Adhesion between Aluminum and Copolymers of Ethylene and Vinyltrimethoxysilane

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Synopsis

The adhesion between aluminum and poly(ethylene-co-vinyltrimethoxysilane) (EVS) and poly(ethylene-co-butylacrylate-co-vinyltrimethoxysilane) (EVSBA), respectively, have been studied. For comparison an ordinary low density polyethylene (LDPE), a poly(ethylene-co-butylacrylate) (EBA), and an ionomer regarded as a bonding polymer were studied as well. The peel strength of laminates obtained by pressing were measured by a T-peel test. The structure of the fracture surfaces were investigated by reflection-IR, ESCA, and SEM. The peel strength of the LDPE and the EBA samples were 100 and 700 N/m, respectively. Although the amount of vinylsilane was low, about 0.2–0.3 mol %, its presence had a pronounced influence on the adhesion: 1800 and 3000 N/m for EVS and EVSBA, respectively. This is even higher than the value observed for the ionomer, 1560 N/m. Although there was a marked difference in surface topology, the SEM and ESCA analysis showed that the fracture was cohesive for both EVS and EVSBA. Immersion in water at 85°C increased the peel strength even more, especially in the case of EVSBA (up to 9000 N/m), in contrast to what is normally observed with aluminum polyethylene laminates. The results suggest that strong and nonhydrolyzable bonds, e.g., covalent bonds, have been formed across the polymer–metal interface for the ethylene copolymers containing vinylsilane.

INTRODUCTION

The adhesion between polyethylene and aluminum is important in many applications, especially in the packaging field. Untreated polyethylene has poor adhesion properties due to low surface energy. However, through introduction of polar groups at the polymer surface the peel strength of polyethylene aluminum laminates can easily be improved. Most modification methods involve oxidation of the polymer surface.[1] An alternative is to use copolymers with comonomers containing polar groups. We have recently showed that the effect on adhesion of different functional groups in ethylene copolymers increase in the following order:[2]

$$-\mathrm{H} \ll -\mathrm{O}-\mathrm{COCH_3} < -\mathrm{COOC_4H_9} < -\mathrm{COONa} \approx -\mathrm{OH} < -\mathrm{COOH}.$$

Although the polar groups introduced at the surface provide stronger bonds across the interface, e.g., hydrogen bonds, these bonds are often easily hydrolyzed. To obtain sufficient wet strength of the laminates, strong chemical links, e.g., covalent bonds, between the polyethylene and aluminum surfaces would be necessary.[3]

Journal of Applied Polymer Science, Vol. 37, 1269–1285 (1989)

CCC 0021-8995/89/051269-17$04.00

Silane coupling agents are frequently used to promote the adhesion between organic polymers and inorganic substrates, e.g., in fiberglass reinforced plastics. Different theories have been suggested to explain the mechanism of the adhesion promotion by the silane compounds.[4] However, the chemical bonding theory remains the most viable. The silane compounds are considered to chemically link the polymer to the substrate through covalent bonds. The oxane bond between the silane and the surface of the substrate is difficult to detect. Some evidences of such interfacial bonds have, however, been reported, e.g., concerning —Fe—O—Si—,[5] —Si—O—Si—,[6] —Ti—O—Si—, —Al—O—Si—,[7] and —Pb—O—Si—.[8]

In our earlier work concerning adhesion between ethylene copolymers and aluminum the functional groups involved were considered to increase the adhesion mainly through hydrogen bond formation.[2] In this paper we present results obtained with copolymers of ethylene and vinylsilane. Like silane coupling agents, it is possible for these copolymers to improve the adhesion through the formation of covalent bonds across the interface. In that case it would be possible to obtain water resistant laminates of polyethylene and aluminum.

EXPERIMENTAL

Materials

Two silane containing ethylene copolymers were used: poly(ethylene-co-vinyltrimethoxysilane) (EVS) and poly(ethylene-co-butylacrylate-co-vinyltrimethoxysilane) (EVSBA). As reference materials low density polyethylene (LDPE), poly(ethylene-co-butylacrylate) (EBA) and a bonding polymer (Surlyn 1652, DuPont) were included in the study. Except for the latter, the polymers were supplied by Neste Polyeten AB, Sweden. By choosing an EBA polymer with the same butylacrylate content as EVSBA, it is possible to study the effect of the silane groups. Surlyn 1652, an ionomer, was

TABLE I
Data on the Polymers

Polymer	Comonomer content BA[d] (wt %/mol %)	Comonomer content VS[e] (wt %/mol %)	Melt index (g/10 min)	$\bar{M}_w$ 10^{-3} [a] (g/mol)	T_m [b] (°C)	Crystal linity[c] (%)
EVS	—	1.6/0.25	0.5	229	108	39
EVSBA	17/4.4	2.3/0.51	4.0	114	90	19
LDPE	—	—	4.5	364	113	53
EBA	17/4.3	—	4.0	111	99	30

[a] determined by GPC-LS.[9]
[b,c] Determined by DSC.
[d] Butylacrylate.
[e] Vinyltrimethoxysilane.

included because of its good adhesion properties especially against aluminum. Table I summarizes the results from a characterization of the polymers. The films were made by film blowing using extrusion temperatures of 150–180°C to a film thickness of 200 μm. The aluminum foil had a thickness of 300 μm and a purity of 99% Al. It was annealed at 300°C for 24 h in air, and before lamination it was degreased with tetrachlorethylene. The foil was supplied by Gränges Aluminium AB, Sweden.

Adhesion Test

Laminates were made by pressing together an assembly of one plastic film between two aluminum foils, thus providing a laminate with inextensible backing in the following peel test. The pressure used was 1.2 MPa, the pressing time 10 s, and the temperature 250°C. The adhesion was measured with an Instron 1122 by a 180° peel test (T-peel test) with an extension speed of 200 mm/min. The width of the test strips were 25 mm. The reported values of the peel force represent the mean for 10 strips from two laminates. In the wet strength test the samples were immersed in distilled water at 85°C before the peel test.

IR Analysis

A Fourier transform infrared spectrophotometer, Perkin-Elmer 1710, was used at a resolution of 4 cm^{-1}. The reflection analysis were made with an multiple internal reflection (MIR) attachment, at an angle of incidence of 45°. The crystal used was a Perkin-Elmer KRS-5 (tallium iodide–bromide) with the refractive index 2.38.

ESCA Analysis

A Hewlett-Packard ESCA Spectrometer 5950 A, with an AlK_α (1486.6 eV) X-ray source was used. Plastic films as well as fracture surfaces from peel tests were analyzed. Some surfaces were also sputtered with argon ions at a speed of 20 Å/min. The composition at the surface was determined after correction of the signals using yield factors according to Ref. 10.

SEM Analysis

A JEOL JSM-840 scanning microscope was used to analyze the fracture surfaces after peeling as well as the polymer surfaces in the laminates. For the latter purpose, the aluminum foil of the laminates was dissolved in 40% NaOH solution. The resulting free-standing plastic films were in some cases etched with dichromatic sulfuric acid (weight proportions: $K_2Cr_2O : H_2O : H_2SO_4$; $10 : 16 : 200$) for 1 h at 20°C.

RESULTS

Figure 1 illustrates the peel forces obtained with the five polymers. The EVS polymer and the ionomer show about the same adhesion to the aluminum substrate, being quite superior to LDPE and EBA. For EVSBA, on

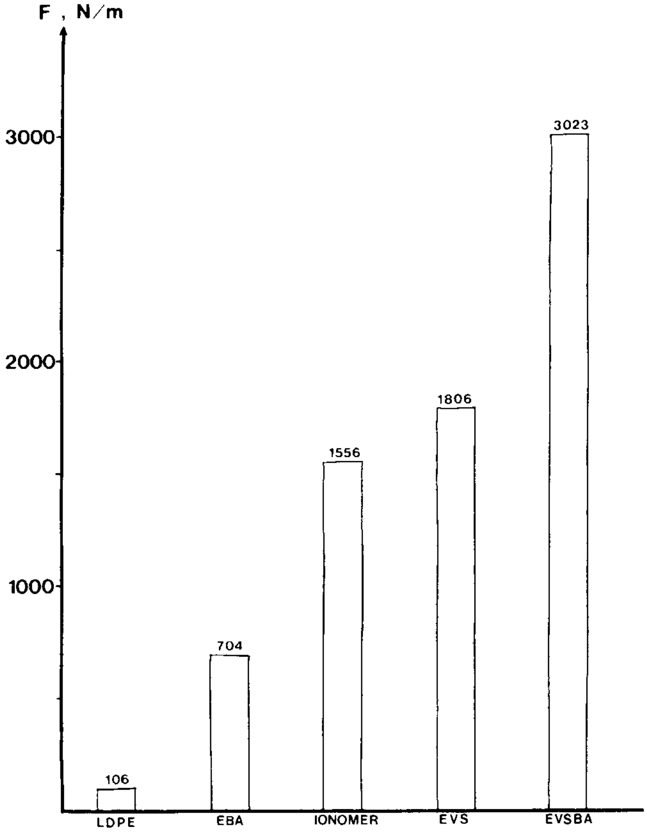


Fig. 1. Peel forces measured with a T-peel test on laminates of the polymers studied.

the other hand, the value is almost twice as high, indicating very strong bonds across the polymer–metal interface.

Visual observation of the peeled laminates indicates that the type of fractures are different for the two silane polymers. A thin polymer layer can be seen on the aluminum side in the case of EVS. However, for EVSBA no such polymer layer is visible. SEM micrographs of the surfaces confirm these observations (Fig. 2). The polymer layer on the aluminum side of a peeled EVS laminate has a very distinct fibrous structure. In the picture of the corresponding EVSBA surface, no distinct polymer layer can be observed. Instead the appearance is similar to that of the original aluminum (see below). Consequently, the fracture of the EVS laminates is clearly cohesive whereas for EVSBA the fracture seems to be adhesive.

ESCA was used to more closely investigate the fracture surfaces of the EVSBA laminates. For comparison the EBA sample was included as well. The results are summarized in Figure 3. The carbon content on the aluminum side of peeled laminates are high for both polymers. Upon etching with argon ions, the carbon content on the EBA sample rapidly diminish to zero. Most likely, this material can be referred to low molecular weight fractions from the

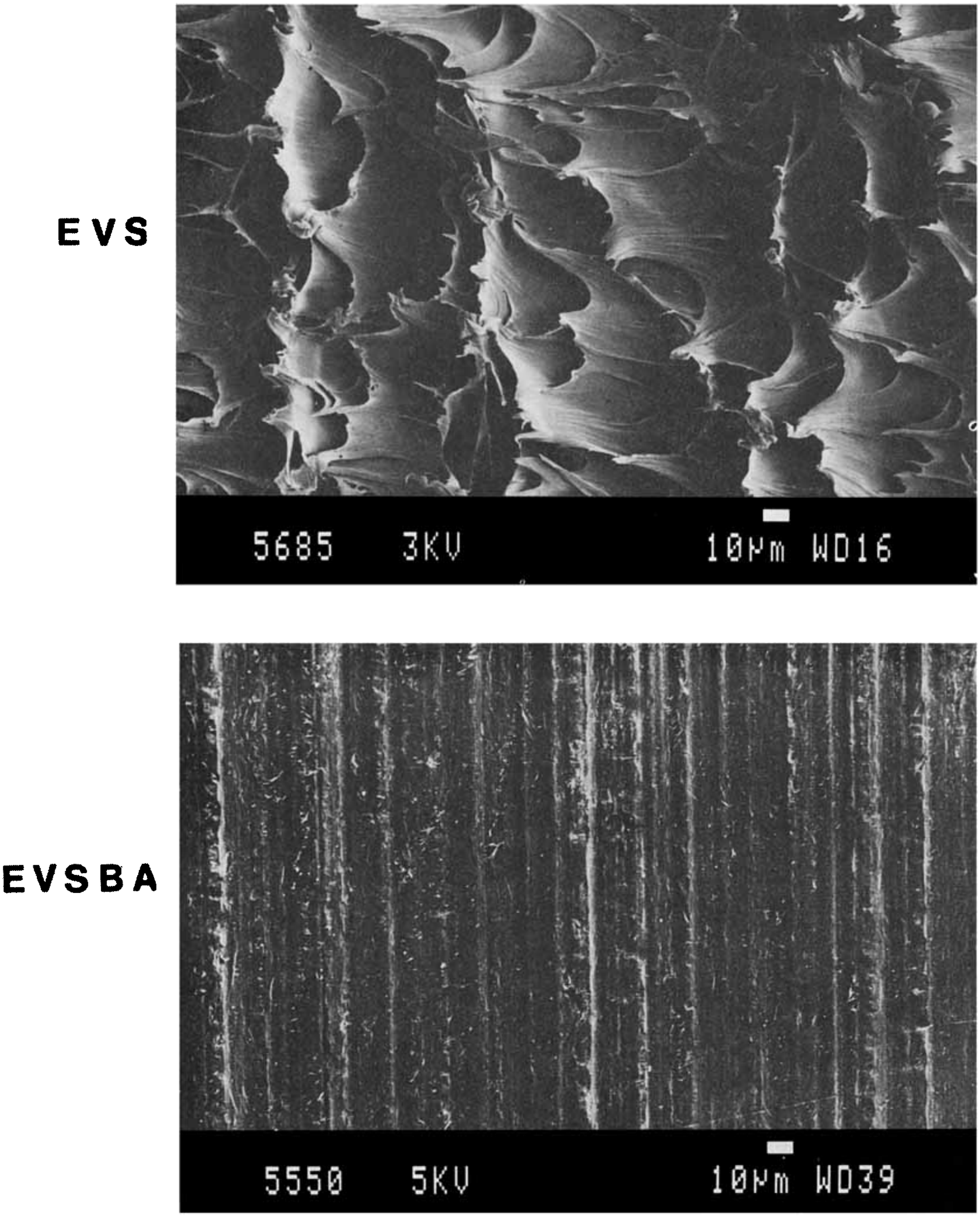


Fig. 2. SEM micrographs of the aluminum side of peeled laminates of EVS and EVSBA.

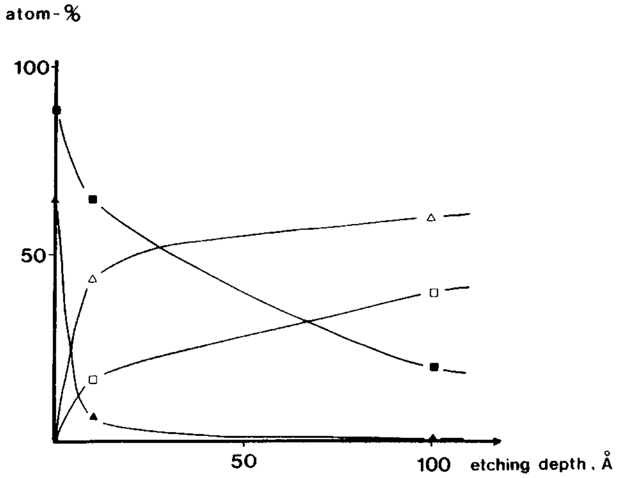
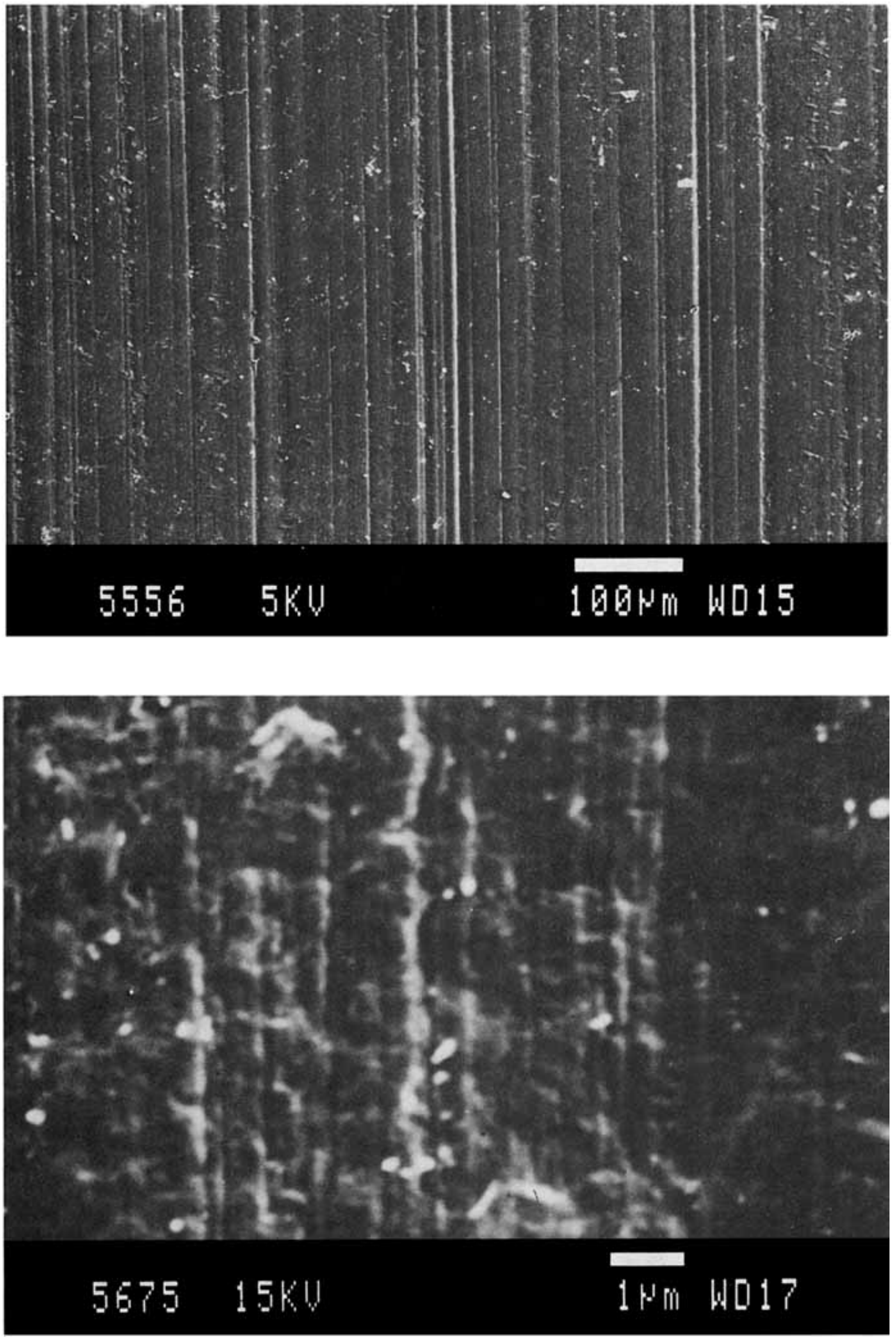


Fig. 3. Content of aluminum and carbon (at. %) on the aluminum side of peeled laminates of EBA and EVSBA measured by ESCA as a function of etching depth: (△,□) aluminum; (▲,■) carbon; (▲,△) EBA; (■,□) EVSBA.

polymer or to contamination after the delamination. For EVSBA, on the other hand, the carbon content decreases much more slowly and is as high as 21 at. % even after 100 Å etching. We therefore consider that the fracture is cohesive for EVSBA but adhesive for EBA.

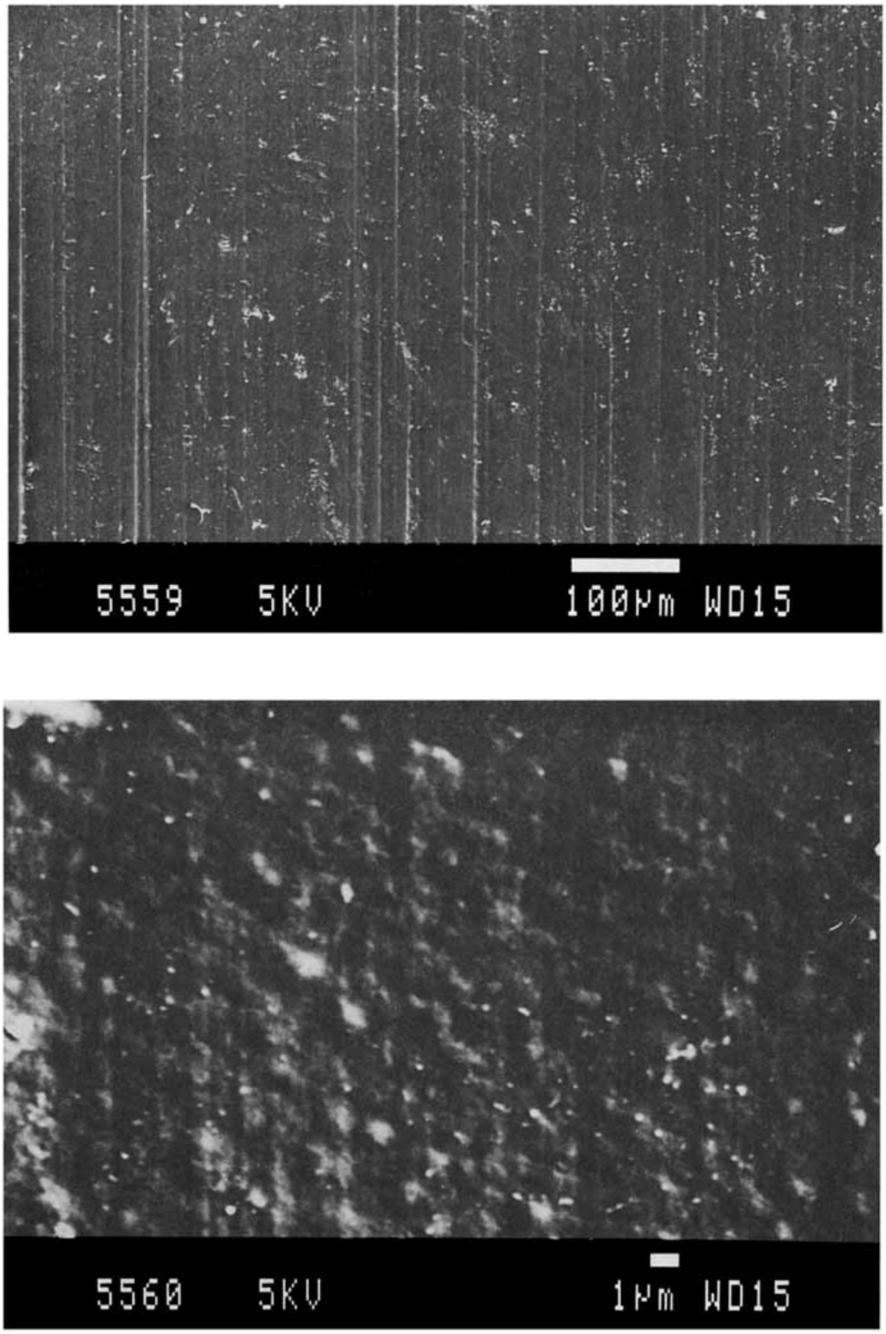
Although both EVS and EVSBA laminates show cohesive fractures, there are obvious differences regarding thickness and appearance of the polymer layers remaining on the aluminum side. The physical structure of the polymer surface in the unpeeled laminates were studied by SEM after dissolving the aluminum with strong NaOH solution. Figure 4 shows the micrographs of the EVS and EVSBA surfaces at two different magnifications as well as the surface of the aluminum foil used. One characteristic feature of these pictures is the distinct grooves of the polymer surfaces, visible even at the larger magnification. These grooves can be related to roller marks on the aluminum surface. This indicates good contact between polymer and metal and thus possibilities for formation of strong bonds across the interface. The uncovered polymer surfaces were further etched with dichromic acid. Since mainly amorphous regions of polyethylene are influenced by this etching,[11] crystalline and amorphous regions can be distinguished. SEM micrographs of etched polymer surfaces are shown in Figure 5. A substantial amount of material is etched away from the surface of EVSBA, changing it from the smooth and featureless structure seen in Figure 4 to a rough surface with deep pits. The surface of EVS is, on the other hand, hardly influenced at all by the acid solution. The surface layer of EVS is thus highly crystalline whereas that of EVSBA has a pronounced amorphous character.

ESCA and MIR was used for a chemical characterization of the silane polymer surfaces. MIR has a penetration depth of a few micrometers and gives thus only an indication of the surface composition. Absorbance spectra of fracture and original film surfaces of EVS and EVSBA can be seen in



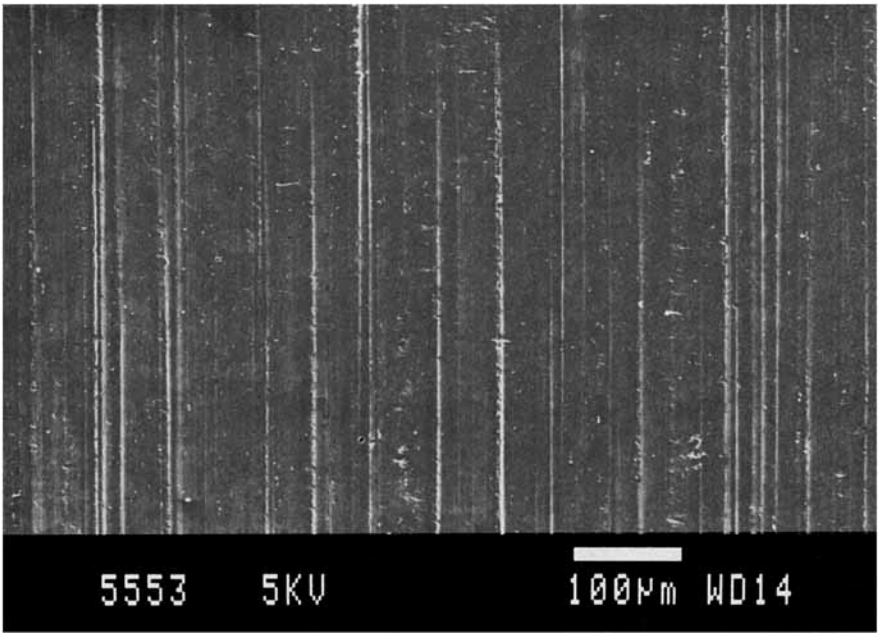
(a)

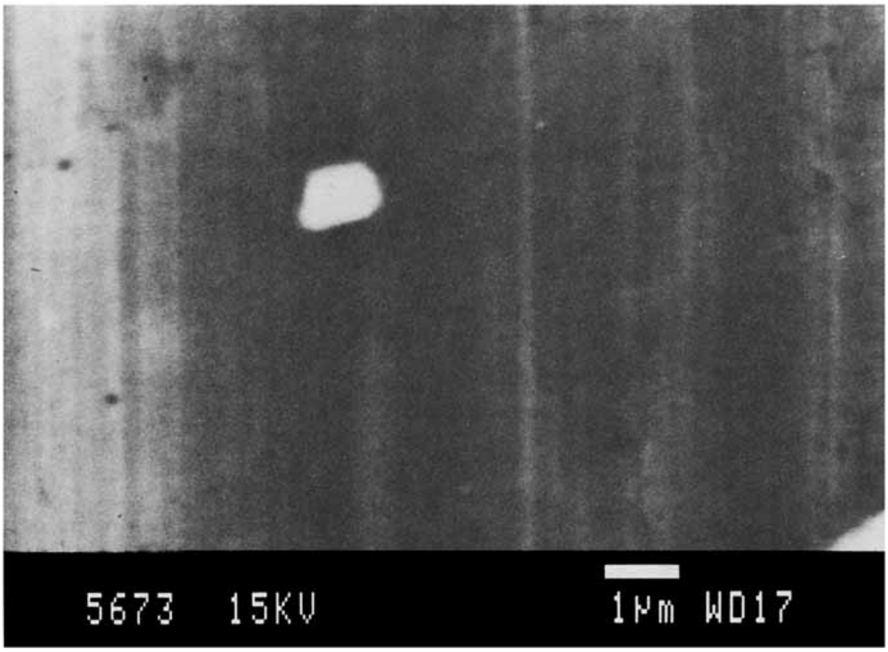
Fig. 4. SEM micrographs: (a and b) polymer surfaces of EVS and EVSBA, respectively, after dissolution of the aluminum foil; (c) aluminum surface.



(b)

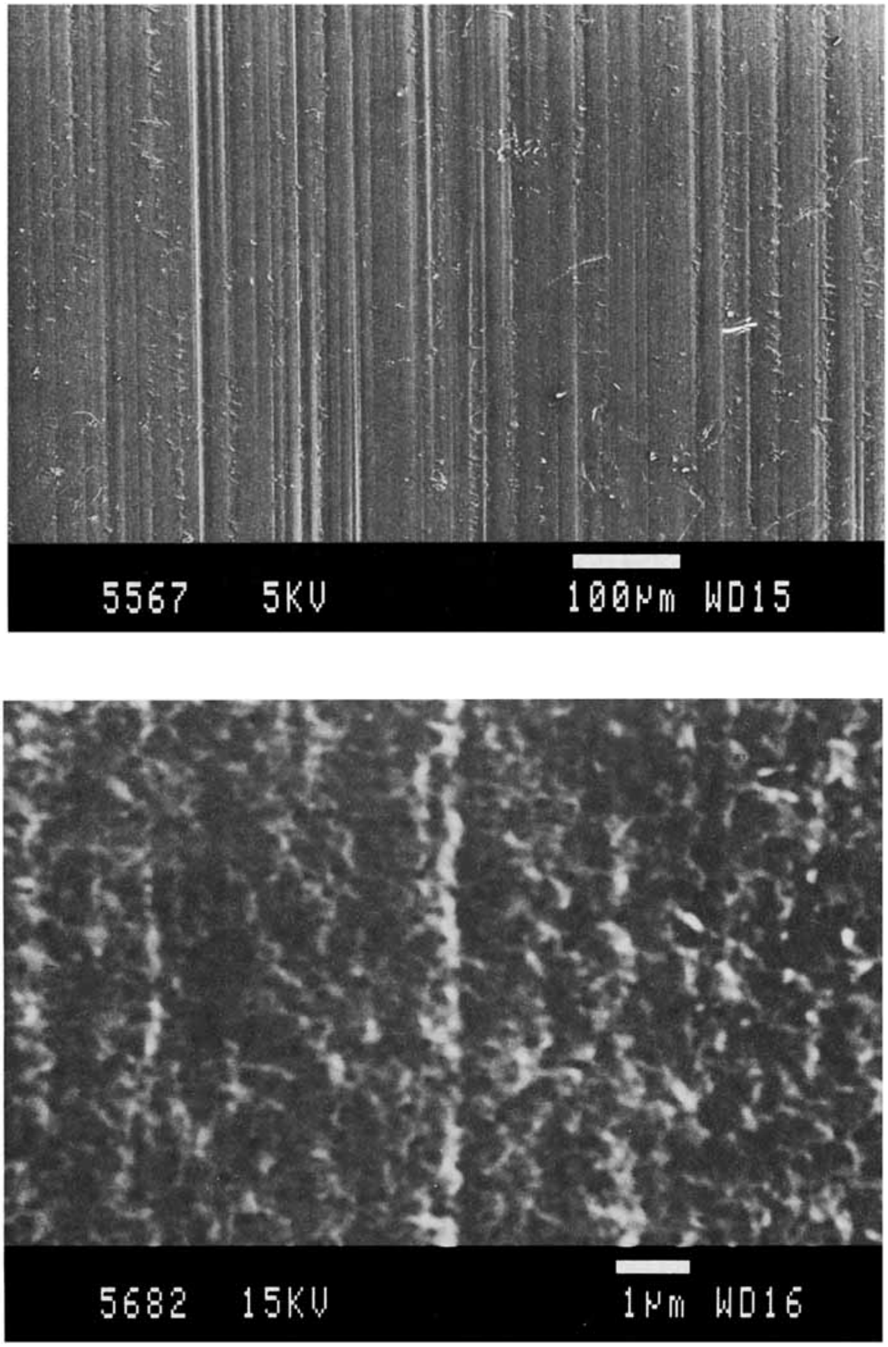
Fig. 4. (*Continued from the previous page.*)





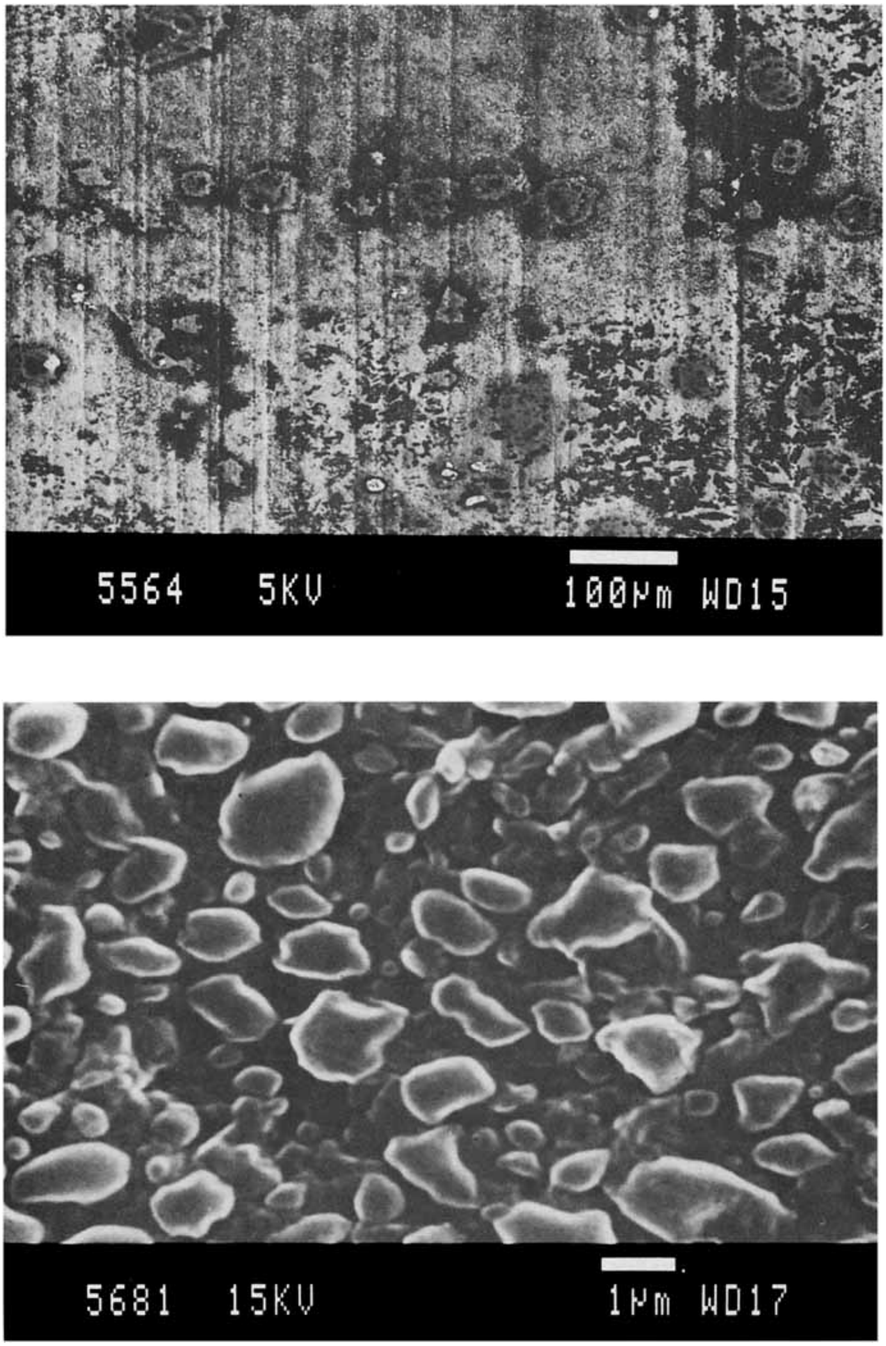
(c)

Fig. 4. (*Continued from the previous page.*)



(a)

Fig. 5. SEM micrographs of the polymer surfaces described in Figure 4 after etching with dichromic acid; (a) EVS; (b) EVSBA.



(b)

Fig. 5. (*Continued from the previous page.*)

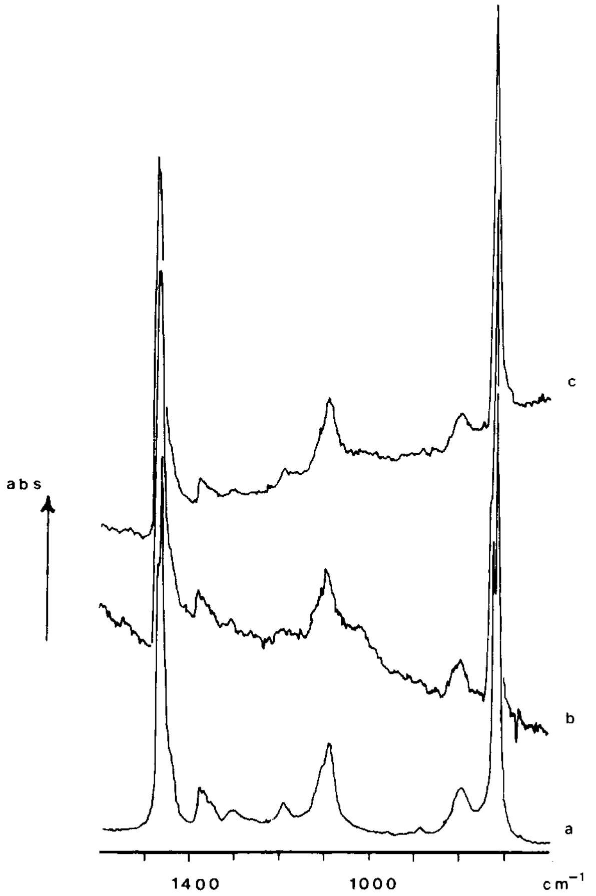


Fig. 6. MIR spectra of EVS: (a) original film; (b) polymer side of peeled laminate; (c) aluminum side of peeled laminate.

Figures 6 and 7, respectively. The polymer layer on the aluminum side of peeled EVSBA laminates was too thin to give an acceptable MIR spectrum. The interesting wave numbers are 600–1600 cm^{-1}, and peak assignments in this region are found in Table II. The relative content of $SiOCH_3$ groups in different surfaces was studied by relating the peak at 800 cm^{-1} to the CH_2 absorption at 1465 cm^{-1}, which was considered to be constant. The results are given in Table III. The $SiOCH_3$ content is particularly low in the polymer layer at the aluminum side of peeled EVS laminates. ESCA analysis indicates a higher total content of Si on this surface (see Table IV). It must be remembered that the penetration depth of MIR and ESCA are totally different, ca. 1–3 μm and 20–50 Å, respectively. Assuming that the polymer layer on the aluminum side is fairly homogenous, these results indicate that the $SiOCH_3$ groups have reacted to a greater extend near the interface.

The results from the wet strength test are summarized in Figure 8, where the peel force is plotted against the time of aging in water. For EVS, an initial slight decrease in peel strength is followed by an increase. After a long time in water, the peel strength exceeds the initial value. MIR spectra of the fracture

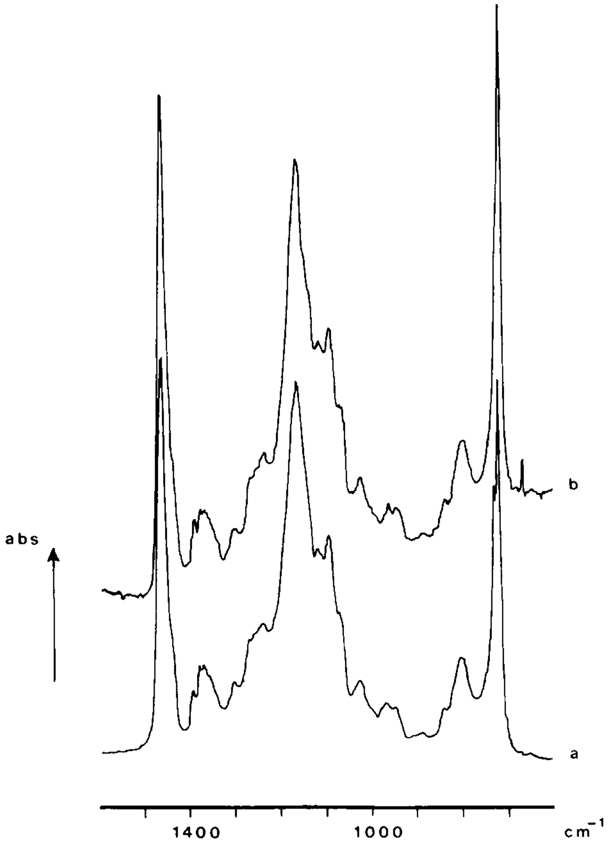


Fig. 7. MIR-spectra of EVSBA: (a) original film; (b) polymer surface of peeled laminate.

TABLE II
IR Peak Assignments for the Silane Group in EVS Polymer[a]

Position (cm^{-1})	Assignment	Group
1190	CH_3 rocking	$SiOCH_3$
1090	Asymmetric Si—O—C stretching	$SiOCH_3$
1030	Asymmetric Si—O—Si stretching	SiOSi
800	Symmetric Si—O—C stretching	$SiOCH_3$

[a] Assignments based on Refs. 12 and 13.

TABLE III
Relative Content of $SiOCH_3$ in Surfaces of EVS and EVSBA Determined by IR

Polymer	Surface	$A(SiOCH_3)/A(CH_2)$
EVS	Film	0.134
	Fracture surface—polymer side	0.104
	Fracture surface—aluminum side	0.072
EVSBA	Film	0.227
	Fracture surface—polymer side	0.170

TABLE IV
Si Content in Surfaces of EVS and EVSBA Determined by ESCA

Polymer	Surface	Si(at. %)
EVS	Film	0.28
	Fracture surface—polymer side	0.26
	Fracture surface—aluminum side	0.35
	Theoretical value	0.15
EVSBA	Film	0.20
	Fracture surface—polymer side	0.40
	Fracture surface—aluminum side	0.50
	Theoretical value	0.21

surfaces at the polymer side are given in Figure 9. A small increase of the Si—O—Si symmetrical stretching at 1030 cm^{-1} can be seen after long time in water, indicating crosslinking. EVSBA shows no minimum in peel strength. After a short delay, the peel strength increases constantly with aging time. After 1 week, the value is almost three times the initial. As the Si—O—Si resonance is hidden by other absorptions in the IR spectrum of EVSBA, the degree of crosslinking could not be followed by the MIR technique. However, the gel content, as measured by GPC, increased from zero in the original film

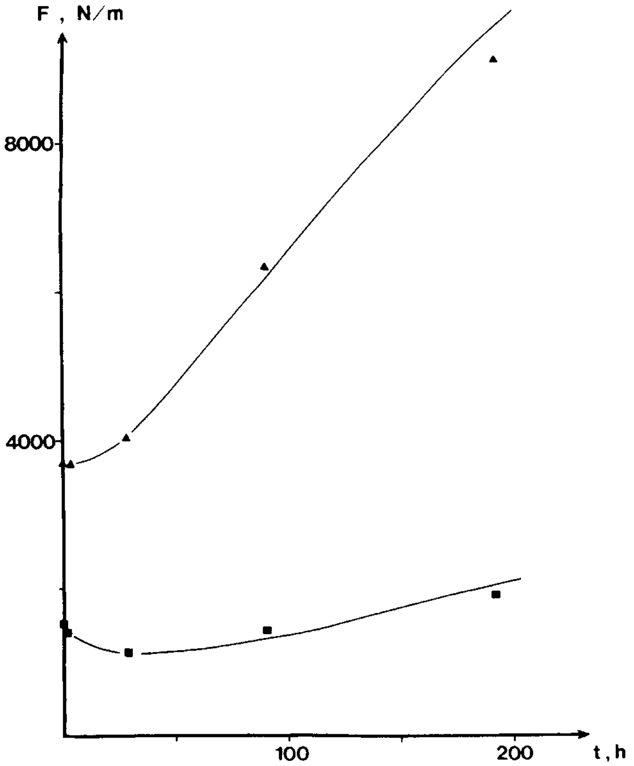


Fig. 8. Peel force of laminates of EVS and EVSBA as a function of aging in water at 85°C; (■) EVS; (▲) EVSBA.

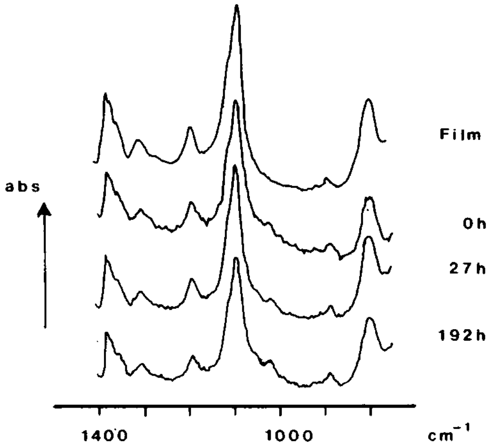


Fig. 9. MIR spectra of EVS; original film and the polymer side of peeled laminates after aging in water at 85°C.

to about 50% after 162 h in water at 85°C. Immersion of the two polymers in water should consequently lead to increased cohesive strength of the films.

DISCUSSION

From a comparison of the peel strength values of EVS and LDPE as well as of EVSBA and EBA, it is obvious that introduction of silane groups in the polymer chain strongly improves the adhesion of polyethylene. Although the silane comonomer content is very low, i.e., 0.2–0.3 mol %, the improvement in adhesion is striking. In addition the ESCA and SEM analysis showed that the fractures of both the silane polymers were cohesive. During the immersion in water the cohesive strength was increased due to crosslinking, leading to higher peel forces. All these results imply that the bonds across the interface are even stronger than indicated by the peel strength. In that case the adhesion obtained with dray samples might be as high as measured after water immersion, i.e., at least 9000 N/m for the EVSBA laminates. Of course, the adhesion could have been increased as well due to further reactions across the interface (see below).

The original structure of the silane group, $SiOCH_3$, should not influence the adhesion between polyethylene and aluminum. It is therefore plausible to assume that these groups have reacted in some way. Possible reactions are:[14] hydrolysis,

$$R{-}SiOCH_3 + H_2O \longrightarrow R{-}SiOH + CH_3OH \tag{1}$$

condensation of silanol groups leading to crosslinking,

$$2\ R{-}SiOH \longrightarrow R{-}Si{-}O{-}Si{-}R + H_2O \tag{2}$$

or of silanol groups in the polymer and hydroxyl groups in the aluminum oxide,

$$R{-}SiOH + Al{-}OH \longrightarrow R{-}Si{-}O{-}Al + H_2O \tag{3}$$

These reactions have in various contexts been considered to improve the adhesion: silanol groups through the possibility to form hydrogen bonds,[15] crosslinking through the removal of weak boundary layers,[16] and covalent bonds through very strong interfacial forces. From the facts that the improvement of the adhesion was very pronounced as well as that the fractures of the laminates were cohesive, it is plausible, however, to assume that covalent bonds have been introduced between the polymer and metal surfaces.

The wet environment tests show that the peel strength of the silane polymer laminates increase when immersed in water. This is in contrast to what usually happens with polyethylene aluminum laminates only held together by polar and hydrogen bonds.[17] Due to the high energy character of the aluminum surface, water has a tendency to accumulate at the interface. This leads to separation of the two materials. The water resistance of the silane polymer laminates indicates unhydrolyzable, or at least not easily hydrolyzed, bonds across the interface. This further support our assumption that reaction (3) does occur between the ethylene vinlysilane copolymers and aluminum.

The difference in peel strength between the two silane polymers is considerable. This is in agreement with what is to be expected from the difference in chemical composition of the two polymers. EVSBA has a higher silane comonomer content and contains, in addition, polar butylacrylate groups. The butylacrylate groups contribute to the adhesion through the possibility of forming stronger bonds across the interface, e.g., dipole–dipole and hydrogen bonds[2] and through the improvement of the wettability of the polymer.[18] Since the fractures are cohesive, the difference in peel strength cannot be interpreted as a difference in adhesion. Instead, the property measured is the cohesive strength of the polymers. As EVS has higher crystallinity as well as higher molecular weight (Table I), the results are confusing. However, although the fractures are cohesive for both the silane polymers, the locus of failure differ markedly, being much closer to the interface for the EVSBA laminates. An explanation for this can be the difference in surface morphology, as revealed by the SEM micrographs of the etched polymer surfaces (Fig. 5). Whereas the EVSBA surfaces are amorphous, the EVS laminates have a pronounced crystalline character at the surface. After pressing, cooling of the laminates is slow. The aluminum surface might therefore induce the formation of a highly crystalline surface layer, e.g., transcrystalline.[19] Due to the higher crystallinity, EVS is more liable to form such surface layers. A strongly crystalline surface layer could lead to the formation of a weaker layer at the transition to the more ordinary spherulitic crystalline structure of the bulk polymer. At such transitions low molecular weight material could be accumulated. This can be an explanation to the large difference in cohesive strength and locus of failures of the two silane polymers. Furthermore, EVSBA seem to undergo crosslinking reactions more easily than EVS.[20]

There are thus several indications of covalent bonds across the interface such as very high peel strength values together with cohesive failures. However, covalent bonds at the interface are difficult to prove. One way could be surface-sensitive IR analysis techniques. With the MIR technique used in this study, the penetration is too deep to give useful information about interfacial phenomena. However, the results from MIR analyses of the silane polymers indicate that methoxysilane groups have been consumed to a greater extend near the interface. This is to be expected since the reactions of the silane group demands the presence of OH groups or H_2O, which can be provided by the aluminum surface. When also taking into account the good contact between polymer and metal, as revealed by SEM (Fig. 4), the conditions for covalent bond formation are favorable.

The conclusion drawn from this investigation is that silane groups in the polymer chain make it possible to form covalent bonds between polyethylene and aluminum. A major advantage of such interfacial bonds is the opportunity to produce water resistant laminates of these materials.

The financial support from Neste Polyethylene Oy, Finland is gratefully acknowledged. The authors also would like to thank Mr. Tore Rönnhult, Department of Engineering Metals for the ESCA analyses, and Mr. Hans Mårtensson, Neste Polyeten AB, for valuable discussions and help with materials.

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Received December 22, 1987
Accepted February 23, 1988