

Impact Strength and Fracture Surfaces of Interfaces Between Polyethylene and Polypropylene and Some Ethylene-Containing Copolymers

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ABSTRACT: The impact strength of annealed interfaces between high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP) and some ethylene-co-vinyl acetate (EVA) and ethylene-co-acrylic acid (EAA) copolymers was obtained using the Notched Izod test. The impact strengths of EVA-HDPE, EVA-LDPE, and EVA-PP interfaces using EVA copolymers with 9 to 27.5 wt % vinyl acetate (VA), and of EAA-PP interfaces using EAA with 3 to 20 wt % acrylic acid (AA), were all equal to or greater than those of the homopolymer used. However, the impact strengths of EAA-HDPE and EAA-LDPE interfaces were all lower than those of pure HDPE or LDPE, with the exception of 3EAA-LDPE. Scanning electron micrographs showed the presence of fibrils and/or voids, mostly on those copolymer-homopolymer fracture surfaces which had high impact strength. X-ray photoelectron spectroscopy of the fracture surfaces showed a greater calculated percentage of AA or VA on both the copolymer and homopolymer sides of the interface than in the bulk for most samples at 15 Å penetration. This greater calculated percentage of AA or VA is probably due to chain scission during sample preparation or fracture, which results in additional acid or alcohol groups at the surface that are calculated as increased VA or AA content. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2221–2235, 1997

Key words: fracture surfaces; impact strength; polyethylene; polypropylene; ethylene-vinyl acetate copolymers; ethylene-acrylic acid copolymers

INTRODUCTION

The use of compatibilizers to increase adhesion between immiscible polymers is a subject of considerable current interest. Generally, it appears that the addition of the right block copolymers

can reduce the interfacial tension and improve the adhesion between the immiscible polymers, thus increasing the compatibility of the blend.^{1–5} In general, the block copolymer compatibilizers are made up of two chemically different blocks, one of which is miscible with one of the immiscible polymers, and the other of which is miscible with the second polymer. Thus the block copolymers, when present at low concentration, are expected to migrate to the interfaces between the immiscible polymers and to stabilize these interfaces.

Recently, several reports have appeared in which random copolymers have been used as polymeric compatibilizers.^{6–8} In a recent article,⁹ we followed up the work in one of these reports, that

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of Swint and colleagues,⁸ who found that a simulated plastics waste mixture containing 70 wt % high-density polyethylene (HDPE), 4 wt % low-density polyethylene (LDPE), 11 wt % polypropylene (PP), and 15 wt % polystyrene could achieve an increased strain to failure without an increase in tensile modulus or yield strength when extruded with 7 wt % of poly(ethylene-co-vinyl acetate) (EVA) containing 27.5 wt % vinyl acetate (VA), 27.5EVA. We⁹ examined annealed interfaces between HDPE, LDPE, and PP with some EVA and poly(ethylene-co-acrylic acid) (EAA) copolymers using optical microscopy, scanning electron microscopy (SEM), and electron microprobe analysis. Transcrystalline zones were observed in a polarizing microscope on the copolymer side of the interfaces between EVA copolymers with ≤ 18 wt % VA or EAA copolymers with ≤ 6.5 wt % acrylic acid (AA) and HDPE or LDPE when the samples were heated above the melting points of both polymers and allowed to cool slowly to room temperature. The crystallization temperatures in the transcrystalline zones were all above those of the bulk copolymers and, in some cases, even above their melting points. Electron microprobe data on EVA-HDPE samples freeze-fractured perpendicular to the interfaces, showed a lower percentage of VA than that in the bulk copolymer in the region corresponding to the transcrystalline zone on the copolymer side of the interface. All of these data together indicated that some polyethylene (PE) molecules had migrated across the interface into the transcrystalline zone. This probability was confirmed by optical microscopy on interfaces between the copolymers and some PE oligomers, which showed that some of these oligomers with molecular weights up to 507 were completely miscible with EVA samples having VA contents up to 18 wt %. Also, calculations using the Flory-Huggins theory indicated that copolymers of low wt % VA or AA should be miscible with low-molecular-weight PE at elevated temperatures. On the other hand, optical microscopy of EAA or EVA interfaces with PP showed the formation of influxes of copolymer into the PP side of the interface, resulting in mechanically interlocked interfaces. These results implied that there might be a strengthening of the interface between the copolymers and the PEs due to diffusion of PE into the copolymer side of the interface, and between the copolymers and PP because of the mechanical interlocking of these interfaces. In this article we examine these interfaces further by measuring their Izod impact strength as well

as the appearance and compositions of the fracture surfaces from the impact test.

EXPERIMENTAL

Materials

Table I lists the source code and molecular weight data of all the commercial polymer samples used in this work. Molecular weights, when listed, were determined by gel permeation chromatography (GPC) in this work or were provided by the suppliers. Samples were used as received.

Gel Permeation Chromatography

A Waters (Milford, MA) GPC, interfaced with a NEC IBM AT-compatible computer, using a single linear column (Ultrastayragel, molecular weight range 2×10^3 to 4×10^6), and a Waters R40 Differential Refractometer were used for molecular weight determinations of those samples that were soluble in chloroform. Calibration was done using poly(methyl methacrylate) (PMMA) standards ranging in molecular weight from 2.2×10^4 to 3.3×10^5 . The molecular weights are thus not absolute, but in terms of PMMA.

Notched Izod Test

To prepare samples for the Notched Izod test, EAA, EVA, HDPE, LDPE, or PP pellets were placed in a $6 \times 1.2 \times \sim 0.25$ -cm bar mold. Samples were pressed at approximately 20°C above the melting temperature of each of the polymers. A Model M Carver Press (Fred S. Carver, Inc., Menomonee Falls, WI) was used. The temperature was monitored by an Omega (Omega Engineering, Inc., Stamford, CT) Model 650 digital thermometer with Type J thermocouple. Samples were pressed at 600 psi between Teflon cloth after triple-plated ferrotype plates (Testrite Instrument Company, Inc., Newark, NJ) were placed on top of and under the samples. The molded samples were cooled on a laboratory bench. When cooled, the molded bars of copolymers and homopolymers were cut in half with a clean razor blade. Combinations of all copolymer and homopolymers were then placed together in the same mold. All samples with HDPE and LDPE were pressed at 160°C. Samples with PP were pressed at 200°C. All samples were pressed for 15 s at 1200 psi, the pressure was quickly relaxed to allow the release of air

Table I Polymers Used in This Work

Code	Polymer	Source	$M_w \times 10^{-3}$	M_w/M_n
9EVA ^a	9 wt % VA	SPP ^b		
14EVA ^a	14 wt % VA	SPP ^b		
18EVA ^a	18 wt % VA	SPP ^b		
27.5EVA ^a	27.5 wt % VA	Exxon ^c	10.1 ^d	2.8 ^d
3EAA ^e	3 wt % AA	Dow ^f	85.7 ^g	4.7 ^g
6.5EAA ^e	6.5 wt % AA	Dow ^f	79.1 ^g	4.2 ^g
9.7EAA ^e	9.7 wt % AA	Dow ^f	94.4 ^g	4.9 ^g
20EAA ^e	20 wt % AA	Dow ^f	76.8 ^g	4.6 ^g
PP	Polypropylene	Exxon ^c		
HDPE	High Density Polyethylene	Phillips ^h	123 ^g	7.1 ^g
LDPE	Low Density Polyethylene	Exxon ^c	97 ^g	5.3 ^g

^a Ethylene–vinyl acetate copolymer.

^b Scientific Polymer Products, Ontario, NY.

^c Exxon Chemical Co., Houston, TX.

^d Determined in this work.

^e Ethylene–acrylic acid copolymer.

^f Dow Chemical Co., Midland MI.

^g Data provided by the supplier.

^h Phillips Plastics Corp., Phillips, WI.

bubbles, then the samples were pressed for 30 s at 10^4 psi. The molds were rapidly quenched in a cold-water bath, then the samples were removed from the mold, dried, and stored in a vacuum oven. Notched Izod tests were conducted on an Impact Tester TIM No. 43-1 (Testing Machines, Inc., Amityville, NY) using a 2-lb pendulum. Bar samples were notched at the interface using a notching cutter, Model TMI 22-05 (Testing Machines, Inc., Amityville, NY). During notching, each sample was sandwiched between similar bars of pure HDPE to maintain the sample's stability. All copolymer–HDPE, copolymer–PP, and homopolymer–homopolymer tests were conducted at 25°C immediately after the sample was notched. Because LDPE does not fracture at room temperature, all tests of samples that included LDPE were conducted at -20°C . To perform the Notched Izod tests at -20°C , the impact tester chamber containing the vise jaw was completely lined with insulation and covered with an insulated cover. Liquid nitrogen was forced through a hole in the front of the chamber. The temperature of the impact testing chamber was monitored by a digital thermometer with a thermocouple inserted into the sample chamber. EVA–LDPE, EAA–LDPE, and pure LDPE samples were notched, then placed in the vise jaw in the cooled chamber for 30 min to equilibrate to -20°C . The top of the chamber was then quickly removed and the pendulum allowed to strike the sample. In all cases, the EVA or EAA portion of the sample was

mounted in the vise jaw of the impact tester, with the pendulum striking the HDPE, LDPE, or PP side of the sample bar. The number of samples of each combination tested was between five and 15.

Scanning Electron Microscopy

A Zeiss CMS 950 scanning electron microscope (Karl Zeiss, Jena, Germany) was used to study the fractured interfaces. Samples were pressed against carbon tape, then mounted on aluminum stubs. Approximately 200 Å of gold was deposited on all samples by a Denton Desk II sputter coater with a gold target. Coated samples were observed and photographs were taken using a Polaroid instant camera. Photographs were taken of areas about 5 mm away from the original position of the notch.

X-ray Photoelectron Spectrometry

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin–Elmer model (Norwalk, CT) 1257 ESCA spectrometer. The spectrometer was interfaced with a Domain 3000 computer and Perkin–Elmer software was used for processing data. Data analysis was performed on unsmoothed curves. The instrument uses a monochromatic Mg anode which was operated at 15 kV and 200 watts. The analysis spot size was 1×1 mm. Pressure in the source chamber was approximately 10^{-9} Torr. Samples were neutralized by

Table II Characteristics XPS Core Level Binding Energies of Polyethylene, PVA, and PAA

Polymer	Peak	Binding Energy (eV)
Polyethylene	$\overline{\text{C}}\text{H}_x$	285.00
	$\overline{\text{C}}\text{H}_x$	285.00
	$\overline{\text{C}}\text{C}=\text{OO}$	285.48
	$\overline{\text{C}}\text{OC}=\text{O}$	286.63
PAA	$\overline{\text{C}}=\text{OO}$	289.17
	$\overline{\text{C}}\text{H}_x$	285.00
	$\overline{\text{C}}\text{C}=\text{OO}$	286.22
	$\overline{\text{C}}=\text{OO}$	289.18

flooding with electrons and were analyzed at three angles relative to the sample surface: 15, 45, and 75 degrees, corresponding to approximately 15, 42, and 58 Å¹⁰ depth penetration into the sample. Attempts were made to study the (visually) smoothest portions of the surfaces.

Quantification of the VA or AA content on the surfaces of the fractured interfaces of copolymer–HDPE and copolymer–LDPE samples from the Notched Izod tests was accomplished by resolving the component peaks in the C_{1s} signal. First, curve fitting for the pure PE, poly(vinyl acetate) (PVA), and poly(acrylic acid) (PAA) was performed to determine the positions of the component peaks in this signal; these are shown in Table II. The fracture surfaces were then analyzed using these peaks. The percent of VA or AA on each surface was calculated using the $\overline{\text{C}}\text{OO}$ carbon peak relative to all other carbon peaks. After we assumed that all the carbons in the different chemical environments had the same sensitivity factor,¹¹ we set the intensity (*I*) of each carbon peak from the XPS C_{1s} spectra equal to the number of moles of the group responsible for that peak in 100 g of analyzed sample:

$$I_{\text{COO}} = w_{\text{VA}}/86 \quad (1)$$

$$I_{\text{CO}} = w_{\text{VA}}/86 \quad (2)$$

$$I_{\text{CH}} = 2w_{\text{VA}}/86 + 2(1 - w_{\text{VA}})/28 \quad (3)$$

where w_{VA} is the weight percent VA in the sample, 86 is the molecular weight of the VA repeat group, and 28 is the molecular weight of the ethylene repeat group. Since only carbon peaks were investigated, the sum of $I_{\text{COO}} + I_{\text{CO}} + I_{\text{CH}}$ is 100. Using this information and eqs. (1)–(3), one may solve for w_{VA} in terms of I_{COO} :

$$w_{\text{VA}} = (0.0714I_{\text{COO}})/(1.16 + 0.025I_{\text{COO}}) \quad (4)$$

In the same way, the expression for obtaining the weight percent AA at the surface becomes

$$w_{\text{AA}} = (0.0714I_{\text{COO}})/(1.39 + 0.0297I_{\text{COO}}) \quad (5)$$

where w_{AA} is the weight percent AA in the surface sample investigated.

Differential Scanning Calorimetry (DSC)

Thermal transitions of thin slices from all copolymer and homopolymer fracture surfaces were studied using a Perkin–Elmer DSC7 Differential Scanning Calorimeter interfaced with a NEC Multisync II computer. Samples were cut directly from the fractured sample with a clean razor blade. All thermograms were first runs, obtained at a heating rate of 10°C min⁻¹. Nitrogen was used as the purge gas in the glove box. Thermal analysis software used for processing the data was present on the hard drive of the computer.

RESULTS AND DISCUSSION

Notched Izod Tests on Copolymer–Homopolymer Interfaces

Up to this time, this test has been generally applied to molded, homogeneous homopolymer specimens or polymer blend specimens but not to the interfacial regions between two polymers. A double cantilever beam test geometry¹ has been developed by others to characterize the fracture toughness of polymer–polymer interfaces reinforced with block copolymers. This test uses a razor blade as a wedge; we attempted a wedge cleavage test with a blunter wedge. This blunter wedge, when driven into the interface at 0.2 in min⁻¹, always caused asymmetric cleavage, with crack propagation into the less-crystalline side of the interface. The Notched Izod test was the only test that caused cleavage of all our samples along the interface and that gave reproducible results. We understand that the resulting numbers cannot be easily interpreted in terms of material parameters, but we feel that they nevertheless allow comparisons to be made between the different interfaces. After fracture using the Notched Izod test, visual observation of all copolymer–HDPE, copolymer–LDPE, and copolymer–PP interfaces showed, within the error of any visual observa-

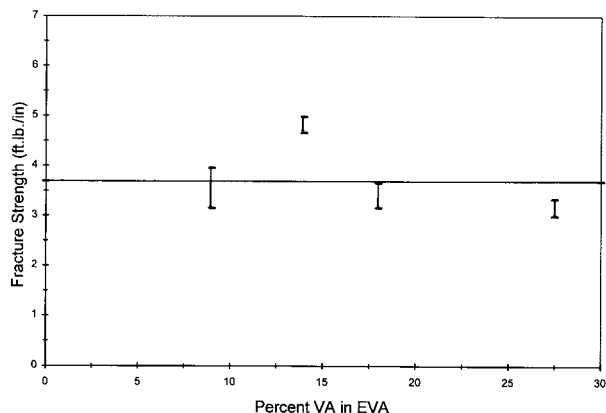


Figure 1 Notched Izod test data for EVA-HDPE interfaces. Error bars represent standard error of the mean. The straight line represents the impact strength of pure HDPE.

tion, that fracture occurred at the interface and did not occur through the bulk copolymer or homopolymer.

Figures 1 through 6 compare the impact strengths of the different copolymer-homopolymer interfaces with that of the pure homopolymer. Figure 1 shows that those copolymers which exhibited transcrystalline zones with HDPE (9EVA, 14EVA, and 18EVA) had the same or slightly higher impact strengths than pure HDPE. However, the interface between 27.5EVA and HDPE, which did not exhibit a transcrystalline zone in the optical microscope but which showed a gradual increase in the percent VA on the EVA side of the interface over approximately 15 μm until the bulk VA content was observed in electron microprobe studies, had an impact strength almost as high as pure HDPE. This demonstrates the excellent adhesion between all these copolymers and HDPE. This excellent adhesion was also evidenced by the fact that some specimens of 9EVA-HDPE, 14EVA-HDPE, and 18EVA-HDPE did not break completely but exhibited a hinged or partial break. These samples had impact strengths about 50% greater than those that fractured completely; these data are not included in Figure 1. Figure 2 shows that the EVA-LDPE interfaces had impact strengths very close to or greater than that of pure LDPE.

Figure 3 shows that the EAA-HDPE interfaces had much lower impact strengths than the EVA-HDPE interfaces or pure HDPE. Optical microscopy studies carried out earlier⁹ showed very thin transcrystalline zones in 3EAA-HDPE and inconsistent transcrystalline zones in 6.5EAA-

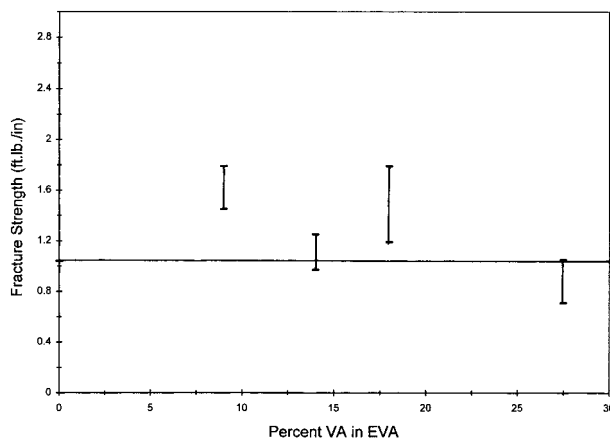


Figure 2 Notched Izod test data for EVA-LDPE interfaces. Error bars represent standard error of the mean. The straight line represents the impact strength of pure LDPE.

HDPE. Figure 4 shows that the Notched Izod tests performed on most EAA-LDPE interfaces also showed slightly lower impact strengths than pure LDPE. Only the 3EAA-LDPE interfaces had a significantly higher impact strength than pure LDPE, possibly approaching that of pure 3EAA, which, unfortunately, could not be measured because this copolymer did not fracture under our conditions.

Figures 5 and 6 show that the impact strengths of the EVA-PP and EAA-PP interfaces were similar to or greater than that of pure PP.

For comparison with the copolymer-homopolymer interfaces, the impact strengths of the interfaces between the different homopolymers were also obtained. The data are shown in Table III,

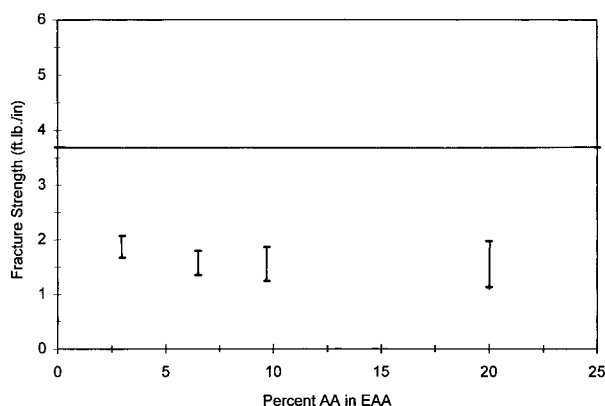


Figure 3 Notched Izod test data for EAA-HDPE interfaces. Error bars represent standard error of the mean. The straight line represents the impact strength of pure HDPE.

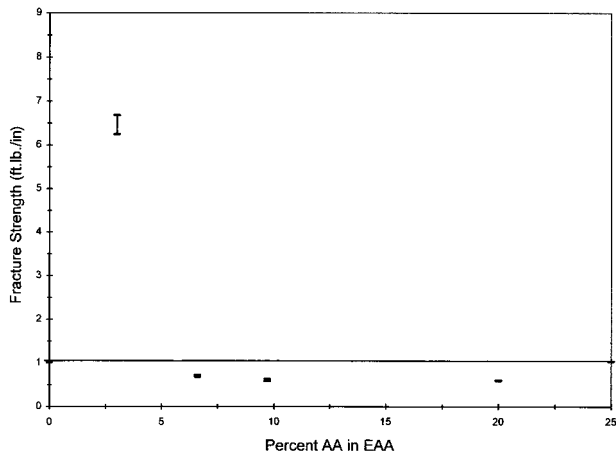


Figure 4 Notched Izod test data for EAA-LDPE interfaces. Error bars represent standard error of the mean. The straight line represents the impact strength of pure LDPE.

where they are also compared with the data on the pure homopolymers. Only the HDPE-LDPE interface had a higher impact strength than either homopolymer alone.

SEM of Fracture Surfaces

As stated above, all SEM pictures were taken about 5 mm away from the original notch. Fracture surfaces became much smoother in areas that were farther away from the notch, indicating that the fracture mechanism may be different in those areas. Nevertheless, it appeared useful to compare the fracture surface morphologies of the

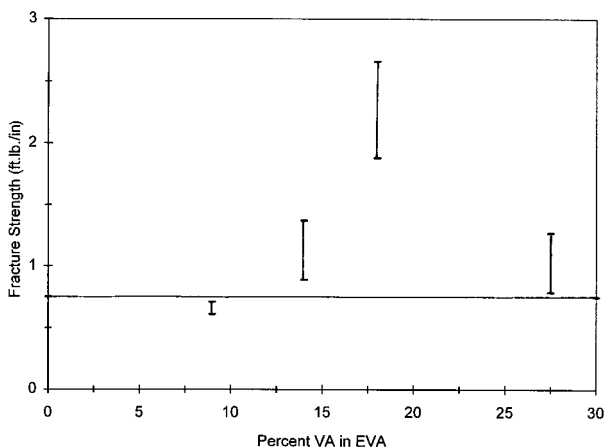


Figure 5 Notched Izod test data for EVA-PP interfaces. Error bars represent standard error of the mean. The straight line represents the impact strength of pure PP.

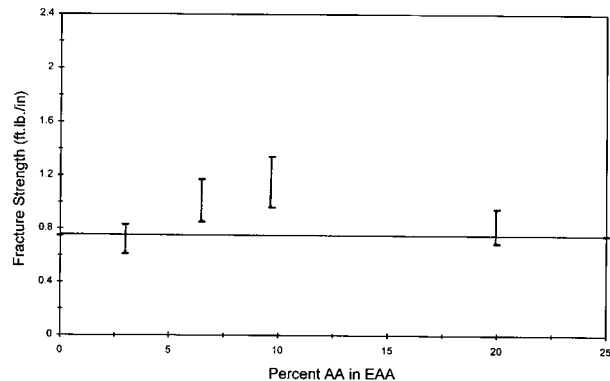


Figure 6 Notched Izod test data for EAA-PP interfaces. Error bars represent the standard error of the mean. The straight line represents the impact strength of pure PP.

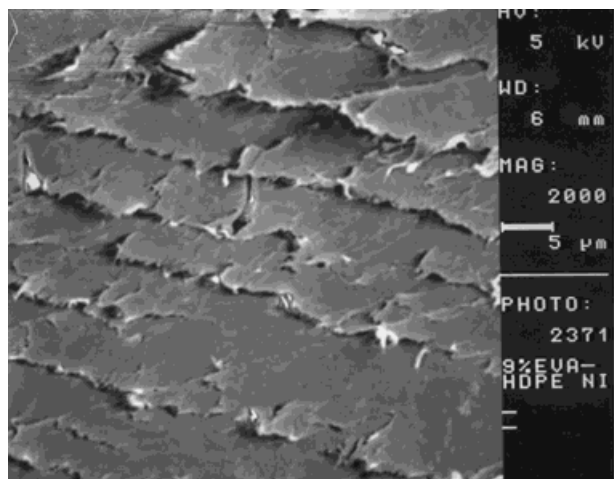
different samples in the “5 mm from the notch” areas. In those areas, samples of 9EVA-HDPE, 14EVA-HDPE, and 18EVA-HDPE had a fracture mechanism that resulted in a fibrous appearance on each side the interface. That is, there appeared to be fibrils standing up from the surface of the interface on both sides of the interface of 9EVA-HDPE (as shown in Fig. 7) and 14EVA-HDPE (not shown). These fibrils appear only on the 18EVA side (Fig. 8) of the 18EVA-HDPE interface but are particularly evident there, whereas the HDPE side appears to have voids. As shown in Figure 9, the 27.5EVA-HDPE fracture interface surfaces have a “flatter” appearance.

In most cases, the corresponding fracture surfaces from the Notched Izod tests of the EVA-LDPE interfaces had a “flatter” appearance than the corresponding EVA-HDPE interfaces but with some fibril structure on the surface that was

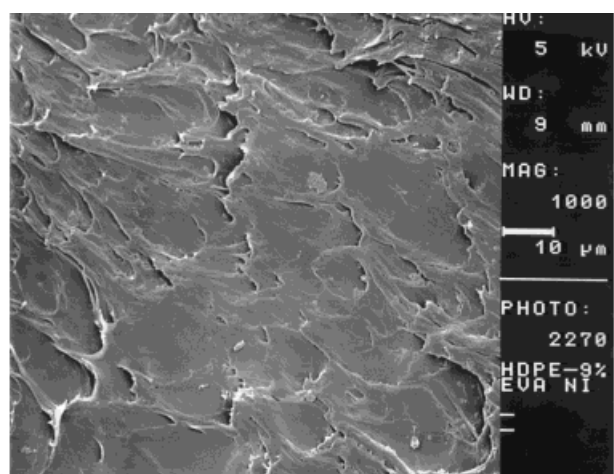
Table III Room Temperature Notched Izod Test Impact Strengths of Homopolymer-Homopolymer Interfaces and of Pure Homopolymers

Interface	Impact Strength (ft lb in. ⁻¹)
HDPE	3.69 ± 0.35
LDPE (at -20°C)	1.04 ± 0.14
PP	0.75 ± 0.06
HDPE-LDPE	4.33 ± 0.75
HDPE-PP	0.47 ± 0.01
LDPE-PP	0.50 ± 0.01

Error limits are standard deviations.



(a)



(b)

Figure 7 SEM of both fracture surfaces of the 9EVA–HDPE interface: (a) HDPE surface; (b) 9EVA surface.

quite evident on the EVA side of the 27.5EVA–LDPE interface, as shown in Figure 10.

The SEM photographs of the fracture surfaces of the EVA–PP samples revealed pullout of EVA influxes from the PP side of the interface, leaving voids on the PP side, probably between spherulites, as shown in Figure 11 for the 18EVA–PP sample.

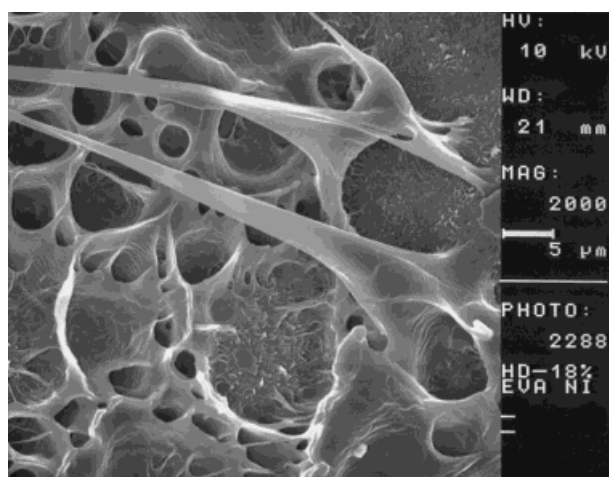
Figure 12 shows that the fracture surfaces from 3EAA–HDPE had a “fibrous” texture similar to that found for some of the 27.5EVA–HDPE fracture surfaces [Fig. 9(a), especially]. This “fibrous” texture became “flatter” as the percent AA increased in the sample.

The EAA–LDPE fracture surfaces looked relatively flat. However, as the percent AA increased,

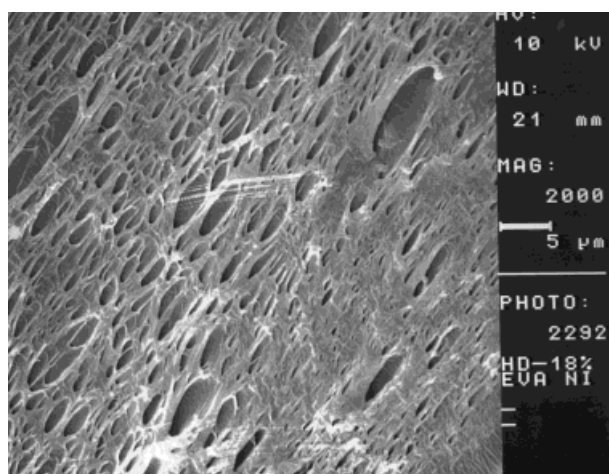
a few random fibrils appeared on the EAA side of 6.5EAA–LDPE and 9.7EAA–LDPE interfaces, with more and larger fibrils on the 20EAA–LDPE fracture surfaces, as shown in Figure 13.

The EAA–PP fracture surfaces did not exhibit as many or as large pullout sections of EAA on the EAA side of the interface as was apparent with the EVA–PP surfaces. Also, only very few small voids were evident on the PP side of the interface. The 3EAA–PP fracture surfaces, as shown in Figure 14, exhibited the largest density of voids and pullout.

Figure 15 shows the fracture surfaces of an HDPE–LDPE sample, both of which exhibit pullout and voids. Figure 16 shows those of an HDPE–PP sample; neither surface shows major



(a)



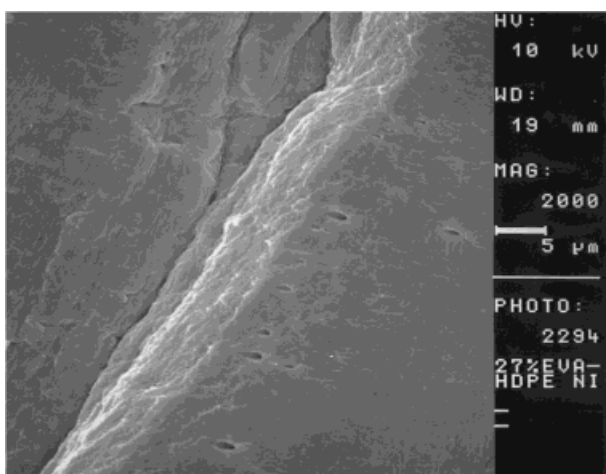
(b)

Figure 8 SEM of both fracture surfaces of the 18EVA–HDPE interface: (a) 18EVA surface; (b) HDPE surface.

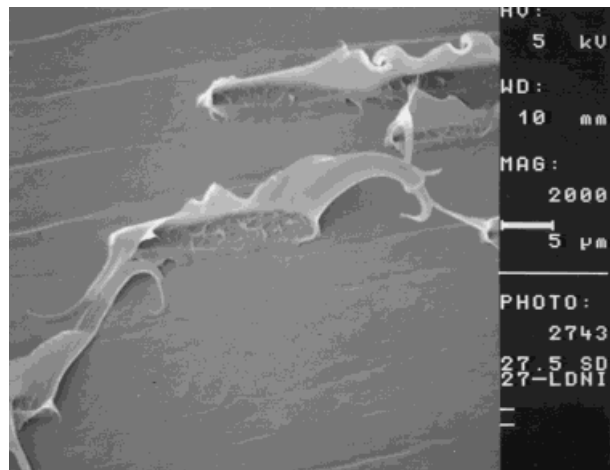
features. Figure 17 shows the fracture surfaces of an LDPE–PP sample; here, one may observe a large section of pullout on the LDPE surface, with a large void visible on the PP side of the interface. We may recall that, among the homopolymer–homopolymer interfaces, only the HDPE–LDPE interface had an impact strength greater than that of either homopolymer alone. This is also the interface that has pullout and voids on both fracture surfaces.

XPS of Fracture Interface Surfaces between Copolymers and Homopolymers

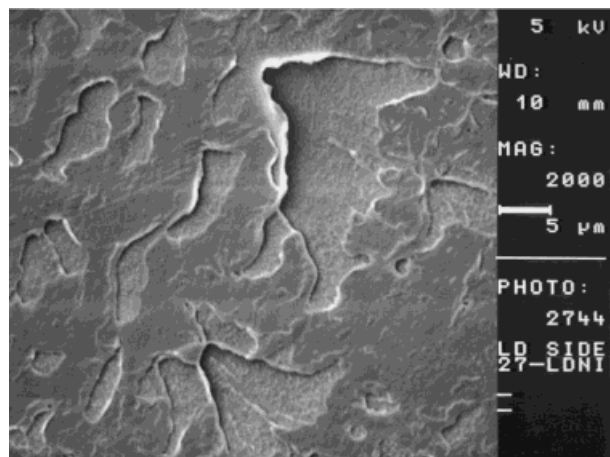
The XPS analysis of the fracture surfaces was an attempt, only somewhat successful, to find the



(a)

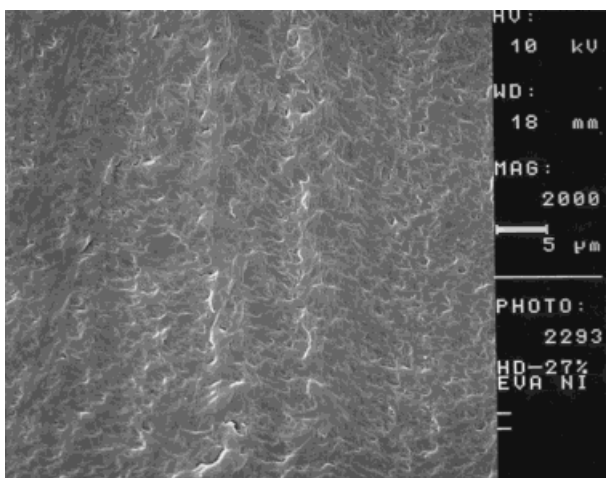


(a)



(b)

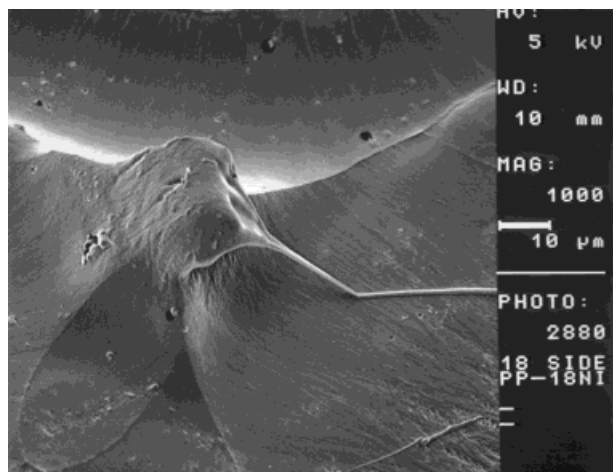
Figure 10 SEM of both fracture surfaces of the 27.5EVA–LDPE interface: (a) 27.5EVA surface; (b) LDPE surface.



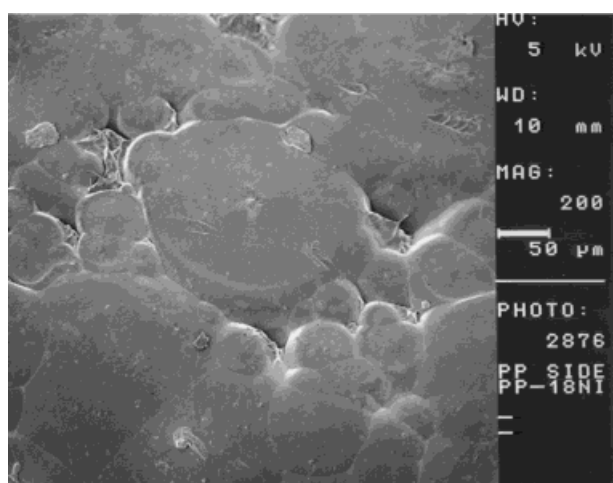
(b)

Figure 9 SEM of both fracture surfaces of the 27.5EVA–HDPE interface: (a) 27.5EVA surface; (b) HDPE surface.

composition of the 60 Å or so below the these surfaces. All the fracture surfaces from the Notched Izod test were examined using XPS, again about 5 mm from the original notch whenever possible, and the weight percent VA or AA was calculated at each penetration depth. The percent of error for each surface was 1 wt % due to sample variations. XPS analysis was performed in several places on each sample, as well as on several samples of the same type. While the exact percentages were not always precisely the same from sample to sample and from area to area on the same sample, the same trends were always observed. Figures 18 through 20 show the results for three types of fracture surfaces: Figure 18 for EVA–HDPE, Figure 19 for EAA–LDPE, and Figure 20



(a)

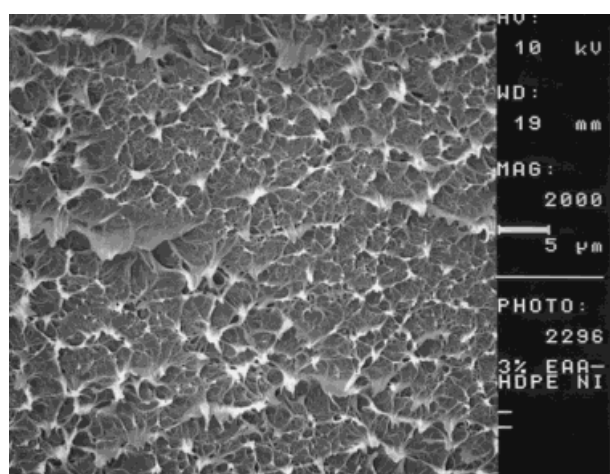


(b)

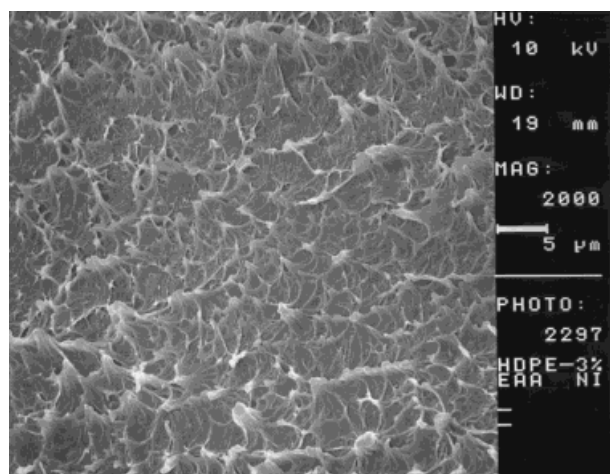
Figure 11 SEM of both fracture surfaces of the 18EVA–PP interface: (a) 18EVA surface; (b) PP surface.

for EVA–PP fracture surfaces. The other three, EAA–HDPE, EVA–LDPE, and EAA–PP, are not shown because they are very similar to those shown. The most noticeable feature in Figures 18 through 20 is the large calculated weight percent VA or AA at 15 Å penetration at most copolymer–homopolymer interfaces. (The line at zero in these figures denotes the original interface before fracture.) The large calculated values of the percent VA or AA at the fracture surfaces can be explained by the formation of free radicals in the process of fracture because of chain scission. These free radicals react differently depending on the temperature and the means of fracture. For example, the primary radicals may convert to secondary

radicals by transfer of a hydrogen atom along a chain or by the abstracting of hydrogen from a neighboring chain. This occurs when polymers are fractured at low temperatures in an inert atmosphere or when the temperature is increased while the sample is still under vacuum. These free radicals may then recombine with hydrogen, or recombine with oxygen when the fracture takes place at normal temperatures in the presence of air. The combination with oxygen forms peroxy radicals, which can further react to form acid or alcohol groups. During our sample preparation, the copolymer and homopolymer bars were first cut with a razor blade then reinserted back into the molds. After laminating for 45 s, then cooling in ice water, these samples were fractured by the



(a)

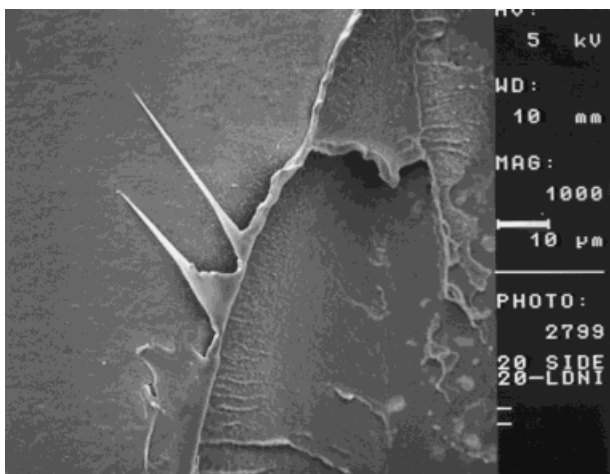


(b)

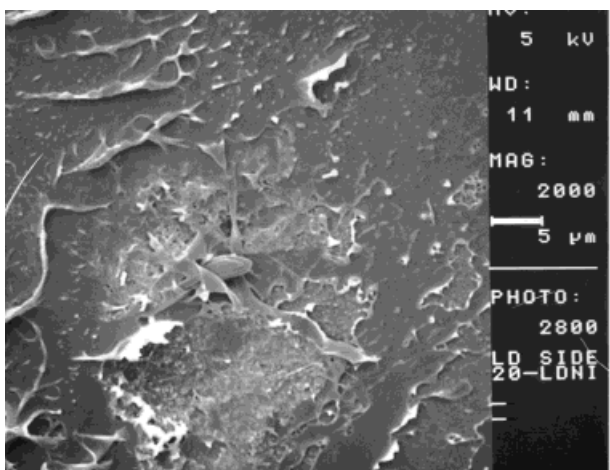
Figure 12 SEM of both fracture surfaces of the 3EAA–HDPE interface: (a) 3EAA surface; (b) HDPE surface.

Notched Izod test. Chain scission during sample preparation (cutting by a razor blade) or fracture (during the Notched Izod test), followed by the formation of acid or alcohol groups from available oxygen in the air, probably caused the observed high intensity of the COO or COH peak at the air surface after fracture. Because the COO peak for an acid and the COO peak for an ester as well as the COH peak are virtually inseparable during XPS curve fitting, the observed COO peak probably consisted of the sum of all these peaks and was calculated as percent VA or AA.

This explanation for the elevated calculated percentages of VA or EA at the Izod fracture surfaces was checked as follows. First, plaques of pure EVA, pure EAA, pure HDPE, pure LDPE,

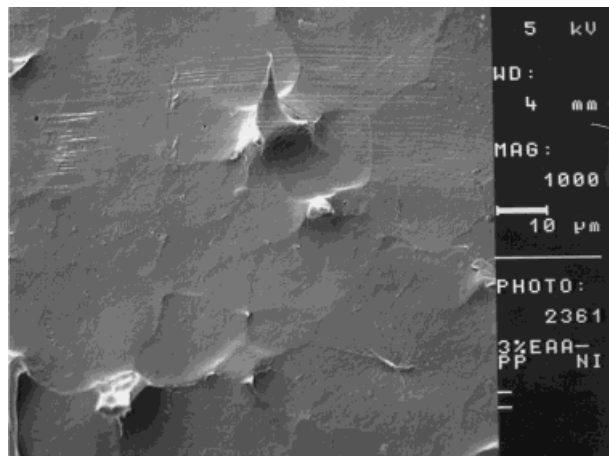


(a)

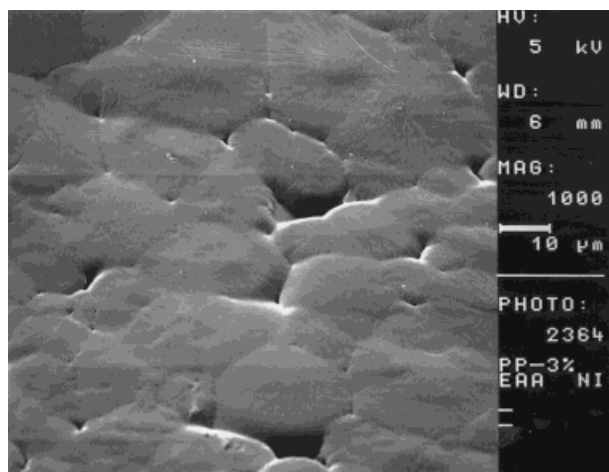


(b)

Figure 13 SEM of both fracture surfaces of the 20EAA-LDPE interface: (a) 20EAA surface; (b) LDPE surface.



(a)

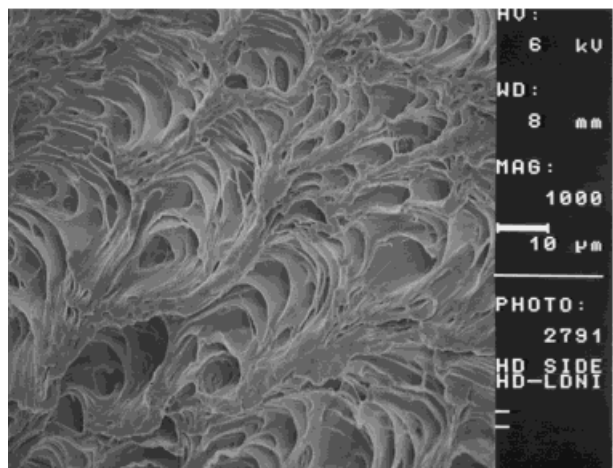


(b)

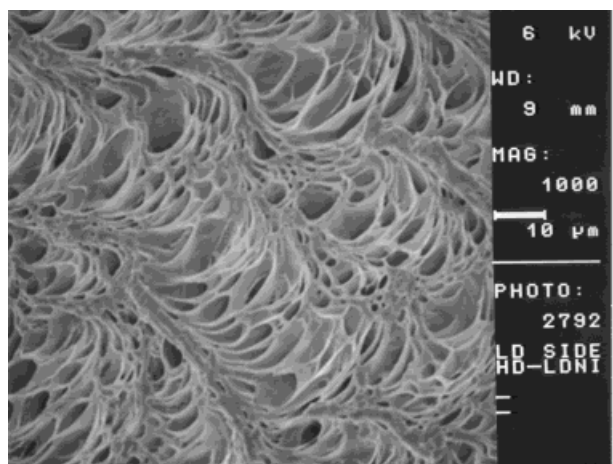
Figure 14 SEM of both fracture surfaces of the 3EAA-PP interface: (a) 3EAA surface; (b) PP surface.

and pure PP were cut with a clean razor blade at room temperature and the cut surfaces were examined using XPS. Then plaques of the pure EVA and EAA copolymers were freeze-fractured under liquid nitrogen and these fracture surfaces were also analyzed by XPS. Surfaces prepared by cutting with a razor blade at room temperature always exhibited a greatly increased intensity of the COO peak whereas samples which were freeze-fractured under liquid nitrogen had the COO peak intensity expected for that sample.

Because of the very high calculated VA content at 15 Å penetration, probably caused by the presence of acid or alcohol groups directly at the fracture surfaces, these groups may also be interfering with the data at 42 and 58 Å penetration; therefore it is very difficult to draw definitive con-



(a)



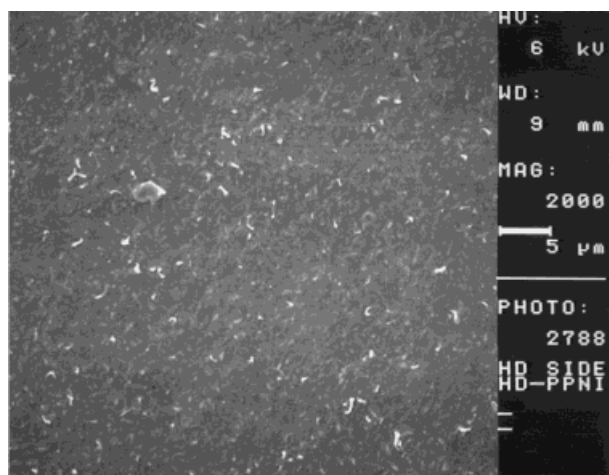
(b)

Figure 15 SEM of both fracture surfaces of the HDPE-LDPE interface: (a) HDPE surface; (b) LDPE surface.

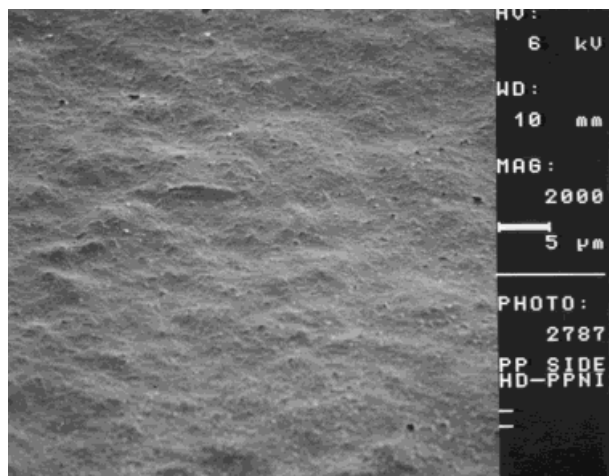
clusions from the XPS data. However, surface roughness is known to enhance the observed intensities of groups directly at the surface at low angles between the X-ray source and the sample surface (low penetration). Fadley and associates¹² found this from analysis of periodic sinusoidal rough surfaces. In the present work, the roughness does not follow a periodic function but the results may be analogous, that is, the groups directly at the surface have artificially high intensities at 15 Å penetration, and appear at much lower intensity at the deeper penetrations.

There are two additional features on Figures 18 through 20 which may be noted. First, on the EVA side of the interfaces in Figure 18, in spite of the elevated calculated weight percent VA right

at the surfaces (15 Å penetration), the calculated percent VA decreases well below the bulk weight percent VA at 42 and 58 Å penetration. This implies a very low weight percent VA just below the fracture surface which may be connected with the migration of PE into the EVA side of these interfaces that was a conclusion in our previous article.⁹ Lowered percentages of VA and AA are also shown on the copolymer sides of the interfaces at the higher penetrations in Figures 19 and 20 in some cases. These data, and possibly some of the data in Figure 18, may have a second explanation connected with the surface roughness shown in the SEM photographs, Figures 7 through 17. Some of the homopolymer from the other side of the fracture surface could be caught in some of

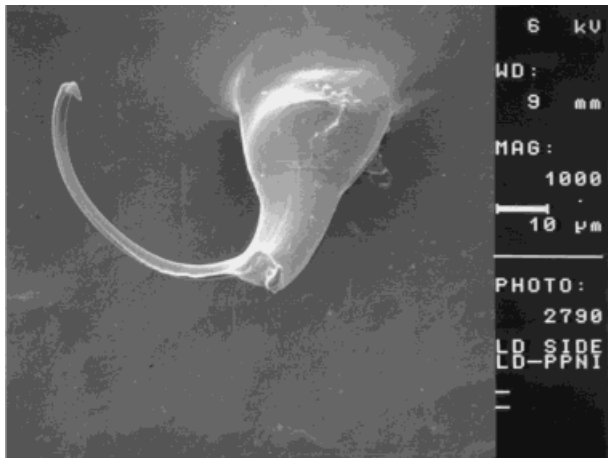


(a)

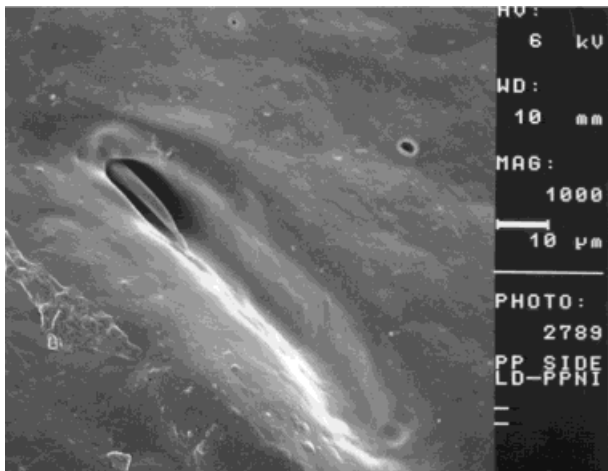


(b)

Figure 16 SEM of both fracture surfaces of the HDPE-PP interface: (a) HDPE surface; (b) PP surface.



(a)



(b)

Figure 17 SEM of both fracture surfaces of the LDPE-PP interface: (a) LDPE surface; (b) PP surface.

the depressions on the copolymer side. (Recall that the X-ray spot in XPS had a 1-mm diameter and examined a surface area that is enormously larger than that shown on any of the SEM pictures.) Although we attempted to obtain XPS data from the smoothest sections of the fracture surfaces, it could not be done using an SEM. Therefore, the sections examined could have been quite rough on the $<100\text{-\AA}$ depth scale examined by XPS.

The second observation from Figures 18 through 20 involves the homopolymer sides of the fracture surfaces. In many cases (e.g., on the HDPE side of the 27.5EVA-HDPE interface in Fig. 18 and generally in Figs. 19 and 20) there is little or no evidence of any copolymer at 58 Å penetration in spite of the surface roughness and

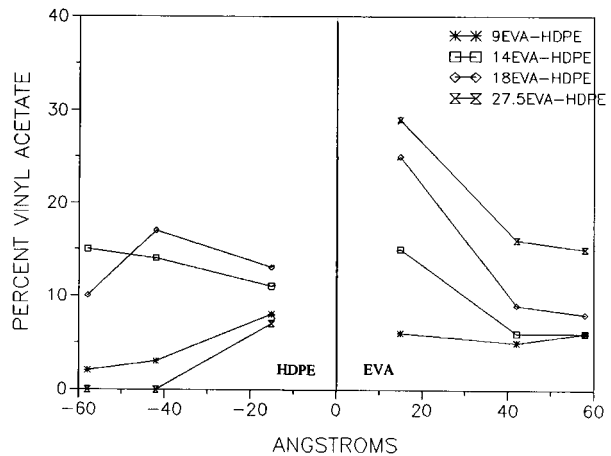


Figure 18 Calculated percent VA versus penetration into both fracture surfaces from XPS data for the EVA-HDPE interfaces.

in spite of the DSC data on material sliced from each fracture surface (discussed below). This was expected, because no copolymer penetration into the homopolymer side of the interface was observed by electron microprobe analysis in our previous study, at least at the μm scale analyzed.⁹ It is, however, hard to understand how the surface roughness could affect the data on the copolymer side of the fracture interface much more than on the homopolymer side.

DSC of Fracture Interface Surface Layers

Table IV shows the results of the first heat in DSC studies done using a thin slice cut from each side of the interface after the Notched Izod test was

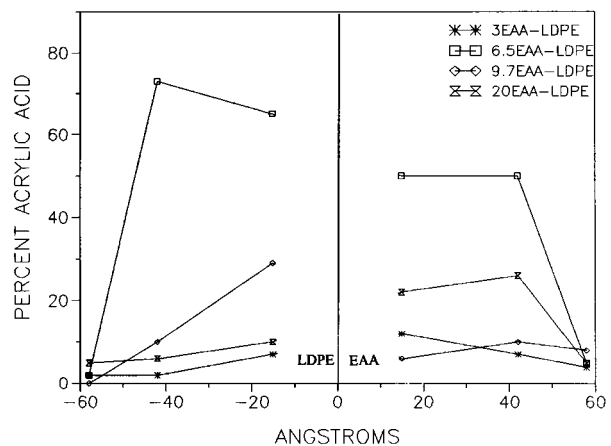


Figure 19 Calculated percent AA versus penetration into both fracture surfaces from XPS data for the EAA-LDPE interfaces.

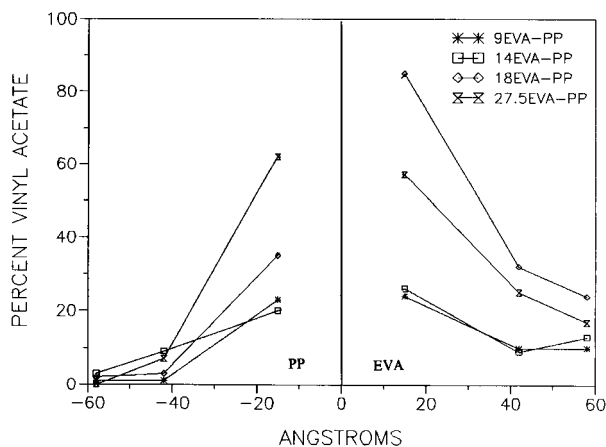


Figure 20 Calculated percent VA versus penetration into both fracture surfaces from XPS data for the EVA-PP interfaces.

performed. These thin slices were, of course, enormously thicker than the highest penetration of the X-ray beam in XPS. In most cases, melting peaks were observed for both components on both fracture surfaces, but the melting peak of the minor component was extremely small. Often, the

heat of fusion of this peak was <2 J/g. (The heat of fusion of HDPE is 245.3 J/g.¹³) The data indicate that, in almost all cases, there was a sufficient amount of the minor component on the other fracture surface to exhibit its own melting peak. This seems hard to reconcile with some of the XPS data which showed a lack of copolymer at the highest penetrations of the X-ray beam. However, careful microscopic observations of the samples prepared for the Izod test indicated that flow of one polymer over the other often occurred near the sample edges on annealing. It is quite possible that fracture at such edges left a small amount of the "other" polymer on each surface.

DSC data were obtained partly in the hope that a separate—or at least a broadened—melting peak could be observed for the polymers in the transcrystalline zones. However, no such separate or broadened peaks were observed, possibly because of the relatively small volume of the transcrystalline zone.

CONCLUSIONS

1. Fracture studies using the Notched Izod test on EVA-HDPE and EVA-LDPE in-

Table IV Melting Data on Thin Slices from Each Fracture Surface from the Notched Izod Test

Fracture Surface From	Side of Interface ^a	Melting Temperatures (°C)	Side of Interface ^a	Melting Temperatures (°C)
9EVA-HDPE	9EVA (93)	95, 133	HDPE (133)	95, 135
14EVA-HDPE	14EVA (91)	88, 130	HDPE (133)	87, 133
18EVA-HDPE	18EVA (83)	83, 132	HDPE (133)	80, 134
27.5EVA-HDPE	27.5EVA (75)	76, 128	HDPE (133)	72, 138
3EAA-HDPE	3EAA (108)	109, 130	HDPE (133)	109, 136
6.5EAA-HDPE	6.5EAA (103)	106, 133	HDPE (133)	shoulder, 135
9.7EAA-HDPE	9.7EAA (97)	99, 130	HDPE (133)	shoulder, 135
20EAA-HDPE	20EAA (96)	96 only	HDPE (133)	shoulder, 136
9EVA-LDPE	9EVA (93)	94, 108	LDPE (111)	93, 109
14EVA-LDPE	14EVA (91)	89, 107	LDPE (111)	90, 109
18EVA-LDPE	18EVA (83)	84, 108	LDPE (111)	82, 107
27.5EVA-LDPE	27.5EVA (75)	73, 105	LDPE (111)	shoulder, 108
3EAA-LDPE	3EAA (108)	110, shoulder	LDPE (111)	shoulder, 109
6.5EAA-LDPE	6.5EAA (103)	106, shoulder	LDPE (111)	shoulder, 106
9.7EAA-LDPE	9.7EAA (97)	105, shoulder	LDPE (111)	shoulder, 109
20EAA-LDPE	20EAA (96)	98, 108	LDPE (111)	shoulder, 109
9EVA-PP	9EVA (93)	94, 163	PP (164)	166 only
14EVA-PP	14EVA (91)	90, 164	PP (164)	88, 167
18EVA-PP	18EVA (83)	83 only	PP (164)	169 only
3EAA-PP	3EAA (108)	109 only	PP (164)	167 only
9.7EAA-PP	9.7EAA (97)	99, 162	PP (164)	168 only
20EAA-PP	20EAA (96)	96, 161	PP (164)	168 only

^a Numbers in parentheses are melting temperatures of the pure polymers; in °C.

- terfaces, using EVA copolymers with 9 to 27.5 wt % VA, showed that all these interfaces had impact strengths equal to or greater than those of the homopolymer present. All these interfaces had shown a zone containing excess ethylene on the copolymer side of the interface in earlier electron microprobe analyses, probably a result of the migration of lower-molecular-weight PE to the EVA side of the interface. In most of these cases, a transcrystalline zone was observed by optical microscopy in earlier work on the copolymer side of the interface. Excess ethylene had been observed throughout the transcrystalline zones. Because of this, we conclude that this ethylene migration is probably connected with the high impact strength of these interfaces.
- EAA-HDPE and EAA-LDPE interfaces, using EAA with 3–20 wt % AA, had lower impact strengths than pure HDPE or LDPE with the exception of 3EAA, which had a much greater impact strength than pure LDPE. Transcrystalline zones had been seen on the copolymer side of many of these interfaces in earlier work, but these were too narrow for electron microprobe analysis. We surmise that either these transcrystalline zones did not contain excess PE or that they were too narrow to provide an increase in impact strength.
 - EVA-PP and EAA-PP interfaces had impact strengths greater than pure PP, probably resulting from the mechanically interlocked interfaces between the copolymers and PP.
 - SEM micrographs showed the presence of fibrils and/or voids, mostly on those copolymer-homopolymer fracture surfaces which had high impact strength. In the case of the fracture surfaces from interfaces that involved copolymer and polyethylene, some of these fibrils may involve the PE that we surmise had diffused into the transcrystalline zone on the copolymer side of the interfaces during annealing. In the case of the fracture surfaces from interfaces that involved copolymer and PP, these fibrils probably arise from the mechanical interlocking of the interfaces during annealing. Yuan and Wool¹⁴ examined strength development at PP-HDPE and at PP-LLDPE (linear low-density polyethyl-

ene) interfaces earlier and reported the conditions under which crystallization at the interfaces occurred. They noted the occurrence of mechanical interlocking and pullout during fracture at these interfaces when crystallization occurred relatively slowly.

- XPS of the fracture surfaces showed a greater calculated percentage of AA or VA on both the copolymer and homopolymer sides of the interface than in the bulk for most samples at 15 Å penetration. This greater calculated percentage of AA or VA is probably due to chain scission during sample preparation and/or fracture which results in additional acid or alcohol groups at the surface that are calculated as increased VA or AA content.
- DSC data obtained on thin slices cut from the fracture surfaces showed the presence of at least a small percentage of the polymer from the other side of the original interface in almost all cases. No data that could be attributed to material specifically in the transcrystalline zones on the copolymer sides of the interfaces could be observed.

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