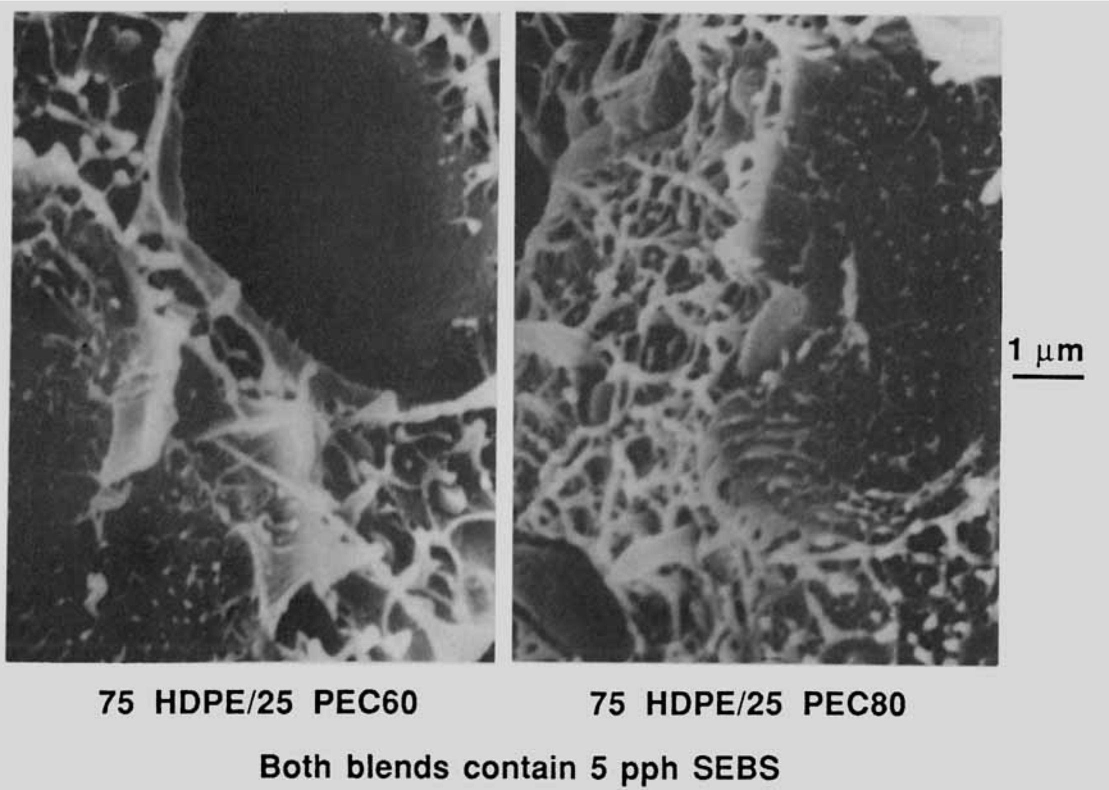


Fig. 12. Cryofracture surfaces of 75 HDPE/25 PS (top) and 75 HDPE/25 PEC80 (bottom) containing 0 and 5 pph SEBS. Samples were strained uniaxially before fracturing at liquid nitrogen temperatures.



75 HDPE/25 PEC60

75 HDPE/25 PEC80

Both blends contain 5 pph SEBS

Fig. 13. Cryofracture surfaces of 75 HDPE/25 PEC60 and 75 HDPE/25 PEC80 containing 5 pph SEBS. Samples were strained uniaxially before fracturing at liquid nitrogen temperatures.

HDPE/25 PEC60 and 75 HDPE/25 PEC80 blends containing 5 pph SEBS (shown in Fig. 13) clearly reveals the fibrils between PEC60 and PEC80 phases and the HDPE matrix. Broken fibrils are also visible on the interior surfaces of the holes remaining in the HDPE matrix after the force of the fracture ripped the dispersed PEC-rich particles from the matrix. This convincing visible evidence of greater adhesion achieved by incorporating PEC into the glassy phase translates quantitatively into reduced volume dilatation and better mechanical properties[16] compared to blends of the same HDPE content based on pure PS as the glassy phase.

To summarize, slopes of the postyield volume strain curves are shown in Figure 14 for blends with either PS, PEC60, or PEC80 as a function of the content of HDPE and SEBS. Most HDPE/PS compositions did not yield except for those containing 20 pph SEBS. In addition to interfacial voiding, the dilatational response observed in HDPE/PS blends is affected by two mechanisms of postyield deformation (shear yielding and crazing) depending on which component forms the continuous phase. Blends with a PS matrix undergo crazing; hence, reduced dilatation may indicate induced shear yielding in addition to any improved interfacial adhesion in the blend. For blends with a HDPE matrix, dilatation is primarily the result of interfacial void formation since crazing of the dispersed phase is unlikely. Reduction of the volume dilatation on addition of SEBS to these blends is due primarily to improved adhesion between the blend components. In all blends, the better adhesion caused by the SEBS compatibilizer shown quantitatively here by stress dilatometry is the primary factor contributing to improved ductility and impact strength reported previously[16] which occurs at the expense of stiffness.

PEC60, PEC80, and HDPE deform by shear yielding; therefore, volume dilatation in these blends must be the result of interfacial voiding. Reductions in the slope of the volume strain curves shown in Figure 14 reflect better adhesion upon the addition of SEBS. The skewed shape of these plots may result from differences in deformability of the individual phases. In blends with a soft matrix (HDPE) and hard dispersed phases (PEC60 or PEC80), the soft matrix will deform around these hard particles. Therefore, volume dilata-

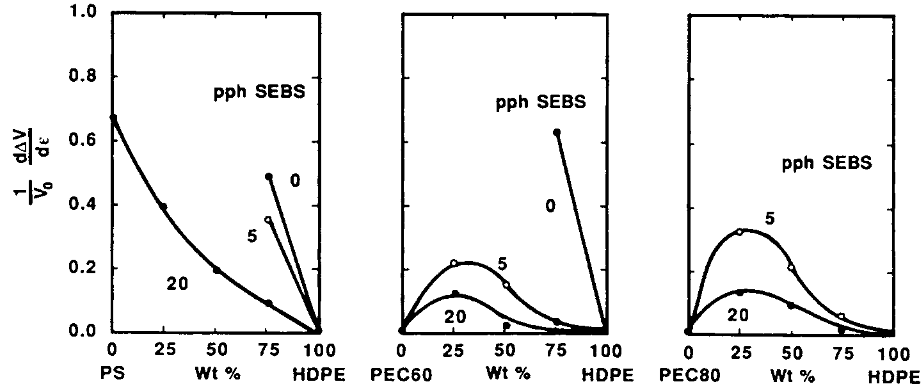


Fig. 14. Postyield slope of the volume strain curve for injection-molded HDPE/PS (left), HDPE/PEC60 (center), and HDPE/PEC80 (right) containing indicated amounts of SEBS.

tion in blends containing 75% HDPE (25% PEC60 or PEC80) should be lower than that for blends of the reverse composition (25% HDPE) which consist of a hard matrix containing a soft dispersed phase.

It is interesting to note that the extent of postyield dilatation decreases as the proportion of PEC in the glassy phase is increased to over 60%. At first sight, this might be thought to occur because adding PEC to the glassy phase tends to promote its deformation by shear yielding rather that crazing. However, the possibility of better adhesion of HDPE to PEC-containing phases caused by SEBS is another factor to be considered in these blends. This is presumed to be caused by the greater affinity for the PS endblocks of SEBS to mix with a phase including PEC rather than PS only. As argued earlier, the driving force for this is the expected exothermic mixing of PS segments with PEC segments;[15,16] whereas, mixing of PS segments from the copolymer with PS homopolymer can only be driven by entropic forces. The results described above suggest this mechanism as an important factor in the decreased dilatation noted. This issue is also believed to contribute to the greater improvements in mechanical properties resulting from the addition of SEBS to blends containing PEC. For example, the Izod impact strength of blends of 75% HDPE containing 5 pph SEBS is increased from approximately 0.5 ft-lb/in. for the blend with 25% PS to nearly 2.8 ft-lb/in. for the blend containing 25% PEC80. Of course, the improvement in ductility of the glassy phase when PEC is present contributes to the overall mechanical performance of these blends.

Compression-Molded Blends

The results given above were obtained with samples prepared by injection molding. Samples of the same blends were also made by compression molding. Table V compares slopes of the volume strain curves of blends containing 50, 75, and 100% HDPE fabricated by both methods. All two-phase blends without SEBS are brittle and fracture before yielding except for injection-molded 75 HDPE/25 PS. For the injection-molded blends, the slope decreases as more SEBS is added. If the HDPE and SEBS contents are held constant, the slope is lower for blends with PEC-rich phases instead of pure PS. The compression-molded blends, on the other hand, do not show the same trends. In general, the slope remains unchanged with each subsequent addition of SEBS and does not depend on the amount of PEC in the amorphous phase.

These results are clearly illustrated by comparing the slopes of injection- and compression-molded blends of 50% HDPE and 50% of either PS, PEC60, or PEC80 containing 5 pph SEBS (Table V). Blends containing PS made by both molding techniques fracture before yielding, but the elongation at failure is greater for blends with PEC-rich phases. This indicates a tendency for the compression-molded materials to show an increased ductility as seen with injection-molded samples; however, the overall levels of elongation at break are lower for the compression-molded specimens. Volume dilatation for the injection-molded materials is small and shows a postyield slope of about 0.2. However, the volume of the same compression-molded compositions begin to increase with a slope of 0.45–0.51 at approximately 2.5% elongational strain.

TABLE V

Comparison of Volume Dilatation of Compression and Injection Molded Blends

Blend composition	$\frac{1}{V_0}\frac{dV}{d\epsilon}$		Blend composition	$\frac{1}{V_0}\frac{dV}{d\epsilon}$	
SEBS pph[a]	Compression molded	Injection molded	SEBS pph[a]	Compression molded	Injection molded
50HDPE/50PS			75HDPE/25PS		
0	b	b	0	b	0.49
5	b	b	5	b	0.35
20	0.45	0.19	20	0.18	0.09
50HDPE/50PEC60			75HDPE/25PEC60		
0	0.73	b	0	b	0.63
5	0.51	0.22	5	0.22	0.03
20	0.41	0.02	20	0.19	0.03
50HDPE/50PEC80			75HDPE/25PEC80		
0	0.68	b	0	b	b
5	0.45	0.21	5	0.2	0.06
20	0.47	0.09	20	0.2	0.02
HDPE					
0	0	0			
5	0.02	0			
20	0.05	0			

[a] Parts per 100 of base blend.

[b] Fractured before yielding.

Figure 15 shows the stress and volume strain responses for blends containing 20 pph SEBS. The slopes of the volume strain curve of the injection-molded blends are reduced to 0.19 for blends containing PS and to 0.02 or 0.09 for blends with PEC60 and PEC80, respectively. Compression-molded samples of this composition yield at about 10% elongational strain, after which the volume increases with a slope of 0.41–0.47. Evidence for improved compatibilization as SEBS is added in the compression-molded blends is reflected by the higher yield strain.

Greater volume dilatation for compression-molded blends compared to the injection-molded counterparts may stem from several causes. As discussed earlier,[15] compression molding of blends involves coalescence of small dispersed particles formed during the high stress extrusion process into larger dispersed phase particles. This effectively decreases the interfacial area per unit volume. It is not clear whether the compatibilizer will be able to remain at the interface during such a reorganization. The flow processes involved in injection molding lead to elongation of the dispersed phases into a fibrillar form and to molecular orientation within each phase. Each of these could result in a tendency for decreased volume dilatation compared to the more isotropic materials made by compression molding. As shown earlier,[16] the molding technique will also affect the crystallinity and the crystalline texture of the HDPE phases. The relative amount of crystallinity and orientation were found to be important factors in the deformation and volume dilatation of styrene-butadiene block copolymers[27,28] that were either injection- or

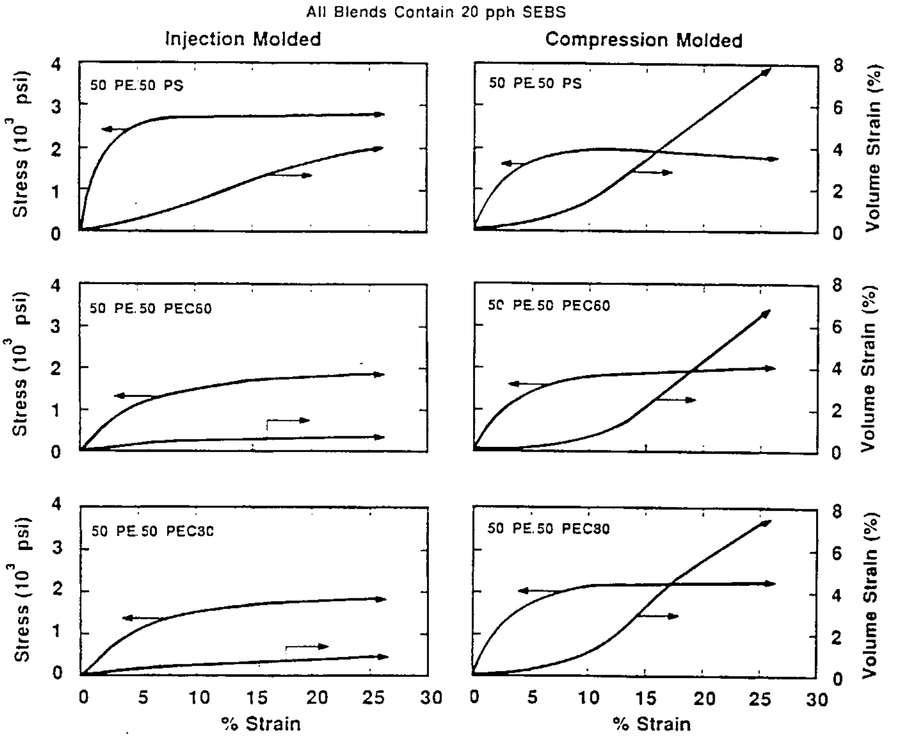


Fig. 15. Stress (left axis) and volume strain (right axis) curves for injection (left) and compression (right) molded blends containing 50% HDPE and 50% of either PS, PEC60, or PEC80, as indicated, with 20 pph SEBS.

compression-molded. Obviously, to understand completely the differences in response for blends made by these two extreme processes would require detailed consideration of issues such as these. The limited results shown here were intended simply to identify these differences and not to provide a detailed interpretation.

SUMMARY

Examination of the postyield volume changes in HDPE/(PEC/PS) blends modified by an SEBS compatibilizer has provided considerable information about the deformation mechanisms of these materials. The results relate directly to the observed mechanical properties of these blends. For miscible PEC/PS blends, increasing the PEC content led to a greater tendency for shear yielding until it became the only mode of deformation in PEC-rich blends. The craze to shear transition occurred between 40 and 60% PEC. Adding SEBS promoted shear yielding in addition to crazing for pure PS and shifted the craze to shear transition in PEC/PS blends to lower PEC concentrations.

Interfacial voiding is an additional volume dilatation mechanism which occurs in HDPE/(PEC/PS) blends. The volume dilatation was reduced as SEBS was added which is evidence for improved interfacial adhesion. For equivalent amounts of HDPE and SEBS, the volume dilatation was lower in blends containing PEC-rich glassy phases compared to those containing only pure PS. This is consistent with better interfacial adhesion when PEC is present in the glassy phase. Visual evidence for better adhesion was seen by SEM photomicrographs of fracture surfaces. This effect is believed to be the result of an extra thermodynamic during force for compatibilization promoted by exothermic mixing of PEC and PS as discussed previously.[15,16] Increased adhesion is believed to be the major factor contributing to improvements in the mechanical properties of these blends.

Compression-molded blends showed greater volumetric dilatation than injection-molded blends of the same composition which may be due to morphological differences.

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