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Interfacial Interactions between Polyethylene and Polypropylene and Some Ethylene-Containing Copolymers

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ABSTRACT: 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 were examined 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 % 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, above the melting points of the bulk copolymers. Electron microprobe data on EVA−HDPE freeze-fractured interfaces showed a percentage of VA less than that in the bulk copolymer in the region corresponding to the transcrystalline zone on the copolymer side of the interface. The data indicated that polyethylene migrated into the transcrystalline zone. This was confirmed by optical microscopy which showed that some PE oligomers with molecular weights up to 507 were completely miscible with EVA samples having VA contents up to 18 wt %. Also, calculations using Flory−Huggins theory indicated that copolymers of low wt % VA or AA should be miscible with low molecular weight PE at elevated temperatures. 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 a mechanically interlocked interface.

Introduction

The use of polymer blends as an economical means or recycling polymer waste is a subject of considerable current interest. However, since many polymers are not miscible with each other, but can be made into useful objects if adhesion between the polymers is improved, the concept of “compatibilization” of immiscible polymers by the addition of block copolymers has been studied quite extensively. The diblock copolymers are usually chosen so that each block is miscible with one or the other of the homopolymers. The diblock copolymer can then reduce the interfacial tension and improve the adhesion between the homopolymers and thus increase the compatibility of the polymer blend.[1−5]

While there is a considerable body of literature on the use of diblock copolymers as “compatibilizers”, there has been very little study of the effect of random copolymers as compatibilizers. Recently, Dai *et al*.[6] and Brown *et al*.[7] have reported that long random copolymers can be more effective than long symmetric block copolymers in strengthening the interface between immiscible homopolymers. It was theorized that the random copolymer could weave back and forth across the interface, forming loops between the copolymer and homopolymer and thus increase the strength of the interface.

This paper examines the interaction of two types of random copolymers, ethylene-*co*-vinyl acetate (EVA) with varying weight percentages of vinyl acetate (VA) and ethylene-*co*-acrylic acid (EAA) with varying weight percentages of acrylic acid (AA) as compatibilizers with high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP), all of which are semicrystalline polymers. EVA is a statistically random copolymer, while EAA is a more “blocky” random copolymer with AA forming longer “blocks” if sufficient acrylic acid is present during polymerization. The interaction of EVA copolymers with HDPE, LDPE, and PP was of particular interest because Swint *et al*.[8] had found that a simulated postconsumer plastic waste mixture containing 70 wt % HDPE, 4 wt % LDPE, 11 wt % PP, and 15 wt % polystyrene (PS) which mimicked the postconsumer plastic waste in New York state could achieve a greatly increased strain to failure without a large increase in tensile modulus or yield strength when extruded with 7 wt % of an EVA containing 27.5 wt % VA (27.5EVA). The aim of the current work was to obtain information about the molecular interaction of the copolymers mentioned above (when used as polymeric compatibilizers) with the homopolymers at the interfaces in order to gain an understanding of the reasons for the compatibilizing power of the EVA with this polymer mixture. A knowledge of the molecular interaction at the interface should also allow for the design of better compatibilizers in the future.

Although the mixture studied by Swint *et al*.[8] included PS, no data are given in this paper on the interaction between the random copolymers and PS because preliminary work using the ASTM D3803-91 Qualitative Peel Test showed either no adhesion (in most cases) or very little adhesion between the copolymers studied and PS.

Experimental Section

Materials. Table 1 lists the source code and molecular weight data for all the commercial polymer samples used in this work. Molecular weights, when listed, were determined by gel permeation chromatography (GPC) in this work or provided by the suppliers. Most samples were used as received.

Partial Fractionation of 9EVA.[9] 9EVA (1.4 g) was dissolved in 40 mL of xylene (reagent grade, Fisher Scientific, Pittsburgh, PA) at 130 °C in a 250 mL Erlenmeyer flask, and 20 mL of preheated ethylene glycol (reagent grade, J. T. Baker,

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Table 1. Information on Polymers Used in This Work

code	polymer	source	$10^{-3} M_w$	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^{d}	10.1^{c}	2.8^{c}
33EVA^{a}	33 wt % VA	SPP^{b}	94^{c}	2.8^{c}
40EVA^{a}	40 wt % VA	SPP^{b}	73^{c}	2.4^{c}
45EVA^{a}	45 wt % VA	SPP^{b}	197^{c}	4.3^{c}
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^{d}		
HDPE	high-density polyethylene	Phillips^{h}	123^{g}	7.1^{g}
LDPE	low-density polyethylene	Exxon^{c}	97^{g}	5.3^{g}
2000PE	polyethylene	polysciences^{i}	2.00^{g}	
hexatriacontane	hexatriacontane	Aldrich^{j}	0.50699^{g}	1.0
N-tetracosane	*N*-tetracosane	Aldrich^{j}	0.4894^{g}	1.0

[a] Ethylene–vinyl acetate copolymer. [b] Scientific Polymer Products, Ontario, NY. [c] Determined in this work. [d] Exxon Chemical Co., Houston, TX. [e] Ethylene–acrylic acid copolymer. [f] Dow Chemical Co., Midland, MI. [g] Data given by the supplier. [h] Phillips Plastics Corp., Phillips, WI. [i] Polysciences, Warrington, PA. [j] Aldrich, Milwaukee, WI.

Danvers, MA) was slowly added to the solution. The mixture was stirred and heated at 135 °C until the solution was clear. The temperature was adjusted to 124 °C, and the solution was allowed to stand until phase separation occurred. The clear lower layer was removed with a pipet, and a precipitate was obtained after addition of methanol (reagent grade, absolute, J. T. Baker). Three additional fractions were then obtained from the upper layer, but the sample was not completely fractionated. The fractions were dried in air.

Gel Permeation Chromatography (GPC). A Waters GPC (Milford, MA), interfaced with a NEC, IBM AT compatible computer, using a single linear column (Ultrastyragel, molecular weight range 2×10^3–4×10^6), 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 (Polysciences, Inc., Warrington, PA) ranging in weight from 2.2×10^4 to 3.3×10^5. All molecular weights are thus not absolute, but in terms of PMMA.

Fourier Transform Infrared Spectroscopy (FTIR). A Perkin-Elmer (Norwalk, CT) PE-1800 spectrometer, interfaced with a Perkin-Elmer 7700 professional computer using Perkin-Elmer version 3.00 software, was used in the range 4000–500 cm^{-1}.

Differential Scanning Calorimetry. Thermal transitions of all copolymer and homopolymer samples were studied using two different Perkin-Elmer DSC7 differential scanning calorimeters (DSC): one interfaced with an IBM 386 personal computer and one interfaced with a NEC Multisync II computer. Samples were cut with a clean razor blade directly from the copolymer and homopolymer pellets as received from the suppliers. All thermograms were obtained at a heating rate of 10 °C/min. Samples were then cooled at a rate of 10 °C/min to obtain a second thermogram during cooling. Nitrogen was used as the purge gas in the glovebox for both instruments. Thermal analysis software used for processing the data was present on the hard drives of the computers.

Optical Microscopy. Optical microscopy was done using a Leitz (Ernst Leitz, Wetzlar, Germany) Laborlux 12 Pol S microscope with crossed polarizer and analyzer. The microscope was equipped with a Leitz microscope heating stage 350. The temperature of the heating stage was controlled by a Partlow MIC 6000 (Upstate Technical Equipment, Syracuse, NY) microprocessor-based profiling controller. Copolymer–homopolymer interfaces were photographed using a 35 mm SLR camera with a magnification of 0.35×. Two different objectives lenses were used: a 10× and a 32× magnification. The eyepiece magnification was always 10×. To observe the morphology of freshly prepared interfaces between the homopolymers and the copolymers, thin sections of each polymer were first cut and then placed side-by-side on a glass slide covered with a cover slip. Most of the samples were received as pellets, and thin sections were cut directly from the pellets. The hexatriacontane and *n*-tetracosane oligomer samples were received in powder form, however, and the interfaces with these oligomers could be prepared more directly. This was done by placing the oligomer powder on top of a 1 in. diameter circular plaque of the desired copolymer in a circular mold, heating to 150 °C for 5 min in an oven purged with nitrogen, cooling, and then cutting perpendicular to the interface with a clean razor blade. Such a slice was then placed on a glass slide with the interface perpendicular to the slide. Each glass slide that contained a homopolymer–copolymer interface was then placed on the hot stage on the optical microscope and heated to the temperature of interest at a rate of 10 °C/min, held for 1 min at that temperature, and then allowed to cool while the formation of the interface was observed.

Wavelength Dispersive Electron Microprobe. Microprobe analysis was performed on a UT JEOL (Peabody, MA) 733 microprobe with an accelerating voltage of 8 kV, a beam diameter of 1 μm, and a sample current of 5–6 nA. Data reduction was performed using Tracor Northern Software which corrected for atomic number, adsorption, and fluorescence. The instrument was calibrated using carbon-coated SiO_2 for oxygen analysis and carbon-coated graphite for carbon analysis. Reflecting crystals for isolation of X-rays peculiar to oxygen and carbon, placed at fixed position at an angle of 40°, were lead laurate for analysis of oxygen and led stearate for analysis of carbon. The pressure in the source chamber was maintained at approximately 10^{-5} Torr during analysis. The maximum allowable time of electron beam penetration was 40 s. To prepare samples for the electron microprobe, pellets of the copolymer and homopolymer (as received from the suppliers) were compression molded in a 1.1 cm radius by 0.1 cm thickness circular mold at approximately 20 deg above the melting temperature of crystalline samples or at 100 °C in the case of the fully amorphous copolymer samples for 10 min in a Model M Carver Press (Fred S. Carver, Inc., Menomonee Falls, WI). 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 were placed on top and under the samples. The molded samples were cooled on a laboratory bench. Combinations of all binary combinations of the circular molded copolymers and homopolymers were then placed together in a 1.1 cm radius by 0.2 cm thickness circular mold. Samples were again placed between Teflon cloth and ferrotype plates, but now they were compressed at 600 psi at 210 °C for 30 min and cooled to room temperature on a laboratory bench. The laminated samples were removed from the molds and freeze-fractured perpendicular to the interface in liquid nitrogen. The freeze-fractured samples were coated with an approximately 200 Å layer of carbon using an Edwards Model carbon coater

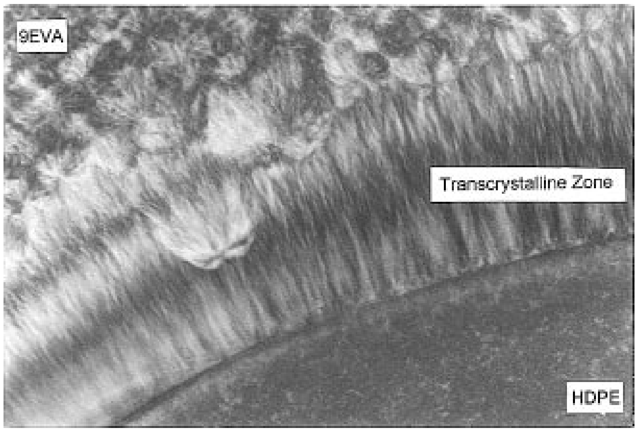

Figure 1. Optical micrograph of the 9EVA−HDPE interface after heating to 150 °C and then cooling to room temperature.

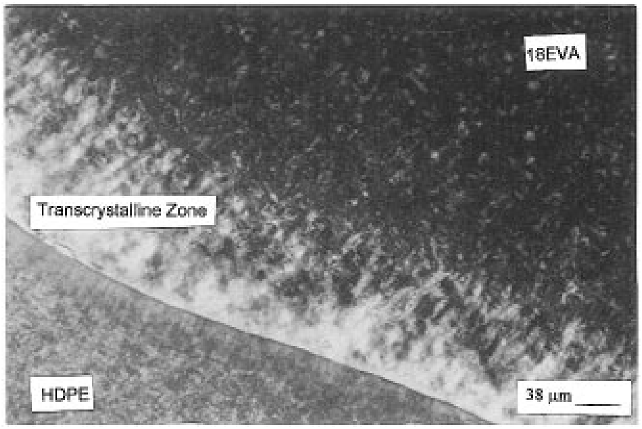

Figure 2. Optical micrograph of the 18EVA−HDPE interface after heating to 150 °C and then cooling to room temperature.

(Ernest F. Fullam, Latham, NY) and were then glued to epoxy stems with epoxy glue and allowed to dry for 24 h before introduction into the probe.

Scanning Electron Microscopy. A Zeiss CMS 950 scanning electron microscope (Karl Zeiss, Jena, Germany) was also used to study the freeze-fractured interfaces. Samples were pressed against carbon tape and then mounted on aluminum stubs. Approximately 200 Å of gold was deposited on all samples using a Denton Desk II sputter coater (Denton Vacuum Co., Cherry Hill, NJ) with a gold target. Coated samples were observed and photographs were taken using a Polaroid instant camera.

Results and Discussion

Copolymer−Polyethylene Interfaces by Optical Microscopy. The birefringence observed with the optical microscope showed that transcrystalline zones formed at those copolymer−HDPE and copolymer−LDPE interfaces where the ethylene content of the copolymer was relatively high. These transcrystalline zones always formed on the copolymer side of the interfaces and appeared in two general forms: tightly packed or relatively diffuse, probably depending on the density of the nuclei at the interface. Figure 1 shows a tightly packed transcrystalline zone on the EVA side of an HDPE−9EVA interface, while Figure 2 shows a less densely packed transcrystalline zone on the EVA side of an 18EVA−HDPE interface. One may also note the presence of birefringence from spherulites in the bulk of both polymers away from the transcrystalline zones. The EVA−HDPE transcrystalline zones ranged in width between 60 and 150 µm. (See Table 2, which shows the range in width of the transcrystalline zones in various interfaces.) In the case of EVA−LDPE interfaces, transcrystalline zones formed only between 9EVA and LDPE and these were relatively diffuse (see Figure 3) and very narrow (5−15 µm). See also Table 2.

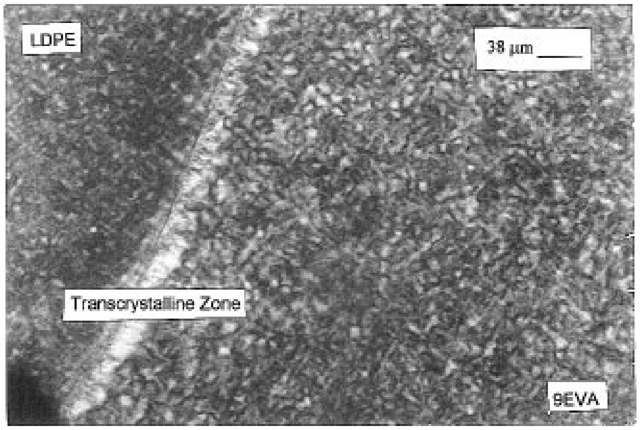

Figure 3. Optical micrograph of the 9EVA−LDPE interface after heating to 150 °C and then cooling to room temperature.

Transcrystalline zones between EAA and HDPE formed only in those EAA copolymers with low weight percentages of AA: 3EAA−HDPE and 6.5EAA−HDPE. Figure 4 shows the 6.5EAA−HDPE interface with a very narrow transcrystalline zone which did not appear to be densely packed. Extremely narrow (<5 µm), sporadic transcrystalline zones formed at the interfaces between 3EAA and LDPE and 6.5EAA and LDPE (see Table 2). The birefringence in these samples appeared as a white line on the EAA side of the interface.

When the copolymers contained more than 18 wt % VA in EVA or 6.5 wt % AA in EAA, transcrystalline zones did not form against any of the homopolymers.

Table 2 shows that all the transcrystalline zones observed crystallized above the crystallization temperature of the neat copolymer as measured by DSC. In

Table 2. Crystallization Temperature, T_c, and Melting Temperature, T_m, of the Neat Copolymers Compared with the Crystallization Temperatures of Transcrystalline Zones in the Same Copolymers at Interfaces with HDPE or LDPE

interfaces observed	T_c of neat copolymer (*C*)[a]	T_m of neat copolymer (*C*)[a]	T_c of transcrystalline zone (°C)	width of transcrystalline zone (µm)
9EVA−HDPE	73	93	107−92	100−150
14EVA−HDPE	70	91	101−88	80−120
18EVA−HDPE	62	83	100−69	60−120
9EVA−LDPE	73	93	91−88	5−15
3EAA−HDPE	89	108	95−89	15−20
6.5EAA−HDPE	81	103	90	10−15
3EAA−LDPE	89	108	∼90	<5
3EAA−2000PE	89	108	∼120	5−10
9EVA−2000PE	73	93	122−119	30−175
14EVA−2000PE	70	91	112−105	30−60

[a] Obtained using DSC.

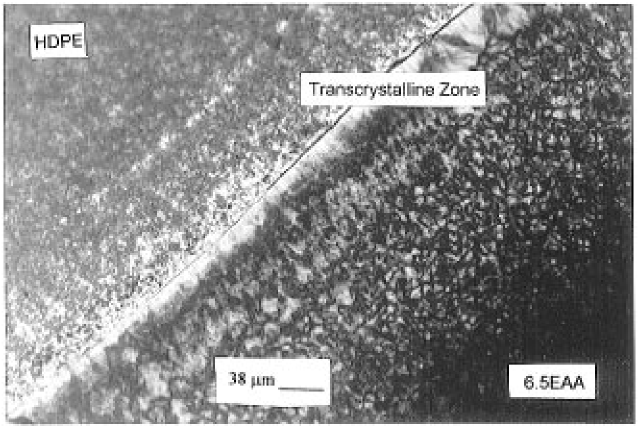

Figure 4. Optical micrograph of the 6.5 EAA–HDPE interface after heating to 150 °C and then cooling to room temperature.

some cases (9EVA, 14EVA, and 18EVA against HDPE), the transcrystalline zone crystallized above the observed *melting* temperature of the neat copolymer as obtained by DSC. These observations strongly imply that one or both of the following occurred: (1) the copolymers that formed transcrystalline zones were compositionally polydisperse enough to fractionate in the transcrystalline zone, with the molecules containing higher EA or AA content diffusing out of this zone while it was molten, or (2) some PE molecules, possibly lower molecular weight ones in these commercial polydisperse samples, diffused into the copolymer side of the interfaces while the whole sample was molten. Both types of diffusion should result in an increase in crystallization temperature on the copolymer side of the interface, similar to that observed (see Table 2).

The possible compositional heterogeneity of the 9-EVA copolymer was examined by analyzing the FTIR spectra of the fractions obtained by the method shown in the Experimental Section of this paper. It has been shown[10] that the frequencies of the rocking vibrations of the methylene group in these copolymers are related to the number of successive methylene groups in different parts of each molecule. The absorbance at 797 cm^{-1} comes from isolated methylene groups, corresponding to head to tail addition of VA monomers during polymerization. The absorbance at 743 cm^{-1} comes from two neighboring methylene groups, corresponding to head to head addition of two VA monomers; the absorbance at 725 cm^{-1} corresponds to three successive methylene groups in the copolymer, and the absorbance at 720 cm^{-1} corresponds to more than five successive methylene groups in the copolymer. The relative absorption of each sample at these three frequencies is directly related to the ratios of these different "types" of methylene groups in the sample. Although the original 9EVA sample had about 40% of its methylene groups in clusters of greater than five, the four fractions contained only about 30% of such clusters. This indicates that the original sample had a much broader composition distribution than one would surmise from the reported r_1 and r_2 values, each equal to 1, for free radical polymerization of ethylene and vinyl acetate.[11] Wu *et al.*[12] have indicated that both a molecular weight and a composition distribution is possible in the commercial polymerization of such a copolymer if polymerization continues during the pressure let-down at the end of the polymerization process.

In spite of the fact that 9EVA, at least, appears to have an appreciable composition distribution, it seems unreasonable to suppose that the composition distribution in this and the other copolymer samples is the only explanation for our experimental results. If the copolymer molecules with the higher ethylene content should become concentrated in the transcrystalline zones, then the copolymer molecules with the lower ethylene content would have to be concentrated at the ends of the transcrystalline zones. Although this may occur to some extent (see the section on Electron Microprobe Data below), it is unlikely that this is the whole story.

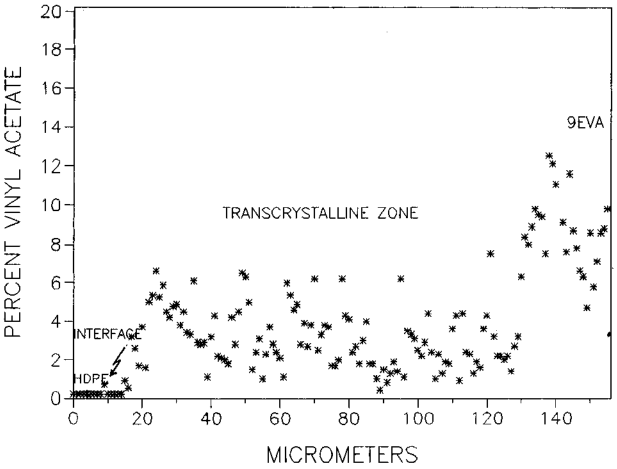

Figure 5. Percent vinyl acetate *versus* location across the interface of a freeze-fractured 9EVA–HDPE sample using the electron microprobe.

Thus, a number of experiments were done to test the hypothesis that some PE molecules diffused across the copolymer/homopolymer interfaces at high temperatures, before the homopolymers crystallized. For example, if this hypothesis is true, then transcrystalline zones should not form when the homopolymer sample that is laid up against the copolymer is not melted before the (molten) sample of copolymer is allowed to cool and crystallize. Exactly this, the lack of any transcrystallinity at all, was observed with EVA9 and EVA14 placed against an HDPE sample where a large transcrystalline zone usually formed. Unfortunately, this experiment is not conclusive, because, in the absence of melting and recrystallization, nuclei suitable for the formation of the transcrystalline zone may have had no chance to form along the interface.

Electron Microprobe Data. The electron microprobe could be used to study the oxygen/carbon (O/C) ratio across the interfacial region, even though the spatial resolution is much worse than might be expected from the beam diameter of 1 μm; the beam spreads below the sample surface, making the spatial resolution ~5 μm. Therefore, the electron microprobe could only be used to provide useful information on the fracture surfaces of those samples that had transcrystalline zones greater than 20 μm. This meant that none of the copolymer/LDPE or EA/homopolymer samples were studied using the microprobe (the EA copolymers were not stable under the electron beam and could not have been studied for that reason alone). For the samples containing the EVA copolymers, the O/C ratio should be directly proportional to the VA/E ratio; thus, the data in Figures 5–8 are shown as % VA versus distance, as the electron beam crossed the homopolymer/copolymer interface. This interface could be observed as a very sharp demarcation in the SEM micrographs visible during the experiment. At this point it is interesting to note that all SEM micrographs, for example, Figure

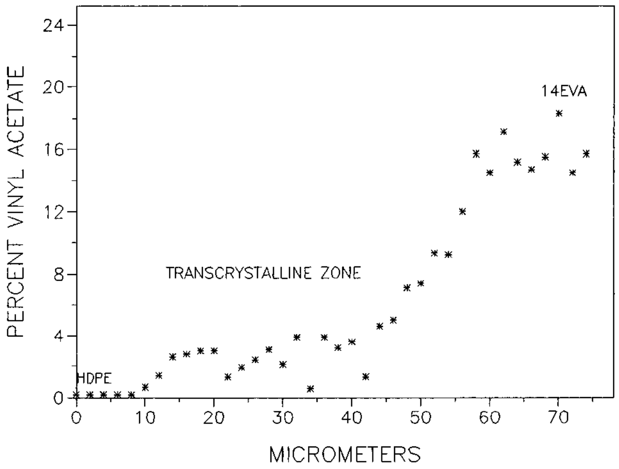

Figure 6. Percent vinyl acetate versus location across the interface of a freeze-fractured 14EVA–HDPE sample using the electron microprobe.

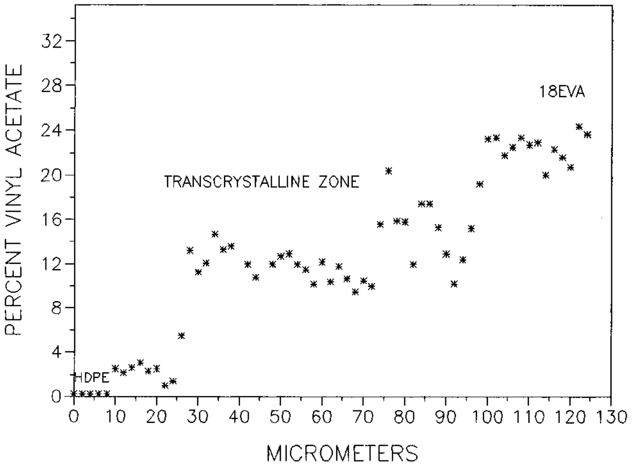

Figure 7. Percent vinyl acetate versus location across the interface of a freeze-fractured 18EVA–HDPE sample using the electron microprobe.

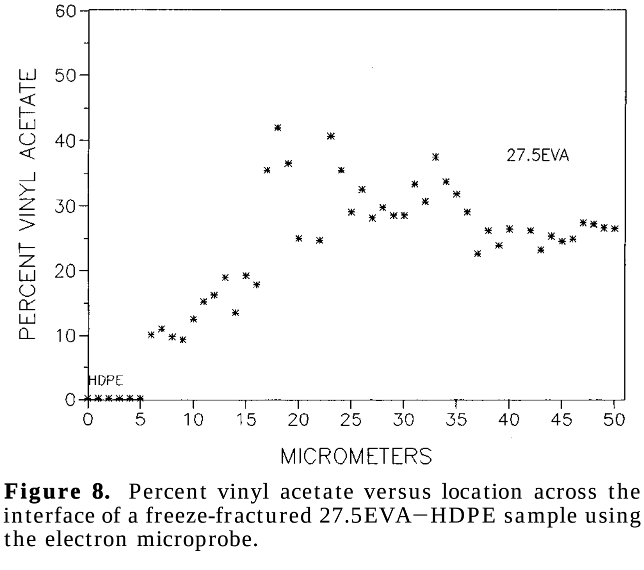

Figure 8. Percent vinyl acetate versus location across the interface of a freeze-fractured 27.5EVA–HDPE sample using the electron microprobe.

9, revealed a sharp interface in the samples, including those with transcrystalline zones. In addition, there was no evidence of a difference in topography between the transcrystalline zone and the bulk of the copolymer.

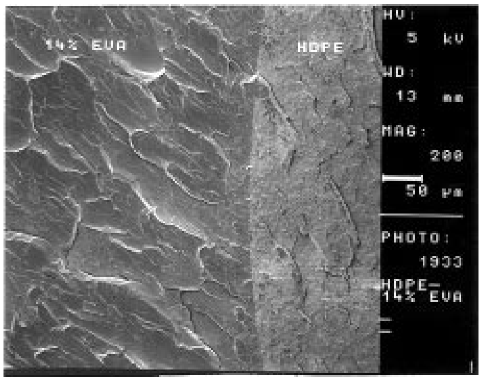

Figure 9. SEM micrograph of freeze-fractured 14EVA–HDPE interface.

In general, as shown by Figures 5–7, there was a "depletion" in the percent VA in the region corresponding to the width of the transcrystalline zone. Figure 5, for example, shows the percent VA versus location across the 9EVA–HDPE interface. The width of the zone with "depleted" VA content is approximately 125 μm, corresponding to the with of the transcrystalline zone which was observed by optical microscopy (see Figure 1). On all three figures, we may note the total absence of oxygen on the HDPE side of the interface. The experimental error in the % VA is high, but the difference between the low % VA near the interface, followed by the higher % VA, very close to 9 wt %, at the end of the presumed transcrystalline zone is outside experimental error. In the case of the 14EVA and the 18EVA, the results indicate that there might have been a small amount of fractionation of the EVA between the transcrystalline zone and the portion of the sample farther from the interface, but as mentioned above, it is very difficult to believe that this alone could be responsible for the optical microscopy, the melting and crystallization data, and the electron microprobe data.

Figure 8 shows electron microprobe data for the 27.5EVA–HDPE sample which did not exhibit transcrystallinity. Nevertheless, there was 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.

Polyethylene–Copolymer Miscibility. Since, if some PE molecules migrated over into the transcrystalline zone, there should be some miscibility between the copolymers and low molecular weight PE, some experimental data were collected on interfaces between the copolymers and 2000 molecular weight PE (2000PE). Transcrystalline zones were obtained with 9EVA, 14EVA, and 3EAA. These zones were of the same order of magnitude as those formed against HDPE. Electron microprobe experiments revealed very broad zones of decreased VA content on the EVA side of the interfaces for 9EVA–2000PE (200 μm) and 14EVA–2000PE (50 μm). Optical microscopy experiments using oligomers of polyethylene (*n*-tetracosane and hexatriacontane) resulted in the disappearance of the interfaces with 9EVA, 14EVA, and 18EVA. Experiments with 25EVA, 27.5EVA, 28EVA, and 33EVA produced diffuse interfaces. Above 33EVA, the interfaces appeared sharper. The interface remained intact for 2EAA and 6.5EAA against the polyethylene oligomers but appeared "diffuse" or "smudged out". Above 6.5 wt % AA, the interface were sharper.

SEM micrographs of the interface area of the EVA–oligomer samples showed a "blended in" appearance and electron microprobe data indicated very broad areas ranging in width up to 1000 μm where the % VA increased gradually until the bulk wt % VA was

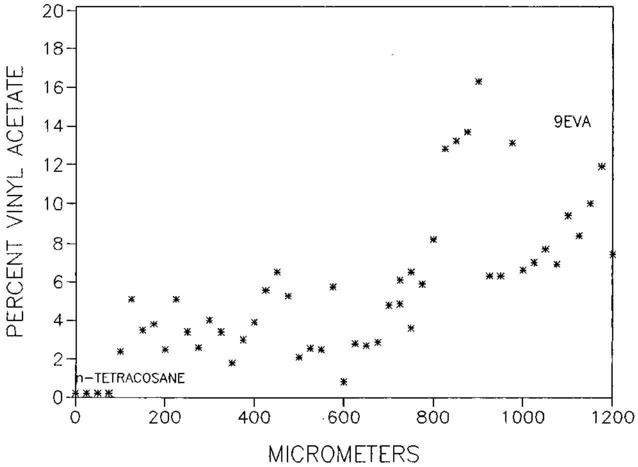

Figure 10. Percent vinyl acetate versus location across the interface of a freeze-fractured 9EVA−*n*-tetracosane sample using the electron microprobe.

observed. Figure 10 shows the percent VA versus location on the sample for a 9EVA−*n*-tetracosane sample.

Transcrystalline Zone. Previous work by others has indicated that a transcrystalline layer is formed when massive numbers of nuclei are formed on a surface such that the crystallites are forced to grow normal to the surface.[13] Transcrystalline zones have been found to range in width from 10 to 100 μm and have been found in polyethylene, polypropylene, polyamide, and polyurethane systems when crystallizing conditions induce a high density of nuclei on the melt surface.[13] These transcrystalline zones have mechanical properties such as tensile yield strength, elongation at yield, and impact strength[14−16] that are all greater than those of the bulk phase that exists far from the surface. Therefore, the presence of a transcrystalline zone at an interface may contribute toward the improvement of adhesion at an interface between the polymers studied in this work. As it happened, however, no transcrystalline zones formed at interfaces between LDPE and HDPE with the 27.5EVA which was found to be a good compatibilizer for a mixture containing these polymers by Swint *et al.*[8]

Many factors have been presented as the reason for high degrees of nucleation which then form transcrystalline regions. These have included: (1) the surface free energy of the nucleating surface,[9,17−19] (2) the influence of the surface morphology which governs the nucleation process,[20] (3) the presence of a temperature gradient at the surface of the melt which allows for supercooling of the melt surface and therefore increasing the nucleation rate,[21,22] (4) the presence of stresses at the surfaces or in the interior of a viscous melt which may cause many nucleating sites,[23,24] (5) crystal unit cell similarities or chemical similarities between the nucleating surface and the polymer which undergoes transcrystalline growth,[25−27] and (6) the presence of internal surfaces, such as fibers or fillers, which may induce dense nucleation.[22,28] However, the present experiments suggest another possible reason for the formation of a transcrystalline zone: that is, it may be a consequence of the migration of some of the polyethylene molecules from HDPE or LDPE into the copolymer side of the interface while the polyethylene was still molten. After this migration, the bulk of the polyethylene crystallized, followed by nucleation of the migrating and already migrated polyethylene; then the transcrystalline zone, which contained the migrated and migrating PE molecules, formed. These migrating PE molecules were probably the lower molecular weight ones in these commercial samples. While it was not possible to perform electron microprobe analysis of the EAA−polyethylene samples, this explanation of the migration of polyethylene across the interface into the EAA side of the interface also appears reasonable.

This explanation is also reinforced by the disappearance of the interface of 9EVA ad 14EVA with oligomers of polyethylene. The disappearance of the interface indicates some degree of miscibility of PE in the copolymer at temperatures at which both components are molten. We have thus examined the miscibility of EVA and EAA with PE in the amorphous state theoretically using the Flory−Huggins theory.[29]

Calculated Interaction Parameters. Calculations of the interaction parameters between the copolymers and polyethylene were done by the method described by Krause[30] for mixtures containing random copolymers using Hildebrand solubility parameters. The Hildebrand solubility parameters of the homopolymers were calculated using

$$\delta = \frac{\rho \sum F_i}{M} \tag{1}$$

where δ is the solubility parameter of the polymer, $\sum F_i$ is the sum of the molar attraction constants of all the groups in the repeat group of the polymer, M is the molecular weight of the repeat group, and ρ is the density of the polymer at the temperature of interest. Hoy's tables[31] were used for the group molar attraction constants. The solubility parameters of the (random) copolymers are

$$\delta_c = \sum \delta_i \phi_i^c \tag{2}$$

where δ_c is the solubility parameter of the copolymer, δ_i is the solubility parameter of the homopolymer corresponding to repeat group i, and ϕ_i is the volume fraction of repeat group i in the copolymer. The polymer$_1$−polymer$_2$ interaction parameter, χ_{12}, is

$$\chi_{12} = \frac{V_r(\delta_1 - \delta_2)^2}{RT} \tag{3}$$

where the δ_i are the solubility parameters of the two homopolymers or copolymers in question, R is the gas constant, T is the absolute temperature, and V_r is a reference volume, taken as 100 cm^3 for polymers. Calculations were made for 25 °C and for 140 °C. The densities used[32] at 25 and at 140 °C, respectively, were 0.965 and 0.855 g cm^{-3} for polyethylene, 1.19 and 1.09 g cm^{-3} for PVA, and 1.41 and 1.3 g cm^{-3} for PAA. The value at 140 °C for PAA was only an estimate, based on the reduction in density between the two temperatures for PVA. Since PAA can H-bond with itself, values of its solubility parameter were calculated for both the completely H-bonded and the completely non-H-bonded state and then used to calculate the interaction parameters shown in Table 3. These could now be compared with the calculated critical interaction parameters for various combinations of polymer molecular weights, as follows:

$$\chi_{cr} = \frac{1}{2}[x_1^{0.5} + x_2^{0.5}]^2 \tag{4}$$

Table 3. Calculated Interaction Parameter for Mixtures of the Different Copolymers with Polyethylene at 25 and at 140 °C

copolymer	χ at 25 °C	χ at 140 °C
9EVA	0.020	0.0073
14EVA	0.049	0.019
18EVA	0.091	0.029
27.5EVA	0.21	0.075
3EAA	0.0016	0.00029
3EAA (IHB)[a]	0.0015	0.00029
6.5EAA	0.0075	0.0015
6.5EAA (IHB)[a]	0.0068	0.0010
9.7EAA	0.017	0.0073
9.7EAA (IHB)[a]	0.016	0.0049
20EAA	0.071	0.069
20EAA (IHB)[a]	0.065	0.0049

[a] Internally hydrogen-bonded.

Table 4. Critical Interaction Parameters for Polymer–Polymer Mixtures Containing Polymers Having Different Molecular Weights

molecular weight of polymer 1	molecular weight of polymer 2	χ_{cr}
10^3	10^4	0.087
10^3	10^5	0.060
10^4	10^4	0.020
10^4	10^5	0.0087
10^5	10^5	0.0020

where χ_{cr} is the critical interaction parameter and the x_i are the degrees of polymerization of the polymers in terms of a hypothetical repeat unit with molar volume V_r. These calculated critical interaction parameters, shown in Table 4, are the ones a mixture must have in order to be just barely miscible at all proportions. If a mixture has a larger value of χ than χ_{cr}, it will no longer be miscible at all concentrations. If $\chi \gg \chi_{cr}$, then there will be no noticeable miscibility at all. The molecular weights in this table were arrived at as follows: If an approximate density of 1 g cm^{-3} is assumed for each polymer, and since the degrees of polymerization in eq 4 are in terms of repeat units with volumes equivalent to 100 cm^3 mol^{-1}, the molecular weights are equal to 100 times the degrees of polymerization in eq 4. Table 4 shows the calculated interaction parameters for our different polymer mixtures at 25 and 140 °C. Comparing the values in these two tables, let us remember that a value of χ (from Table 3) which is less than χ_{cr} of a polymer/polymer mixture with particular molecular weight values (from Table 4) means that these two polymers should be miscible in all proportions if they have the molecular weights shown. In our cases, the molecular weights shown may refer to particular weight fractions of the copolymer and of the PE that we used.

Since most of our copolymers (see Table 1) have molecular weight averages in the vicinity of 10^5, it is of great interest to compare the calculated copolymer/homopolymer values of χ with the χ_{cr} calculated for a mixture of molecules with molecular weight 10^5, representing the copolymer, with molecules having molecular weight 1000 or 10^4, representing molecules diffusing into the copolymer from the PE. For such mixtures, only the 9EVA, the 14EVA, and EAA copolymers containing ≤9.7 wt % AA are predicted to be completely miscible with the PE molecules. For mixtures of polymer molecules with molecular weights 1000 and 10^4, however, all the EVA and all of the EAA copolymers listed should be miscible in all proportions. In addition, partial miscibility is expected when the χ of the mixture is not appreciably greater than the χ_{cr} calculated. More details can be found in ref 29. Within the limits of Flory–Huggins theory, then, we have shown that the lower molecular weight chains of the polyethylene are at least partially miscible in some of the EVA and EAA copolymers at elevated temperatures, providing a driving force for migration of low molecular weight molten polyethylene molecules across the interface.

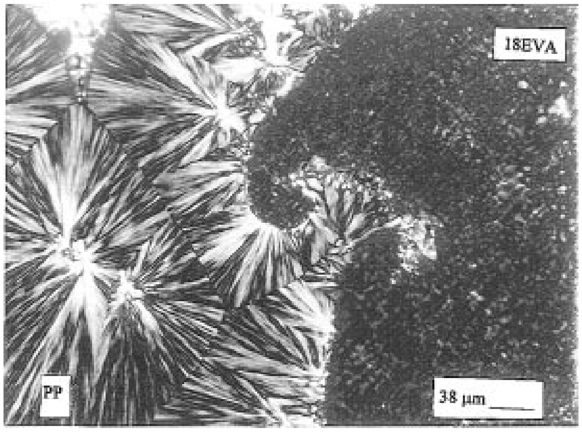

Figure 11. Optical micrograph of an 18EVA–PP interface after heating to 190 °C, then holding at 136 °C for 2 h, and then cooling to room temperature.

Interfacial Zone Width. Differences in miscibility alone are not enough to explain the relative narrowness of the transcrystalline zones in EVA–LDPE, EAA–HDPE, and EAA–LDPE samples. Several reasons can be presented for this narrowness. (1) Unlike the EVA–HDPE transcrystalline zones, these transcrystalline zones formed below the melting temperature of the copolymer (see Table 2). The transcrystalline zones could thus form and propagate only in a very narrow temperature range. (2) In the case of LDPE, the molecules are branched and cannot diffuse as well as HDPE. (3) The chemical properties of EAA are distinct from those of EVA. The acid units are capable of inter- as well as intramolecular hydrogen bonding. The acid groups probably form dimers in the amorphous region of the copolymer. These dimers can then act as cross-links between and within the molecules which may hinder the migration of polyethylene through the EAA copolymer and limit the formation of transcrystalline regions. Diffusion is further restricted with LDPE which also has side groups. Therefore, those EAA–LDPE interfaces which are capable of transcrystalline growth are even narrower than the corresponding EAA–HDPE samples. (4) In addition, the "blockiness" of the EAA copolymers may have an effect on the miscibility with low molecular weight polyethylene molecules. In block copolymers, homopolymer–copolymer solubility depends on the length of the block which makes up the same repeat unit as the homopolymer. Thus the length of the AA blocks could restrict the amount of polyethylene that diffuses into the EAA side of the interface.

Copolymer–PP Interfaces. Although no transcrystalline regions were observed at interfaces between the EVA and EAA copolymers and PP, mechanically interlocked interfaces were observed under the optical microscope at all EVA–PP or EAA–PP interfaces when the samples were heated to 190 °C, above the melting temperature of the PP, cooled slowly to 136 °C and held for times ranging from 30 min to 2 h at that temperature. Figures 11 and 12 show these influxes in samples of 18EVA–PP and of 3EAA–PP.

Similar results were observed by Wool[33,34] and Galeski[35,36] at LDPE–PP interfaces. They postulated that

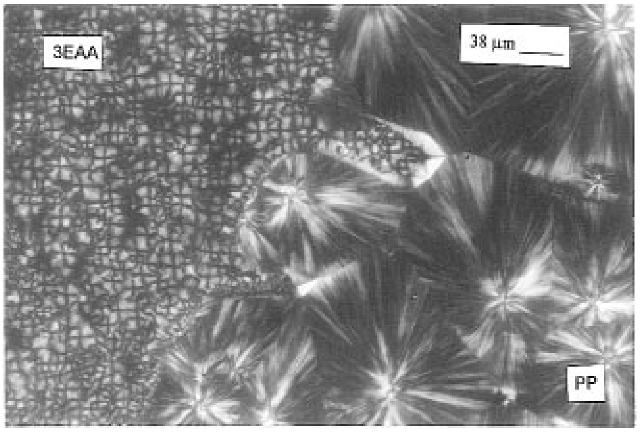

Figure 12. Optical micrograph of a 3EAA–PP interface after heating to 190 °C, then holding at 136 °C for 2 h, and then cooling to room temperature.

during the crystallization of polypropylene, the density decrease of the polypropylene resulted in volume contractions at the polypropylene/LDPE interface. These volume contractions created voids along the interface which allowed for the flow of the still molten low-density polyethylene into the voids which resulted in a mechanically interlocked interface when the low-density polyethylene crystallized. In our samples, the copolymers have taken the role of the LDPE discussed above.

When the interfaces were cooled from 190 °C without holding at 136 °C for a long time, the influxes of the copolymer into the PP were not evident under the optical microscope. As the time for crystallization of the PP at 136 °C was increased, a larger number and larger, often pear-shaped, influxes of the copolymer resulted. In many cases, these influxes reached several micrometers in the PP matrix. A mechanically interlocked interface should increase the adhesion at the interface between two polymers.

Conclusions

1. Transcrystalline zones formed on the copolymer side of the interfaces between EVA copolymers with ≤18 wt % EA or EAA copolymers with ≤6.5 wt % 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 on a microscope hot stage. The crystallization temperatures in the transcrystalline zones were all above those of the bulk copolymers, and, in some cases, above the melting points of the bulk copolymers.

2. Electron microprobe data on EVA–HDPE freeze-fractured interfaces showed a percentage of VA less than that in the bulk copolymer in the region corresponding to the transcrystalline zone on the copolymer side of the interface.

3. Conclusions 1 and 2 indicated that either (a) the copolymer fractionated in the transcrystalline zone, leaving molecules with higher ethylene content in this zone while pushing molecules with lower ethylene content to the end of the transcrystalline zone away from the interface with PE or (b) low molecular weight molecules of PE diffused across the interface to take part in the crystallization of the transcrystalline zone or (c) both.

4. The possibility of copolymer fractionation in the samples was confirmed for 9EVA by a partial solvent fractionation of this sample and by examination of the electron microprobe data that showed an ethylene content somewhat greater than that of the bulk sample at the ends of the transcrystalline zones away from the interfaces, *except* when 9EVA was the copolymer examined.

5. The possibility of polyethylene migration into the transcrystalline zone was confirmed in two ways. First, optical microscopy showed that *n*-tetracosane and hexatriacontane, PE oligomers with molecular weights up to 507, were completely miscible with EVA samples having VA contents up to 18 wt % although transcrystalline zones were observed when a 2000 molecular weight PE was used. Second, calculations using Flory–Huggins theory and Hildebrand solubility parameters indicated that copolymers of low wt % VA (in EVA) and low weight percent AA (in EAA) should be miscible with low molecular weight PE at elevated temperatures. Therefore, the formation of the transcrystalline zone is probably due mostly to the migration of low molecular weight polyethylene across the interface into the copolymer while the PE is still molten.

6. Nevertheless, SEM revealed a sharp interface after freeze-fracturing at all interfaces between the copolymers and HDPE or LDPE, probably because high molecular weight PE molecules were immiscible with the copolymers.

7. 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 a mechanically interlocked interface. This was observed only after holding the sample at the crystallization temperature of PP for at least 30 min after heating to 190 °C.

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