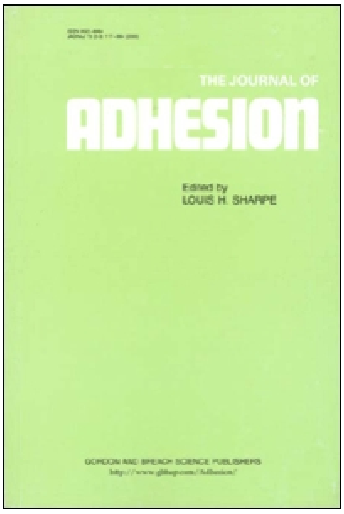

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An FT-IR Study on Interfacial Interactions in Ethylene Copolymers/Aluminium Laminates in Relation to Adhesion Properties

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An FT–IR Study on Interfacial Interactions in Ethylene Copolymers/Aluminium Laminates in Relation to Adhesion Properties

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The effect of three different functional groups in ethylene copolymers on the adhesion with aluminium was studied. The interface in polymer/metal laminates was analyzed by FT–IR, and the adhesion mechanism for each functional group was evaluated. Laminate samples were prepared by solution casting or by hotpressing polymeric film onto the aluminium substrate. In the latter case, the interface was exposed by solvent extraction. The interfacial structures developed by the different copolymers were correlated to the mechanical strength of hotpressed laminates, which was measured by a peel test. The polymer surfaces were further characterized by contact angle measurements.

Polar functional groups, carboxylic acid and butyl ester in hotpressed laminates were found to form Lewis acid/base interactions with the aluminium oxide. The strength of the interfacial interactions was correlated to the concentration and acidity/basicity of the group, the acid group being the most efficient. A silane functional group provided strong adhesion to the laminates at a much lower concentration than the polar groups. Silanols as well as Al–O–Si linkages were detected at the polymer/aluminium interface.

KEY WORDS Polyethylene; functional groups; aluminium; laminate; adhesion; interfacial interactions.

INTRODUCTION

The adhesion of unmodified polyethylene to a high energy surface such as a metal is generally very low due to its nonpolar character. In polyethylene/aluminium laminates, a common material for packaging, the bond strength can be improved by surface oxidation of the polymer.[1,2] This has been commercially utilized for a long time and several different theories have been forwarded to explain the increased bond strength, e.g. improved mechanical strength of the interfacial layer,[3,4] surface energy considerations,[5] mechanical locking[6] and specific interactions across the interface.[1,2,7,8] These theories have been described and evaluated in a review by Brewis and Briggs.[1] Although all factors must be considered in each specific case, the new possibilities to form interfacial bonds are accepted as an important explanation to the increased bond strength, see e.g. Refs. 8 and 9.

An alternative to surface oxidation is to use copolymers of ethylene and monomers containing polar groups that can provide stronger bonds to the metal, thus increasing the adhesion. The bond strength of laminates between aluminium and different copolymers depends strongly on the type of functional group.[10] This was suggested to be mainly due to different strength of the interfacial bonds that the functional groups were involved in. In a recent study, we showed that the bond strength of polyethylene/aluminium laminates can be improved dramatically by the introduction of a silane functional group in the polymer.[11] In addition, the wet strength of the laminates was excellent. We suggested that the polymer was chemically linked to the metal surface *via* the silane groups.

In this study, Fourier transform infrared spectroscopy (FT–IR) has been used to analyze the interface of laminates composed of ethylene copolymers and aluminium. In addition, the surfaces of the copolymers have been characterized by contact angle measurements. The purpose was to study the effect of different functional groups in polyethylene on the adhesion to aluminium on a molecular basis, and to correlate the interfacial interactions with the bond strength of the laminates. A peel test was used to study the mechanical strength of the laminates. Infrared spectroscopy is a useful tool in these attempts since information on the interactions of a specific group with its surrounding molecules can be obtained. Interfacial studies on the interaction between polymers or coupling agents and aluminium include, for example, inelastic tunneling spectroscopy (IETS)[12,13] and FT–IR spectroscopy.[14–16] Some evidence of interfacial covalent bonds between silanes and inorganic substrates using FT–IR has been reported.[17–19]

In order to simulate the laminate structure, a polymer which contained a corresponding functional group was adsorbed on a flat surface. The experimental difficulties due to the low surface area of a flat surface and the low comonomer content were minimized by employing reflection–absorption spectroscopy (RAS), which is useful for studying thin coatings on reflecting substrates such as metals.[20] In addition, a high sensitivity FT–IR spectrometer was used to detect the functional groups at very low concentrations.

EXPERIMENTAL

Materials

Three different ethylene copolymers were used; poly(ethylene-co-vinyltrimethoxysilane) (EVS, Neste Polyeten AB), poly(ethylene-co-butyl acrylate) (EBA, Neste Polyeten AB), and poly(ethylene-co-acrylic acid) (EAA, Dow

TABLE I
Data on polymers used

Polymer	Content of comonomer, mole%	Melt index g/10 min	Crystallinity[a] %
LDPE	—	4	45
EBA-1	0.7	3.5	47
EBA-2	1.8	1	36
EBA-3	3.7	4	30
EAA-1	1.2	11	37
EAA-2	2.4	9	31
EAA-3	3.7	5	28

[a] DSC

Chemicals Inc.). Data on composition and melt flow index are given in Table I. The samples designated EVS, EAA-3, and EBA-3 were used in the FTIR study. All samples were utilized in the study of contact angles. A silane model compound, octyltrimethoxysilane, was purchased from Fluka AG and used as received. Aluminium plates were supplied by Gränges Aluminium AB, Sweden, and had a reported purity of at least 99%. Two different thicknesses were used; 1 mm for the solution cast polymer films and 0.15 mm for the hotpressed films and the model compound. All solvents were of spectrometric grade.

Sample preparation

Two different kinds of laminates were prepared for the study of the polymer/aluminium interface; solution cast polymer films on the aluminium substrate and hotpressed laminates. The 1 mm aluminium plates were mechanically polished using a chromium oxide polishing powder. The thinner aluminium plates had initially a very smooth surface and were consequently not polished. To remove eventual grease and to create a well-defined oxide layer the aluminium plates were then heat treated at 350°C in air for 24 h. Finally, the plates were cleaned with tetrachloroethylene in an ultrasonic bath and dried in air. For solution casting the polymers were dissolved in p-xylene at 120°C (concentration *ca.* 0.1 g/l). In order to prevent rapid crystallization of the polymer, the aluminium plates were preheated to 120°C. To obtain a uniform thickness of the polymer layer, the solvent was evaporated in a nearly saturated environment. Films with different thicknesses were obtained by varying the volume of applied solution. The hotpressed laminates were obtained by pressing a 50 μm thick polymer film onto an aluminium plate for 10 s in a hydraulic press heated to 250°C. The interface was then exposed by repeated fast dissolutions of the main part of the polymer film in hot xylene, thus only leaving tightly bound polymer at the interface. Excess xylene was removed by evacuation in a desiccator. Octyltrimethyoxysilane, the model compound, was deposited onto clean aluminium plates by spreading the pure compound directly on the substrate, rapidly heating the plate to approximately 150°C, and then removing excess compound by rinsing repeatedly in toluene. The samples were then stored under vacuum. In some experiments water treated aluminium plates were used. They were prepared by immersion in distilled water at 95°C for 20 s prior to the lamination preparation.

Infrared spectroscopy

For the depth profile study, a Bomem DA-3 FT–IR spectrometer with a narrow band, liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector was used. The specific detectivity D* was $3 \times 10\,\mathrm{cm\,Hz^{1/2}/W}$. All spectra of the solution cast films were recorded with this spectrometer. In order to reduce water vapour in the background, the spectrometer was evacuated to 0.4 torr. The infrared radiation was p-polarized by a KRS-5 polarizer. The sample spectra obtained from the polymer film on the aluminium substrate were ratioed to the reference spectra from the clean aluminium plates prior to coating.

A Perkin–Elmer 1800 FT–IR spectrophotometer with a room temperature triglycerin sulfate (TGS) detector was used to obtain spectra of the hotpressed laminates and the model compound using continuous dry air purge. Spectra of the aluminium plates were taken before coating and after hotpressing or model compound adsorption. The difference spectrum, representing the thin polymer or model compound layer, was obtained by a digital subtraction of the coated sample and the bare aluminium spectra. Since the sample preparation did not induce any changes on the aluminium plates that could be detected by FT–IR, a scaling factor of 1 was used.

In all cases, an external reflection attachment was used at an incident angle at 75°. The spectral resolution was $4\,\mathrm{cm^{-1}}$ and 500 scans were coadded to improve signal-to-noise ratio. The thickness of the polymeric layers were very small, 2–200 nm. In order to obtain reliable results, all experiments were repeated several times. The discussed features concerning the spectra are constrained only to reproducible effects. All spectra are shown in the absorbance mode and ΔA represents the difference between the maximum and minimum absorbances of the spectrum.

Contact angle measurement

The measurements were made on polymer film (extrusion blown) surfaces using a Ramé–Hart Contact Angle Goniometer. Three different contact liquids were used; distilled water, dimethylsulfoxide (DMSO), and *N*-methylpyrrolidone (NMP). 5–10 μl of the liquid, depending on the diameter of the droplet formed, was placed on the substrate and the advancing angle was obtained by refilling the droplet. The contact angle given is the average of 20 measurements. In all cases the standard deviation was less than 1.5°.

RESULTS

Carboxylic acid and ester functional group

The RAS spectrum of a solution cast film of EAA on an aluminium substrate is illustrated in Figure 1. Spectral regions showing characteristic carbonyl (1700–1750 cm^{-1}) as well as hydrocarbon bands (—CH_2—: 2920, 2850, 1546 cm^{-1}) are plotted. The approximate film thickness as calculated by mass balance from the preparation data is 20 nm. Figure 2 shows spectra of the carbonyl region of films with different thickness of the acid copolymer. By varying the film thickness, the polymer near the interface can be compared with the bulk polymer. The spectrum of the thickest film, representing the bulk, is dominated by one band in the carbonyl region, 1705 cm^{-1}. When the film thickness is reduced, a second band at 1738 cm^{-1} can be seen. The band at 1705 cm^{-1} can be assigned to the antisymmetric C=O stretching mode in dimeric carboxylic acid and the one at 1738 cm^{-1} to the C=O stretching mode of free carboxylic acid.[21]

The corresponding spectra of the copolymer containing ester groups (EBA) are shown in Figure 3. The bulk spectrum has a single carbonyl band at 1735 cm^{-1} representing the C=O stretching mode of the ester group. On approaching the interface, a shoulder at a lower wavenumber is growing and, for very thin films, a new band around 1727 cm^{-1} is distinguishable. The lower band could represent carbonyl involved in hydrogen bonding with surface AlOH groups or in electron donation to the O—Al—O groups.

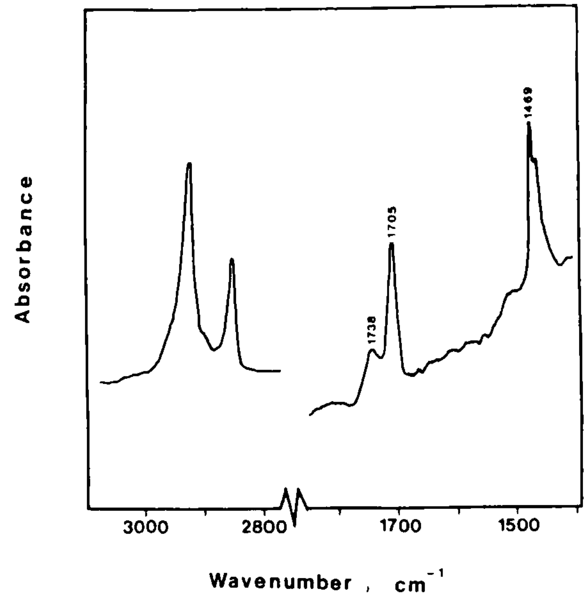

FIGURE 1 RAS spectrum of a 20 nm solution cast film of EAA-3 on aluminium: 3000–2800 cm^{-1}, $\Delta A = 0.075$; 1800–1400 cm^{-1}, $\Delta A = 0.015$.

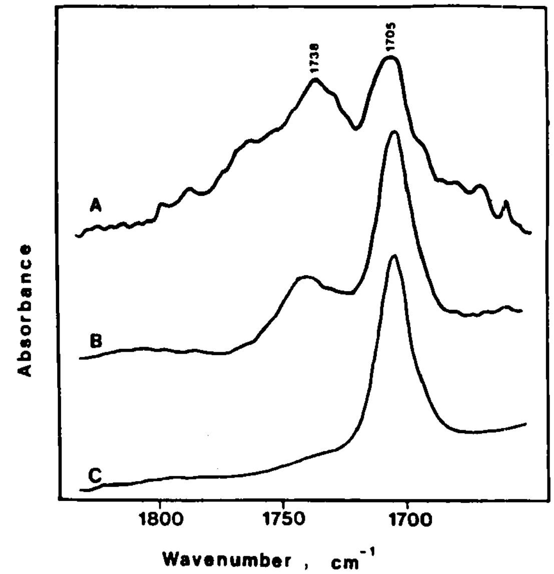

FIGURE 2 Effect of film thickness on the RAS spectra of solution cast films of EAA-3 on aluminium: A, 3 nm, $\Delta A = 0.0013$; B, 20 nm, $\Delta A = 0.010$; C, 150 nm, $\Delta A = 0.065$.

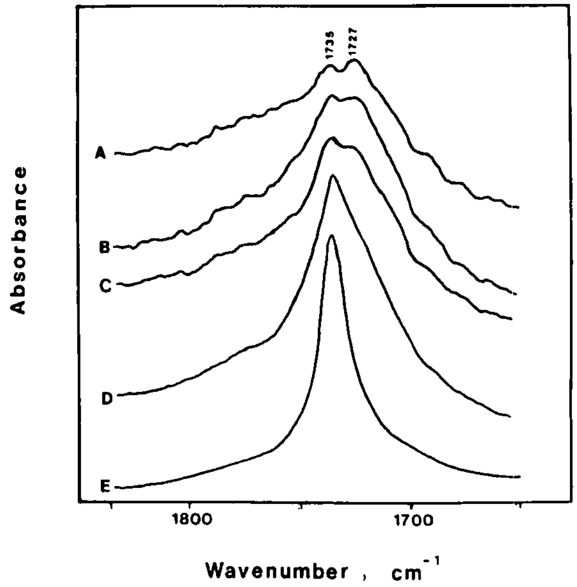

FIGURE 3 Effect of film thickness on the RAS spectra of solution cast films of EBA-3 on aluminium: A, 2 nm, $\Delta A = 0.0010$; B, 4 nm, $\Delta A = 0.0060$; C, 10 nm, $\Delta A = 0.0105$; D, 20 nm, $\Delta A = 0.018$; E, 100 nm, $\Delta A = 0.044$.

In practice, the polymer comes into contact with the substrate in the form of a melt and not as a solution. In order to be able to correlate the interfacial structures of these copolymers with the adhesion and bond strength of real laminates, hotpressed laminates were prepared in addition to the solution cast films discussed above. The interface was then exposed by dissolving the polymeric film except for material tightly bound to the aluminium. In Figure 4, difference spectra of the interfacial region of hotpressed polymer/aluminium laminates are illustrated for EBA and EAA. A weak shoulder at lower frequency is observed in the 1735 cm^{-1} band of the ester copolymer. The shoulder becomes more obvious when a Fourier self-deconvolution procedure is performed, Figure 5. The acid copolymer, spectrum B in Figure 4, shows a band at 1705 cm^{-1}, originating from dimeric acid, as well as a shoulder at higher frequency. For the aluminium plates that were treated with water prior to the preparation of laminates by hotpressing, a broad band around 1590 cm^{-1} is seen for both the acid and the ester groups indicating carboxylate formation, Figure 6.

In the interpretations above it has been assumed that the changes observed in the carbonyl band can be related to interactions between the functional group and the substrate. Any other possible changes in the polymer structure must, however, be considered as well. As the sample preparations involves a heat treatment in air the polymer might be oxidized resulting in a new carbonyl resonance. Although 250°C is used in the hotpressing, the heating-up time at 250°C is considerably shorter. According to earlier results obtained at our laboratory[22–24] the conditions used should not cause the development of an

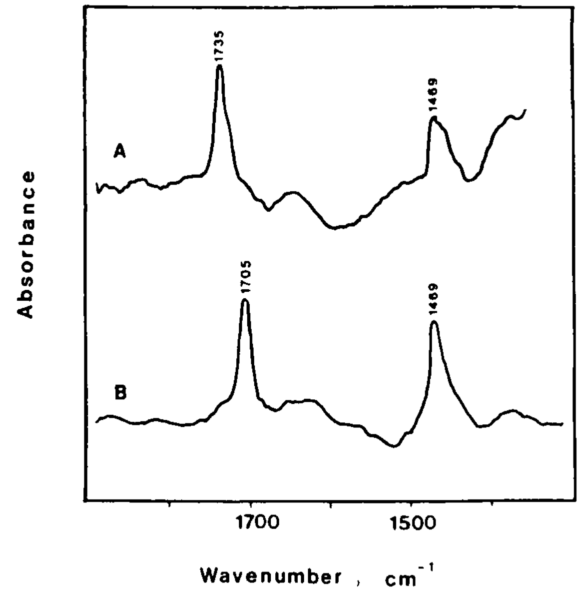

FIGURE 4 RAS difference spectra of residual polymer after solvent extraction of polymer films hotpressed onto aluminium: A, EBA-3, $\Delta A = 0.0016$; B, EAA-3, $\Delta A = 0.0025$.

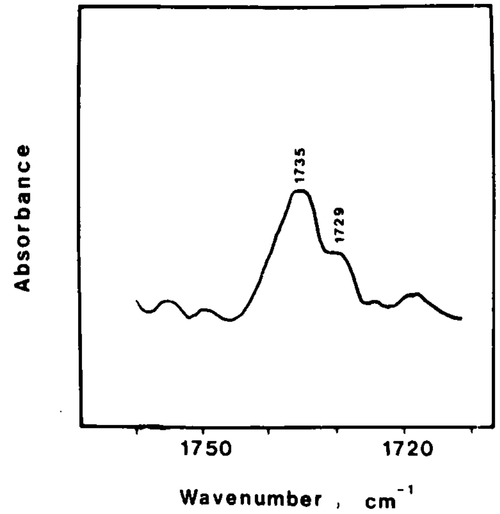

FIGURE 5 RAS difference spectrum of EBA-3 sample in Figure 4 after digital deconvolution of the carbonyl band; $\Delta A = 0.0025$.

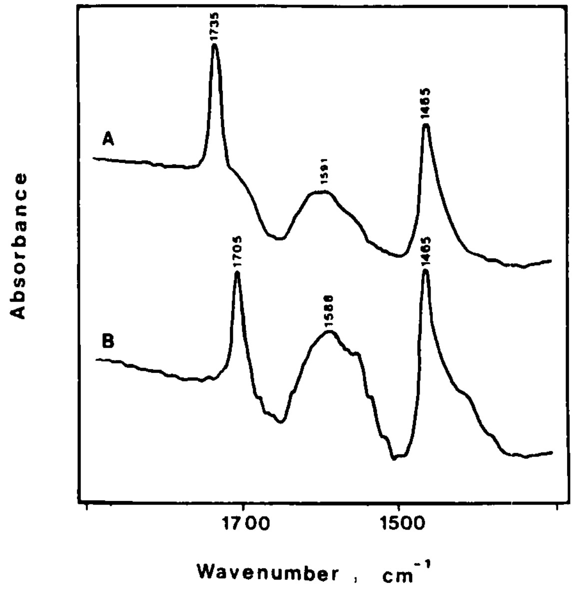

FIGURE 6 RAS difference spectra of residual polymer after solvent extraction of polymer films hotpressed onto water treated aluminium: A, EBA-3, $\Delta A = 0.0135$; B, EAA-3, $\Delta A = 0.0135$.

observable carbonyl band. This would normally be centered around 1720 cm^{-1}. It can, on the other hand, not be excluded that the aluminium surface might have a catalytic effect on the oxidation. The oxidation mechanism of EAA and EBA should, however, not differ too much, and in both cases a carbonyl band centered around 1720 cm^{-1} is expected. With regard to the quite opposite behaviour observed for the carbonyl band in the interface region of EAA and EBA, *c.f.* Figures 2 and 3, oxidation of the polymer can not explain the unique spectra observed for the thinnest films. As a further confirmation it can be mentioned that solution casting of polyethylene under similar conditions did not lead to increased carbonyl absorption in the thinnest films.

Silane functional group

Figure 7 illustrates the transmission spectrum of the copolymer containing the silane groups, as well as the RAS difference spectrum of the interfacial material in a laminate made by hotpressing the same polymer. Using X-ray photoelectron spectroscopy (XPS or ESCA), the thickness of the polymer layer is estimated to be about 2.5–5.0 nm measuring the relative carbon and aluminium intensities after different degrees of argon ion sputtering.[25] The characteristic absorptions of silanes are found in the 800–1200 cm^{-1} region. Even though the content of silane is very low, *ca.* 0.3 mole-%, bands due to the trimethoxysilane group can easily

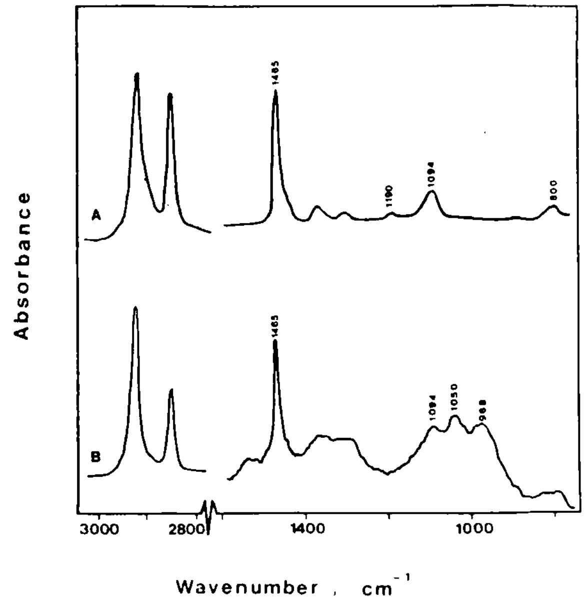

FIGURE 7 Spectra of EVS: A, transmission spectrum, $\Delta A = 1.06$ (3000–2800 cm^{-1}), $\Delta A = 0.47$ (1500–800 cm^{-1}); B, RAS difference spectrum of residual polymer after solvent extraction of polymer film hotpressed onto aluminium, $\Delta A = 0.0160$ (3000–2800 cm^{-1}), $\Delta A = 0.0024$ (1500–800 cm^{-1}).

be found in the transmission spectrum (spectrum A); 1190 cm^{-1} (the —CH_3 rocking in Si—O—CH_3), 1094 cm^{-1} (the antisymmetric Si—O—C stretching), and 800 cm^{-1} (the symmetric Si—O—C stretching).[26,27] However, the strong absorption is to be expected since IR absorptions of linkages involving silicon atoms are several times more intense than the corresponding bands from a carbon linkage.[28] The reflection spectrum of the interfacial material of the same copolymer is more complex with new bands around 1050 and 970 cm^{-1}. The new IR bands found in the reflection spectrum can be due to changes during hotpressing, not only in the silane groups but also in the polyethylene main chain and on the aluminium surface. As mentioned in the Experimental part the latter can be excluded. The heat treatment is far to mild to cause any further changes in the oxide, which was formed by heating at 350°C for 24 h. In an attempt to distinguish bands specific to the silane groups, a low molecular weight silane compound, octyltrimethoxysilane, was used. In order to simulate the hotpressing procedure, a very thin layer of this compound was deposited on a hot substrate. The difference reflection spectrum of the thin film is shown in Figure 8 together with a transmission spectrum of the model compound. The silane-related bands in the transmission spectrum are the same as in that of the silane-modified polymer (the bands at 1190, 1090, and 800 cm^{-1}). In addition, the appearance of a shoulder at 1025 cm^{-1}, representing the antisymmetric Si—O—Si stretching,[26,27] indicates that some silanol formation with further condensation to siloxane has occurred. By comparing the bulk (A) and the interface (B) spectra, a new band at 968 cm^{-1} is seen in the interface spectrum.

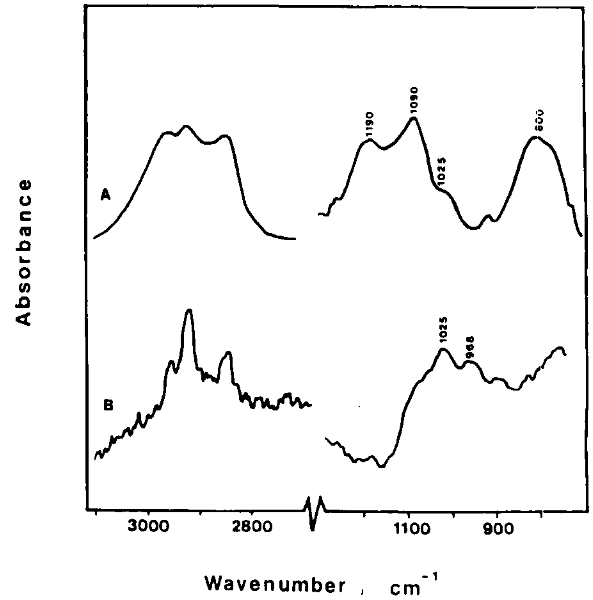

FIGURE 8 Spectra of octyltrimethyoxysilane: A, transmission spectrum, $\Delta A = 0.46$ (3000–2800 cm^{-1}), $\Delta A = 0.50$ (1300–800 cm^{-1}); B, RAS difference spectrum of model compound deposited on aluminium, $\Delta A = 0.0006$ (3000–2800 cm^{-1}), $\Delta A = 0.0016$ (1300–800 cm^{-1}).

DISCUSSION

The main issue of this work is to correlate the interaction, as measured by FT-IR spectroscopy, between different functional groups in ethylene copolymers and aluminium with the adhesion in the same systems. To estimate the adhesion we have used the bond strength of hotpressed metal/polymer/metal laminates measured in a *T*-peel test. The effect of different degrees of extension of the polymers should thus be minimized. In Figure 9 the peel force is plotted against the content of comonomer for EVS, EAA, and EBA copolymers (data taken from Refs. 10 and 11). Observe that EAA and EBA are represented at three different levels of comonomer (four including LDPE). The polymers used for the present IR study are those with the highest concentration of the comonomer in question. It should also be noted that the failure is cohesive for the EVS sample as well as the EAA with the highest content of comonomer,[11] i.e. the adhesive strength is expected to be higher than that indicated by the peel strength. All other samples, on the other hand, give adhesive failures. It is thus reasonable to regard the peel strength values as a measure of the adhesion. Although EAA-3 shows a cohesive failure the linear relation in Figure 9 indicates that this effect could be extrapolated to acid contents higher than 2 mole% acrylic acid. It should, however, be remembered that the adhesion of EAA-3 in fact should be higher than that corresponding to the peel strength.

It is evident that there is a substantial difference in the ability of the three functional groups to increase the bond strength between polyethylene and

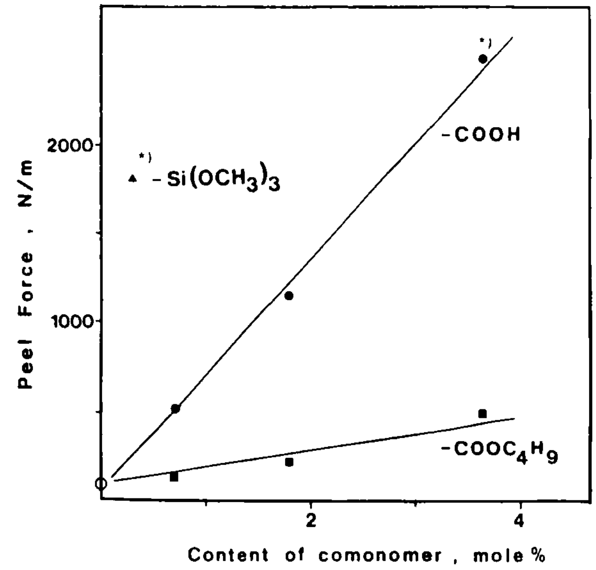

FIGURE 9 Effect of different functional groups in polyethylene on the adhesive strength of hotpressed aluminium/polymer/aluminium laminates (250°C, 10 s); *) cohesive failure; from Refs. 10 and 11.

aluminium. The carboxylic group is much more effective than the ester group. Furthermore, the silane group provides high bond strength to the laminate at a much lower concentration. It is essential for our purpose, that the bond strength data in Figure 9 can be used as a measure of the adhesion, instead of reflecting the mechanical properties of the polymer.[4] With increasing content of comonomer, the crystallinity, and thus the cohesive strength of ethylene copolymers, decreases, i.e. it should not explain the increased peel strength. Furthermore, the relatively moderate increase in modulus and strength of EAA compared to EBA, is not at all proportional to the 6–7 times increase in adhesive strength. The low comonomer content of EVS implies that the mechanical properties should be similar to the reference LDPE. Crosslinking *via* the silane groups leads to a 30–40% increase in the tensile strength,[29] but the initial modulus should not be affected by the quite loose network (0.3 mole-% silane). Although the increase in peel strength, from 100 to 1800 N/m, is dramatic, the increase in adhesive strength is even higher as the EVS sample shows cohesive strength is even higher as the EVS sample shows cohesive failure far from the interface.[11] Furthermore, the wet strength of EVS/aluminium laminates is excellent in contrast to what is observed for other ethylene copolymers. We have, therefore, suggested that the silane groups can form strong bonds across the polymer-metal interface.[11] Increased bond strength is often observed for sharp interfaces when small amounts of functional groups, capable of forming bonds across the interface, are introduced. The opinion, that this can be related to increased interfacial interactions, i.e. increased adhesion, is now accepted, see e.g. Refs. 8 and 9.

The spectra of the thin solution cast films of carboxylic acid copolymer, Figure 2, showed two bands in the carbonyl region that were assumed to be due to free and dimeric acid groups. In the bulk polymer, the carboxylic acid groups exist predominantly in the dimeric form, although a small band around 1740 cm^{-1} indicates a minor fraction of free acid. The increased amount of free acid at the interface can be attributed to interfacial hydrogen bonds between the hydroxyl groups of the acid and the surface AlOH groups, or eventually Al—O—Al, thus setting some of the carbonyl groups "free." Another possibility is that the band at 1738 cm^{-1} represents the carbonyl in an interfacial ester link between the polymer and the metal originating from a reaction between surface AlOH group and hydroxyls of the acid groups. Adsorption of low molecular weight carboxylic acids onto aluminium oxide formed on aluminium in air in ambient atmosphere has, however, shown that formation of carboxylate is favoured.[30] In any case, both possibilities should provide strong interactions across the interface.

Surprisingly, the spectrum of the interface of a hotpressed laminate with the same copolymer shows predominantly the dimeric form of the carboxylic acid groups, Figure 4B. This observation can be explained by the fact that extremely dilute polymer solutions were used for the film casting. In the dilute solution, the strong dimers can dissociate and the free carboxylic acid can form interfacial bonds. However, the conditions used in the hotpressing (250°C, 10 s) seem not to be enough to break the very strong hydrogen bonds between two carboxylic acid groups. An alternative explanation is that the mobility of the acid groups in the

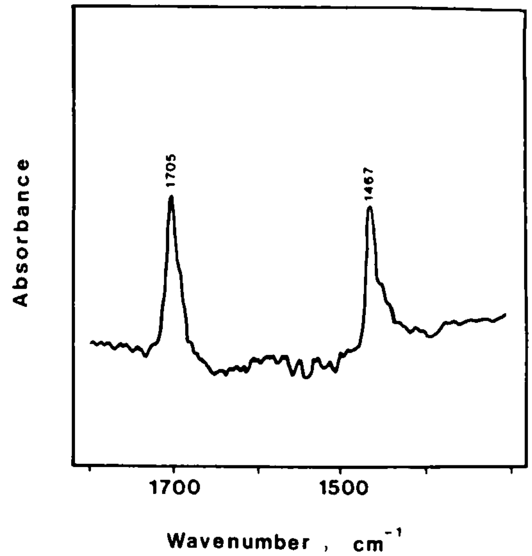

FIGURE 10 RAS difference spectrum after residual EAA polymer on aluminium after peel test of hotpressed laminate; $\Delta A = 0.0120$.

melt is not sufficient to allow a preferential adsorption of the acid groups during the 10 s pressing time. In any case, there seems to be a low concentration of interfacial hydrogen or covalent bonds between hydroxyls of the acid and the aluminium oxide in hotpressed laminates.

The acid copolymer with the highest content of comonomer, EAA-3, gave a cohesive failure in the peel test. Figure 10 shows the RAS spectrum of the thin polymer layer left on the aluminium. By relating the absorbance of the carbonyl peak with that of other films, the thickness can be estimated to 15–20 nm. Comparison with the spectrum of the polymer layer left on the aluminium after dissolution in xylene, Figure 4B, indicates no obvious difference that can be related to the dissolution procedure. A more close inspection shows, however, that the carbonyl peak of the peel test sample is askew with increased absorption on the low frequency side. This indicates that the carbonyl in the acid dimers might be involved in an interaction similar to that of the carbonyl in EBA, see below.

The carbonyl of the ester copolymer gives two absoptions in the IR spectrum at low film thicknesses, both for solution cast films (Figure 3) and hotpressed laminates (Figure 4A). The downshift of the carbonyl frequency at the interface can be attributed to some interaction with the aluminium oxide of the substrate. Possible interactions include electron donation to the polar metal oxide or hydrogen bonding to surface hydroxyls. Both these would lower the carbonyl frequency.[31]

Water is easily adsorbed on the high energy surface of the aluminium plates when exposed to ambient air, and can later react with aluminium oxide to form

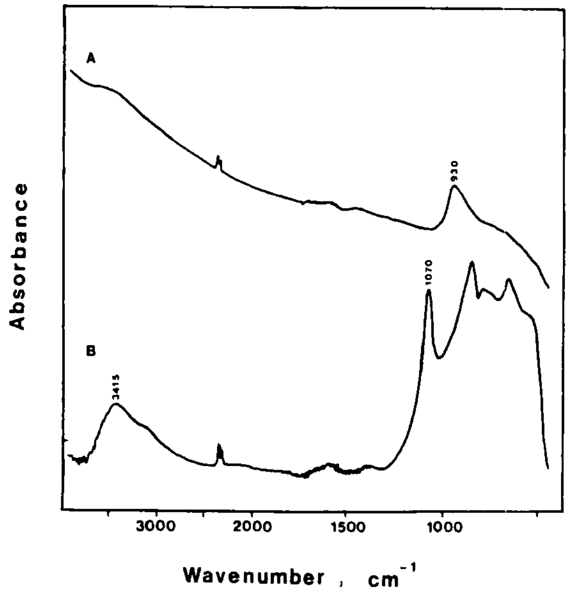

FIGURE 11 RAS spectra of aluminium: A, standard aluminium foil, $\Delta A = 0.040$; B, water-treated aluminium foil, $\Delta A = 0.127$.

hydroxyl groups. The amount of surface hydroxyls on the oxide formed in air seems to be low, Figure 11A (—OH; 3415 and 1070 cm^{-1}). The effect of a high surface hydroxyl content on the ester and the acid groups was studied by treating the aluminium with water prior to hotpressing. A large amount of hydroxyl groups is then introduced at the surface, Figure 11B, by the formation of an oxide that could be described as pseudobohemite,[32] AlOOH. In contact with this modified surface, both the ester and the acid groups show a strong tendency for carboxylate formation, Figure 6. However, no carboxylate can be found at the interface of the laminates with the original aluminium plates.

Considering the discussion above, it is thought that the dominant form of interaction in the hotpressed laminates of EBA, and eventually EAA as well, is some interaction *via* the carbonyl oxygen, but not with a hydrogen donor. The shift to lower frequencies observed for the ester group can in general terms be described by partial donation of the free electron pair. This might be described as a dipole/dipole interaction, in agreement with the discussion of solvent affects on the carbonyl absorption.[31] Alternatively, it can also be discussed in terms of Lewis acid/base interactions, which would be in line with the suggestion of Fowkes and coworkers[33,34] that acid-base interactions are essential in determining the adhesion strength. The ester group is a Lewis base, and in complexes with strong Lewis acids,[35] e.g. BF_3 and $AlCl_3$, the carbonyl frequency shift is of the order of 70–180 cm^{-1}. The shift observed in this investigation is only 8 cm^{-1}, indicating a much weaker interaction. It should also be pointed out that the aluminium oxide formed on aluminium generally is considered to be a donor.[33,36]

In the Brønstedt acid-base definition, on the other hand, it is considered amphoteric,[37] and the presence of weak Lewis acid sites can not be excluded.

Carboxylic acid groups are of course to be considered as Lewis acids, but it should be remembered that most of the acid groups of EAA exist as dimers. The carbonyl oxygen of the dimers might well act as an electron donor similar to those in the ester groups. Although the nature of the interaction thus could be similar for both kinds of functional groups, carboxylic acid groups improve the adhesion of polyethylene to aluminium much more effectively than ester groups, Figure 9. In order to study further the surface character of the EAA and EBA copolymers, contact angle measurements were performed. Three different liquids, distilled water, dimethylsulfoxide (DMSO), and N-methylpyrrolidone (NMP), were used. In the case of water, a strongly hydrogen bonding liquid, there is just a slight decrease in the contact angle with increasing content of comonomer compared to the reference surface of pure polyethylene, Figure 12. The small effect observed in the advancing contact angle of water when introducing small amounts of a high-energy contaminant on a low-energy surface is well known.[38]

A drastic decrease in contact angles with increased content of carboxylic acid is, however, seen for the two strongly polar organic liquids, DMSO and NMP, Figure 13. In contrast to water these will not contribute with hydrogen in a hydrogen bond. The copolymers with the ester group, on the other hand, show the same behaviour for all liquids. Both the DMSO and NMP are generally considered as Lewis basis in agreement with the larger effect observed for the acidic copolymer, EAA. Although weaker, they can, however, also act as acids,

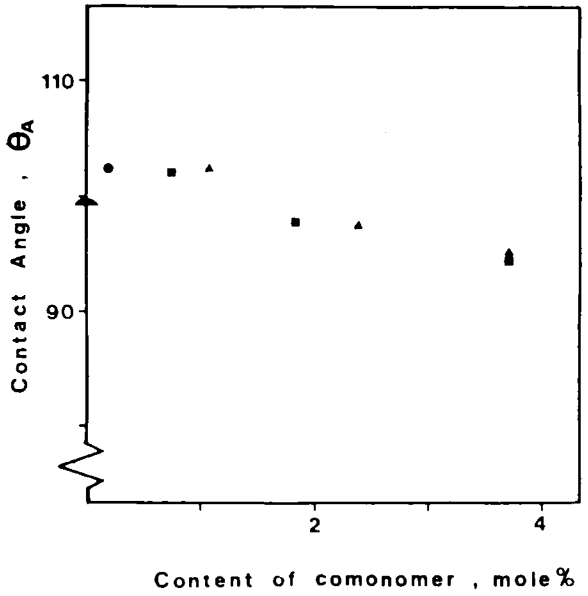

FIGURE 12 Advancing contact angle of distilled water in contact with polymer film surfaces: △, EAA; ■, EBA; ●, EVS; ▲, LPDE.

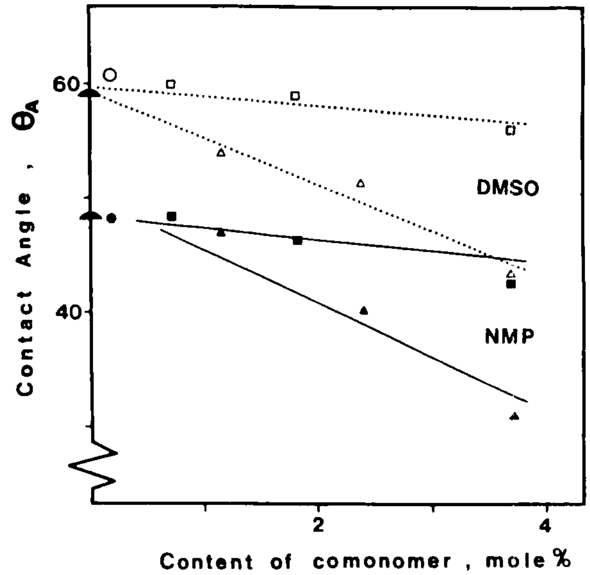

FIGURE 13 Advancing contact angles of DMSO and NMP in contact with polymer film surfaces: △ ▲, EAA; □ ■, EBA; ○ ●, EVS; ▲, LPDE.

c.f. the donor and acceptor numbers given by Gutmann,[39] Table II, which explains the change in contact angle for the copolymer with basic groups, EBA. For a liquid which mainly act as an acceptor, dinitrobenzene, the largest effect of comonomer was instead observed for EBA: LDPE, $\Theta = 44^\circ$; EAA-3, $\Theta = 40^\circ$; EBA-3, $\Theta = 38^\circ$. This is in agreement with the expected higher donor capacity of EBA. In the case of EAA the contact angles of the different liquids thus show that EAA mainly interacts as a Lewis acid, although a certain donor capacity cannot be excluded.

It should also be noted that using the non-polar liquid methylene iodide the same contact angle, within the experimental errors, was observed for all samples, 54°. This indicates that the non-polar or dispersive component of the surface tension, γ^d, should be the same for all samples.[40] The difference in contact angle observed using e.g. DMSO could, on the other hand, be related to differencies in the acid-base contribution to the work of adhesion[33] between the liquid (L) and

TABLE II
Donor and acceptor numbers[39] of liquids used for contact angle measurements

Compound	Donor number	Acceptor number
DMSO	29.8	19.3
NMP	27.3	13.3
nitrobenzene	4.4	14.8

the solid (S), W^{ab}:

$$W^{ab}_{SL} = W_{SL} - W^{d}_{SL} = \gamma_L(1 + \cos\Theta) - 2(\gamma^d_L\gamma^d_S)^{1/2}$$

where d stands for the dispersive component of the work of adhesion, W_{SL}, or of the surface tension, γ. The more marked decrease in Θ with increased comonomer content observed for EAA thus corresponds to a larger value of W^{ab}, indicating that the acid groups interact much more effectively than the ester groups. This parallels the stronger interactions with aluminium observed for the acid groups as demonstrated by the peel strength results in Figure 9. The work of adhesion for a given surface (against a liquid) can be related to the specific efficiency and the concentration of the functional group in question. The differencies in W^{ab}, as given by the contact angle for a polar liquid, e.g. DMSO, will thus be a measure of both these parameters.

Using published[41] data on γ_L, γ_L and γ_S, W^{ab} was calculated for the polymers used in the contact angle measurements. For LDPE and the EBA samples with lowest content of comonomer negative values of W^{ab} were obtained. This is, however, strongly depending on the values used for the constants. As it is the *changes* in the acid-base contribution to the work of adhesion that are important in this investigation, all values were increased by an arbitrary factor (2). Values of the adhesive strength in laminates against aluminium were not available for all copolymers. Instead, interpolation was made in Figure 9 in order to obtain peel strength data for the relevant comonomer concentrations. The relation between W^{ab} for polymer-DMSO and the peel strength data for aluminium/polymer/aluminium laminates is given in Figure 14. All data points

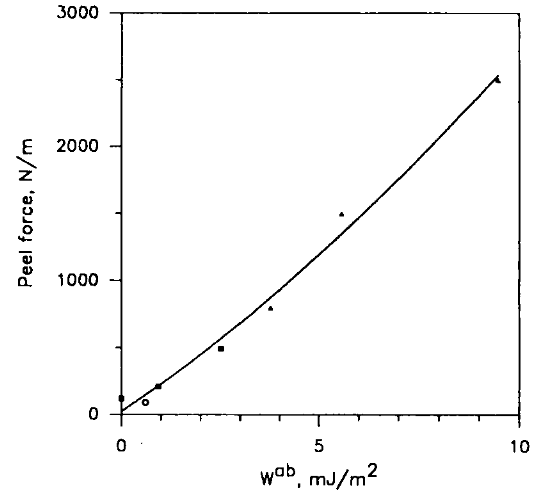

FIGURE 14 The relation of the peel force strength data in Figure 9 and the acid-base contribution to the work of adhesion (DMSO-polymer) according to equation given in text (all W^{ab} values increased by 2 mJ/m^2): ▲, EAA; ■, EBA, ○, LPDE.

follow the same correlation which is a further confirmation that the interaction in the adhesion mechanism of the two copolymers is similar in nature.

Compared with carboxylic acid and ester groups, the efficiency of the methoxysilane groups is considerably higher. The infrared spectrum of the silane copolymer at the aluminium interface, Figure 7B, shows some specific bands that are not found in the bulk polymer, spectrum A. Methoxy-silanes are relatively easily hydrolyzed to silanols while the condensation reaction is considerably slower.[42] Since water is adsorbed on aluminium surfaces, silanols are expected to be formed readily in the interface region during hotpressing of the silane copolymer to aluminium. The band at 1050 cm^{-1} can be assigned to the Si—OH deformation mode.[43]

There are several possibilities for the silanols to react further at the interface. Interfacial hydrogen bonds can be formed between the silanol groups and the aluminium oxide. Silanols can also react with each other producing crosslinks, or with surface hydroxyls forming interfacial covalent bonds, Si—O—Al. In a previous study using Fourier transform infrared diffuse reflectance spectroscopy (DRIFT), a band at 963 cm^{-1} was tentatively assigned to the interfacial Si—O—Al stretching mode.[19] The position for the band, around 960 cm^{-1}, was also in agreement with theoretical calculations using a simple harmonic oscillator model. Since the broad band around 970 cm^{-1} is found in the interface spectra of both the silane copolymer and the model compound, we assume that this band is indeed due to the interfacial covalent bonds formed with the aluminium substrate. We assume that interfacial hydrogen bonds in addition to the covalent bonds account for the dramatic improvement of the adhesion of polyethylene to aluminium when silane functional groups are used. Since the silane group is effective at very low concentrations, it is reasonable to conclude that strong interfacial chemical links are involved in the adhesion mechanism of these laminates.

CONCLUSIONS

By using a film casting procedure to prepare samples for reflection infrared spectroscopy, the adhesion mechanism of a polymer in contact with some substrate can be studied. However, to allow for a correlation between the spectroscopic study and the macroscopic properties of a hotpressed laminate, e.g. peel strength, it is of course important that the conditions for the formation of the interfacial regions are similar in both cases. In this work, casting from dilute solutions did not show the same molecular behaviour as meltpressing EAA, one of the polymers studied. Although convenient to form thin layers of controlled thickness the former method could thus not be used for a comparison with peel test results obtained with hotpressed laminates.

The effect of three different groups on the adhesion of polyethylene to aluminium has been studied. It was concluded that the polar groups, carboxylic acid and butylester, predominantly interact with the aluminium oxide *via* Lewis acid/base interactions. The strength of the interfacial interactions between the polymer and the metal depends on the acidity/basicity and the concentration of the functional group, the acid group being the most efficient. The silane group shows a remarkable improvement of the adhesion of polyethylene at much lower concentrations than the polar groups. Since silanols and Si—O—Al linkages were detected in the spectrum of the silane copolymer/aluminium interface, we conclude that interfacial hydrogen and covalent bonds account for the adhesion in this system. This conclusion is confirmed by the fact that the silanes are effective at very low concentrations and consequently very strong bonds must have been formed across the interface.

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