Mechanical Properties of Poly(ethylene terephthalate) Modified with Functionalized Polymers

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ABSTRACT: This study examined the effect of blending poly(ethylene terephthalate) (PET) with 5% of a functionalized polymer. The blends were characterized by particle size and size distribution, unnotched tensile behavior, toughness, and notch sensitivity. The improved properties of blends that incorporated a functionalized elastomer were consistent with *in situ* formation of a graft copolymer by reaction with PET end groups. Triblock copolymers were examined that had styrene end blocks and an ethylene/ butylene midblock (SEBS) with grafted maleic anhydride. The present study extended previous investigations that focused on level of grafting to examine the effects of component molecular weight and PET hydroxyl-to-carboxyl end-group ratio. Increasing the molecular weight of the SEBS and decreasing the hydroxyl-to-carboxyl ratio of the PET increased the effectiveness of the SEBS. In addition, a mix of an unfunctionalized SEBS with a functionalized SEBS was more effective than a single SEBS with the same total anhydride content. The same elastomers were the most effective for modifying a lower molecular weight PET (intrinsic viscosity 0.73) and a higher molecular weight PET (intrinsic viscosity 0.95). Some functionalized polypropylenes included in the study did not enhance the properties of PET. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 203-219, 1999

Key words: poly(ethylene terephthalate) blends; SEBS block copolymers; rubber toughening

INTRODUCTION

Several studies have described the effect of blending poly(ethylene terephthalate) (PET) with up to 5 wt % of a functionalized triblock copolymer.¹⁻⁴ The triblock copolymers in these studies had styrene end blocks and an ethylene/butylene midblock (SEBS) that was grafted with maleic anhydride. Improved properties with these and other blends of PET that incorporated functionalized polymers^{5–8} were consistent with *in situ* formation of a graft copolymer by reaction with PET end groups. It appeared that the graft copolymer acted as an emulsifier to decrease the interfacial tension and promote adhesion.

Although it can be anticipated that the amount of graft copolymer formed by reaction of PET and a functionalized SEBS will affect both particle size and interfacial strength, increasing the anhydride concentration in the SEBS did not strongly affect blend rheology.^{3,4} In contrast, particle size was strongly dependent on elastomer functionality: the higher the functionality, the smaller the particle size and the narrower the particle size distribution. These trends were at-

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		IV					Grafted Anhydride
Material	Identification	(dL/g)	M_w	M_n	OH/COOH	S/EB	(wt %)
Cleartuf [®] 7207	PET72	0.73	49,000	24,000	_	_	_
Traytuf [®] 9506	PET95	0.95	90,000	37,000	4.0	_	
PET 2.2	PET2.2	0.95	91,000	37,000	2.2	_	
PET 4.9	PET4.9	0.97	95,000	38,000	4.9		
Kraton [®] 1921X	SEBS1		73,000	71,000	_	28/72	1.0
Kraton [®] 1924X	SEBS1h		136,000		_	13/87	1.0
Kraton [®] 1901X	SEBS2		77,000	75,000	_	28/72	2.0
Kraton [®] B 51-4	_		73,000	70,000	_	28/72	4.5
Kraton® G 1652	_		77,000	75,000	_	28/72	0
1 : 1 blend of Kraton® B 51-4	SEBS2m					28/72	2.2
and Kraton® G							
Polybond® 3002	PP0.2		440,000		_	_	0.2
Polybond® 3150	PP0.5		330,000		—		0.5

Table I Material Characteristics

tributed to an increase in the degree of grafting. Notched tensile tests differentiated among the blends in terms of their toughness. The most effective was the SEBS with only 1% anydride. The decrease in toughness with increasing functionality was attributed to decreasing particle size.

Variables other than the amount of grafting are also expected to influence the effectiveness of functionalized SEBS for toughening PET. These include the molecular weight of the components, and the hydroxyl-to-carboxyl end-group ratio of the PET. The present study extends previous investigations to examine these variables. The experimental design builds on the earlier finding that SEBS with 1% anhydride is the most effective for toughening PET. In addition, the possibility is examined that a mix of an unfunctionalized SEBS with a functionalized SEBS may be more effective than a single SEBS with the same total anhydride content. Some functionalized polypropylenes are also included in the study.

MATERIALS AND METHODS

The polymers used in this study are listed in Table I. Several poly(ethylene terephthalate) (PET) resins were provided by the Shell Chemical Company, as were triblock copolymers that had styrene end blocks and an ethylene/butylene midblock (SEBS). Some of the SEBS elastomers were functionalized with grafted maleic anhydride. The functionalized polypropylenes were produced by the Uniroyal Chemical Company. In the first series of samples, two PETs of different molecular weight (PET72 and PET95) were blended with 5 wt % of functionalized polymer. Four blends prepared with the SEBS elastomers compared the effect of anhydride concentration (SEBS1 and SEBS2) and the effect of molecular weight (SEBS1 and SEBS1h); also, an SEBS with no functionality was blended with an equal amount of an SEBS with 4.5% anhydride (SEBS2m) to achieve about the same anhydride content as SEBS2. Two blends were prepared with 5 wt % of a functionalized polypropylene (PP0.2 and PP0.5). In the second series of samples, PET95 and two PETs with approximately the same molecular weight as PET95 but differing in the OH/ COOH ratio (PET2.2 and PET4.9) were blended with 5 wt % of SEBS1h and SEBS2m, the elastomers that gave the best properties with PET95.

The PET was vacuum dried for 15 h at 130°C; the other components were vacuum dried for 15 h at 80°C. The PET was melt blended with 5 wt % of functionalized polymer in a Haake Rheomex TW 100 twin-screw extruder. The processing conditions for the PET72 blends were as described previously.^{2,3} The barrel temperature was 280°C, and the screw speed was 35 rpm. For PET95 blends, the barrel temperature was 290°C, and the screw speed was 45 rpm. These processing parameters were selected after preliminary studies to determine the effect of processing temper-

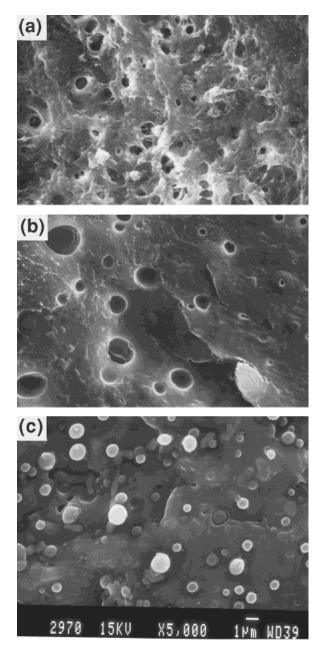


Figure 1 Scanning electron micrographs of freeze fractured surfaces. (a) PET95 with 5 wt % SEBS1h etched to remove the elastomer; (b) PET95 with 5 wt % SEBS2 etched to remove the elastomer; and (c) PET95 with 5 wt % PP0.5.

ature on PET95 molecular weight. The pelletized blends were injection molded into a family mold that consisted of a 3.18 mm-thick type I tensile bar (ASTM D638), a 3.18 mm-thick Izod bar (ASTM D256), and a 50-mm diameter disc 1.27 mm thick for the puncture test. The Battenfeld Unilog 4000 injection molding machine was operated with a barrel temperature of 265°C, nozzle temperature of 270°C, mold temperature of 21°C, and injection pressure of 1350 psi. Notches were prepared according to ASTM D256.

For particle size determination, an Izod bar was immersed in liquid nitrogen for 30 min and freeze fractured. Blends with SEBS were etched with THF for 8 h at ambient temperature to remove the elastomer. After drying in vacuum, the fracture surfaces were coated with gold and examined in the JEOL 840A scanning electron microscope. Particle size distributions were obtained by measuring at least 600 particle diameters.

Thermal properties were determined with a Perkin-Elmer DSC 7 using a heating/cooling rate of 10°C/min. Specimens weighing 5–10 mg were cut from the center of Izod bars. The crystallinity of the injection molded bar was determined from the difference between the melting enthalpy and the enthalpy of cold crystallization. The residual crystallinity was between 13 and 21% based on a heat of fusion of 122 J/g for PET.

Tensile tests were carried out on unnotched type I tensile bars equilibrated under ambient conditions using strain rates of 100%/min and 1000%/min. Five specimens were tested for each condition. Tensile tests were also performed on notched tensile bars. The notch was machined according to ASTM D256. The distance between grips was 10 cm, and the crosshead speed was 500 mm/min. Tests were made at 25 and 0°C. Specimens were equilibrated in the environmental chamber of the Instron machine at the test temperature for 30 min before testing. Fracture surfaces of specimens tested at 0°C were examined in the reflection optical microscope (OM) and in the SEM. Some of the fracture surfaces were examined in the OM before and after etching with THF at 59°C for 4 h.

Puncture tests were carried out on a DYN-ATUP[®] 8250 instrument following ASTM D3763. The plunger was dropped a height of 300 mm, which produced a velocity of 1.5×10^5 mm/min on impact. The plunger had a hemispherical tup with a 12.7-mm diameter. Five specimens were tested at 25 and -29° C. The specimens were maintained at temperature overnight before testing. The notched Izod impact strength was measured on specimens equilibrated under ambient conditions. The tests were made at ambient temperature using a TMI No. 43-1 impact tester with an impact speed of 3.33 mm/s. Five specimens were tested.

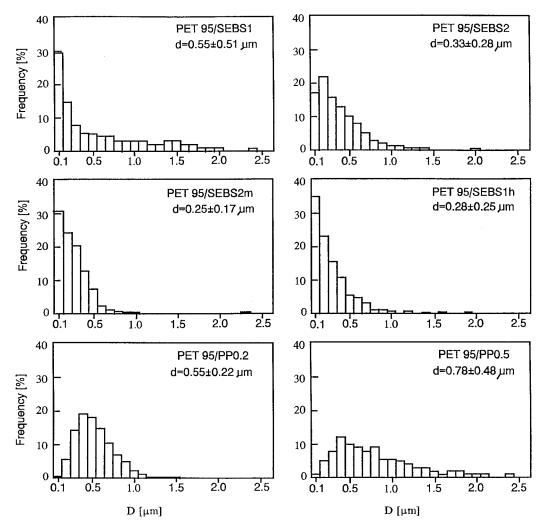


Figure 2 Particle size distributions in PET95 blends.

RESULTS AND DISCUSSION

Blends of PETs with Different Molecular Weight

Blend Characterization

Brittle freeze-fracture surfaces showed the functionalized polymer to be dispersed as spherical particles in all the blends. The blends of PET95 with SEBS were etched to remove the elastomer. The size and shape of the remaining circular holes indicated that the elastomer particles were smaller and more uniform in size in the blend with SEBS1h [Fig. 1(a)] than in the blend with SEBS2 [Fig. 1(b)]. Because the blends with functionalized polypropylene were not etched, the freeze-fracture surface contained particles of PP0.5 that were spherical with a fairly broad size distribution [Fig. 1(c)]. The smooth surfaces of the particles suggested that they were not strongly adhered to the matrix.

The particle size distributions for the PET95 blends are given in Figure 2. Of the SEBS blends, the one with SEBS2m had the smallest average particle size and essentially no particles larger than 1.0 μ m. The average particle size and the number of larger particles in the distribution increased from SEBS2m to SEBS1h to SEBS2 to SEBS1. The particles of SEBS1 had a very broad distribution with a large number of particles in the 1.0- to 2.5- μ m size range.

The same blend compositions were prepared with PET72, a lower molecular weight resin. The particle sizes for PET95 and PET72 blends are summarized in Tables II and III, respectively. Average particle sizes of SEBS1 and SEBS2 were very similar in PET95 and PET72. For example,

Material	Elastomer	Elastomer Functionality	Particle Diameter (µm)
PET72/SEBS1	5% Kraton® 1921X	1 wt % MA	0.58 ± 0.22
PET72/SEBS1h	5% Kraton [®] 1924X	$1 ext{ wt \% MA}$	0.37 ± 0.21
PET72/SEBS2	5% Kraton [®] 1901X	$2 \mathrm{~wt} \ \% \mathrm{~MA}$	0.35 ± 0.19
PET72/SEBS2m	2.5% Kraton® B51-4	4.5 wt % MA	0.48 ± 0.22
	2.5% Kraton [®] G1652	unfunctionalized	
PET72/PP0.2	5% PP3002	0.2 wt % MA	0.91 ± 0.36
PET72/PP0.5	5% PP3150	0.5 wt $\%~{\rm MA}$	0.80 ± 0.34

Table II Particle Size in PET72 Blends

the particle size of SEBS1 was $0.55 \pm 0.51 \ \mu m$ in PET95 compared to 0.58 \pm 0.22 μ m in PET72. This was also very similar to the 0.60 \pm 0.23 μ m reported previously for the particle size of SEBS1 in PET72.³ Similarly, the particle size of SEBS2 was 0.33 \pm 0.28 μ m in PET95 compared to 0.35 \pm 0.19 μ m in PET72 and 0.33 \pm 0.28 μ m reported previously for SEBS2 in PET72.³ The larger average particle size and slightly broader size distribution in SEBS1 blends compared to SEBS2 blends were attributed to a lower level of grafting with SEBS1.³ Although the average particle sizes in PET72 and PET95 were essentially the same, the PET95 blends had a somewhat broader particle size distribution, with more particles larger than 1 μ m, than the PET72 blends. In contrast to SEBS1 and SEBS2, particle sizes of SEBS1h and SEBS2m were significantly smaller in PET95 than in PET72.

Stress-Strain Behavior

Tensile deformation of PET and all the blends was characterized by formation of a macroshear band at the yield point. The engineering stress dropped to about half the yield stress as the macroshear band formed. A neck then propagated from one side of the macroshear band. If the neck was stable, it propagated at a constant engineering stress all the way to the end of the gauge section. The necked region then uniformly strain hardened with a small increase in stress until the neck started to propagate again from the other side of the macroshear band. This was accompanied by a small stress drop, and was followed by a second region of cold drawing. When the entire gauge section had necked, there was a region of uniform strain hardening that terminated when the specimen fractured at one end of the neck.²

In stress-strain measurements carried out at a strain rate of 100%/min, the yield stress of PET72 was slightly higher than the yield stress of PET95; the draw stresses were not significantly different. The primary difference was in the stability of the propagating neck. The unmodified, higher molecular weight PET95 fractured during strain hardening after the entire gauge section had necked; in contrast, the lower molecular weight PET72 fractured at the end of the neck after the neck had propagated only a short distance. As a result, the fracture strain of PET72 was much lower than the fracture strain of PET95. The higher ductility of PET95 was attrib-

Table III Particle Size in PET95 Blends

Material	Elastomer	Elastomer Functionality	Particle Diameter (µm)
PET95/SEBS1	5% Kraton® 1921X	1 wt % MA	0.55 ± 0.51
PET95/SEBS1h	5% Kraton [®] 1924X	1 wt % MA	0.28 ± 0.25
PET95/SEBS2	5% Kraton [®] 1901X	2 wt % MA	0.33 ± 0.28
PET95/SEBS2m	2.5% Kraton® B51-4 2.5% Kraton® G1652	4.5 wt % MA unfunctionalized	0.25 ± 0.17
PET95/PP0.2	5% PP3002	0.2 wt % MA	0.55 ± 0.22
PET95/PP0.5	5% PP3150	0.5 wt $\%~{\rm MA}$	0.78 ± 0.48

Material	Yield Stress (MPa)	Fracture Strain (%)	Yield Stress (MPa)	Fracture Strain (%)
	$\varepsilon = 3$	100%/min	$\varepsilon = 10$	000%/min
PET72	58.5 ± 1.0	92 ± 1	57.5 ± 1.0	58 ± 14
	$(60 \pm 1)^{a}$	(96 ± 1)	(63 ± 1.0)	(35 ± 15)
PET72/SEBS1	52.0 ± 0.5	890 ± 22	51.3 ± 0.5	109 ± 7
	(51 ± 1)	(890 ± 28)	(57 ± 1)	(135 ± 78)
PET72/SEBS1h	50.3 ± 0.5	908 ± 40	50.2 ± 0.3	423 ± 28
PET72/SEBS2	52.1 ± 0.5	730 ± 55	51.8 ± 0.3	$13\pm~5$
	(53 ± 0)	(712 ± 51)	(58 ± 1)	(159 ± 50)
PET72/SEBS2m	51.1 ± 0.4	860 ± 15	49.5 ± 0.5	190 ± 35
PET72/PP0.2	54.2 ± 0.3	857 ± 21	51.3 ± 0.9	15 ± 5
PET72/PP0.5	55.0 ± 0.3	825 ± 10	52.8 ± 0.6	111 ± 10

Table IV Effect of Blending on Tensile Properties of PET72 at 25°C

^a Values in parentheses from ref. 3.

uted to the larger number of entanglements, which increased the stability of the neck during cold drawing.

Addition of 5% SEBS decreased the yield stress by about 10% (Tables IV and V), but did not significantly affect the draw stress. The major effect of blending was on neck stability, as indicated by the fracture strain. In stress-strain tests carried out at a strain rate of 100%/min, all the blends of PET72 were ductile and fractured after the entire gauge section had necked. In contrast, only two SEBS blends, those with SEBS1h and SEBS2m, produced an increase in the fracture strain of PET95 [Fig. 3(a)]. Blending with SEBS1 or SEBS2 decreased the fracture strain. Blends with SEBS1 and SEBS2 typically fractured during the first cold-drawing region, and blends with PP0.2 and PP0.5 typically fractured in the second cold drawing region. Because the elongation at break depended on the length of the cold-drawn

gauge section, the fracture strain values reported for these blends have a large standard deviation.

When the strain rate was increased from 100%/ min to 1,000%/min, the yield stress increased and the fracture strain decreased. All the materials yielded with formation of a macroshear band, then fractured in the cold-drawing region before the propagating neck reached the end of the gauge section. The site of fracture was the propagating end of the neck. The fracture strain essentially measured the distance the neck propagated before fracture, and thus indicated the relative stability of the neck. The results confirmed trends observed in the lower strain rate experiments. For example, SEBS1h and SEBS2m increased the fracture strain of PET95; the other functionalized polymers including SEBS1 and SEBS2 produced a decrease in the fracture strain [Fig. 3(b)].

Material	Yield Stress (MPa)	Fracture Strain (%)	Yield Stress (MPa)	Fracture Strain (%)
	$\varepsilon = 3$	100%/min	$\varepsilon = 10$	000%/min
PET95	56 ± 1	615 ± 205	60 ± 2	119 ± 35
PET95/SEBS1	49 ± 1	62 ± 36	53 ± 1	57 ± 42
PET95/SEBS1h	49 ± 1	809 ± 57	50 ± 1	250 ± 87
PET95/SEBS2	49 ± 1	277 ± 249	54 ± 1	23 ± 5
PET95/SEBS2m	50 ± 1	758 ± 11	55 ± 1	163 ± 55
PET95/PP0.2	51 ± 1	440 ± 320	57 ± 1	$24\pm~7$
PET95/PP0.5	54 ± 1	651 ± 118	53 ± 1	62 ± 42

Table V Effect of Blending on Tensile Properties of PET95 at 25°C

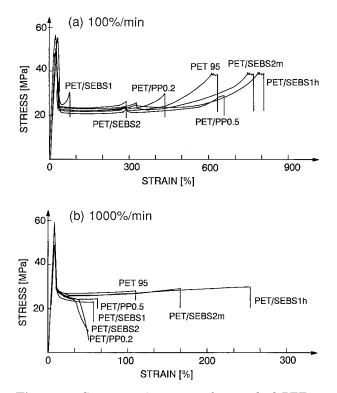


Figure 3 Stress-strain curves of unnotched PET95 and PET95 blends at two strain rates: (a) 100%/min; and (b) 1000%/min.

Toughness

High-speed puncture fractures of PET95 and the SEBS blends at 25°C were all ductile with essentially the same fracture energy (Table VI). Blending with functionalized polypropylene embrittled PET95, as indicated by the occurrence of brittle fractures at 25°C and a significant decrease in the fracture energy. At a lower temperature, -29° C, PET95 was brittle, as were the blends with

SEBS1 and SEBS2 (Table VII). In contrast, blends of PET72 with SEBS1 and SEBS2 tested under the same conditions as the PET95 blends exhibited some ductile puncture fractures at $-29^{\circ}C.^{3}$ About half the specimens of PET95 with SEBS1h and SEBS2m fractured in a ductile manner. It would appear that these blends were close to the brittle-to-ductile transition. When ductile fractures were observed, the fracture energy increased accordingly. This demonstration that only SEBS2m and SEBS1h improved the properties of PET95 was consistent with the results of unnotched tensile tests.

Uniaxial tension and puncture impact were both methods that tested toughness under conditions that did not emphasize notch sensitivity. Without blending, PET95 formed a stable neck in uniaxial tension, whereas PET72 did not, and as a result, unnotched PET95 appeared more ductile than unnotched PET72. However, puncture tests did not differentiate PET72 and PET95, and both were ductile at 20°C, and at -29°C both were brittle with about the same fracture energy.³ However, PET95 was not as easily toughened with SEBS as PET72. This was clearly revealed in the results of both uniaxial tension and puncture impact tests of the blends with SEBS1 and SEBS2. These elastomers increased the neck stability of PET72, but actually decreased the neck stability of PET95 in unaxial tension. In addition, ductile puncture fractures of PET72 blends with SEBS1 and SEBS2 were observed at $-29^{\circ}C$,³ whereas all the corresponding PET95 punctures were brittle. These effects could not be attributed to differences in average particle size, which was essentially the same in PET72 and PET95. The particle size distribution might have been impor-

Table VI Effect of Blending on Puncture Strength of PET95 at 25°C

Material	Failure Type	Maximum Load (N)	Total Energy (J)
PET95	5 ductile	1219 ± 30	13.5 ± 0.5
PET95/SEBS1	5 ductile	1219 ± 42	12.5 ± 0.9
PET95/SEBS1h	5 ductile	1228 ± 25	12.7 ± 0.6
PET95/SEBS2	5 ductile	1219 ± 25	13.1 ± 0.6
	5 ductileª	$1119 \pm 49^{\mathrm{a}}$	$12.2\pm0.4^{\mathrm{a}}$
PET95/SEBS2m	5 ductile	1185 ± 40	12.1 ± 0.6
PET95/PP0.2	1 ductile, 4 brittle	1074 ± 112	4.7 ± 3.6
PET95/PP0.5	5 ductile	1002 ± 349	6.8 ± 5.7

^a Blending and testing repeated.

Material	Failure Type	Maximum Load (N)	Total Energy (J)
PET95	5 brittle	475 ± 193	0.8 ± 0.3
PET95/SEBS1	5 brittle	251 ± 110	0.4 ± 0.2
PET95/SEBS1h	5 brittle	371 ± 219	0.6 ± 0.3
PET95/SEBS2	3 ductile, 2 brittle	1679 ± 344	10.0 ± 6.5
	2 ductile, 3 brittle ^a	$1418 \pm 188^{\mathrm{a}}$	$7.7\pm5.4^{ m a}$
PET95/SEBS2m	3 ductile, 2 brittle	1746 ± 258	10.3 ± 5.4
PET95/PP0.2	5 brittle	110 ± 14	0.2 ± 0.1
PET95/PP0.5	5 brittle	92 ± 13	0.2 ± 0.1

Table VII Effect of Blending on Puncture Strength of PET95 at -29°C

^a Blending and testing repeated.

tant. It was possible that larger particles were particularly detrimental in PET95.

Related to this point, the fairly broad particle size distributions of SEBS1 and SEBS2 in PET95 included many particles larger than 1 μ m, whereas the two elastomers that improved the puncture impact toughness of PET95, SEBS1h and SEBS2m, had the smallest average particles sizes and also had very few particles larger than 1 μ m. A direct comparison of SEBS1 with the higher molecular weight SEBS1h was complicated by the higher rubber content of SEBS1h, which by itself, could have affected particle size and properties. It should be noted that the blending conditions (290°C/45rpm) were chosen to minimize molecular weight loss of the PET95, and not for optimum dispersion of SEBS. Although blending conditions did not have much effect on dispersion of SEBS in PET72,² the effect might have been larger with the more viscous PET95.

Notch Sensitivity of PET95 Blends

Notched Tensile Behavior

Blending PET with 5% of an SEBS elastomer did not significantly improve the notched Izod impact strength. This was consistent with previous observations that 5% SEBS was not sufficient to change the failure mode of PET in an Izod test from brittle to ductile. It should be noted that 5% was considerably less than the 20% used in studies where enhanced Izod impact toughness of PET was demonstrated.¹ Because the Izod test conditions were too severe to evaluate the effect of blending on the notch sensitivity, specimens with the V-shaped Izod notch were tested in tension at two temperatures using a testing rate lower than the effective rate of the Izod test.

Representative stress-displacement curves of PET95 and the blends at 25°C are shown in Figure 4. The shape of the stress-displacement curve and the appearance of the fracture surface were used to categorize the fractures as ductile or brittle. Ductile fractures exhibited a maximum in the stress-displacement curve; localized yielding resulted in pulled out material and considerable "sucking in" at the fracture site; in addition, the entire fracture surface was stress-whitened. In contrast, brittle specimens were those that fractured at the maximum stress; the brittle fracture surfaces were not entirely stress-whitened, although there was usually some stress-whitening at the notch root that marked a region of slow crack growth. At 25°C, all five specimens of the blend with SEBS2m and two of the five specimens of the blend with SEBS1h were ductile (Table VIII). In contrast, PET95 and all the other blends fractured in a brittle manner, although the blends fractured at a higher extension than PET95. In tests at 0°C, PET95 and all the blends appeared brittle (Table IX), although the blends with

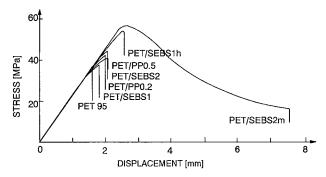


Figure 4 Stress-displacement curves of notched PET95 and PET95 blends at 25°C.

Material	Fracture Mode	Yield Stress (MPa)	Fracture Stress (MPa)	Fracture Extension (mm)	Fracture Energy
PET95	4 brittle		42.0 ± 2.8	1.4 ± 0.5	0.9 ± 0.5
PET95/SEBS1	4 brittle	_	44.9 ± 1.0	1.9 ± 0.1	1.3 ± 0.2
PET95/SEBS1h	2 ductile	53.8 ± 1.2	_	2.9 ± 0.5	5.3 ± 2.6
	3 brittle	_	45.9 ± 5.8	2.2 ± 0.3	1.8 ± 0.3
PET95/SEBS2	5 brittle	_	44.2 ± 1.8	2.0 ± 0.1	1.5 ± 0.1
PET95/SEBS2m	5 ductile	56.8 ± 5.6	_	7.7 ± 2.8	7.3 ± 3.1
PET95/PP0.2	5 brittle	_	42.8 ± 0.8	2.0 ± 0.1	1.5 ± 0.1
PET95/PP0.5	5 brittle	_	40.6 ± 1.2	2.1 ± 0.1	1.3 ± 0.1

Table VIII Effect of Blending on Notched Tensile Properties of PET95 at $T = 25^{\circ}$ C

SEBS2m started to yield at the notch root before they fractured and much of the fracture surface was stress-whitened with some "sucking in." It appeared that SEBS2m and SEBS1h, the only two modifiers that improved the performance of PET95 in unnotched tests, were also the most effective in reducing the notch sensitivity.

Fractography

Surfaces of notched specimens fractured at 0°C all showed a region of slow crack growth at the notch root with a region of fast crack growth further from the notch. The size and texture of the slow crack growth region varied with sample composition. The smooth texture of the PET95 specimen was characteristic of slow crack growth through a preexisting craze [Fig. 5(a)].^{4,9} The size and shape of the preexisting craze were revealed by the boundary of the smooth region; in this example, the length of the craze was about 0.9 mm at fracture. At higher magnification, the region of craze fracture did not exhibit the fibrillated texture that is characteristic of fracture through the craze fibrils. Instead, the smooth, featureless surface texture indicated that the

crack path followed the interface between the craze and the surrounding bulk material. Fracture surfaces of blends with functionalized polypropylene revealed that these blends also fractured through a preexisting craze, although the preexisting craze was longer than in unmodified PET95 [Fig. 5(b)]. The fracture surface of the PP0.2 blend was very similar to that of the PP0.5 blend in Figure 5(b).

The slow crack growth region of the SEBS blends indicated ductile tearing rather than craze fracture [Fig. 5(c)–(f)]. The region of ductile fracture was characterized by stress-whitening and some "sucking in" of the edges. The main features were a small region of shear tearing that extended across the specimen width at the notch root, and further from the notch a much larger elongated region that usually contained the parabolic markings that are indicative of secondary cracks. Although all the fractures were classified as brittle, a larger slow crack growth region correlated with higher fracture stress, fracture displacement, and fracture energy (Table IX). The blend with SEBS2m had the largest slow crack growth region [Fig. 5(c)]. On this surface, the

Fracture Fracture Stress **Fracture Extension** Fracture Mode Material (MPa) (mm)Energy PET95 2.2 ± 0.5 1.6 ± 0.6 5 brittle 41.5 ± 6.4 PET95/SEBS1 5 brittle 38.4 ± 3.6 2.2 ± 0.4 1.5 ± 0.4 PET95/SEBS1h 5 brittle 47.9 ± 1.5 3.4 ± 0.4 3.0 ± 0.4 PET95/SEBS2 5 brittle 48.2 ± 2.3 3.1 ± 0.3 2.7 ± 0.3 50.1 ± 1.3 3.1 ± 0.2 2.8 ± 0.3 PET95/SEBS2m 5 brittle 46.1 ± 2.1 $2.4\,\pm\,0.2$ 2.0 ± 0.3 PET95/PP0.2 5 brittle 45.4 ± 2.1 2.5 ± 0.2 2.0 ± 0.2 PET95/PP0.5 5 brittle

Table IX Effect of Blending on Notched Tensile Properties of PET95 at $T = 0^{\circ}$ C

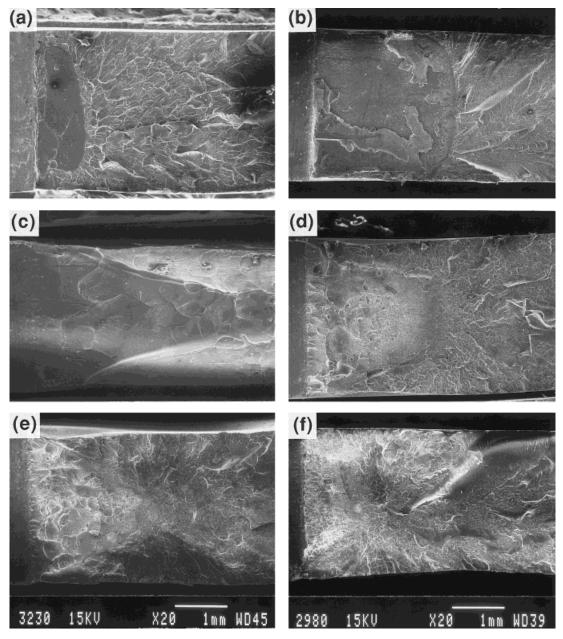


Figure 5 Low-magnification scanning electron micrographs of PET95 and PET95 blends fractured at 0°C. (a) PET95; (b) PET95 with 5 wt % PP0.5; (c) PET95 with 5 wt % SEBS2m; (d) PET95 with 5 wt % SEBS1h; (e) PET95 with 5 wt % SEBS2; and (f) PET95 with 5 wt % SEBS1. The crack propagated from the notch on the left.

parabolic markings became more numerous as the distance from the notch root increased and the stress intensification ahead of the crack increased. The size of the slow crack growth region gradually decreased as the elastomer changed from SEBS2m to SEBS1h to SEBS2 to SEBS1. Decreases in length of both the shear tearing region and the larger elongated region contributed to the overall decrease in size of the slow crack growth region. Higher magnification of the region adjacent to the notch root revealed highly drawn ligaments without extensive cavitation. In contrast, the larger elongated region was characterized by profuse cavitation. These features suggested that the blends fractured through a preexisting damage zone of the type previously described for blends of other ductile thermoplastics, such as polycarbonate and PVC,^{10–12} which are also very notch sensitive. In these polymers, the damage zone con-

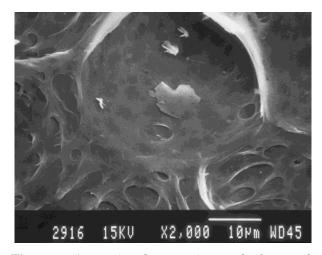


Figure 6 A scanning electron micrograph of a secondary crack from the slow crack growth region of PET95 with 5 wt % SEBS1h.

sists of two regions: a shear yielding region at the notch root, and a cavitated zone that begins some distance from the notch root. Yielding first occurs at the notch root as two families of slip lines that grow out of the notch surface. This yielding mode is referred to as core yielding. Cavitation of the elastomer subsequently initiates some distance ahead of the notch root where the stress state is more severe. Cavitation relieves the triaxiality and permits the matrix to shear yield. The distance between the notch root and the onset of cavitation increases with the cavitation resistance of the elastomer, and in general, a larger distance is indicative of better toughness as long as the cavitation stress remains well below the crazing stress of the matrix.¹⁰ The correlation between toughness and onset of cavitation was tested with the SEBS blends by measuring the length of the uncavitated shear yielding region on the fracture surface. This length decreased from 0.7 mm (SEBS2m) to 0.4 mm (SEBS1h) to 0.3 mm(SEBS2) to less than 0.05 mm (SEBS1), a trend that paralleled decreases in fracture stress and fracture energy.

In general, secondary cracks were more numerous and appeared closer to the notch root as the size of the slow crack growth region decreased. A magnification of a typical secondary crack in Figure 6 shows that they initiated from flaws that were up to 10 μ m in diameter. These particulate flaws were removed by exposure of the fracture surface to THF, indicating that they were large pieces of elastomer. Although these large particles (~10 μ m) were too rare to appear in the particle size distribution, the blends that had more large particles (1.0 to 2.5 μ m) in the particle size distribution also had more secondary cracks.

Blends of PETs with Different Hydroxyl-to-Carboxyl End-Group Ratio

Blend Characterization

The particle size distributions of SEBS2m and SEBS1h in PET2.2 and PET4.9 are plotted in Figure 7. A major feature that distinguished the PET2.2 and PET4.9 blends from the PET95 blends was the absence of particles in the 1.0-2.5- μ m range. Otherwise, the average particle size of an SEBS was in the same range in all the PETs. It might be anticipated that the higher hydroxyl concentration of PET4.9 and greater potential for graft formation would result in smaller particle sizes. This occurred in the SEBS2m blends where the average particle size in PET4.9 was significantly smaller than in PET2.2 (Table X). However, the average particle size of SEBS1h

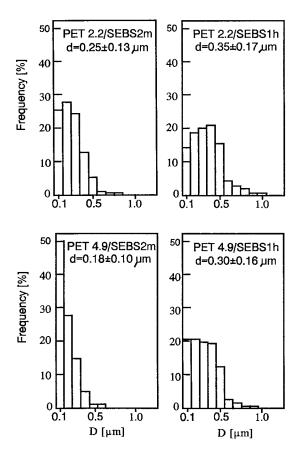


Figure 7 Particle-size distributions of SEBS2m and SEBS1h in PET2.2 and PET4.9 blends.

Material	PET IV	PET OH/ COOH	Elastomer	Elastomer Functionality	Particle Diameter (µm)
PET95	0.95	4.0	_	_	
PET2.2	0.95	2.2	_	_	_
PET4.9	0.97	4.9	_	_	_
PET95/SEBS1h	_	_	5% Kraton [®] 1924	1 wt % MA	0.28 ± 0.25
PET2.2/SEBS1h	_	_	5% Kraton [®] 1924	1 wt % MA	0.35 ± 0.17
PET4.9/SEBS1h		_	5% Kraton [®] 1924	1 wt % MA	0.30 ± 0.16
PET95/SEBS2m	—	—	2.5% Kraton® B51-4 2.5% Kraton® G1652	4.5 wt % MA unfunctionalized	0.25 ± 0.17
PET2.2/SEBS2m	_	—	2.5% Kraton® B51-4 2.5% Kraton® G1652	4.5 wt % MA unfunctionalized	0.25 ± 0.13
PET4.9/SEBS2m	—	—	2.5% Kraton [®] B51-4 2.5% Kraton [®] G1652	4.5 wt % MA unfunctionalized	0.18 ± 0.10

Table X Effect of Hydroxyl-to-Carboxyl End Group Ratio on Particle Size

in PET4.9 was only slightly smaller than in PET2.2.

Toughness

All the PETs were brittle in notched tensile tests at 25°C. Blending with SEBS decreased the notch sensitivity, and some of the blends were ductile at 25°C (Fig. 8). Blends of PET95 and PET2.2 with SEBS2m were ductile; the PET95 blend fractured at a higher strain on average (7.4 compared to 5.4) and the combination of higher yield stress and higher fracture strain produced a higher fracture energy for the PET95 blend with SEBS2m than for the PET2.2 blend (7.3 compared to 3.7) (Table XI). In contrast, the blend of PET4.9 with SEBS2m was brittle.

Of the blends with SEBS1h, only the blend of PET2.2 was consistently ductile. The blends of PET95 and PET4.9 produced a mixture of brittle and ductile fractures at 25°C (Table XI). All the blends were brittle at 0°C; however, the blend of PET2.2 had a longer stress-whitened zone (about half the fracture surface) than blends of either PET95 or PET4.9 (less than a quarter of the fracture surface). Considering the results with both SEBS1h and SEBS2m blends, the overall trend appeared to be that PET2.2 blends were the most ductile, PET4.9 blends were the least ductile, and PET95 blends were intermediate. The trend in increasing ductility correlated with decreasing hydroxyl end-group content.

The yield stress, obtained from the stress-displacement curve of notched specimens that exhibited ductile fractures, was about 20% lower for PET2.2 and PET4.9 blends than for PET95 blends. For this reason, comparisons between PET2.2 and PET4.9 were probably more meaningful than comparisons that included PET95. In this context, it was clear that blends of PET2.2

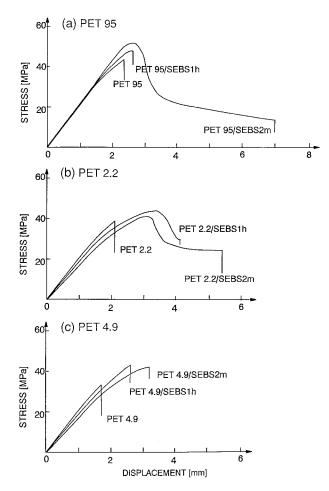


Figure 8 Stress-displacement curves of notched PETs and their blends with SEBS2m and SEBS1h at 25°C: (a) PET95; (b) PET2.2; and (c) PET4.9.

Material	Fracture Mode	Yield Stress (MPa)	Fracture Stress (MPa)	Fracture Extension (mm)	Fracture Energy
PET95	4 brittle ^a	_	42.0 ± 2.8	1.4 ± 0.5	0.9 ± 0.5
	3 brittle		44.8 ± 1.2	2.4 ± 0.3	1.8 ± 0.2
PET2.2	3 brittle	_	37.8 ± 3.9	2.1 ± 0.4	1.5 ± 0.4
PET4.9	3 brittle	_	$33.2\pm~0.1$	1.7 ± 0.1	1.1 ± 0.1
PET95/SEBS1h	$2 \; \text{ductile}^{\text{a}}$	53.8 ± 1.2	_	2.9 ± 0.5	5.3 ± 2.6
	3 brittle ^a	_	45.9 ± 5.8	2.2 ± 0.3	1.8 ± 0.3
	1 ductile	52.0	_	2.9	3.6
	3 brittle	_	43.7 ± 1.3	2.5 ± 0.2	2.0 ± 0.3
PET2.2/SEBS1h	3 ductile	42.2 ± 1.2	33.1 ± 16.8	4.2 ± 1.6	3.1 ± 1.0
PET4.9/SEBS1h	1 ductile	42.0	_	2.6	2.0
	3 brittle	_	42.6 ± 2.0	2.6 ± 0.3	2.0 ± 0.3
PET95/SEBS2m	5 ductile^{a}	56.8 ± 5.6	_	7.7 ± 2.8	7.3 ± 3.1
	3 ductile	53.5 ± 1.6			
PET2.2/SEBS2m	4 ductile	41.0 ± 0.4	_	5.4 ± 2.9	3.7 ± 1.6
PET4.9/SEBS2m	3 brittle	—	$40.5\pm~0.5$	3.1 ± 0.2	2.2 ± 0.2

Table XI Effect of Hydroxyl-to-Carboxyl End-Group Ratio on Notched Tensile Properties at $T = 25^{\circ}$ C

^a Data from Table VIII.

were more ductile than blends of PET4.9. At 25°C, PET2.2 blended with SEBSm was ductile and PET4.9 blended with SEBS2m was brittle. Similarly, all the specimens of PET2.2 blended with SEBS1h were ductile compared to only one of four specimens of PET4.9 blended with SEBS1h. Athough all the compositions exhibited brittle fracture at 0°C, fracture surfaces of PET2.2 blended with SEBS1h exhibited considerably more stress-whitening than fracture surfaces of PET4.9 blended with SEBS1h. The fracture stress, fracture strain and fracture energy of the PET2.2 blends were correspondingly higher (Table XII).

Fractography

Surfaces of notched PET2.2 and PET4.9 specimens fractured at 0°C exhibited typical craze features [Fig. 9(a) and (b)]. The length of the preexisting craze was 1 mm or less. The slow crack growth regions of the PET2.2 and PET4.9 blends with SEBS1h are compared in Figure 9(c) and (d). The PET2.2 blend surface was characteristic of

Table XII Effect of Hydroxyl-to-Carboxyl End Group Ratio on Notched Tensile Properties at 0°C

Material	Fracture Mode	Fracture Stress (MPa)	Fracture Extension (mm)	Fracture Energy
PET95	5 brittleª	41.5 ± 6.4	2.3 ± 0.5	1.6 ± 0.6
	3 brittle	47.0 ± 1.2	2.6 ± 0.2	2.2 ± 0.1
PET2.2	3 brittle	36.7 ± 1.3	1.9 ± 0.1	1.3 ± 0.0
PET4.9	3 brittle	46.3 ± 0.2	2.5 ± 0.1	2.0 ± 0.1
PET95/SEBS1h	5 brittle ^a	47.9 ± 1.5	3.4 ± 0.4	3.0 ± 0.4
	3 brittle	49.3 ± 2.3	3.4 ± 1.0	3.0 ± 1.1
PET2.2/SEBS1h	3 brittle	49.3 ± 0.9	3.3 ± 0.1	2.9 ± 0.1
PET4.9/SEBS1h	3 brittle	43.9 ± 2.6	2.6 ± 0.5	2.0 ± 0.5
PET95/SEBS2m	5 brittle ^a	50.1 ± 1.3	3.1 ± 0.2	2.8 ± 0.3
	3 brittle	51.6 ± 1.3	3.5 ± 0.4	3.2 ± 0.4
PET2.2/SEBS2m	3 brittle	48.8 ± 1.3	3.3 ± 0.2	2.8 ± 0.2

^a Data from Table IX.

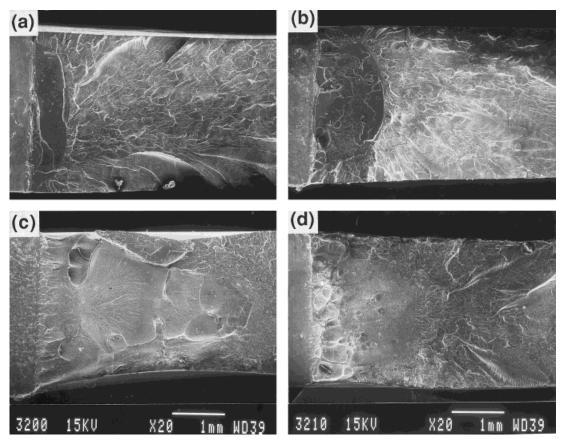


Figure 9 Low-magnification scanning electron micrographs of PET2.2, PET4.9 and their blends with SEBS1h fractured at 0°C. (a) PET2.2; (b) PET4.9; (c) PET2.2 with 5 wt % SEBS1h; and (d) PET4.9 with 5 wt % SEBS1h. The crack propagated from the notch on the left.

ductile tearing through a preexisting cavitated damage zone. The core yielding region at the notch root was quite long, more than 0.5 mm, and was followed by an elongated zone with several parabolic shapes caused by secondary cracks. There was also noticeable "sucking in" of the sides in the slow crack growth region. In contrast, the PET4.9 blend surface had almost no core yielding region, and there were numerous parabolic markings that indicated where secondary cracks initiated close to the notch and grew almost to the notch root before they impinged on the primary crack.

Higher magnification micrographs in Figure 10 compare the texture at various locations in the slow crack growth region of the blends with SEBS1h. The core yielding region at the notch root [position I in the schematic Fig. 10(a)] was only present in the PET2.2 blend. The texture consisted of highly drawn PET ligaments [Fig. 10(b)]. There was little evidence of cavitation, and

indeed, numerous uncavitated elastomer particles were visibly incorporated into the drawn PET ligaments. The absence of profuse cavitation was confirmation that failure occurred under mainly plane stress conditions in this region. The texture further from the notch root on the surface of a secondary crack [position II in Fig. 10(a)] showed profuse cavitation with numerous drawn out and fractured ligaments. Comparable regions from the fracture surfaces of the PET4.9 blend and the PET2.2 blend in Figure 10(c) and (d), respectively, showed striking differences. The PET2.2 blend surface was uniformly cavitated with many drawn-out PET ligaments. In contrast, a similar region of the PET4.9 blend surface was not as uniformly cavitated, the PET ligaments were less numerous, and they frequently had clumps of uncavitated SEBS1h particles attached. Near the end of the slow crack growth region [position III in the schematic Fig. 10(a)], the surfaces showed the initial stages of cavitation [Fig. 10(e) and (f)].

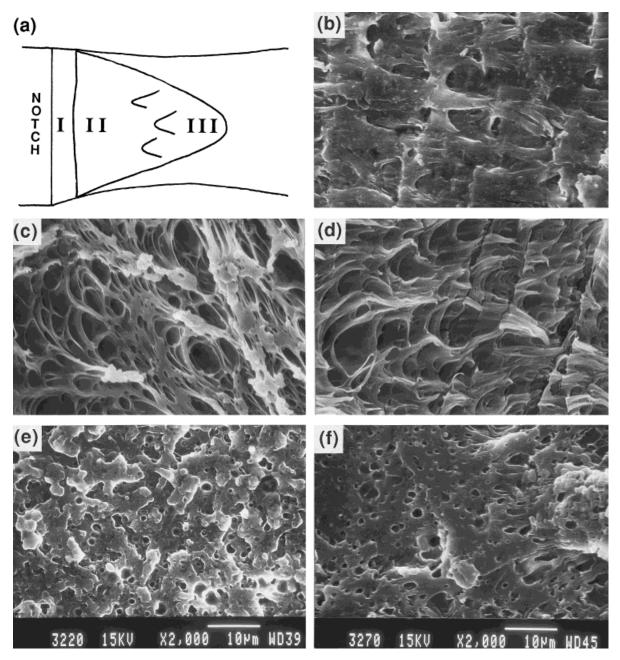


Figure 10 Higher magnification scanning electron micrographs of the slow crack growth region in Figures 9(c) and (d). (a) Schematic representation of the slow crack growth region with positions I, II, and III identified; (b, d, and f) PET2.2 with 5 wt % SEBS1h at positions I, II, and III , respectively; and (c, e) PET4.9 with 5 wt % SEBS1h at positions II and III, respectively.

On the PET2.2 blend surface, the numerous circular holes indicated the beginning of overall cavitation. In some areas the cavities had become elongated as the matrix started to draw into ligaments. A comparable region of the PET4.9 blend surface was less cavitated. Numerous uncavitated particles were in evidence, often these uncavitated particles were clustered together in small clumps. The roughness of the PET4.9 blend surface indicated that matrix fracture was more brittle than in the comparable region of the PET2.2 blend.

Because there were no large differences in the particle size and particle size distribution of

SEBS1h in PET2.2 and PET4.9 blends, these factors could not completely account for the striking differences in the fracture behavior. Assuming that PET4.9 formed more copolymer by reaction with SEBS1h than PET2.2 did, it can be speculated that the increased amount of copolymer affected particle-particle interactions without affecting particle size. For example, it was possible that the amount of copolymer formed in PET4.9 was sufficient to interconnect the elastomer particles. Although clumping of SEBS1h particles was not apparent in the etched brittle fracture surfaces used to measure particle sizes, it was possible that in tension the interconnections inhibited deformation of the matrix between particles and caused the particles to adhere together in clumps as the blend deformed.

CONCLUSIONS

Previous studies established the effectiveness of functionalized SEBS for enhancing the toughness of PET.²⁻⁴ The present study extended these previous investigations that focused on level of grafting to examine the effect of other variables, including PET molecular weight, SEBS molecular weight, and PET hydroxyl-to-carboxyl end group ratio. The results are summarized as follows:

- 1. Toughness enhancement of a higher molecular weight PET (PET95 with intrinsic viscosity 0.95) was achieved by addition of 5% SEBS elastomer. However, the intrinsically greater tensile toughness of the higher molecular weight PET95 was not of obvious advantage in the modified polymer. By comparing results presented here and in previous studies, it appeared that blends of the lower molecular weight PET72 (intrinsic viscosity 0.73) with SEBS generally performed as well or better than those of the higher molecular weight PET95 in both notched and unnotched tensile tests. There was no clear relationship to particle size, although it was speculated that large particles (greater than $1 \mu m$) in the particle size distribution were detrimental to PET95.
- 2. Two approaches to increasing the grafting level in this system independently of other variables entailed increasing the anhydride content of the SEBS, as in previous studies, and increasing the hydroxyl-to-carboxyl end-group ratio of the PET. Not surpris-

ingly, the two approaches had different effects on particle size. The former was accompanied by decreasing particle size with increasing anhydride concentration, whereas increasing hydroxyl-to-carboxyl number had no effect on particle size or size distribution. Nevertheless, in both cases, increasing the potential grafting level resulted in poorer properties, although the causes may have been different. The deterioration in properties of PET72 with increasing SEBS functionality was attributed to an increase in the cavitation resistance above the optimum level for this system. Increasing the ratio of hydroxyl end groups appeared to produce particle-particle interconnections that inhibited the toughening mechanisms.

3. Examination of fracture surfaces revealed evidence of a preexisting damage zone at the notch root in even the most brittle fractures. Subsequent fractographic analysis provided insight into the mechanisms of energy absorption and toughness enhancement under a triaxial stress state. Crazing produced the most brittle fractures. Blending PET with an SEBS elastomer changed the deformation mechanism in the damage zone from crazing to cavitation and shear yielding. The apparent toughness of a blend depended on the extent to which the damage zone developed before a catastrophic crack initiated. The fracture surfaces provided evidence that toughening of PET with functionalized SEBS elastomers was mechanistically analogous to rubber toughening of other ductile thermoplastics.

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