

The Effect of Corona Discharge Treatment of Ethylene Copolymers on Their Adhesion to Aluminum

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Synopsis

The efficiency of different techniques to obtain improved adhesion in polyethylene–aluminum laminates have been studied. Both surface treatments, such as thermal oxidation and corona discharge, and the use of copolymers with polar comonomers, i.e., vinyl acetate (EVA) and butyl acrylate (EBA), have been included. Thermal oxidation performed by high temperature extrusion including an ozone shower seems to be more effective than corona discharge. In a model experiment thermal oxidation was studied in more detail. The adhesion, as measured by a T-peel test, increased with the content of carbonyl measured by reflexion IR, except for relatively long thermal treatments. In the latter case molecular scission gave a large fraction of low molecular weight material with low cohesive strength. For EBA and EVA the peel strength increased linearly with the bulk concentration of comonomer from about 100 N/m for untreated polyethylene to 450 and 300 N/m, respectively, at 5 mol % comonomer. Corona discharge treatment of these copolymers had, however, a most remarkable effect on the adhesion properties. The increases, relative to untreated EBA and EVA, were much more dramatic compared to polyethylene, e.g., three to four and less than two times, respectively. The higher values obtained with EBA are suggested to be due to the conversion of acrylate groups into carboxylic acid. In the case of EVA, loss of acetic acid might instead decrease the content of polar groups.

INTRODUCTION

Laminates of polyethylene and aluminum are extensively used, e.g., for food packaging. The combination provides a sealable material with good barrier properties. The adhesion strength between the two materials is, however, too low for many applications. Several different techniques are used in the industry to promote the adhesion, and a number of theories intended to explain their effect have been discussed. This is discussed in a recent review by Brewis and Briggs¹ with the emphasis put on polyethylene and polypropylene surfaces. In most cases the improved adhesion can be related to surface oxidation.

In extrusion coating of polyethylene onto aluminum, it is common practice to use a high extrusion temperature to ensure oxidation. Sometimes an ozone stream is introduced between the die and the nip rolls. Another possibility is to use a corona discharge. The effect of the latter was earlier a matter of dispute, as the techniques used to determine an eventual oxidation, e.g., reflexion IR, gave inconsistent results. ESCA (electron spectroscopy for chem-

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ical analysis) analysis with its low penetration depth, 20–50 Å, has, however, positively shown that corona discharge leads to surface oxidation.^{1,2} By specific labelling and subsequent ESCA analysis it has also been possible to identify and quantify hydroxyl, carbonyl, carboxyl, hydroperoxides, etc. on the surface of corona-treated polyethylene.^{3–5}

Polar groups may also be introduced by copolymerization, which changes the bulk of the polymer. Ethylene copolymers containing vinyl acetate (EVA) or acrylic acid (EAA), as well as partly saponified EAA (ionomers), are examples of polyolefines with increased adhesion properties.

In this paper we have compared the efficiency of different methods to improve the adhesion between polyethylene and aluminum. We have used the peel strength of laminates obtained under favorable conditions, i.e., static pressing, as a relative measure of the interfacial forces. To obtain increased adhesion we have used high temperature oxidation, corona treatment, and ethylene copolymers with polar comonomers, in particular EVA and poly(ethylene-co-butyl acrylate) (EBA).

EXPERIMENTAL

Materials

The aluminum foil used meets the Swedish specification of SIS aluminum 4010 (99% Al), and was kindly supplied by Gränges Aluminum AB, Sweden. The thickness was 70 μm and before use the foil was degreased using tetrachloroethylene.

Nine different polyethylenes and copolymers have been used. Some specifications are given in Table I. The major part of the data was obtained with the LDPE, EBA 1–3, and EVA 1–3 samples. The two last samples in Table I were used for comparison purpose mainly. LDPE-ox was flat extruded at 330°C using an ozone shower, while the ionomer was a Surlyn sample with zink as counterion.

In most cases film was obtained from the polymers by blow extrusion at 165°C, except for LDPE-ox and the LDPE samples used to test the effect of

TABLE I
Data on Polymers Used

Sample	Content of comonomer (mol %)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\lambda \times 10^4$ ^a	$[\eta]$ (dL/g)	MI	T_m (°C)
LDPE	—	20.5	224	3.5	0.80	4.5	111
EBA 1	0.74	31	224	1.9	1.08	0.25	107
EBA 2	1.84	29	163	1.9	0.97	0.9	103
EBA 3	3.91	27	148	3.2	0.81	4.5	98.5
EVA 1	0.49	20.5	100	1.5	0.88	1.5	111
EVA 2	1.59	21	229	2.5	0.94	2.0	104
EVA 3	6.02	25	167	1.8	0.98	1.7	86
LDPE-ox	—	21	517	5.8	0.86	—	105.5
Ionomer	—	—	—	—	—	5.0	97

^a Long chain branching index.⁶

thermal oxidation. For the latter purpose films were instead prepared by pressing at 170°C and 20 MPa for 90 s between Teflon sheets. The thickness of the polymer films were $200 \pm 20 \mu\text{m}$.

Surface Modifications

Surface modifications were made by thermal and corona discharge treatments. For the thermal oxidation an ordinary thermostated oven operating at 300°C was used. The film samples were placed on Teflon sheets and kept in the oven for 20, 30, 40, and 120 s. Thereafter, the films were turned over, and the other side was exposed for the same periods of time. In a blank test with inert atmosphere ($\text{N}_2, \text{O}_2 < 5 \text{ ppm}$), no structural changes could be detected by ESCA measurements, which also showed that no external contamination was introduced in the film pressing.

The corona discharge treatment was performed using a commercial aggregate (Sherman Treaters Ltd., Model GT40) giving an output tension of 15 kV at 17 kHz and having an electrode distance of 1 cm. Input currents of 1 or 2 A (maximal 4 A) were used and the roll speed was 1 m/s.

Preparation and Testing of Laminates

The film samples were placed between two aluminum foils ($20 \times 20 \text{ cm}$), and the assembly was pressed together for 3 s in a press heated to 300°C using a pressure of 5 MPa. Before testing, the laminates were conditioned for 7 days at $50 \pm 3\% \text{ RH}$ and $23 \pm 1^\circ\text{C}$, according to ASTM D 1876-72. During the first 2 days the peel forces increased somewhat to a constant value.

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, expressed in N/m, represent the mean from measurements of 12 strips from two laminates.

Characterization

The content of comonomer in the EBA and EVA samples were determined by $^1\text{H-NMR}$ using a Varian XL200. Spectra were obtained from 3% (w/v) solutions in 1,2,4-trichlorobenzene/benzene- d_6 (3:1) at 90°C. The melting behavior was determined by calorimetry using a Perkin-Elmer DSC-2. A sample of about 5 mg was used, and the heating rate was 10 K/min. All runs were performed in a nitrogen atmosphere, and before analysis all samples were given the same thermal treatment by rapid heating to 150°C and cooling down to room temperature in a controlled manner. The crystallinity was calculated from the area of the melting endotherm using *n*-dotriacontane as a reference.

To determine the molecular weight distribution (MWD), gel chromatography (GPC) and viscometry were used. Details of the GPC analysis have been given earlier.⁶ A Waters Associates GPC Model 200 operating at 135°C with trichlorobenzene as solvent was used for the process. The column combination consisted of five Styragel columns with permeabilities ranging from 10^3 to 10^7 \AA , giving good separation in the molecular weight range of interest. The setup also contained a SEPEMA on-line viscometer of Ubbelohde type includ-

ing a syphon with a volume of 4.95 mL (V_s). The effluent time of pure solvent was 199.50 ± 0.01 s. The intrinsic viscosity ($[\eta]$) was calculated according to

$$[\eta] = \frac{\sum \Delta t \cdot V_s}{t_0 \cdot c_0 \cdot V_i}$$

where Δt is the time difference between solution and pure solvent for each fraction, c_0 is the concentration of polymer in the injected solution, and V_i the injected volume. To calculate MWD and molecular weight averages, the computer program devised by Drott and Mendelson⁷ was used, assuming trifunctional branch points. The calibration curve for linear polyethylene was obtained via the universal calibration curve as described earlier.⁶

To follow structural changes on the polymer surfaces MIR and ESCA spectra were recorded. ESCA spectra were obtained with a HP 5950A spectrometer using an AlK_{α} source (1486.6 eV) operating at 800 W with a background pressure of 10^{-10} torr. To calculate the composition, 1 and 2.5 were used as yield factors for O_{1s} and C_{1s} , respectively.⁸ MIR spectra were obtained with a Perkin-Elmer 399 IR spectrometer using a multiple reflexion accessory with a KRS-5 crystal. The degree of oxidation was determined by the relative content of carbonyl as measured by the ratio between the absorbances for C=O stretching in ketone (1720 cm^{-1}) and C—H bending in methylene (1465 cm^{-1}).

RESULTS AND DISCUSSION

First of all, we would like to stress that all peel tests have been performed with laminates prepared by static hot pressing. The peel forces presented should thus be regarded as optimum values, and they do not necessarily reflect what can be obtained in a continuous process. It should also be pointed out that the use of two aluminum layers implies that the substrate as well as the backing were inextensible. Differences in the bulk properties of the polymers may, however, have caused different degrees of plastic yielding in the delamination zone, thus influencing the peel force.

The values obtained with LDPE, LDPE-ox and the ionomer illustrate the range of the peel force achieved under the given conditions, see Table II and Figure 1. Typically, values of ca. 100 N/m or somewhat lower were obtained for untreated polyethylene, while the ionomer chosen as a reference showed much better adhesion, about 650 N/m using the pressing conditions in question. In order to minimize oxidation, these polymer films had been

TABLE II
Peel Forces Obtained with LDPE, LDPE-ox, and the Ionomer

Sample	Peel force (N/m)
LDPE	86
LDPE, corona-treated (1 A)	150
LDPE, corona-treated (2 A)	162
LDPE-ox	274
Ionomer	647

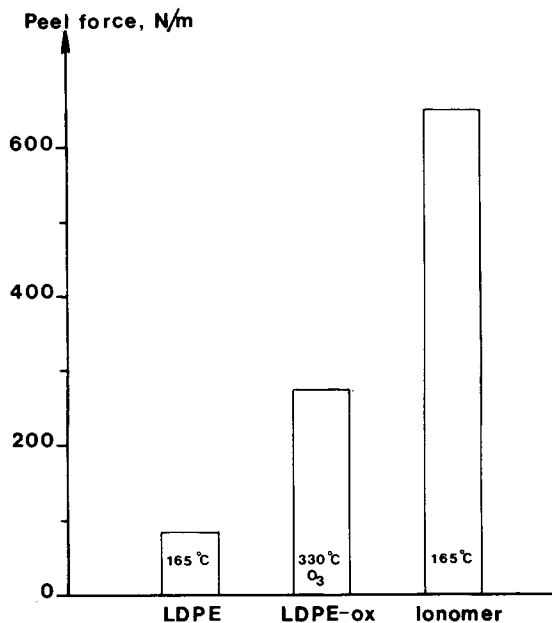


Fig. 1. Peel forces of laminates obtained from LDPE, LDPE-ox, and the ionomer. The temperatures and the presence of ozone during the film blowing indicated in the figure.

prepared at mild conditions (165°C). It should be mentioned that the peel force for the ionomer increases considerably if the pressing time is increased from 3 to 10 s, up to about 1600 N/m, while that of polyethylene is unchanged.

The third sample in Figure 1 illustrates what can be achieved by high temperature extrusion, 330°C, and ozone flushing. The oxidation was easily detected by the presence of a carbonyl absorption in a reflexion IR spectrum. Another common technique to improve the adhesion is to use a corona discharge, which does not, however, seem to be as efficient as the high temperature oxidation (Table II). MIR spectra did not reveal any sign of oxidation, but, as mentioned in the Introduction, ESCA analysis has clearly demonstrated that corona treatment leads to oxidation in a very thin surface layer.^{1,2}

To learn more about the limitations of thermal oxidation, we made some model experiments involving a short treatment at 300°C in an ordinary forced-air oven. The film samples were 200 μm thick and the heating-up time for the bulk was about 2 min. The time of treatment is therefore a relative measure only. MIR spectra of the treated samples show that the absorbance in the carbonyl region increased substantially (see Fig. 2). For short times ketones dominate, but at longer times other groups become visible as well. The carbonyl index, used as a measure of the oxidation, increased from 0.04 in the original sample to 1.50 after 120 s. The peel force of laminates prepared from the heat treated samples increased as well, but only up to 40 s (Table III).

If the peel force is plotted against the carbonyl index, Figure 3 is obtained. The linear relation indicates that the improved adhesion can be related to the

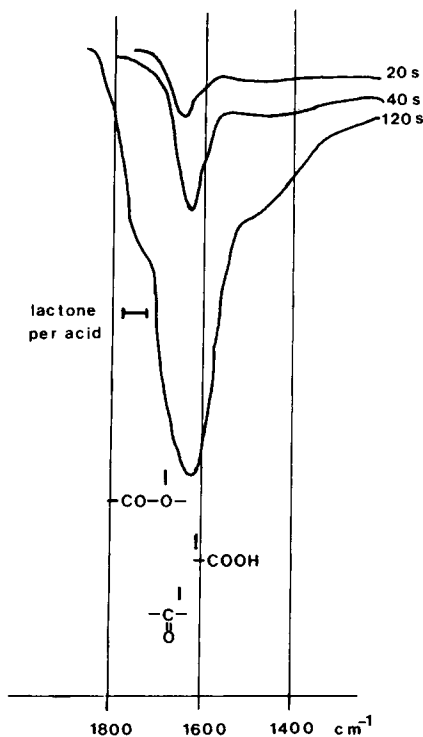


Fig. 2. Change in the infrared spectra in the range $1600\text{--}1800\text{ cm}^{-1}$ for LDPE samples heated in air.

amount of polar groups introduced in the surface. Similar relations between the degree of oxidation and the adhesion between polyethylene and aluminum in laminates have been observed earlier.⁹ The divergence at high values of the carbonyl index could be a result of the analysis depth of MIR, i.e., $1\text{--}3\text{ }\mu\text{m}$. It must be remembered, however, that oxidation of polyethylene leads to chain scission as well,¹⁰ which is demonstrated by the MWDs in Figure 4. The tendency is obvious even at short times, but the 2-min sample is more drastically influenced. Besides longer heating time, this sample has also experienced a higher temperature due to the heating-up effect, which should give more scissions.¹¹ As expected,¹⁰ molecular enlargement occurs as well. It

TABLE III
The Effect of Thermal Treatment of LDPE at 300°C in Air
on the Carbonyl Index and the Adhesion

Time (s)	Carbonyl index ^a	Peel force (N/m)
—	0.04	86
20	0.06	108
30	0.09	139
40	0.12	192
120	1.50	191

^aSee text.

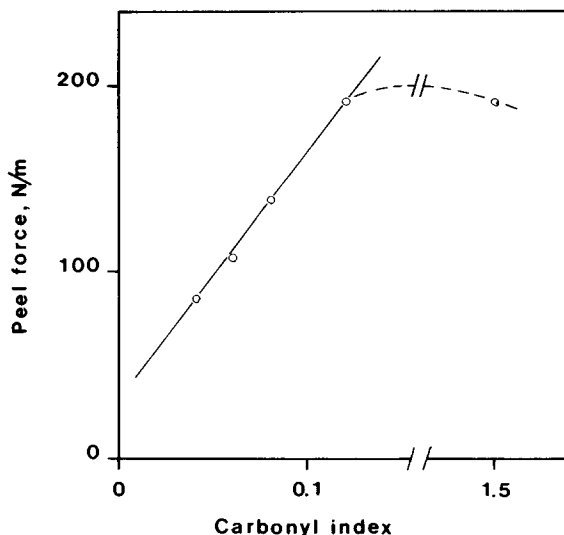


Fig. 3. The relation between the peel force and the carbonyl index (see Experimental) of LDPE samples heated in air at 300°C. Observe the change in scale.

may be assumed that the huge fraction of low molecular weight material at least partly is enriched in the surface layer. The positive effect of the increased amount of polar groups is thus counterbalanced by decreased cohesive strength. Although this model experiment is not directly comparable with extrusion coating, it demonstrates the necessity to optimize the processing conditions properly.

The oxidation processes discussed above may lead to problems with taste and odor. Use of copolymers with polar comonomers is an alternative to obtain increased adhesion without surface oxidation. We have investigated the effect of the concentration of comonomer on the adhesion to aluminum for EBA and EVA (see Fig. 5). EVA is known to give improved adhesion and

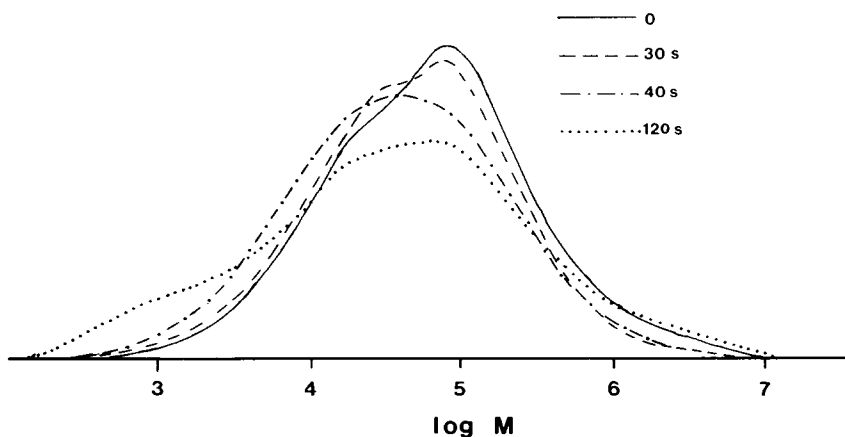


Fig. 4. Change in the MWD for LDPE samples heated in air at 300°C: (—) 0 s; (---) 30 s; (-·-) 40 s; (···) 120 s.

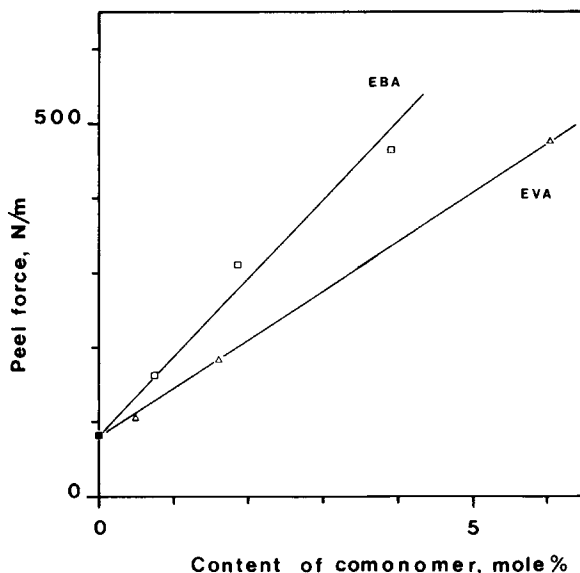


Fig. 5. The relation between the peel force and the content of comonomers for laminates of EBA and EVA: (■) LDPE.

EBA seems to be still better. The attainable peel force is clearly higher than that observed after thermal oxidation or corona discharge of polyethylene. The linear relation between the peel force and the content of comonomer indicates that the adhesive strength should be proportional to the surface concentration of functional groups.

The oxidation processes lead to the introduction of several structures containing oxygen¹: hydroxyl, carbonyl, carboxyl, hydroperoxides, etc. Very little, however, is known about their relative contribution to the increased interfacial strength. In copolymers like EBA and EVA, one functional group should be dominant, facilitating an evaluation of the efficiency of respective group. The relation between adhesive bond strength and concentration of functional groups can most often be expressed by¹²

$$\sigma_f = \sigma_{f_0} + kC^n \quad (1)$$

where σ_f is the adhesive strength at a concentration of functional groups equal to C , σ_{f_0} is the adhesive strength at zero concentration, and k and n are constants. Normally, n is found in the range 0.6–1. The results shown in Figure 5 indicate that n should be equal to 1 for both copolymers, assuming the surface concentration of functional groups to be proportional to the bulk concentration. This is somewhat higher compared to, e.g., the lap shear strength of aluminum/epoxy/aluminum and steel/polyvinyl formal/steel, where $n = 2/3$ was observed.^{13,14}

The higher efficiency of EBA might seem somewhat surprising as the ester linkage is common to both polymers. One possible explanation could be that the surface enrichment of functional groups is higher for EBA compared to EVA. Another is that EVA tends to expel acetic acid at temperatures above

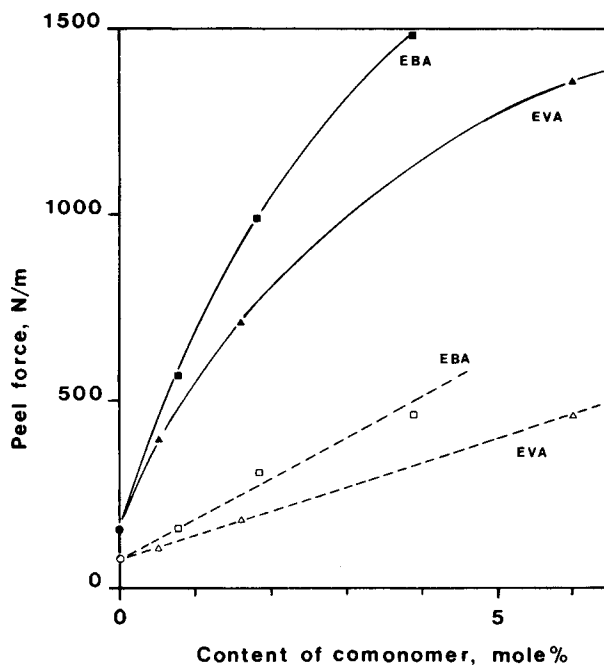


Fig. 6. Space filling models of the most favorable conformations of EBA and EVA.

150°C, leaving a C=C in the chain.¹⁵ It cannot be excluded that this reaction, which diminishes the concentration of polar functional groups, is catalyzed by the metal surface. In EBA, on the other hand, the corresponding reaction starts above 250°C and leaves carboxylic groups in the polymer chain.¹⁵ This should instead tend to increase the bond strength.

The difference in the direction of the ester linkage should furthermore affect the steric crowding around the carbonyl oxygen. A calculation based on molecular mechanics showed that the conformations represented by the space-filling models in Figure 6 should be the most favorable. It is obvious that the carbonyl oxygen is more close to the neighboring chain atoms in EVA. The ability to participate in interactions with atoms in the metal surface could thus be somewhat higher for the carbonyl in EBA.

Although EBA and EVA might give better adhesion against aluminum, compared to surface oxidized polyethylene, they are not as effective as EAA or ionomers. We have tested if corona discharge can be used to further improve the adhesion properties of EBA and EVA. The peel forces measured for LDPE, EBA, and EVA before and after corona discharge treatment at low levels are given in Table IV. The increase in adhesion strength is dramatic for the copolymers, up to a factor of 3–4, compared to less than 2 for polyethylene. The results obtained at the highest current used are summarized in Figure 7. The adhesion strength at the highest concentration of comonomer is well above that observed for the reference ionomer under the lamination conditions in question.

The remarkable effect of corona discharge treatment on the adhesion properties of EBA and EVA can reasonably be referred to the higher content

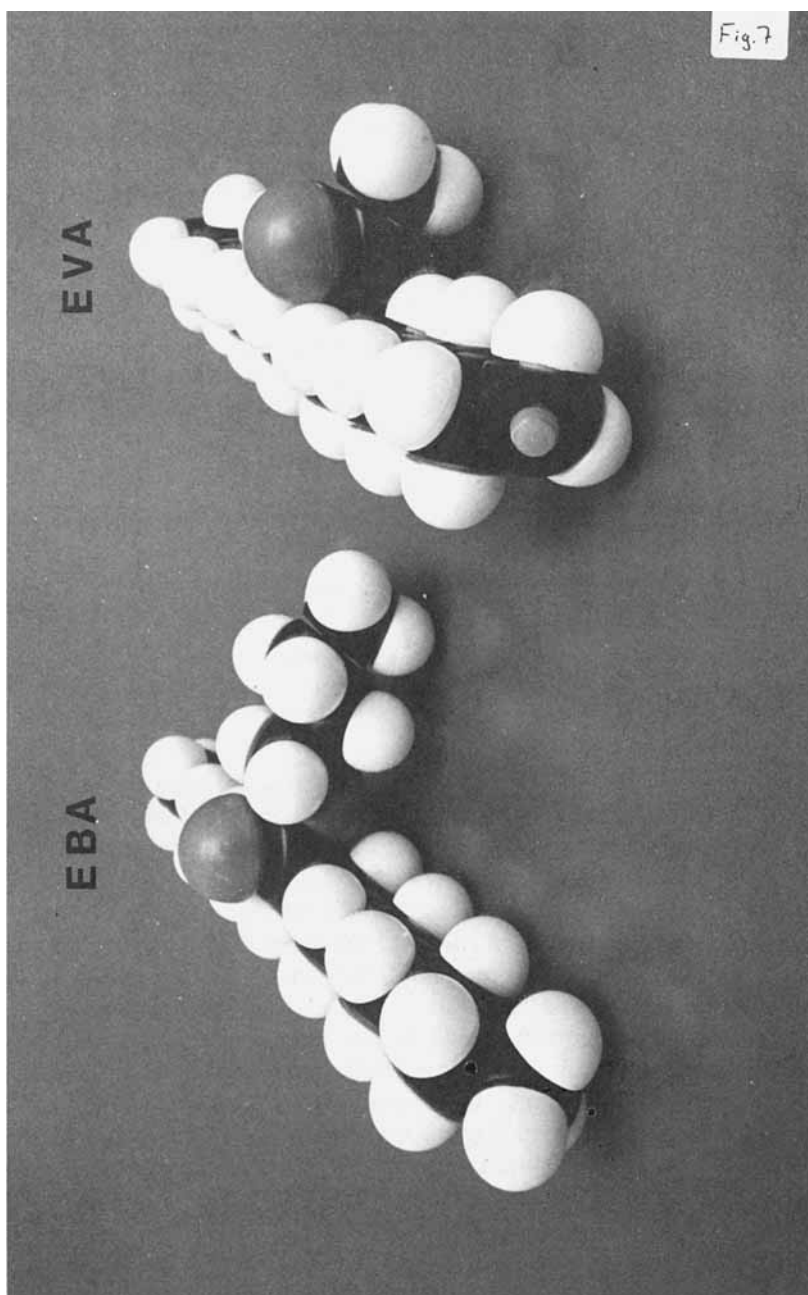


Fig. 7. The effect of corona discharge treatment of EBA and EVA on the peel force: (---) untreated samples; (—) treated samples.

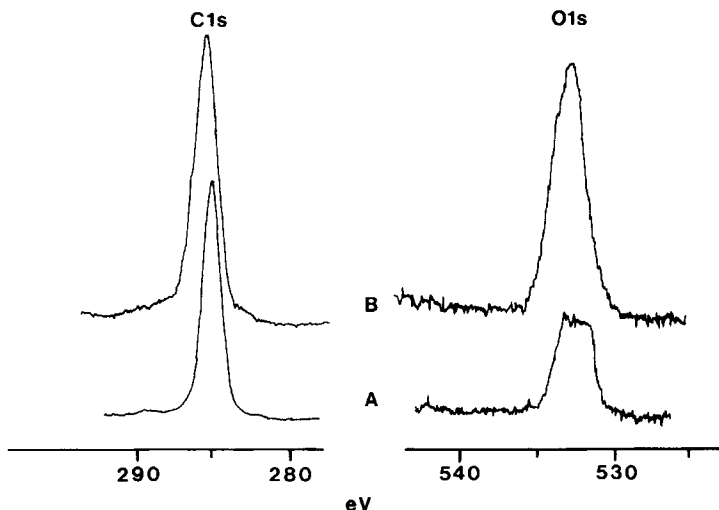


Fig. 8. Change in the ESCA spectra of EBA-2 in the C_{1s} and O_{1s} regions due to corona discharge treatment: (A) untreated sample; (B) treated sample.

TABLE V
Content of Oxygen in the Surface of EBA 2 before
and after Corona Treatment

Sample	Content of oxygen (at. %)			Peel force (N/m)
	—C— <u>O</u> —	—C= <u>O</u>	Total O	
Theoretical	0.8	0.8	1.6	—
Untreated	1.5	1.5	3.0	311
Corona treated	3.5	5.9	9.4	990

former was considered to be most important. At present, we are working with surface hydrolysis of EBA and EVA in order to further explore their capabilities as bonding polymers. The surfaces should be dominated by a single polar group, i.e., carboxylic acid and hydroxyl, respectively, which would facilitate an evaluation of functional group efficiency. The results will be published soon.

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