

Functional Group Efficiency in Adhesion between Polyethylene and Aluminum

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Synopsis

The effect of different functional groups on the adhesion between polyethylene and aluminum has been studied. Poly(ethylene-co-butyl acrylate) (EBA) and poly(ethylene-co-vinyl acetate) (EVA) were used as such and provided polyethylene surfaces with two different kinds of ester groups, butyl ester and acetate, respectively. By alkaline hydrolysis in an organic solvent the surface functionality could be changed to carboxylate and hydroxyl, respectively. Finally, acid washing converted the carboxylate groups into carboxylic acid. The effect of the surface treatments were followed by reflection IR. T-peel tests of laminates made of the original, as well as the surface-treated polymers, and aluminum allowed an evaluation of the specific contribution to the adhesion for the groups in question. The peel strength increased linearly with the bulk concentration of comonomer in the original EBA and EVA samples. The values increased from about 100 N/m for polyethylene up to 2500 N/m in the case of 3.7 mol % of carboxylic acid. The efficiency of the investigated functional groups increased in the following order: $-H \ll -O-CO-CH_3 < -CO-O-C_4H_9 < -COONa \approx -OH < -COOH$.

INTRODUCTION

Whether a polyolefin is used as substrate or adhesive, its bondability characteristics are usually not good enough. For a long period of time, several effective pretreatments have been used in the industry to improve the adhesion properties of polyolefins, e.g., corona discharge treatments, high temperature oxidation, flame treatments, and chromic acid etching. The method of choice normally depends on the shape and size of the object.

Although surface oxidation reasonably should occur in most of these treatments, there has been a lot of discussion about the reason why the adhesion of polyolefins is improved. Several suggestions have been forwarded: improved wettability due to increased surface energy, removal of weak boundary layers, increased possibilities to mechanical keying due to morphological changes, and increased interaction across the interface as a result of the introduction of specific functional groups onto the polymer surface. These theories have been described and evaluated in a recent review by Brewis and Briggs.¹

With the advent of ESCA (electron spectroscopy for chemical analysis) the possibilities of elucidating changes in the surface composition of polymers submitted to various treatments were considerably improved. It is obvious that the pretreatments mentioned above lead to the introduction of polar groups including carbonyl, carboxylic acid, hydroxyl, hydroperoxides, amino,

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and sulfonic acids. It is also clearly demonstrated that the adhesion of polyolefins is related to the oxidation level of the surface.¹⁻⁴ Furthermore, the performance of ESCA in the detection of surface functional groups has been extended by using derivatization techniques. This results in the incorporation of specific labels for functional groups in the surface.⁵⁻⁷ However, it is very difficult to determine the specific contribution of individual groups to the observed increase in adhesion. Very recently a few attempts to such correlations have been published involving polyethylene-epoxy⁸ and polyethylene-aluminium⁵ interfaces.

In an earlier paper,⁹ we showed how the adhesion between aluminum and polyethylene increased with the content of butylacrylate (EBA) and vinylacetate (EVA) as comonomers. The acrylate group had a somewhat higher efficiency. Most remarkable was that corona discharge treatment of these copolymers was much more effective than with polyethylene. In fact, the observed peel strengths exceeded those obtained with an ionomer under the conditions used. Most likely, the distinct improvements observed for EBA and EVA can be related to increased sensitivity towards oxidation as well as conversion of acrylate and acetate groups into carboxylic acid and hydroxyl, respectively. In the present paper we present results from an investigation involving alkaline hydrolysis of EBA and EVA surfaces and its effect on the adhesion to aluminum. In this way, some of the functional groups suspected of being responsible for the increased adhesion upon corona treatment would be more specifically introduced onto the surface. Furthermore, a comparison between the peel forces obtained with EBA, EVA, and their modified counterparts have allowed an evaluation of the specific contribution to the adhesion between polyethylene and aluminum for the functional groups in question.

EXPERIMENTAL

Materials

The aluminium foil used was kindly supplied by Gränges Aluminium AB, Sweden. The thickness was 300 μm and the foil was heated at 300°C for 24 h. The content of other elements was (wt %): Cr, 0.001; Fe, 1.04; Mn, 0.16; Si, 0.032; Ti, 0.017; and Zn, 0.014. Before being used the foil was degreased with tetrachloroethylene and wiped with acetone.

The polymers used included: one low density polyethylene (LDPE) and three poly(ethylene-co-butylacrylate) (EBA 1-3) from Neste Polyethylene AB and three poly(ethylene-co-vinylacetate) (EVA) from Esso Chemicals. All polymers were free from additives like antioxidants and antiblocking agents. Some specifications are given in Table I. Film was obtained from the polymers by blow extrusion at 165°C. The thickness of the film was ca. 200 μm .

Hydrolysis

Surface hydrolysis was performed by treating the film in a solution of NaOH in water or *i*-propanol at 40-60°C. The concentration of alkali was 6 and 0.1-0.2 mol/L, respectively. After hydrolysis the films were thoroughly rinsed with distilled water. To exchange Na with H the saponified EBA

samples were treated with 0.1M HCl at 50°C for 2 h, and thereafter rinsed with water.

Preparation and Testing of Laminates

The film samples were placed between two aluminum foils (20 × 20 cm) and the assembly was pressed together for 10 s in a press heated to 250°C using a pressure of 5 MPa. Before testing the laminates were conditioned for 7 days at 50 ± 3% RH and 23 ± 1°C.

The adhesion was measured by a T-peel test using an Instron tensile machine. The speed of the crossheads was 200 mm/min, and the width of the test strips was 25 mm. The reported values of the peel force (N/m) represent the mean from measurements of 12 strips from two laminates.

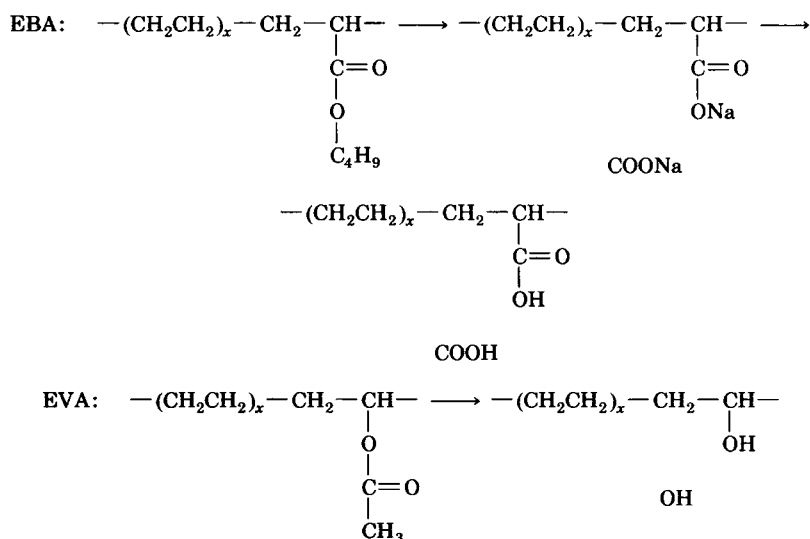
Characterization

The polymers were characterized using gel chromatography, calorimetry, and NMR. Details of the analysis have been given earlier.⁹ To follow the structural changes induced by the hydrolysis MIR spectra were recorded with a Perkin-Elmer 399 IR spectrometer using a multiple reflection accessory with a KRS-5 crystal.

RESULTS AND DISCUSSION

Hydrolysis

With the reagents used, the following reactions should occur:



EBA and EVA and their modified counterparts, COONa, COOH, and OH, would thus allow an evaluation of the contribution to adhesion for butyl ester, acetate, carboxylate, carboxylic acid, and hydroxyl. In order not to change the structure and properties of the bulk, we intended to perform a surface hydrolysis only. The reactions were therefore made with samples of blown

TABLE I
 Data on Polymers Used

Sample	Content of comonomer (mol %)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$[\eta]$ (dL/g)	T_m (°C)	Crystallinity (%)
LDPE	—	14.2	189	0.84	113	53
EP ^a 1	0.70	15.1	124	0.84	110	47
EL . . 2	1.81	24.8	180	0.90	103	36
EBA 3	3.65	17.3	122	0.81	99	30
EVA 1	0.48	20.5	100	0.88	111	49
EVA 2	1.37	19.8	214	0.92	106	44
EVA 3	6.02	24.9	167	0.98	86	22

film, which later were used to obtain laminates by hot pressing. Using EBA-2, we tested a wide range of reaction conditions and followed the extent of reaction with MIR.

In a heterogenous reaction between a polymer surface and a solution, the nature of the solvent might be much more important than for the corresponding reaction performed in a homogenous system. The reaction rate should, e.g., increase with the swelling power of the solvent. The MIR spectra (see Fig. 1), of samples treated at 50°C for 24 h using two different solvents clearly demonstrate this effect. The extent of hydrolysis can be followed by a decrease of the ester carbonyl (1740 cm^{-1}) and a parallel increase in carboxy-

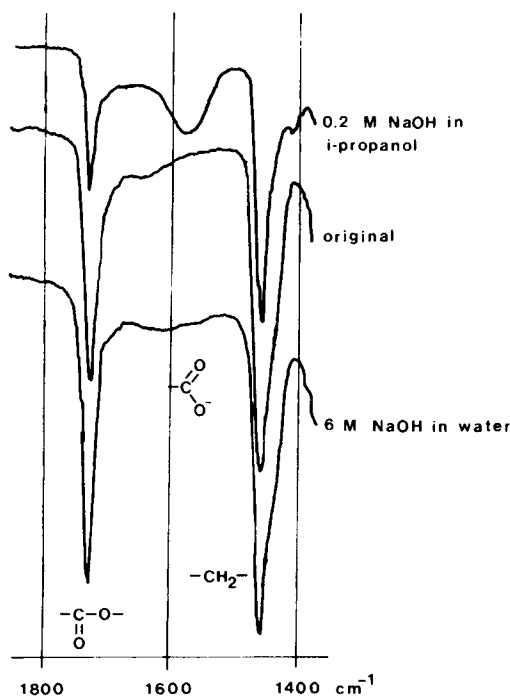


Fig. 1. Change in infrared spectra of EBA-2 in the region $1400\text{--}1800 \text{ cm}^{-1}$ due to alkaline hydrolysis using water ($6M$ NaOH) or *i*-propanol ($0.2M$ NaOH) as solvent; temperature 60°C .

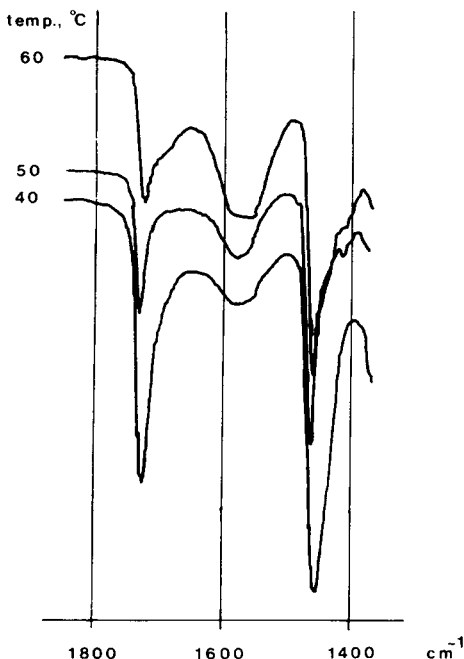


Fig. 2. Change in infrared spectra of EBA-2 in the region $1400\text{--}1800\text{ cm}^{-1}$ due to hydrolysis at different temperatures; *i*-propanol, $0.2M$ NaOH.

late (1575 cm^{-1}) using the C—H stretch at 1465 cm^{-1} as reference. Although the concentration of alkali in water was as high as 6 mol/L , hardly any hydrolysis could be detected. Using *i*-propanol as solvent, on the other hand, a substantial conversion was obtained with only 0.2 mol/L NaOH. Obviously, the organic solvents penetrate the polymer much better, resulting in a higher concentration of reactant at the locus of reaction. In patents¹⁰ describing the production of ionomers from ethylene-acrylate copolymers, the use of, e.g., alcohols is indeed recommended.

We have also tested the effect of temperature on the hydrolysis of EBA in *i*-propanol. As expected, the degree of conversion increased with increasing temperature (Fig. 2). Besides an increased rate constant, this could also be due to increased availability and mobility of ester groups.

Figure 3 shows the carbonyl region of MIR spectra of EBA-2 hydrolyzed with $0.11M$ NaOH in *i*-propanol at 60°C for 1–24 h. After 1 h the extent of reaction is almost too low to allow a discrimination with the original sample. With increasing time, however, the absorbance of carboxylate grows and that of ester carbonyl diminishes. A plot of these absorbances relative to the reference peak at 1465 cm^{-1} indicates that the reaction rate decreased after about 10 h. However, it must be remembered that the spectra were obtained using the MIR technique, which has a penetration depth of a few micrometers. The decreased rate can instead be taken as an indication that the reaction was approaching 100% conversion within the depth of observation. Most likely, the reaction proceeded even deeper but without contribution to the MIR spectra.

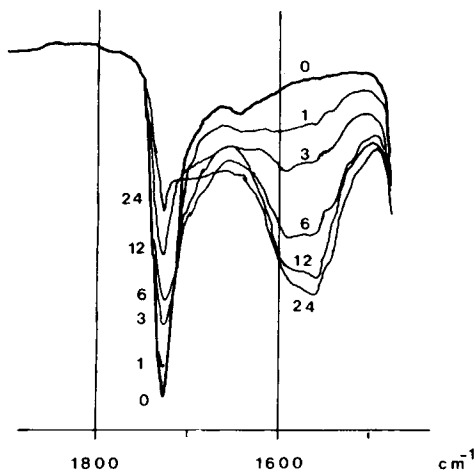


Fig. 3. Change in infrared spectra of EBA-2 in the region $1500\text{--}1800\text{ cm}^{-1}$ as a function of hydrolysis time (h); *i*-propanol, $0.11M$ NaOH, 60°C .

Although 1 h of reaction is too short to induce any changes in the MIR spectrum, the adhesion properties should, on the other hand, mainly be related to structural changes in a very thin surface layer, i.e., 100 \AA or less. To monitor the extent of surface reaction, we have used the peel strength of laminates. The hydrolysis of EBA-2 clearly improved the adhesion to aluminum, and the maximum strength was reached after a reaction time of 1–2 h (Fig. 4). Somewhat more than 1 h thus seems to be enough to obtain 100% conversion in the surface. After 1 h, the MIR spectrum only indicates a very limited change, which suggests that the reaction so far had been restricted to the surface. However, to ensure complete surface hydrolysis we used 21 h as reaction time for the samples used to obtain the data on adhesion discussed in the next section.

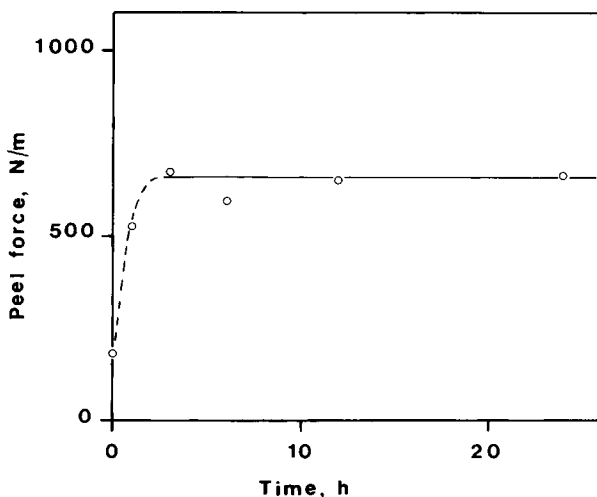


Fig. 4. The relation between the peel force of laminates and the time of hydrolysis of EBA-2; *i*-propanol, $0.11M$ NaOH, 60°C .

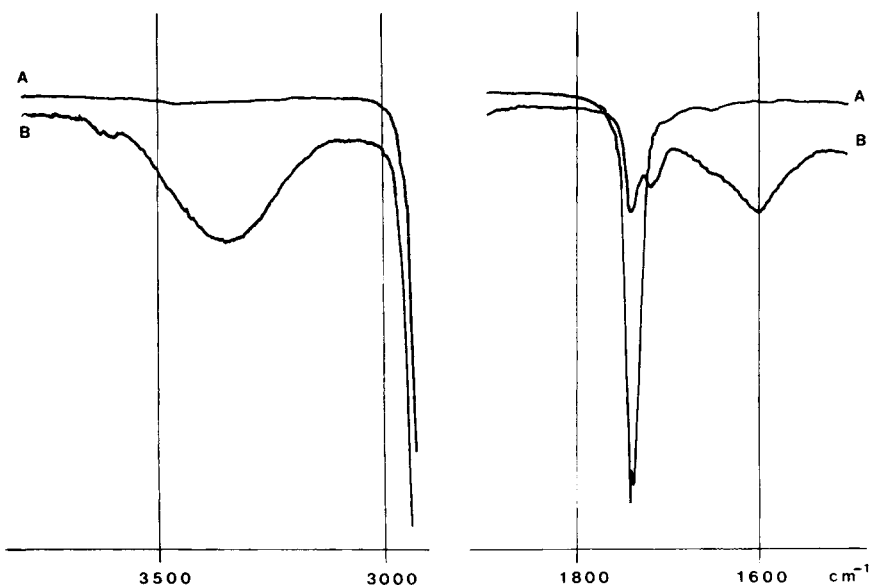


Fig. 5. Change in infrared spectra of EVA due to alkaline hydrolysis at 60°C for 21 h using *i*-propanol (0.11M NaOH) as solvent: (A) original sample; (B) hydrolyzed sample.

Without further investigation we used 0.11M NaOH in *i*-propanol at 60°C to hydrolyze EVA-2 as well. Relevant parts of the MIR spectra of an original and a hydrolyzed sample are given in Figure 5. The disappearance of acetate groups is indicated by the decreased absorption due to $-\text{CO}-$ (1720 cm^{-1}) while $-\text{OH}$ groups become visible at 3300 cm^{-1} .

Adhesion

To evaluate the adhesion a T-peel test was used, and the results are given in Table II and Figure 6. Independent of functional group, the peel strength increases with the bulk concentration of the comonomer. Later investigations have shown that the fracture was adhesive in most cases. An obvious exception was COOH-3, which showed cohesive fracture. Formation of blisters did also interfere with the results for this sample. Most likely, the blisters were

TABLE II
Peel Forces for EBA and EVA and Their Modified Counterparts

Sample	Content of comonomer (mol %)	Peel force (N/m)				
		Original	Hydrolyzed samples			
			Saponified	Acidified		
LDPE	—	75				
EBA 1	0.70	119	COONa 1	224	COOH 1	516
EBA 2	1.81	211	COONa 2	474	COOH 2	1164
EBA 3	3.65	493	COONa 3	1146	COOH 3	1361
EVA 1	0.48	95				
EVA 2	1.37	132	OH 2	419		
EVA 3	6.02	423				

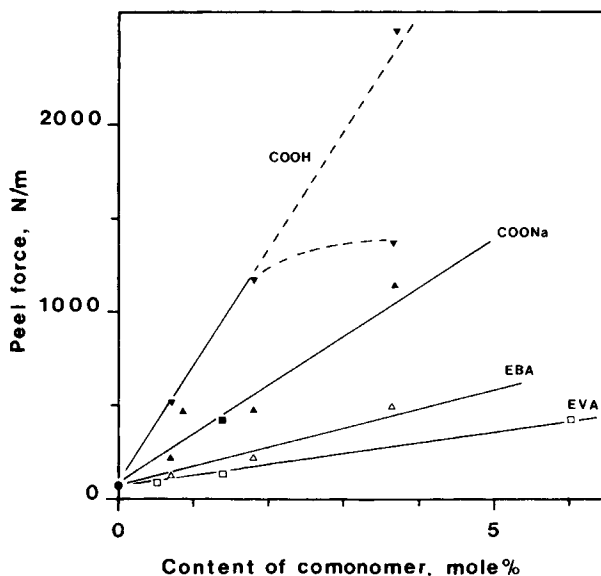


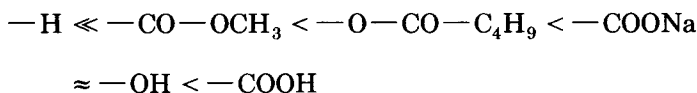
Fig. 6. The relation between the peel force and the content of comonomers for laminates of EBA and EVA and their modified counterparts; (Δ , \square) untreated samples; (\blacktriangle , \blacktriangledown , \blacksquare) treated samples.

caused by insufficient removal of butanol or solvent after the hydrolysis. To extend the range of COOH—concentration we have therefore added the result obtained with a sample of EAA containing 3.7 mol % acrylic acid. Although cohesive fracture was observed, the peel strength of this sample coincides with the trend given by COOH-1 and COOH-2. The cohesive fracture indicates that the adhesion strength could have been even higher.

The concentration values given in Figure 6 represent the bulk concentrations. The original film samples of EBA and EVA were obtained by film extrusion and the crystallization might have induced a fractionation leading to surface enrichment of functional groups. Using ESCA, we have earlier observed that the surface concentration of butylacrylate in EBA-2 was about two times higher than that of the bulk.⁹ However, we have assumed that the degree of enrichment is proportional to the bulk concentration. The conditions used during hydrolysis—increased temperature and a polar environment—might also have increased the surface concentration of functional groups by migration.¹¹ Considering the differences noted in connection with Figures 4 and 5, it can be suggested, however, that migration only occurs in a relatively thin layer. Eventually, a similar effect is obtained when the polymer melt is in contact with the polar aluminum surface during processing. However, it can not be excluded that the efficiency of the functional groups are somewhat overestimated for the treated samples in Figure 6. The differences between the various functional groups are, on the other hand, obvious and allow an evaluation of their relative efficiency concerning adhesion to aluminum.

With regard to functional groups, the surfaces of EVA, EBA, and their modifications should be dominated by one single structure in each case. This is a much more simple situation compared to that encountered after various

surface treatments, facilitating an evaluation of the efficiency of different groups. The specific contribution to adhesion against aluminum increases in the order:

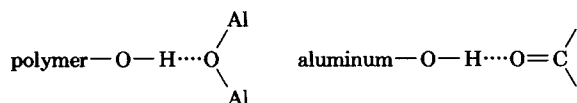


The high efficiency of, e.g., carboxylic acid is known (see, e.g., Ref. 12) and is utilized in EAAs and ionomers, which are considered as bonding polymers. In a recent work the effect of single functional groups on the adhesion of polyethylene to epoxy was discussed.⁸ Similar to our results, $-COOH$ was found to be more efficient than $-OH$. Carbonyl in isolated keto groups gave still higher adhesion. The latter group has also been suggested to have a more general importance in adhesion.¹³

In another recent work Delamar et al.⁵ studied the effect of thermal oxidation and corona treatment on the adhesion between aluminum and polyethylene in laminates obtained by extrusion. By mixing ordinary LDPE with LLDPE they could change the content of functional groups in the surface as determined by specific derivatization and subsequent ESCA analysis. First of all, the adhesion was found to be dependent on the total content of oxygen on the polymer surface. Regarding specific groups, the best correlation was obtained to the sum of the concentrations of hydroxyl and carbonyl groups. The amount of carboxylic acid was almost constant, and no statement was made concerning its participation to the adhesion. On the other hand, our results undoubtedly show that carboxylic acid must be considered to be even more efficient than hydroxyl.

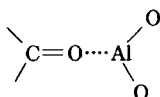
In the discussion above, it has been assumed that the peel strength can be related to the surface chemistry alone. With increasing content of comonomer the crystallinity decreases which increases the tendency to yielding. The use of two aluminum layers implies that substrate as well as backing are inextensible, which minimizes the effect of yielding. However, irreversible work due to yielding in the delamination zone could contribute to the peel force. For the changes induced by the surface hydrolysis, e.g., $EBA \rightarrow COONa \rightarrow COOH$, the bulk properties are not expected to change. This implies that the differences between the functional groups, i.e., a vertical movement in Figure 6, can be related to changes in surface chemistry mainly. For comparisons at different content of comonomer yielding may contribute, but the linear relations indicate a strong correlation between adhesion and concentration of functional groups.

The improved adhesion of polyethylene caused by the various pretreatments is now considered to be mainly due to the introduction of polar groups, some of which are capable of participating in relatively strong specific H bonding interactions.^{1,14} In contact with aluminum, i.e., aluminum oxide, both surfaces may provide the hydrogen, e.g.:

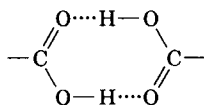


Furthermore, both COOH and OH might react with Al—OH to form covalent bonds across the interface. These bonds would contribute to dry peel strength. However, similar to the other interactions discussed, they are easily hydrolyzed resulting in decreased wet peel strength.

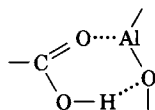
Considering the specific contribution to the adhesion of the nonionic functional groups studied in this investigation two distinct classes can be discerned, butyl ester and acetate, respectively hydroxyl and carboxylic acid. The two former functions cannot contribute hydrogen and show lower adhesion than the two latter. Although hydroxyl groups on the aluminum surface should form hydrogen bonds to EBA and EVA, the concentration of such groups is considered to be rather low for the material used.¹⁵ Another possible interaction would be dipole-dipole forces:



This bond is weaker than the H bonds discussed above, which could explain the lower efficiency of butyl ester and acetate compared to hydroxyl and carboxylic acid. Of the two latter, carboxylic acid is the most efficient, which parallels the differences in H-bond strength observed for low molecular weight alcohols and acids, respectively. This is due to tendency of carboxylic acids to form dimers:



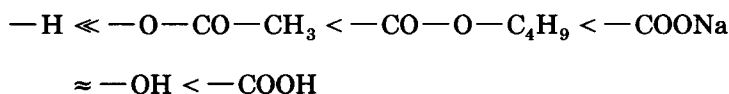
A somewhat similar interaction involving H bonding and dipole-dipole contact can be considered for a carboxylic acid close to a surface of aluminum oxide:



The O—H bond of carboxylic acid is more polarized than that in hydroxyl, which also would contribute to a stronger interaction.

CONCLUSIONS

By using EBA and EVA as well as surface hydrolyzed modifications, it is possible to obtain polyethylene surfaces with a single functional group. T-peel tests of laminates made of such polyethylenes and aluminum have allowed us to evaluate the specific contribution to the adhesion for the groups in question. Their efficiency increased in the following order:



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