

Improved Adhesion Strength Between Aluminum and Ethylene Copolymers by Hydration of the Aluminum Surface

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SYNOPSIS

By immersing aluminum in boiling water, a hydroxyl-covered pseudoboehmite layer is formed on the aluminum surface. The adhesion strength between aluminum foils, hydrated in boiling water for short times, and ethylene copolymers, with vinyl acetate, *n*-butyl acrylate, and acrylic acid, was examined. The laminates were obtained by pressing with 1.2 MPa at 250°C and the peel strengths were measured by a *T*-peel test. By hydrating the aluminum foils, the adhesion strength was doubled for the ester copolymers, while a moderate effect was observed for the acrylic acid copolymer. To understand the adhesion mechanism, the chemical and topographic transformations were followed, using FTIR, SEM, TGA, and BET surface-area analysis. The adhesion mechanism was found to depend on many factors, such as mechanical effects and increased surface area, due to the porosity of the hydrated film formed. The improved adhesion after hydration of the aluminum can also be explained by the fact that new, stronger interactions are formed. A carboxylate formation of carboxylic acid groups and a catalyzed hydrolysis reaction of the ester bond at the interface is also proposed. These reactions change the functionality on the polymer surface and the formation of stronger bonds between the materials is possible. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyethylene–aluminum composite films are important and are widely used, especially in the packaging industry. However, the adhesion between the materials is usually low, due to the low polarity of the polyethylene film. To reach an acceptable level of adhesion strength, it is necessary either to modify the polyethylene or the aluminum surface. One of the most common techniques for increasing adhesion is to introduce polar groups on the polymer surface by oxidation.^{1,2} This can be done by high-temperature extrusion, and the effect can be further improved by ozone treatment of the extruded melt.^{3,4} Another way of obtaining a polar surface is to use a copolymer where the comonomer contains a polar group, for example, acrylic acid or vinyl acetate.

In previous reports, it was found that the effi-

ciency of adhesion depended strongly on the functional group used in the copolymer,⁵ and that Lewis acid-base interactions are formed between the aluminum oxide surface and the functional groups in the copolymer.⁶ An alternative to the modification of polyethylene is to modify the aluminum surface with a coupling agent or another chemical treatment. There exist many coupling agents for this application and, among others, silane^{7,8} and chromium (III) fumarate compounds^{9,10} have been found to form strong assemblies. The improved adhesion strengths in these cases have been explained by a coupling mechanism through interfacial diffusion and interpenetrating crosslinking networks. Good adhesion strength has also been reported¹¹ between polyethylene and acid-anodized aluminum. It was suggested that the mechanism of adhesion involved mechanical keying, due to the penetration of the polymer into the pores of the porous anodic film formed on the aluminum surface.

The aim of this work was to improve the adhesion strength between aluminum and polar ethylene co-

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polymers by increasing the amount of hydroxyl groups on the aluminum surface. By immersing the aluminum in boiling water, an adherent hydroxyl-rich pseudoboehmite layer, containing physically adsorbed water, is formed.¹² An increase in the adhesion strength between hydrated aluminum surfaces and pure polyethylene has been reported.¹³⁻¹⁵ In these cases, long hydration times were used and the increased adhesion strength was suggested to depend on mechanical keying in the porous surface layer that is formed when aluminum is hydrated. Recently it has been shown that strong interactions are formed between a hydrated aluminum surface and functional groups present in ethylene copolymers.¹⁶ This might also have an effect on the adhesion between these materials.

In the present study, the effect of the adhesion strength for aluminum, treated in water for relatively short water boiling times (20–160 sec), has been studied. Many techniques, including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), BET surface-area analysis, and thermogravimetric analysis (TGA), have been used to follow the chemical and topographic changes of the hydrated aluminum surface, as a function of the hydration time. Furthermore, the improved adhesion strength and the complex adhesion mechanism for three polar ethylene copolymers is discussed.

EXPERIMENTAL

Materials

Three different ethylene copolymers were used: poly(ethylene-*co*-vinyl acetate) (EVA), poly-

(ethylene-*co*-butyl acrylate) (EBA), and poly(ethylene-*co*-acrylic acid) (EAA). As a reference material, low-density polyethylene was included in the study. Table I summarizes the comonomer content and some other important specifications of the polymers used. The films used for the testing of the peel strength were made by blown-film extrusion, using extrusion temperatures of 150–180°C, with a film thickness of 200 μm .

An aluminum foil, containing 1.01% Fe, 0.15% Mn, 0.14% Si, and 0.045% Mg, was kindly supplied by Gränges AB, Sweden, and had a thickness of 150 μm . The foils were annealed at 300°C for 16 h in air before hydration or lamination. The annealing has been reported to remove completely all hydrocarbons present from the rolling oil¹⁷ and for that reason the foils were used without further cleaning. The hydration of the aluminum foils was done by immersion in deionized boiling water. Before lamination, the foils were dried in ambient air.

Laminate Preparation and Testing of Peel Strength

The laminates were prepared by pressing one plastic film between two pieces of the 150 μm -thick aluminum foil. When strong bonds between the materials were obtained, this assembly eliminated rupture and extension of the plastic film. The assemblies were pressed together at 250°C for 10 sec at a pressure of 1.2 MPa. After one week at ambient conditions, the peel force was tested in an Instron 1122 by a 180° *T*-peel test, with a crosshead speed of 200 mm/min. The widths of the test strips were 25 mm. The reported values from the peel force measurements represent the mean from ten strips taken from

Table I Data on Polymers Used in the Study

Polymer	Comonomer Content (Wt %)	Comonomer Content ^a (mol %)	Meltindex ^a (g/10 min)	T_m^b (°C)	Crystallinity ^b (%)	Producer
LDPE			4.5	112	45	Neste
EBA-4	17	4.3	4	98	21	Neste
EBA-8	27	7.5	4	93	14	Neste
EVA-7	18	6.7	2	88	19	Exxon
EVA-18	40	17.8	55	54	< 4	Atochem
EAA-1	3	1.2	11	104	36	Dow
EAA-3	6.5	2.6	9	101	29	Dow
EAA-4	9	3.7	10	98	24	Dow
EAA-6	13.5	5.7	11	96	17	Exxon

^a Values from the producers.

^b Determined by DSC with dotriacontane as a reference.

two laminates. The mean standard deviation of all laminates was 62 N/m.

In the wet-strength test, the laminates were immersed for four weeks in deionized water at room temperature before the *T*-peel test. The laminates used in the wet strength test were prepared by pressing a plastic film to one untreated aluminum foil or to one aluminum foil hydrated for 30 sec. This type of laminate was chosen to allow penetration of water through the polymer film, which better imitates real aging conditions.

Sample Preparation for FTIR Analysis

A thin polymer layer on 150 μm -thick hydrated aluminum foil (40 sec hydration time) was prepared by first pressing a polymer film to a foil at 150°C. The low temperature was chosen to reduce the evaporation of the physically adsorbed water from the hydrated surface. After repeated dissolution in hot xylene, during which most of the polymer film was removed from the plate, only a thin layer of tightly bonded polymer remained on the surface. The thin polymer layer on the hydrated aluminum surface was then heated to 250°C in the hot press to simulate lamination conditions. To increase the absorbance of the interesting carbonyl peak, the polymers with the highest content of comonomer were used, as shown in Table I.

Analysis

A FTIR spectrophotometer, Perkin-Elmer 1720 X, with a nitrogen cooled MCT detector was used. The aluminum surfaces, with or without a thin polymer layer, were analyzed in a reflection-absorption spectroscopy (RAS) attachment, with an 80° angle of incidence. This technique performs well on highly reflecting substrates, such as aluminum. In the present study, 50 scans, with a resolution of 4 cm^{-1} , were used. To detect the small peaks in the carbonyl region, it was necessary to reduce the water vapor in the background by dry nitrogen purge of the sample chamber. The spectra of the thin polymer layers on the hydrated aluminum foil were ratioed to the reference spectrum from an uncoated foil with the same pretreatment. For comparison, the bulk spectra of the polymers were obtained by casting onto KBr disks.

The carbonyl absorbance ratio was obtained by dividing the absorbances of the carbonyl and the hydrogen stretching vibrations at 1705–1740 and 2920 cm^{-1} , respectively. For each plate, the ratio

measured after the treatment described above was compared with the corresponding ratio obtained from the transmission spectra of the bulk. The reported ratios represent the mean of three spectra.

A JEOL JSM-840 Scanning microscope was used to study the porous structure formed on the hydrated aluminum foils.

The BET surface area, on 150 μm -thick hydrated aluminum foils, was determined as a function of hydration time in boiling water by gas absorption in a Digisorb 2600. Due to the low surface area of the foil, krypton absorption was utilized. The reported values represent the mean of two measurements.

A Perkin-Elmer TGA 7 was used for the thermal gravimetric analysis (TGA) of the copolymers and of the hydrated aluminum foils. The samples were heated in a nitrogen atmosphere, at 200°C/min to 250°C, and then were maintained at that temperature to simulate the lamination conditions. For the analysis of the content of physically adsorbed water, an aluminum foil with a thickness of 14 μm was used. The weight decrease of the hydrated aluminum foils, representing the physically adsorbed water, was obtained after 1–2 min. The reported values represent the mean of two measurements.

RESULTS

In Figures 1(a) and 1(b), the relationship between the peel force and the hydration time of the aluminum foil in boiling water is shown for the ester and the acid copolymers, respectively. For the ester copolymers, a considerable increase of the peel force was found. For the aluminum foils, hydrated for more than 20 sec, the peel force was more than twice as high, as compared to the untreated aluminum foils. A visual observation of the aluminum side of the *T*-peeled laminate indicated that the failure mode had changed from adhesive to cohesive. This indicates that the true adhesion strengths between the materials is higher than the values obtained from the *T*-peel test.

Cohesive failure is confirmed when the aluminum side is analyzed in FTIR, utilizing the RAS technique. Figure 2 shows the absorbance of the asymmetric $-\text{CH}_2-$ stretching vibration band, from the polymer layer, remaining on the aluminum side after peeling. As described elsewhere,¹⁶ it is possible to obtain a calibration curve between absorbance and thickness by analyzing polymer layers of known thickness, obtained by solution casting. This relation is, however, only linear up to about 1000 Å,¹⁸ but in the present work, a linear relation was assumed for

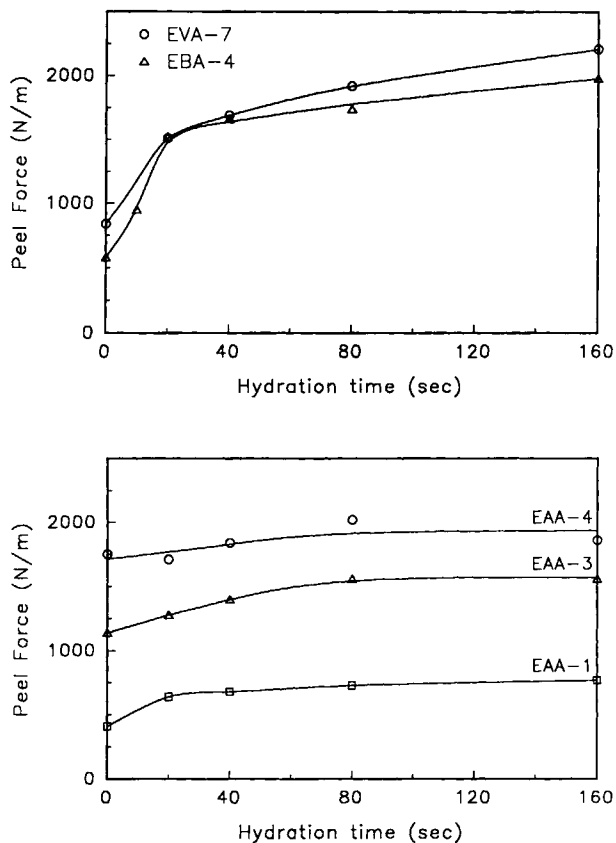


Figure 1 Peel forces for EBA-4, EVA-7, and EAA copolymers, laminated between hydrated aluminum foils, as a function of hydration time: (a) EBA-4 and EVA-7 copolymers and (b) EAA copolymers.

all absorbance values, as shown in Figure 2. It is probable that reported values above 1000 Å should thus be even higher. For all copolymers, the aluminum side with 40 sec hydration time showed absorbances corresponding to several hundreds of

Ångstroms, indicating a cohesive failure. For the untreated aluminum, no polymer was found on the aluminum side for EVA-7, whereas for EBA-4 laminates, a small amount remained. In a previous report,¹⁹ using the same EBA polymer, this small amount was proposed to be due to low molecular weight fractions from the polymer.

The peel force for the acrylic acid copolymers was not improved to the same extent as for the ester copolymers [Fig. 1(b)]. We have earlier found⁵ that EAA-4 gives a cohesive failure when peeled from an ordinary oxidized aluminum surface. The relatively high amount of remaining polymer on the untreated aluminum surface, observed for all EAA samples, as shown in Figure 2, indicates a strong interaction between the acrylic acid group and aluminum oxide. The failure mode for the EAA samples can thus be regarded to be mainly cohesive. The possibilities of forming even stronger bonds, due to the hydration of the aluminum, should not lead to increased peel forces in accordance with the observed results.

The lower peel force for EAA-1 and EAA-3, as compared with EAA-4, may be explained by the lower comonomer content. A possible explanation for this can be that the probability of a molecule being strongly bonded in more than one position to the aluminum oxide surface increases as the comonomer content increases. An interfacial entangled network could then be formed where polymer molecules are entangled into molecules that are bonded in more than one position to aluminum. As the comonomer content increases, the fraction of molecules bonded in more than one position, and the interfacial network density, increase, resulting in a higher cohesive strength. The decreased amount of polymer remaining on the untreated aluminum surface for EAAs with lower comonomer content supports this.

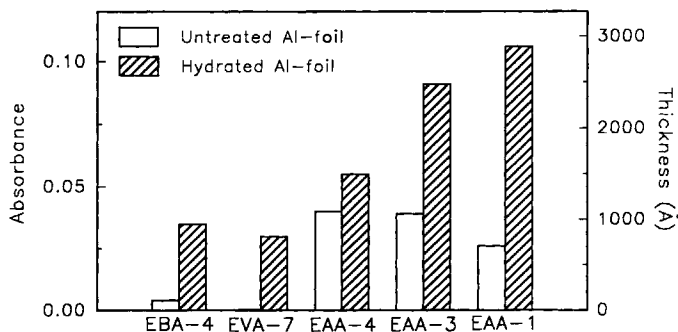


Figure 2 The absorbance of the asymmetric $\text{—CH}_2\text{—}$ stretching vibration mode at 2920 cm^{-1} and corresponding thickness of remaining polymer on the aluminum side after peeling.

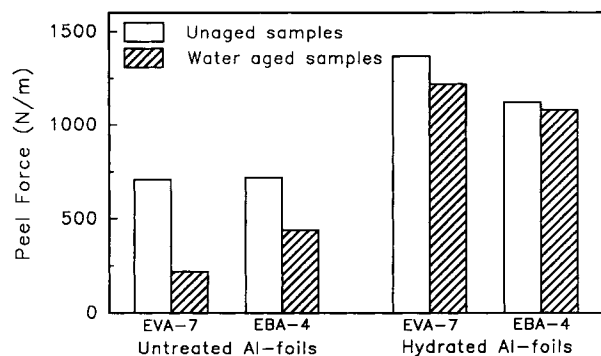


Figure 3 Peel force for the ester copolymers laminated to untreated and hydrated aluminum foils after aging in deionized water at room temperature, as compared with the peel force of unaged samples.

The wet adhesion strength was tested by aging laminates for four weeks in deionized water at room temperature. To obtain maximum exposure to water, the laminates used in this test consisted of one plastic film and one aluminum foil. The reported values of the peel force may, therefore, deviate somewhat from those obtained for the laminates with two aluminum foils. For laminates between the ester copolymers and untreated aluminum, the peel force decreased, due to aging in water (see Fig. 3). For the foils hydrated for 30 sec, no distinct decrease of the peel force was found, which supports the suggestion that these copolymers are more strongly bonded to the hydrated surface. The peel strength for the EAA copolymers were tested for laminates prepared and aged in the same way. In this case, the aging conditions had no effect on the peel force for EAA-1 laminated to either untreated aluminum or hydrated aluminum. The same behavior seemed to be true for the EAA copolymers with higher comonomer content, but rupture of the film, due to the higher cohesive strength, made it difficult to peel these laminates.

DISCUSSION

When aluminum is immersed in boiling water, hydrogen gas evolves from the surface after a few seconds. This is due to the production of an adherent layer of an hydrated aluminum oxide, according to the reaction:



The aluminum and water reaction has been extensively reviewed by Alwitt.²⁰ In boiling water, a poorly

crystallized pseudoboehmite film is formed on the aluminum surface. The chemical composition of this layer can be described as an aluminum oxyhydroxide containing physically adsorbed water.

The formation of the pseudoboehmite film can be followed by means of reflection absorption IR spectroscopy. In the spectrum of an untreated surface, only a weak absorbance at 960 cm^{-1} appears, due to bending modes in the thin aluminum oxide film. After hydration, new absorbances arise,¹⁶ representing hydrogen stretching, physically adsorbed water, and a strong characteristic bending mode of the hydroxyl group at 1080 cm^{-1} . In Figure 4, the absorbance at 1080 cm^{-1} is used to detect and follow the hydration reaction as a function of immersion time in boiling water. The rate of hydroxyl formation is high initially and then decreases, which also can be established by visual observation of the hydrogen gas evolution. The curve in Figure 4 also shows that there is an induction period of about 5–7 seconds, where no reaction occurs. This induction period has been found to vary with temperature and pretreatments of the foil, which is believed to be due to the presence of an oxide film on the metal.^{22,23}

When the aluminum foil is hydrated in boiling water, the topography of the foil is also altered and a highly porous surface is obtained. The appearance of a porous surface was studied by means of SEM and gas absorption and it was found that the topography of the aluminum surfaces altered simultaneously with their chemical conversion. In Figure 5, SEM micrographs of the surface are shown for an untreated aluminum foil and foils with 10–160 seconds of hydration time. From micrographs of hydrated aluminum foils (magnified $10,000\times$), the size of the pores can be estimated to be about $0.1 \mu\text{m}$.

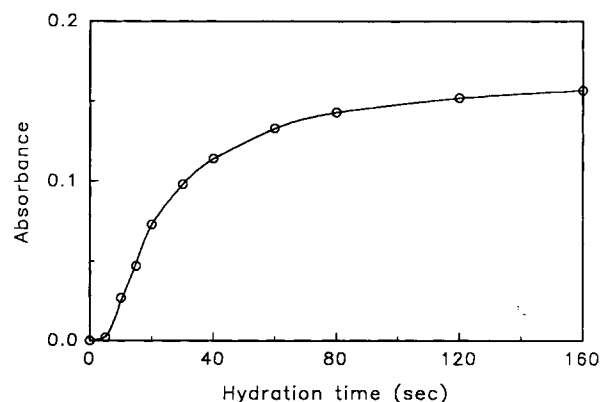


Figure 4 The absorbance of the —OH bending vibration mode at 1080 cm^{-1} , on hydrated aluminum surfaces, as a function of hydration time.

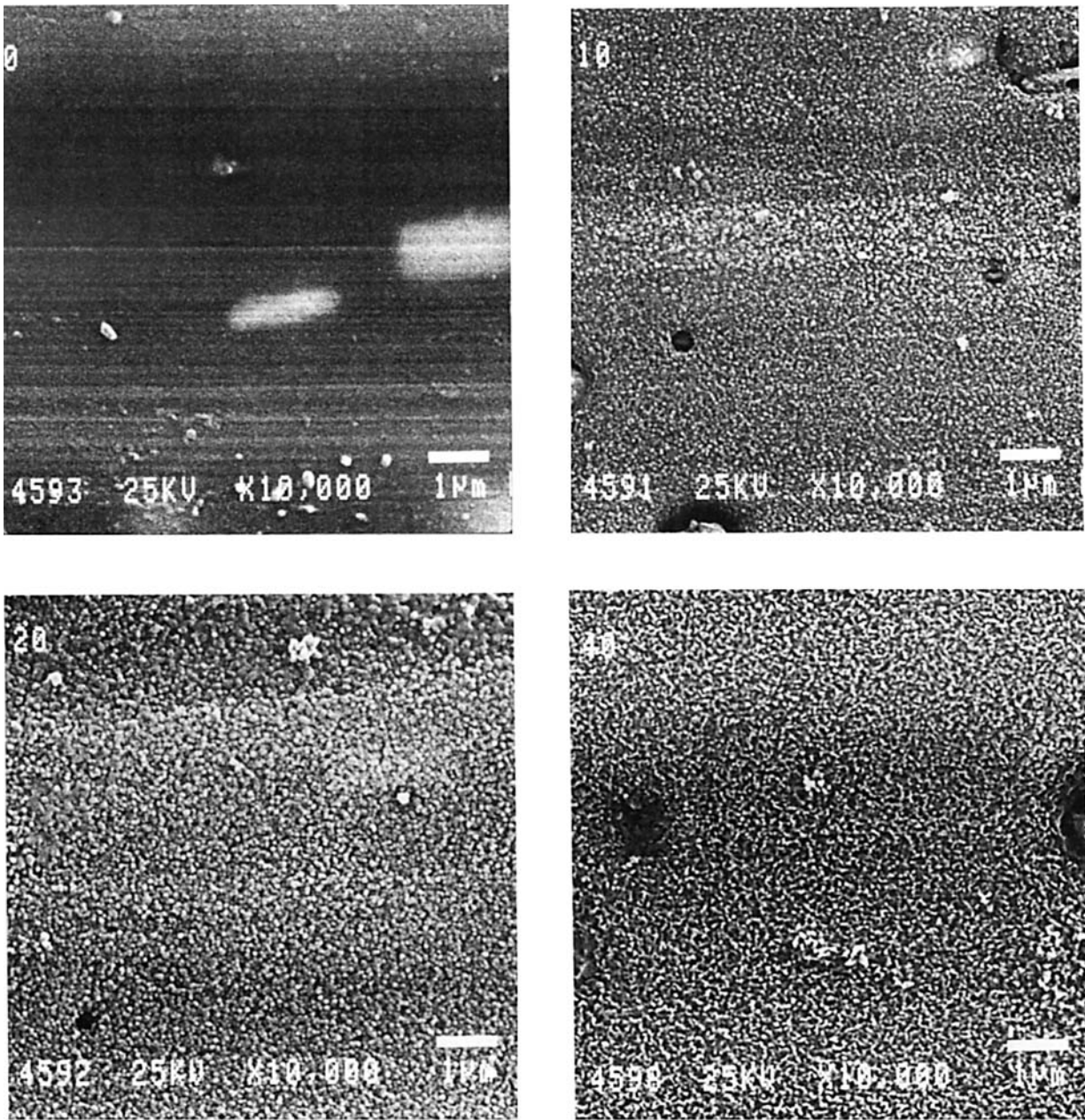


Figure 5 Scanning electron micrographs on aluminum foils: (a) untreated, (b) hydrated for 10 sec in boiling water, (c) 20 sec, (d) 40 sec, (e) 80 sec, and (f) 160 sec.

The improved adhesion strength observed for the ester copolymers may thus be due to both chemical and topographical changes. To investigate how the topographical changes of the surfaces influence the adhesion strength, the peel force was tested for laminates with LDPE as a function of hydration time. From the results, exhibited in Figure 6, it is clear that the peel force increases as an effect of the hy-

dration. When the fracture surfaces were examined, a cohesive failure was obvious. Since LDPE does not contain any polar functional groups, no polar interactions should be present. The increased adhesion strength that was obtained for LDPE can thus be explained by mechanical keying in the porous surface. This also ought to contribute to the increased adhesion strength for the copolymers.

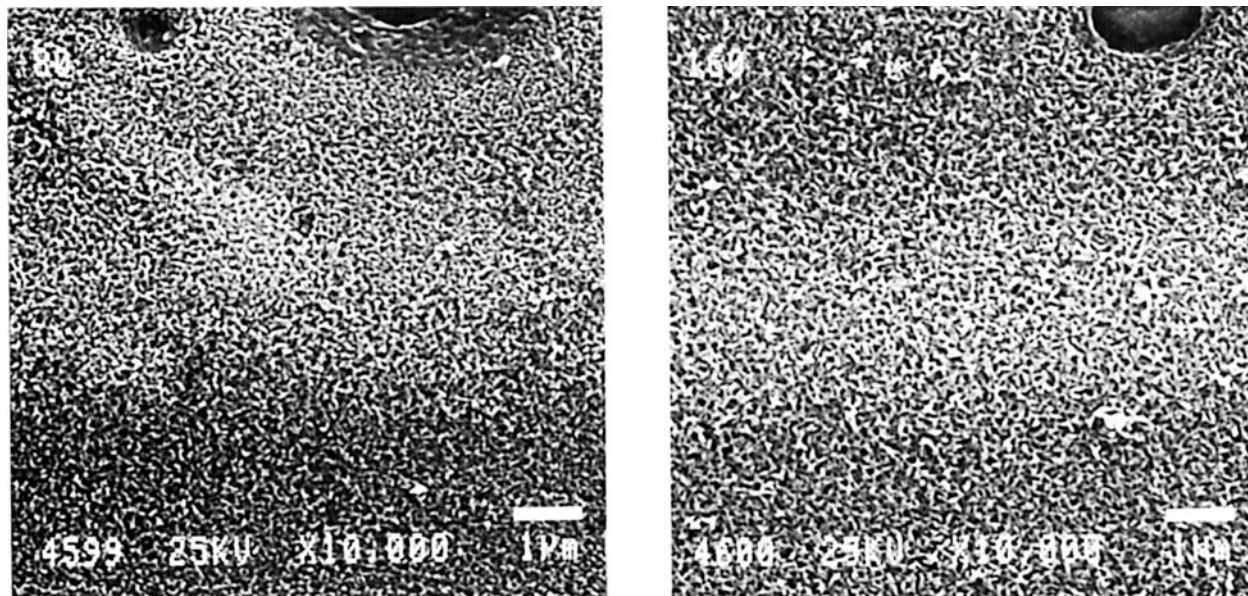


Figure 5 (Continued from the previous page)

BET surface area analysis showed that the hydration increased the surface area by about 20 times (see Fig. 7). At long hydration times, the increase in surface area slowed down, most likely due to the decreased reaction rate described above. The formation of a denser film with decreased porosity at a long hydration time²⁴ may also contribute. However, the increased surface area obtained after hydration increases the contact surface between adhesive and substrate. In turn, the amount of polar or dispersive forces between the materials increases, leading to better adhesion in itself, whether mechanical keying is obtained or not.

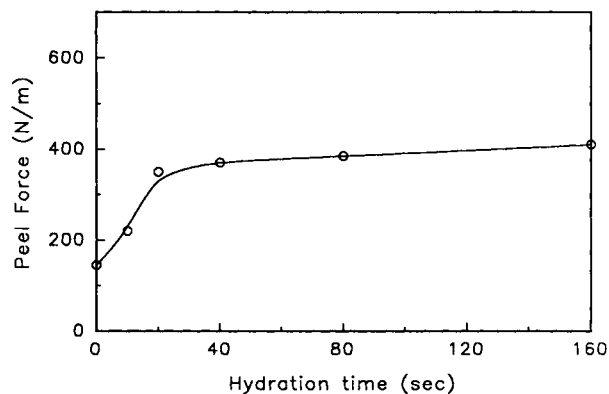


Figure 6 Peel force for LDPE laminated to hydrated aluminum as a function of hydration time.

In a previous report,⁶ it has been stated that the functional groups used in the present study interact via acid-base interactions, with an oxidized aluminum surface. When the amphoteric aluminum oxide surface is hydrated into pseudoboehmite, it becomes more acidic,²⁵ which allows a stronger acid-base interaction to the electron donating carbonyl oxygen in EVA and EBA. This was demonstrated clearly in an FTIR study¹⁶ at the interface between these materials. The interacted carbonyl in EBA was thus displaced 38 cm^{-1} apart from the bulk absorbance, due to a hydrogen bond with the hydroxyl groups on the hydrated surface. In a similar study at the interface on an oxidized aluminum surface,⁶ the carbonyl for the same polymer was displaced at 8 cm^{-1} . The magnitude of the carbonyl displacement has been shown to be directly proportional to the enthalpy of the acid-base interaction by Fowkes et al.^{26,27} Consequently, the modification of the chemical structure on the surface also has a great influence on the adhesion strength and contributes to the improved adhesion.

In the present study, the high temperature used for lamination leads to new interactions at the interface. For a study at the interface, model experiments were made to simulate the lamination conditions, as described in the experimental section. The thicknesses of the polymer layers, that remained on the aluminum surface after dissolution, were estimated as described above to be about $250\text{--}300\text{ \AA}$,

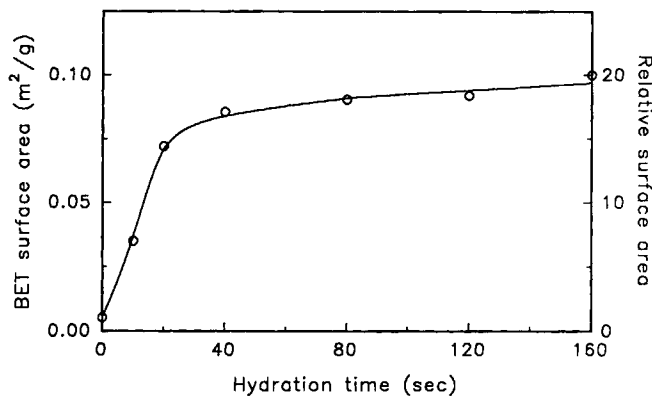


Figure 7 BET surface area on 150 μm -thick aluminum foils as a function of hydration time in boiling water. The right scale represents the relative surface area of the hydrated foils, as compared with an untreated foil.

as related to the projected area. If the increase in surface area is considered, this corresponds to an actual thickness of 10–20 Å. In Figure 8, the carbonyl and hydrogen stretching regions are shown for a thin film of EVA-18 on an aluminum plate, hydrated for 40 sec. In spectrum A, a small peak is visible besides the bulk carbonyl, probably due to an interaction and the formation of a hydrogen bond. Spectrum B represents the same film after 10 sec under a pressure of 250°C, and an immediate decrease of the bulk carbonyl absorbance is observed. In that case, no other peak was visible in this region. For EVA-18, as well as for the other copolymers used, the ratio between the absorbance modes of the C=O stretch (around 1740 cm^{-1}) and the asymmetric $-\text{CH}_2-$ stretch (at 2920 cm^{-1}) was found to de-

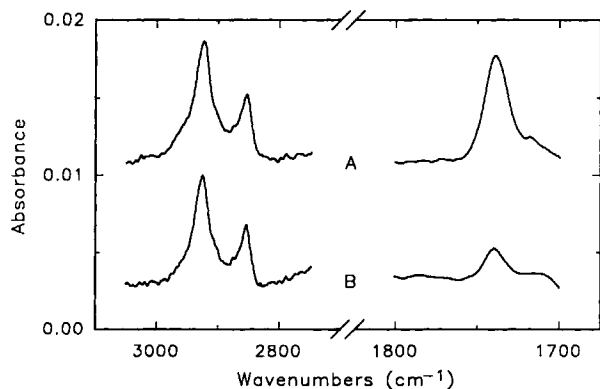


Figure 8 Spectra of hydrogen and carbonyl stretching regions of remaining polymer layer after dissolution. (A) EVA-18 pressed onto the hydrated aluminum plate at 150°C and (B) the same plate after 10 sec in press at 250°C.

crease. This is shown in Figure 9, as a function of time under pressure at 250°C. The quick leveling off to a nearly constant value of the carbonyl ratio indicates a rapid reaction of functional groups in contact with the surface, leaving those groups, which are not in contact with the surface, unchanged.

In a previous study,¹⁶ carboxylate has been shown to form when EAA is cast onto an hydrated aluminum surface. The FTIR spectrum of EAA, after dissolution of a pressed film onto hydrated aluminum, also indicates carboxylate formation.⁶ In work by Schultz et al.,²⁸ the adhesion strength for a laminate, consisting of acrylic acid grafted polyethylene and aluminum, increased after it had been immersed in boiling water. Also in this case, the improvement was explained to be due to a carboxylate formation

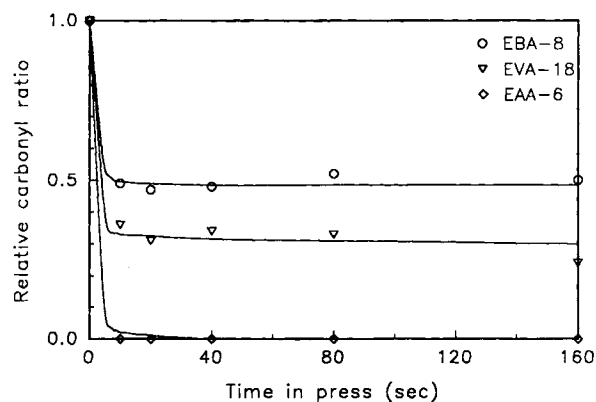


Figure 9 The relation between the carbonyl ratios (1705–1740/2920) of bulk and thin polymer layers, melt pressed on hydrated aluminum foils, as a function of time in the hot press.

between the polymer film and the aluminum surface. Consequently, the disappearance of the carbonyl absorbance, as shown in Figure 9 for EAA-6, is likely due to carboxylate formation with the hydrated aluminum. The formation of a strong ionic bond between the materials should increase the adhesion strength between the polymer and the aluminum surface. In the present study, it was, however, not possible to observe any great improvement due to the fact that cohesive failures were obtained with both untreated and hydrated aluminum.

The decrease of the carbonyl absorbance for the ester copolymers requires a more complex explanation. If there are abstractable hydrogens on the β carbon atom of the ester group, ester copolymers are susceptible to thermal degradation. Acetic acid is thus expelled from the vinyl acetate copolymer and a double bond appears in the polymer chain backbone,²⁹ while a degradation of EBA results in the evolution of butene and the formation of carboxylic acid groups on the polymer chain.^{30,31} The IR spectra of the heat-treated samples did not indicate any occurrence of thermal degradation, that is, vinylene groups or carbonyl formation due to oxidation. Furthermore, a TGA-analysis of EVA-18 and EBA-8 showed that the weight loss after 30 min at 250°C was 0.5% and 0.2%, respectively, which is too low to explain the decrease in carbonyl absorbance (Fig. 9).

It is more likely that the evaporation of the physically adsorbed water from the hydrated surface induces hydrolysis of the ester. The initial weight loss at 250°C, which is due to physically adsorbed water, was determined using a 14 μm -thick aluminum foil, hydrated in boiling water. Together, with the weight increase due to hydration, this allowed calculation of the water and AIOOH content as well as the relative composition of the hydrated film (Table II). The induction period for the foils was 10 sec longer, which could yield small differences as compared with the thicker foil, but the general behavior should be

the same. The amount of evaporated water after 40 sec hydration ($2.8 \mu\text{g}/\text{cm}^2$) is enough to hydrolyze all ester groups in a 3500 Å-thick layer of the sample with the highest comonomer content, EVA-18. It is, however, unlikely that hydrolysis is obtained without any catalyst under these conditions. As already mentioned, it has been shown that the ester carbonyls interact strongly with the hydroxyl groups on the hydrated aluminum surface. It is thus probable that an acid-catalyzed hydrolysis reaction takes place at the interface when water is present.

Hydrolysis of the ester can then explain the decrease in carbonyl absorbance (Fig. 9). In case of EBA, carboxylic acid groups are formed, which immediately react and form carboxylate couplings, as described for EAA. In an earlier FTIR study,⁶ at the interface between EBA and hydrated aluminum in pressed laminates, the formation of carboxylate was found. The ionic bond, formed for EBA at the interface with hydrated aluminum, must be considered to be much stronger than the previously observed acid-base interaction that forms with the untreated aluminum surface.⁶

In the case of EVA-18, a hydrolysis reaction will produce a hydroxyl group on the polymer chain, which has been found to have a better effect on adhesion to an oxidized aluminum surface than the ester group.⁵ Unfortunately, the substrate surface adsorbs strongly in the IR region, where the characteristic absorbances of a C—OH group should appear. For this reason, it has not been possible to confirm this group in EVA with IR spectroscopy. However, the chemical change of the surface after hydration is important for the adhesion mechanism, and contributes to the observed increase of the adhesion strength for both EBA and EVA.

The higher equilibrium level of the carbonyl ratios, shown in Figure 9, obtained for the ester copolymers as compared with the acrylic acid copolymer, may depend on the hydrolysis reaction. For this reaction, the contact with the surface, as well

Table II Compositions and Characteristics of Hydrated Films Formed on a 14 μm -Thick Aluminum Foil

Hydration Time (sec)	Weight Increase (%)	Water Content ^a (%)	H ₂ O ($\mu\text{g}/\text{cm}^2$)	AIOOH ($\mu\text{g}/\text{cm}^2$)	Molar Ratio (AIOOH : H ₂ O)
40	1.11	0.15	2.8	18	1 : 0.52
80	1.32	0.21	4.0	21	1 : 0.63
160	1.64	0.28	5.3	26	1 : 0.69

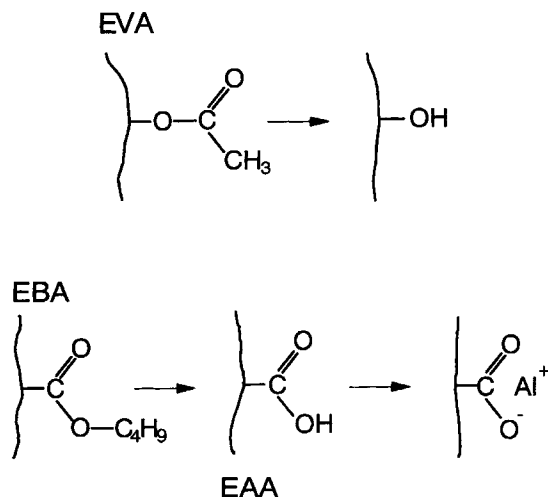
^a Determined by TGA.

as the access of water, are important factors. In the case of EAA, only one of these factors is involved in the formation of carboxylate groups, which probably also occurs more readily and with a higher rate than the hydrolysis reaction.

CONCLUSIONS

In laminates with EBA and EVA, the adhesion strength was found to increase, and it doubled after hydration of the aluminum surface. The failure mode of these laminates was also observed to change from adhesive to cohesive. For EAA, on the other hand, only a moderate effect was observed, because a strong bond already existed to the oxidized aluminum surface. The adhesion strength was found to depend on many factors, due to the fact that a porous surface and a new chemical composition develops after hydration. As shown for LDPE, mechanical keying in the porous surface leads to an increase of the adhesion strength. The higher surface area after hydration increases the contact surface and more adhesion-promoting interactions can be obtained, which improves the adhesion strength.

As a consequence of the chemical modification of the surface, new chemical interactions or bonds were formed between the materials. For EAA, an ionic carboxylate forms at the interface with the hydrated aluminum surface. For the ester copolymers, the high temperature used at the lamination conditions evaporates physically adsorbed water, which was suggested to induce a catalyzed hydrolysis reaction of the ester bond. New functional groups were thus obtained as summarized below:



For EVA, acetic acid is expelled and a hydroxyl

group remains on the polymer chain that may form a stronger interaction to the substrate surface. EBA, on the other hand, was suggested to form a carboxylic acid group, which reacts further with aluminum hydroxyl groups on the surface to form a carboxylate at the interface. Thus, both the hydroxyl group and the ionic carboxylate bond are important factors that also may contribute to the improved adhesion strength observed between the polymers and hydrated aluminum.

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