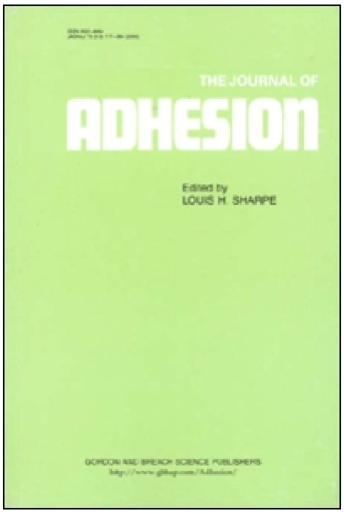

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Adhesion Between Hydrated Aluminium and Ethylene Copolymers Containing Methoxy Silane Groups*

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The peel strength between ethylene copolymers and aluminium has been investigated. The polymers were ordinary LDPE, copolymer with butyl acrylate (EBA), copolymer with vinyltrimethoxysilane (EVS), and copolymer with both comonomers (EVSBA). The aluminium was modified by hydration in boiling water up to 120 s. The strength of melt-pressed laminates was tested with a T-peel test and the failure mechanism was evaluated by FTIR and SEM. The hydration leads to a porous pseudoboehmite with an increased content of Al—OH groups, which causes considerable increases in peel strength for all polymers, in particular for EVS and EVSBA. The mode of failure varied between adhesive and cohesive depending on the surfaces. The introduced porosity contributes with mechanical keying while the Al—OH groups enable polar interactions for EBA and the formation of interfacial covalent bonds for EVS and EVSBA.

KEY WORDS adhesion; ethylene copolymers; hydrated aluminium; laminate; interfacial interactions; mechanical keying.

INTRODUCTION

Aluminium coated with polyethylene is a widely used material combination, especially by the packaging industry. However, adhesion between the materials is generally very low, due to the non-polar character of pure polyethylene. A frequent method to solve this problem is surface oxidation of the polymer *via* corona discharge or thermal treatment, which introduces a number of polar groups onto the polymer surface.[1,2] Grafting monomers with polar groups onto polyolefins also increases the adhesion to aluminium as shown by Schultz *et al.*[3,4] Another method

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*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

**Corresponding author.

is to use coextruded films, where the polymer next to the aluminium surface is a copolymer containing a comonomer with polar groups.

The efficiency of adhesion to aluminium depends strongly on the type and polarity of the functional group in the copolymer.[5] Interfacial studies have also proven that the polar groups are effective against an aluminium oxide surface with Lewis acid-base interactions.[6] Although the polar groups introduced onto the polymer surface initially yield very good adhesion strength by forming strong interactions across the interface, the adhesion strength drops rapidly in many cases to an unacceptable level in liquid media. To obtain satisfactory wet strength it is necessary to combine aluminium and polyethylene with strong chemical links *e.g.* covalent, ionic or possibly a strong hydrogen bond.

Even if polar groups increase the adhesion under dry conditions, that adhesion may be drastically decreased by the presence of water. Kinloch[7,8] and Venables[9] have shown that strong and durable joints are obtained for epoxy systems when phosphoric acid anodised (PAA) aluminium is used. This can be explained by mechanical keying into the porous surface that is formed after the anodising treatment, but also by the fact that PAA aluminium oxide inhibits corrosion with water. Another possibility to prevent the deterioration of adhesion in wet media is to use coupling agents, *e.g.* silane[10,11] and chromium fumarato compounds.[12] Different theories have been suggested to explain the mechanism of adhesion in these cases, the most probable one being that the coupling agent forms covalent bonds to the substrate. The polymer can then combine with the coupling agent by either forming chemical bonds or by developing an interpenetrating crosslinking network.[10,12] Recently it was shown that when ethylene copolymers contain small amounts of vinyltrimethoxysilane comonomer, a considerable improvement of the peel strength to aluminium was obtained.[13] The peel strength was also maintained and even improved after ageing in hot water. For the silane-containing copolymers as well as for the silane coupling agents it is possible to form covalent bonds across the interface because the methoxy silane group reacts with the hydroxy groups on the aluminium surface, which explains the excellent peel strength and hydrolytic stability. However, when the copolymers were used in extrusion coating of aluminium with very short lamination times no obvious difference of the peel strength between polyethylene and the silane copolymers was found.[14] On the other hand, unlike polyethylene, the peel strength for the silane copolymers was observed to increase after ageing in hot water.

On a new aluminium foil manufactured for use in extrusion coating, very few hydroxy groups are generally present on the surface. By introducing more hydroxy groups onto the aluminium surface it is possible to obtain a more reactive surface. This can be done by immersion in boiling water which produces an adherent and porous pseudoboehmite film.[15] For polyethylene laminated to hydrated aluminium surfaces, improved adhesion was obtained, which was explained as due to mechanical keying in the porous surface.[16–18] Recently we have shown that the hydrated surface can form strong hydrogen bonds with ester copolymers and carboxylates with acrylic acid copolymers.[19] In this case the peel strength was also improved, especially for the ester copolymers, and explained to be due to the hydrogen bond, increased surface area as well as mechanical keying.[20] An increase of the content of hydroxy groups should also favour the probability for the aluminium surface to react with the methoxy silane group.

In this study we have examined peel strength between ethylene silane copolymers and hydrated aluminium. The hydration was done by treating the aluminium foil before lamination in boiling water for 10–120 seconds. The strength of melt-pressed laminates was tested with a T-peel test and the failure mechanism was evaluated by FTIR and SEM.

EXPERIMENTAL

Materials

Two silane-containing ethylene copolymers were used: poly(ethylene-co-vinyltrimethoxysilane) EVS, and poly(ethylene-co-vinyltrimethoxysilane-co-butylacrylate) EVSBA. As reference materials low density polyethylene (LDPE) and an ethylene butylacrylate copolymer (EBA) was included in the study. All the polymers used in the study were supplied by Neste Polyethylene AB, Sweden. Table I summarizes comonomer content and some other specifications of the polymers. Films of the enumerated polymers was produced by means of film-blowing at extrusion temperatures of 150–180°C, to a thickness of 200 μm.

An aluminium foil was kindly supplied by Gränges AB, Sweden and had a thickness of 150 μm. The content of other elements was 0.82% Fe, 0.06% Si, 0.004% Mn and 0.002% Mg. Before hydration and lamination the foils were annealed at 300°C for 16 h in air. The annealing has been reported to remove all hydrocarbons present from the rolling oil[21] and for that reason the foil was used without any further cleaning. The hydration of the aluminium foil was done by immersion in deionized boiling water. Before lamination the hydrated foils were dried in ambient air.

Laminate Preparation and Testing of Peel Force

To eliminate rupture and extension of the plastic film, laminates were prepared by pressing one plastic film between two aluminium foils. The assemblies were pressed

TABLE I
Characteristics of the polymers used

Polymer	Comonomer content BA* (mole-%)	Comonomer content VTMS* (mole-%)	Melt index (g/10 min)	T_m (°C)	Crystallinity (%)	$M_w \times 10^{-3}$ (g/mole)
LDPE			4.5	111	44	348
EVS		0.38	0.8	111	40	174
EBA	4.3		4.0	99	21	171
EVSBA	4.4	0.44	4.5	94	15	199

T_m and crystallinity determined by DSC; M_w determined by GPC-LS
*Butyl acrylate and vinyltrimethoxysilane

together for 10 seconds at a pressure of 1.2 MPa. After one week in ordinary laboratory atmosphere the peel force was tested in an Instron 1122 by a T-peel test with a crosshead speed of 200 mm/min. The width of the test strips was 20 mm. The reported values represent the mean of ten strips taken from two laminates.

Analysis

A Fourier Transform Infrared Spectrophotometer, Perkin Elmer 1720 X, with a nitrogen-cooled MCT detector was used. For the analysis of the aluminium surfaces a reflection-absorption spectroscopy attachment (RAS, Spectratech FT-80) was used, with a fixed angle of incidence of 80°. To obtain spectra representing the polymer layer on the aluminium sides the sample spectra were ratioed to the reference spectra of the original aluminium surface. For the analysis of polymer films and thick layers of polymer on the aluminium side an attenuated total reflection (ATR) attachment was used. A zinc selenide prism was used in this case with an angle of incidence of 45°. The analysing depth for this technique is 1–2 μm.

To study the topographical changes due to the hydration and the fracture surfaces of the peeled laminates a JEOL JSM-840 scanning electron microscope (SEM) was used.

RESULTS

LDPE and EVS

In Figure 1 the relation between the peel force and press temperature is shown for LDPE and EVS laminated to untreated aluminium and aluminium hydrated for 60 seconds in boiling water. As expected, the peel force increases at higher temperatures. For both polymers the hydrated surface also yields a higher peel force then the untreated surface, but for EVS pressed at the higher temperatures the difference is not so obvious.

LDPE adheres very poorly to the untreated surface as shown in Figure 1a. Upon hydration the peel force is increased several times, especially at the lower press temperatures. A visual observation of the hydrated aluminium side of a peeled laminate indicated a cohesive failure. To confirm this, the strips were analysed by reflection IR spectroscopy, see Table II. By correlating the absorbance of the —CH_2— stretching mode (2920 cm^{-1}) with the thickness calculated by mass balance, a calibration line following the Beer-Lambert law was obtained for an EBA copolymer (7.5 mole-% butylacrylate).[19] For this polymer the regression coefficient was determined to be 27500 Å per absorbance unit. If we disregard the butylacrylate content and assume the —CH_2— content constant with the polymers, the thickness of the remaining polymer layer can roughly be estimated for the polymers in Table II. However, for this method the relation between absorbance and thickness has been found to be linear only up to 1000 Å,[22] which must be considered for the high absorbance values. It should also be noted that we have assumed a uniform layer. This is probably true for solution-cast layers, but not for the delaminated surfaces that we have studied in this investigation. Nevertheless, we have

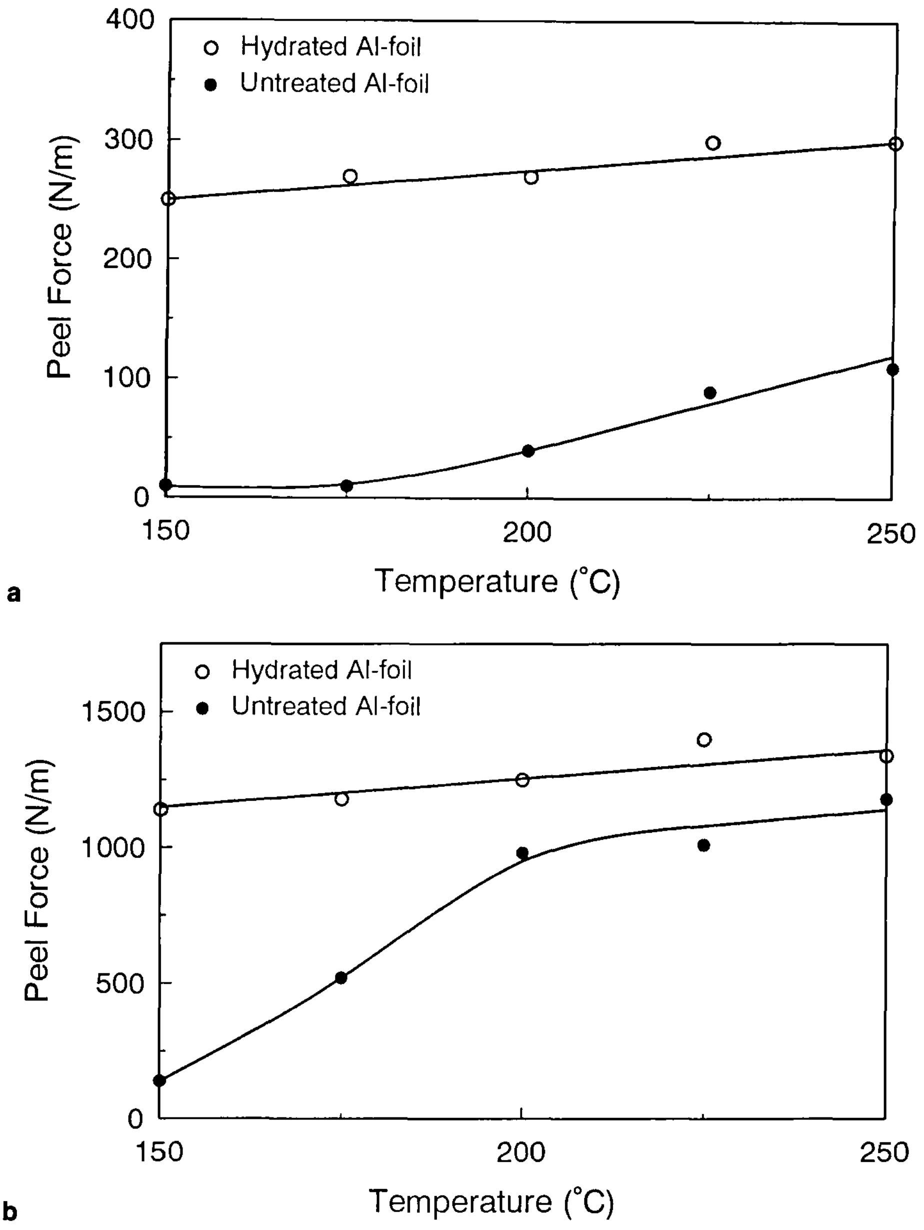


FIGURE 1 The relation between the peel force and press temperature, for untreated aluminium and aluminium hydrated for 60 seconds in water at 100°C, laminated with: a) LDPE; b) EVS.

used this relation to obtain a measure of the amount of polymer remaining at the aluminium side. The absorbances of the —CH_2— stretch at 2920 cm^{-1} on the hydrated aluminium side for the laminates pressed at 150, 200 and 250°C thus corresponds to 2500, 2000, and 2000 Å, respectively, which definitely is enough to regard

TABLE II
Absorbance at 2920 cm^{-1} of remaining polymer layer on the aluminium side after peel test

Hydration time (sec)	Temperature °C	LDPE	EVS	EBA	EVSBA
0	150	0.0014	0.020	0.0042	0.016
0	200	0.0086	0.25	0.0038	0.019
0	250	0.015	0.22	0.0066	0.021
60	150	0.091	>0.25	0.031	0.031
60	200	0.072	>0.25	0.032	0.037
60	250	0.072	>0.25	0.042	0.041

the failure mode as cohesive. A smaller amount of LDPE is also found on the untreated aluminium side, which most probably comes from the amorphous regions in the interphase (see below).

By copolymerizing ethylene with a small amount of vinyltrimethoxysilane (0.4 mol% VTMS) a considerable effect on the peel strength to aluminium can be obtained, see Figure 1b. After delamination of the laminates made with hydrated aluminium a relative thick polymer layer (easily detectable by visual observation) remained in all cases on the aluminium side due to a cohesive failure. The amount of remaining polymer in this case is far too high to get true absorbance values, but they are presented in Table II as well, which clearly demonstrates that a cohesive failure was obtained. An obvious cohesive failure could also be established between EVS and the untreated surface for the laminates pressed at and above 200°C. This explains the small difference in the peel forces for EVS between the hydrated and untreated aluminium surfaces at the higher temperatures.

In Figure 2 the effect of hydration on the peel force is shown for EVS and LDPE. The press temperature was chosen as 175°C in this case due to the cohesive failure at the higher temperatures for EVS laminated to the untreated surface. For LDPE a steady increase of the peel force up to 60 seconds hydration time can be observed, whereafter it remains constant. By means of SEM micrographs of the aluminium side it was easy to establish a cohesive failure at this point, see Figures 3a and 3b. On the aluminium hydrated for 60 seconds a fine fibrillar structure remained on the surface, but the entire surface was not covered. On the untreated aluminium side spots of the polymer may be identified, most probably due to weak layers in amorphous regions. However, we consider the failure mode for LDPE against untreated aluminium as mainly adhesive.

The peel forces for EVS shown in Figure 2 makes a very obvious jump to an almost constant value after 20 seconds hydration time. For the peeled EVS laminates with 20 seconds or more hydration time it is easily established by visual observation that a cohesive failure arises. The location of the cohesive failure far from the interface makes the peel force independent on any further changes of the surface, which explains that it remains at one level. The SEM micrographs of the aluminium side shown in Figures 3c and 3d confirms that two types of fractures are obtained also in this case. Comparing the SEM micrographs of the hydrated aluminium, Figures 3b and 3d, shows that EVS gives a much thicker layer with a rougher fibrillar structure than LDPE.

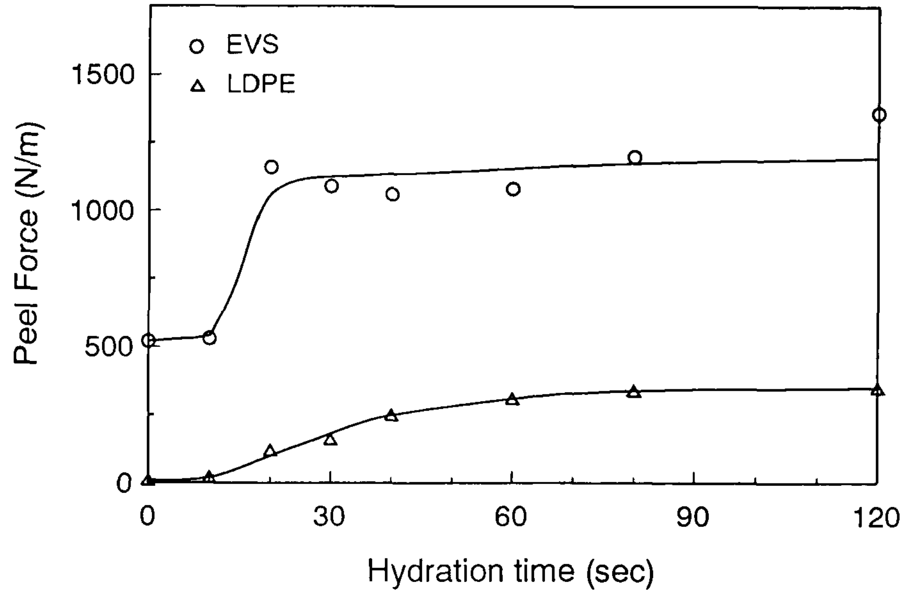


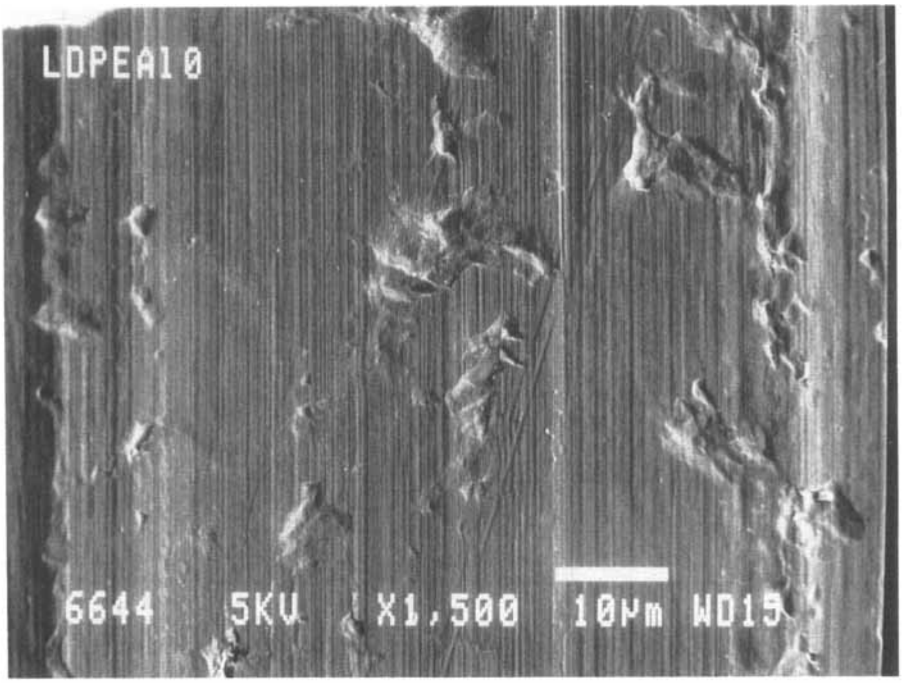
FIGURE 2 Peel force as a function of hydration time at 100°C for LDPE and EVS.

EBA AND EVSBA

In Figure 4 the peel force is shown for systems similar to those in Figure 1, but also containing butyl acrylate (4.3 mol%) as comonomer, *i.e.* EBA and EVSBA. Also in this case it is obvious that increased press temperature improves the peel strength. The effect of hydrating the aluminium surface has a great influence on the peel force also for EBA and improves it several times. Among the laminates with hydrated aluminium EBA seems to be more dependent on the temperature than the others. Also, in this case, a greater amount of polymer remains on the aluminium side after hydration, Table II, indicating a cohesive failure.

When EVSBA was used instead of EBA high values of the peel force were obtained for the hydrated surfaces as well as for the untreated surfaces. For this silane-containing polymer it was not possible to decide whether a cohesive failure was obtained or not with only a visual observation. The IR analysis of the aluminium sides for this polymer also showed low values of polymer on both surfaces, compared with its high peel forces and corresponding values for EVS, Table II. With only this information it is difficult to interpret the failure mode.

For EBA and EVSBA the press temperature was set to 150°C when the effect of hydration time was studied. EBA behaves in a similar way to LDPE; first the peel force increases up to 40 seconds and then remains nearly constant as hydration time increases, see Figure 5. In the SEM micrographs of these laminates no distinct polymer layer can be observed on the peeled aluminium side, and the fracture seems



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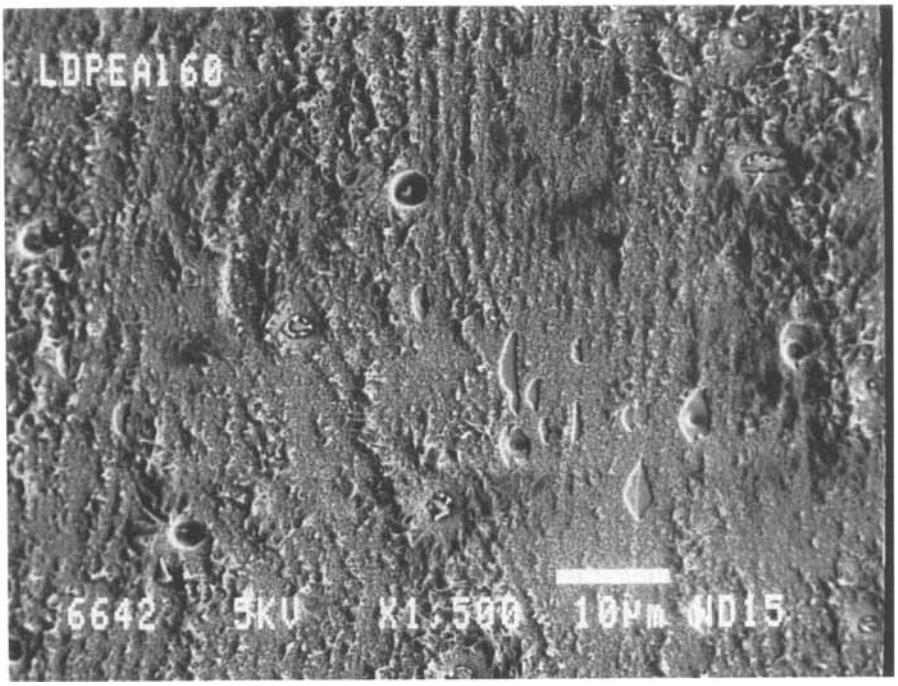


b

FIGURE 3 SEM micrographs of: a) untreated aluminium side peeled from LDPE; b) aluminium side hydrated for 60 seconds peeled from LDPE; c) untreated aluminium side peeled from EVS; d) aluminium side hydrated for 30 seconds peeled from EVS.

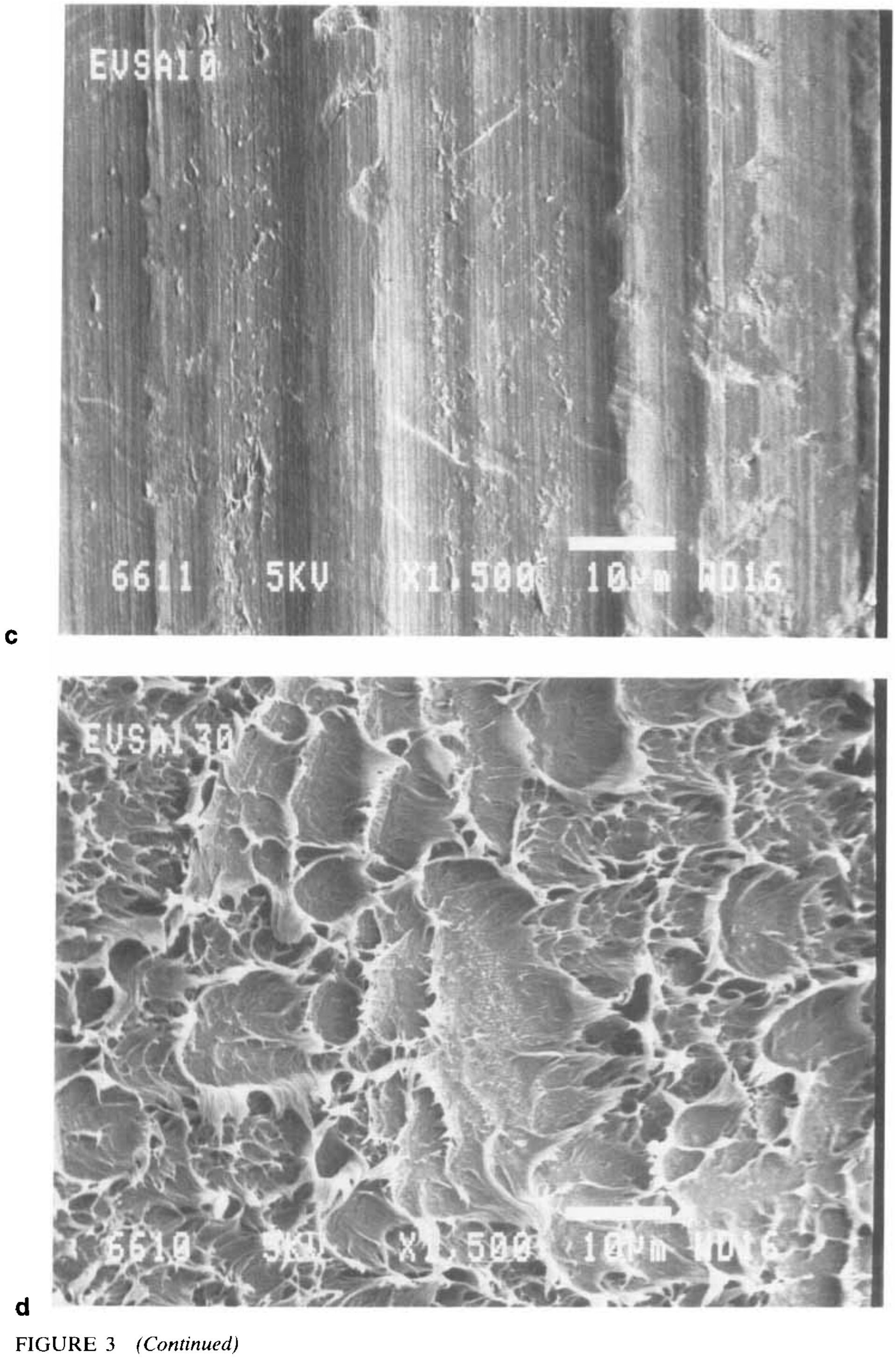
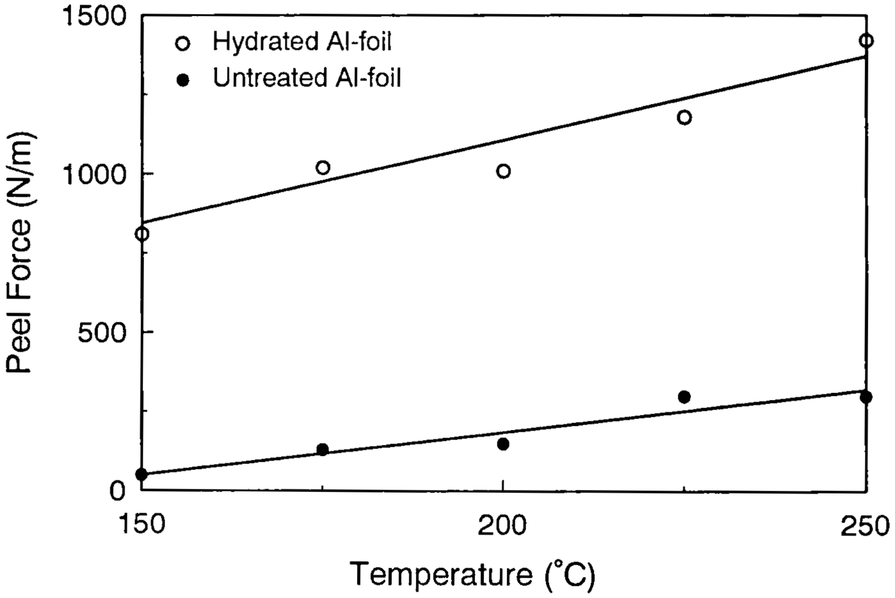


FIGURE 3 *(Continued)*



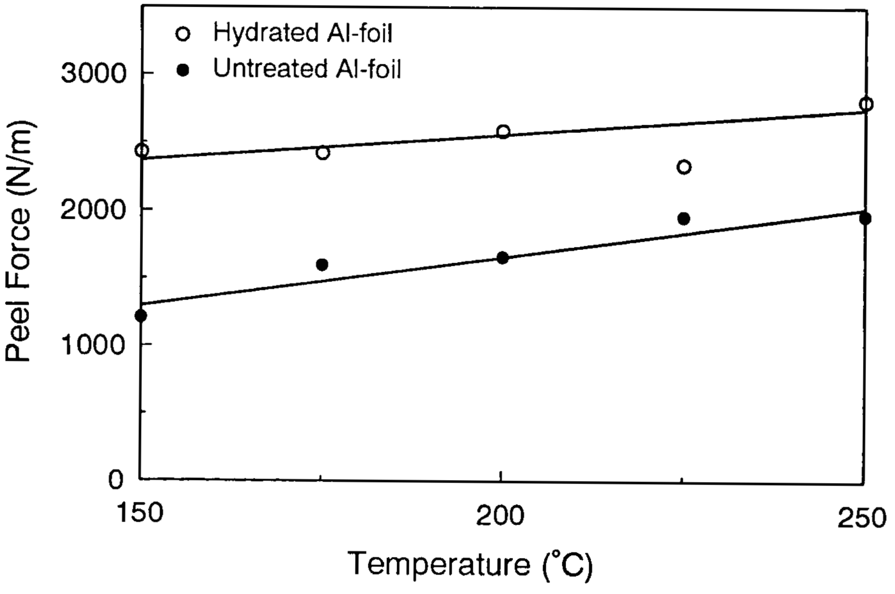


FIGURE 4 The relation between the peel force and press temperature, for untreated aluminium and aluminium hydrated for 60 seconds at 100°C, laminated with: a) EBA; b) EVSBA.

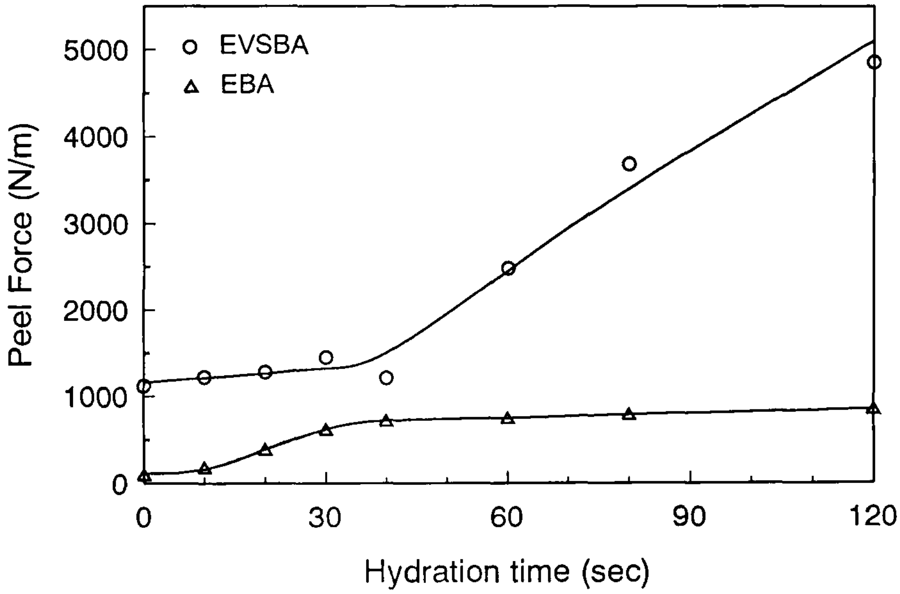


FIGURE 5 Peel force as a function of hydration time at 100°C for EBA and EVSBA.

to be adhesive, see Figures 6a and 6b. The obvious roller marks on the untreated surface disappear upon hydration, due to formation of a rougher porous surface, which explains the difference of the surface structure in the pictures, see Figure 8. (The small circular pits on the hydrated aluminium are unreacted precipitates containing iron.)

The effect of hydration time on the peel strength is very different for EVSBA compared with the other polymers. For the shorter hydration times no obvious effect is seen, but after 40 seconds hydration time an increase is observed. For the laminates with 80 and 120 seconds hydration time the fracture in many of the strips occurred in the bulk of the polymer, and the peel force in this case was measured to be 6800 N/m. For the values of the peel forces presented in Figure 5 for these hydration times, the strips peeled in the interphasial region. In the SEM micrograph of the aluminium side it was not possible to find a polymer layer for the untreated aluminium, see Figure 6c. For the hydrated aluminium we can observe that the pseudoboehmite film has delaminated partially, see Figure 6d. The hydrated structure remaining on the aluminium side dominated the surface, but it is also in this case difficult to find any polymer. The peeled polymer sides of the samples shown in Figure 6 were also analysed by means of SEM. The polymer side of EBA laminated to untreated aluminium showed an even structure similar to the aluminium side in Figure 6a. For EBA and EVSBA laminated to hydrated aluminium, and for EVSBA laminated to untreated aluminium as well, a rough and fibrillar structure was found on the peeled polymer side (for EBA see Figure 10).

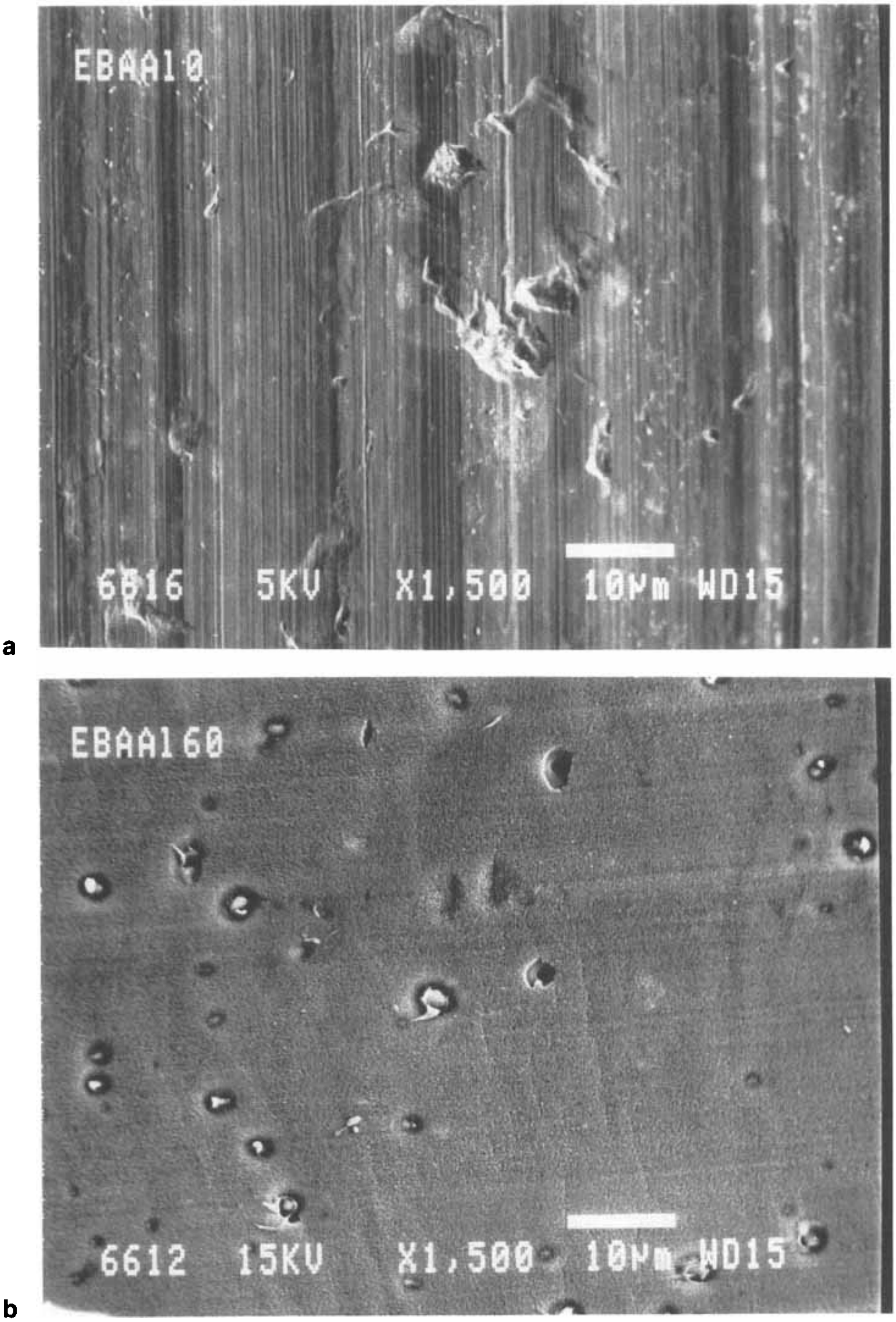


FIGURE 6 SEM micrographs of: a) untreated aluminium side peeled from EBA; b) aluminium side hydrated for 60 seconds peeled from EBA; c) untreated aluminium side peeled from EVSBA; d) aluminium side hydrated for 60 seconds peeled from EVSBA.

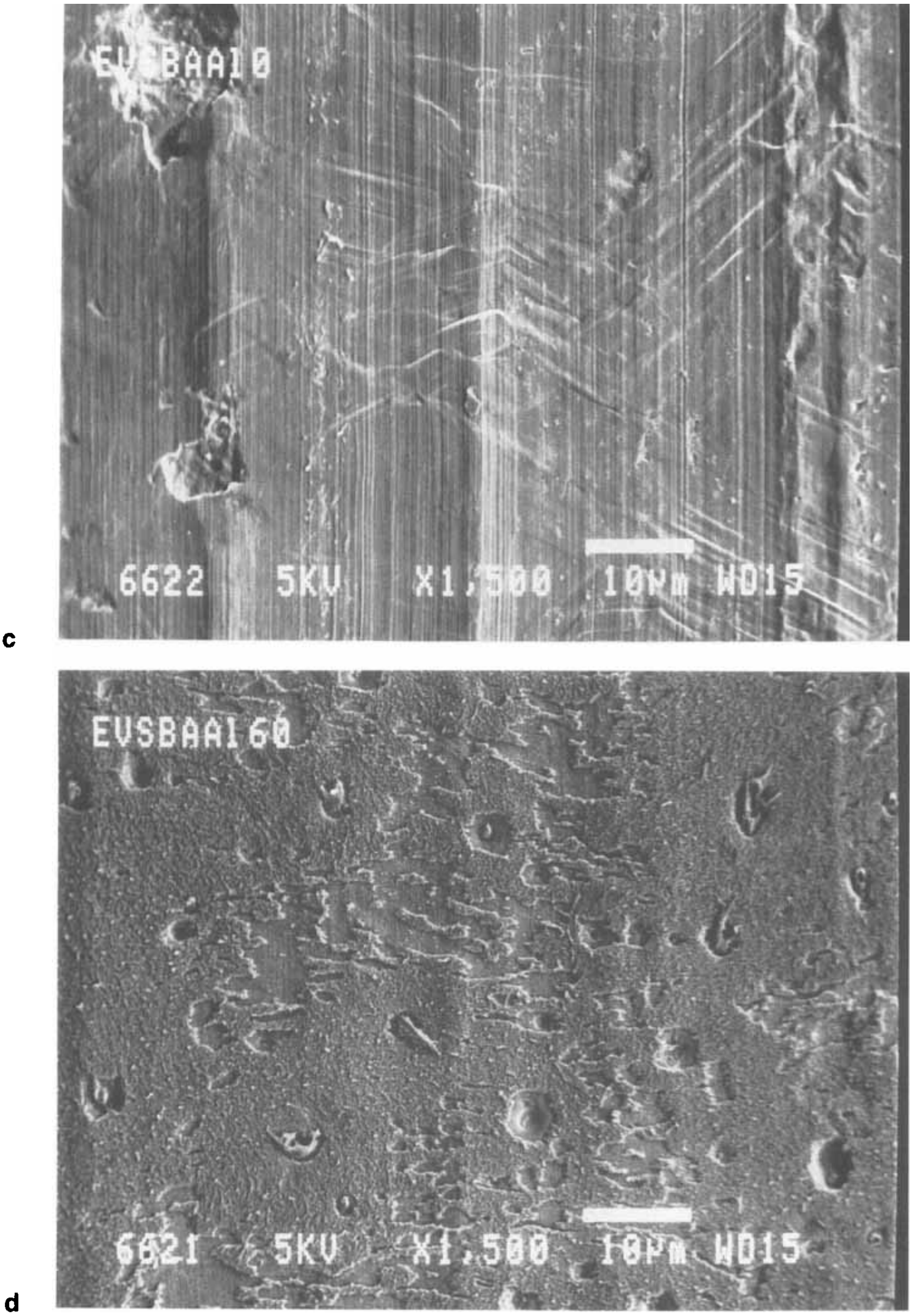


FIGURE 6 *(Continued)*

DISCUSSION

Hydration of Aluminium

The aluminium and water reaction has been extensively reviewed by Alwitt.[23] When aluminium is hydrated in boiling water an adherent layer of a poorly crystallized pseudoboehmite film is formed on the surface according to:

$$Al + 2H_2O \rightarrow AlOOH + 3/2\ H_2$$

The chemical composition of the hydrated film can be described as an aluminium oxyhydroxide containing physically adsorbed water, where the water is bonded with strong hydrogen bridges between layers of boehmite.

FTIR combined with an RAS attachment is a convenient method to study the hydration of the surface. In a previous paper it was shown that the spectrum of an untreated surface only contained a weak absorbance at 960 cm^{-1} due to bending mode in the thin aluminium oxide film.[19] After hydration new absorbances arose representing hydrogen stretching, physically adsorbed water and a strong bending mode of the hydroxy group at 1080 cm^{-1}.

In Figure 7 the absorption of the strong characteristic —OH bending mode at 1080 cm^{-1} is used to detect and follow the hydration reaction as a function of immersion time in boiling water. For the shortest hydration time no reaction occurs due to an induction period. 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

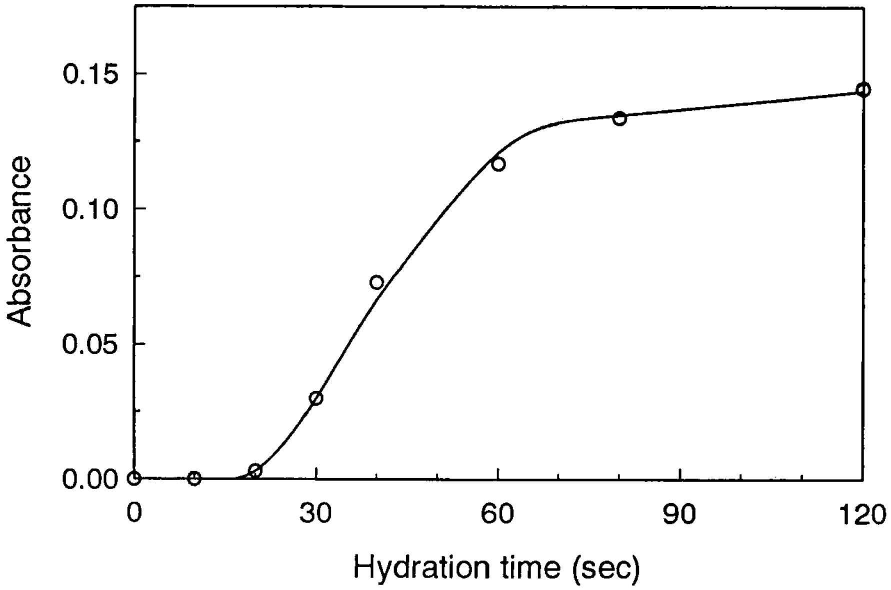


FIGURE 7 The absorbance of the —OH bending at 1080 cm^{-1} for the aluminium surfaces as a function of hydration time at 100°C.

existing oxide film on the metal.[24,25] In a previous report[20] we used a foil with a much shorter and distinct induction time (5–7 seconds) than that found for the foil used in the present study (20–30 seconds). The hydration conditions and the pretreatments of the foils are the same, but the content of alloying elements are different. We suggest that this also may have a great influence on the induction period and that a higher content of alloying elements for the foil used in the previous work gives a shorter induction time. After the induction period hydration starts and the rate of hydroxyl formation is high between 20–60 seconds and then decreases.

Besides the chemical changes that occur during hydration, the surface topography is changed. The importance of the surface topography on the adhesion between polyethylene and copper[26] or aluminium[27,28] has been demonstrated by Packham *et al.* In Figures 8a–d SEM micrographs of the aluminium surface are shown for some selected hydration times. For the aluminium surface hydrated for 30 seconds a rough surface with pseudoboehmite structure is formed but it is not fully developed. At 60 seconds hydration time the entire surface is covered with a porous layer and for longer hydration times no obvious variations in the structure can be observed. From the SEM micrographs the size of the pores, for the surfaces with 60 and 120 seconds hydration time, can be estimated to be about 0.1 μm. In a recent study the BET surface area of hydrated foils was determined.[20] For a fully-developed pseudoboehmite film (at 60 seconds hydration time) it had increased about 20 times compared with the original surface.

LDPE

Hydration of the aluminium foil leads to an increased peel strength for the LDPE laminates, as shown in Figures 1 and 2. It is also easy to establish that the adhesive failure for LDPE against untreated aluminium is changed to a cohesive failure when hydrated aluminium foils are used (see Table II and Figures 3a and 3b). Despite the obvious cohesive failure the peel forces observed for laminates between LDPE and hydrated aluminium are very low, compared with those observed for the other materials. This is unexpected since the bulk tensile strength of the LDPE sample is relatively high, at least compared with EBA and EVSBA, due to the higher crystallinity. Schonhorn *et al.*[29,30] have shown that high energy surfaces such as aluminium may induce crystallization of polyethylene with high degree of crystallinity, which produces a transcrystalline layer. We have earlier observed also that low density polyethylenes with nearly the same crystallinity as in the present study form transcrystalline layers against aluminium foil.[13] The relatively high amorphous content of LDPE would probably produce a weak layer in the transition to the ordinary spherulite crystalline structure in the bulk. A higher crystallinity at the surface may also cause internal stresses in the interphasial region, which also may lead to deterioration of the cohesive strength in that.

Due to the lack of polar groups in LDPE no polar interactions should be present against the aluminium foil. We, therefore, assume that the change in chemical composition of the surface is less important than the topographical change. By

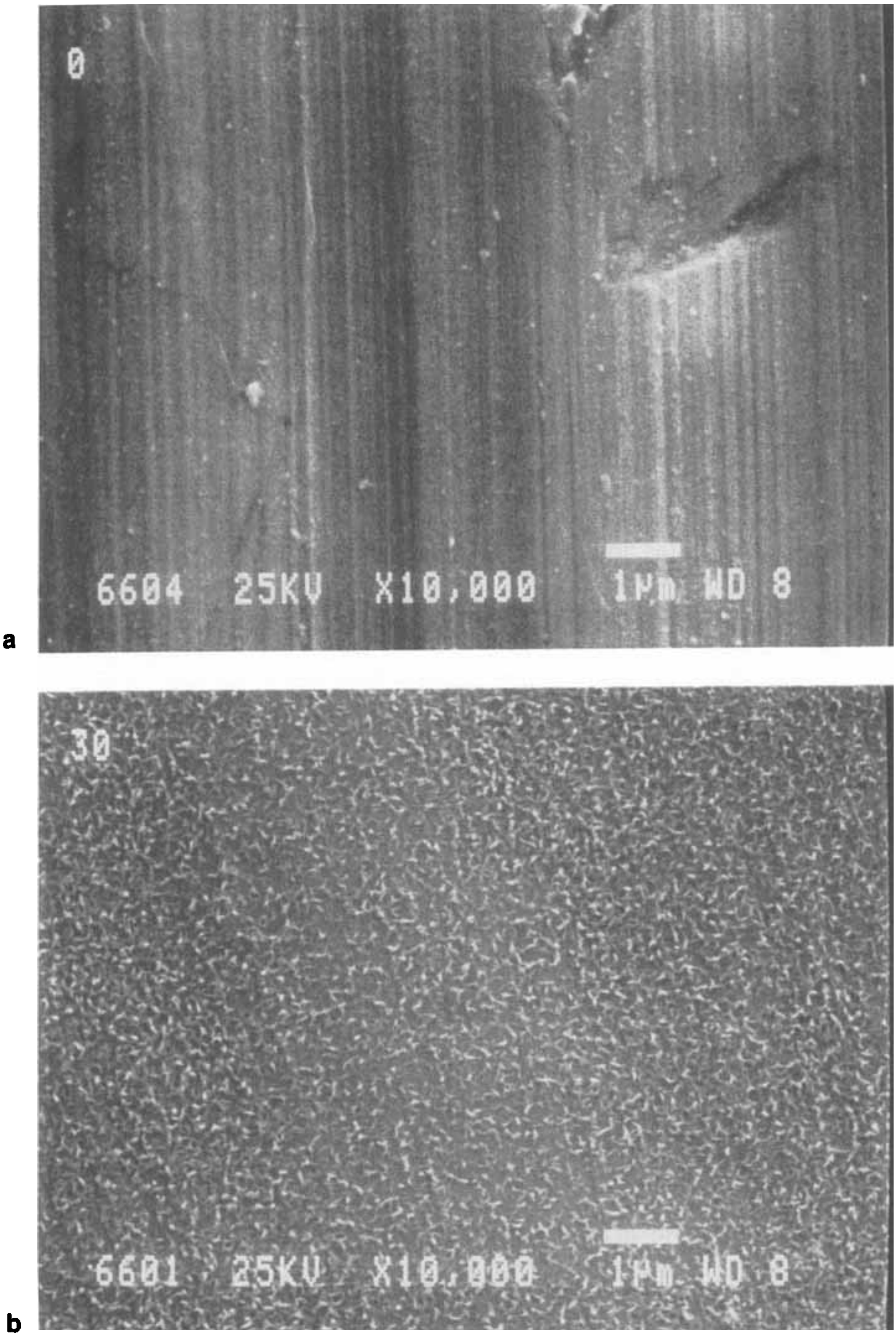


FIGURE 8 Scanning electron micrographs on aluminium foils: a) untreated; b) hydrated for 30 seconds; c) 60 seconds; d) 120 seconds.

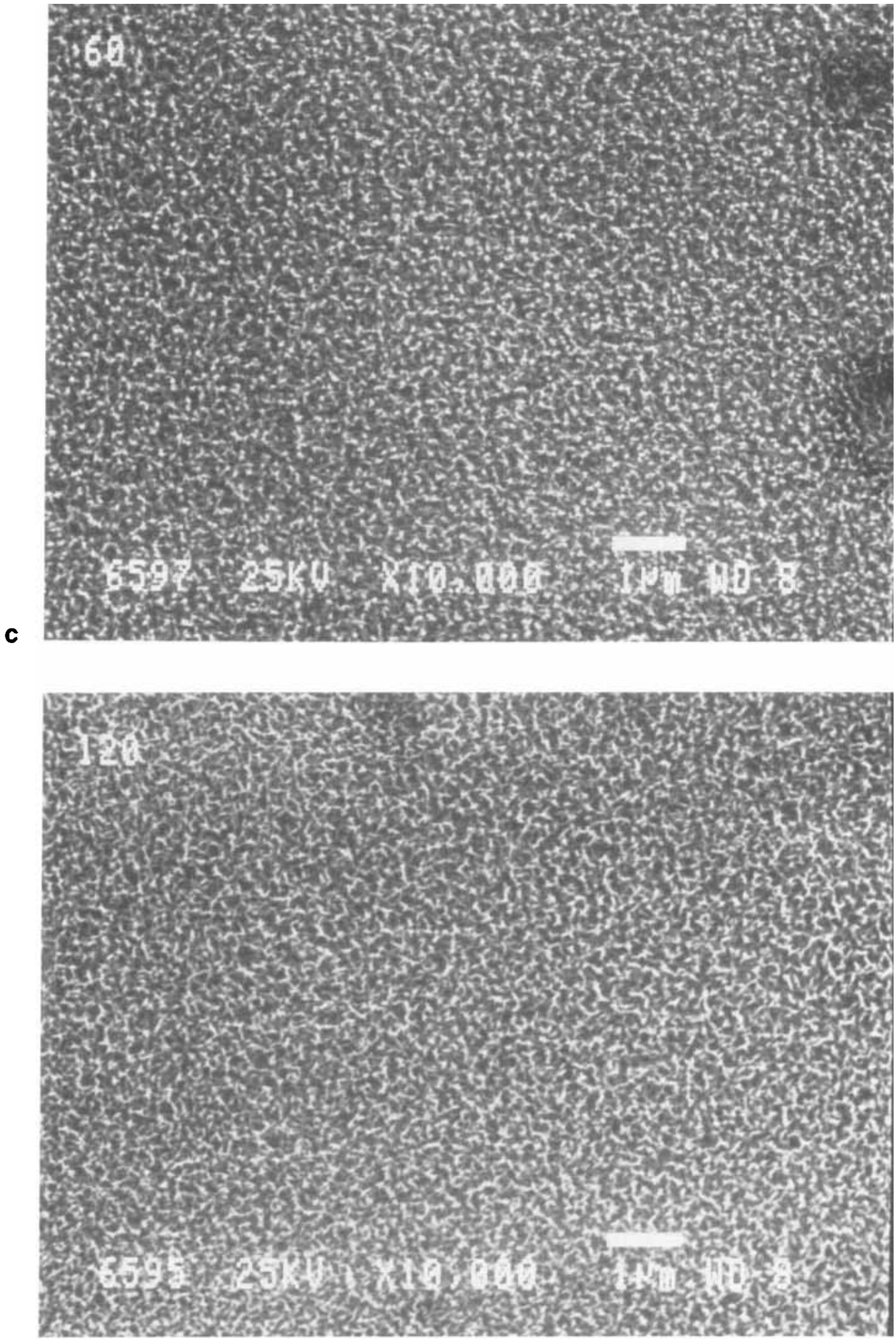


FIGURE 8 *(Continued)*

means of the SEM micrographs in Figures 8a–d it is easy to correlate the peel strength with the surface roughness. At 30 seconds hydration time a rougher surface has developed on the aluminium foil but it is not fully developed. An obvious increase of the peel strength could also be observed at this point, but it continues to increase for longer hydration times. However, the change in appearance of the foils between 60 and 120 seconds hydration time is minor. No obvious increase for the corresponding values of the peel forces could be observed either. This points to the fact that the topographical change of the surface leads to keying of LDPE in the hydrated laminates. The "degree of keying" is also increased until the pseudo-boehmite film is fully developed. As mentioned in the Introduction, mechanical keying has been used by other authors to explain the adhesion mechanism between hydrated aluminium and LDPE.[16–18]

EBA

The importance of polar groups at the interface to obtain acceptable adhesion between polyethylene and aluminium has been discussed in many publications. The properties of different functional groups in ethylene copolymers have also been evaluated.[5] For EBA the carbonyl in the butyl acrylate group has been shown to form a Lewis acid-base interaction with aluminium in an oxidised aluminium surface.[6] For this reason, the change in chemical composition may be more important for the adhesion in laminates with EBA then in the case of LDPE. The different peel forces against untreated and hydrated aluminium are very obvious for EBA, Figure 4a. The effect of hydration time was also studied, and the peel strength increases in a similar way as for LDPE, see Figure 5. The increased content of hydroxy groups on the surface may be one important factor for the improved peel strength, but the mechanical keying found for LDPE must also have an influence on the adhesion. Due to the formation of a porous surface layer after hydration the surface area also increases. This should also lead to greater contact surface between the materials and probably even better adhesion, due to the possibility of forming a larger number of interactions.

In a recent study it was shown that the carbonyl interacted very strongly with hydroxy groups on a hydrated aluminium surface.[19] In the spectrum of the interface two peaks were visible in the carbonyl region, one representing ordinary bulk carbonyls and the other, displaced 38 cm^{-1}, due to strongly hydrogen/bonded carbonyls. In a similar study,[6] but on an oxidised aluminium surface, the interacting carbonyls were displaced 8 cm^{-1}. The magnitude of the displacement is directly proportional to the enthalpy of the acid-base interaction.[31,32] Consequently, it is very probable that the chemical transformation of the surface contributes to the improvement of the peel strength. When EBA is laminated at 250°C with hydrated aluminium it has also been suggested that a carboxylate coupling forms to the hydrated surface.[6,20] This reaction is probably favoured at the higher temperatures used in this study. This may explain the great difference of the obtained peel forces at 150 and 250°C.

For the laminates that were pressed at 250°C a partial delamination of the hydrated surface could be observed, see Figure 9a. On the corresponding polymer

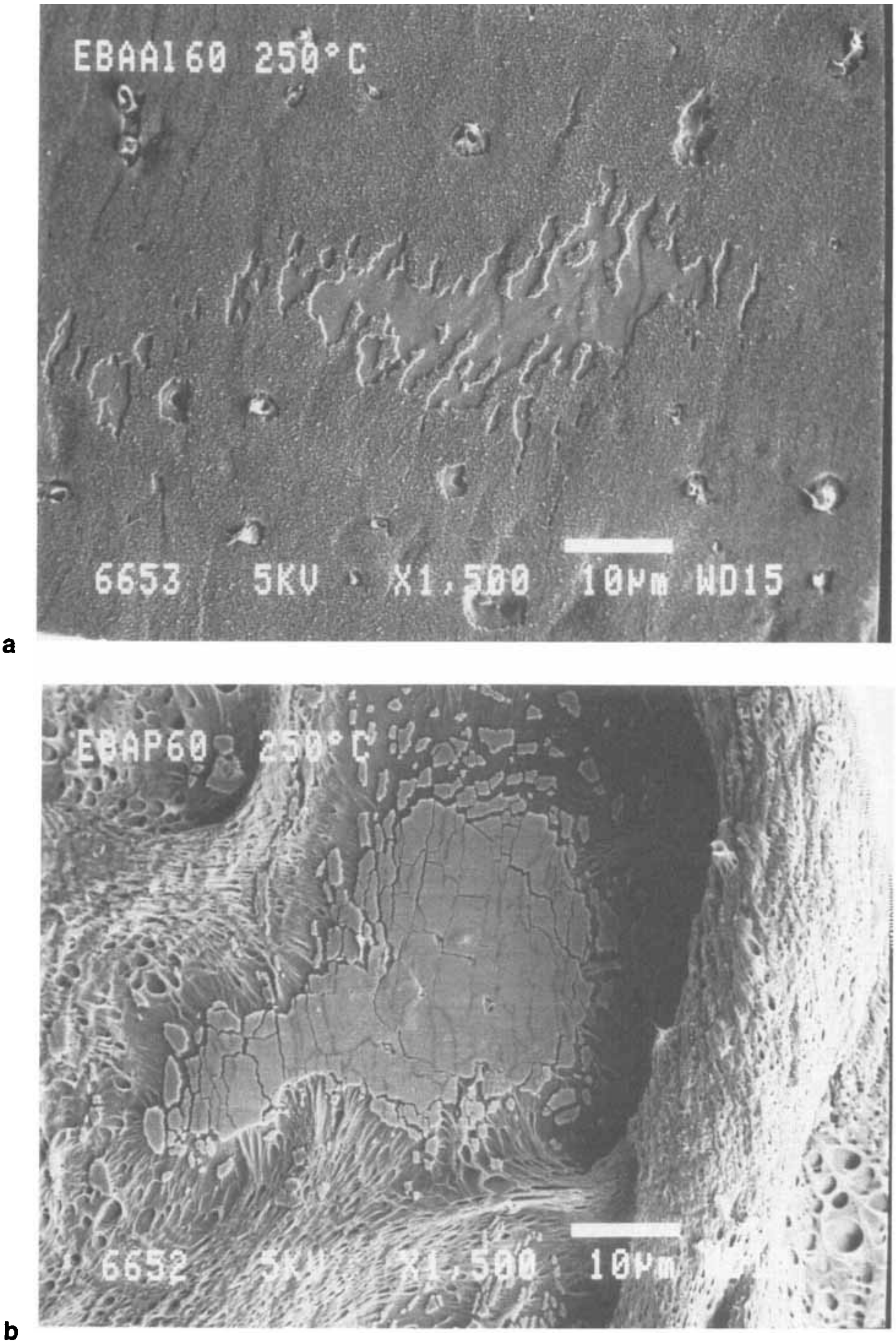


FIGURE 9 Fracture surfaces of an EBA laminate pressed at 250°C to aluminium hydrated for 60 seconds: a) aluminium side; b) corresponding polymer side.

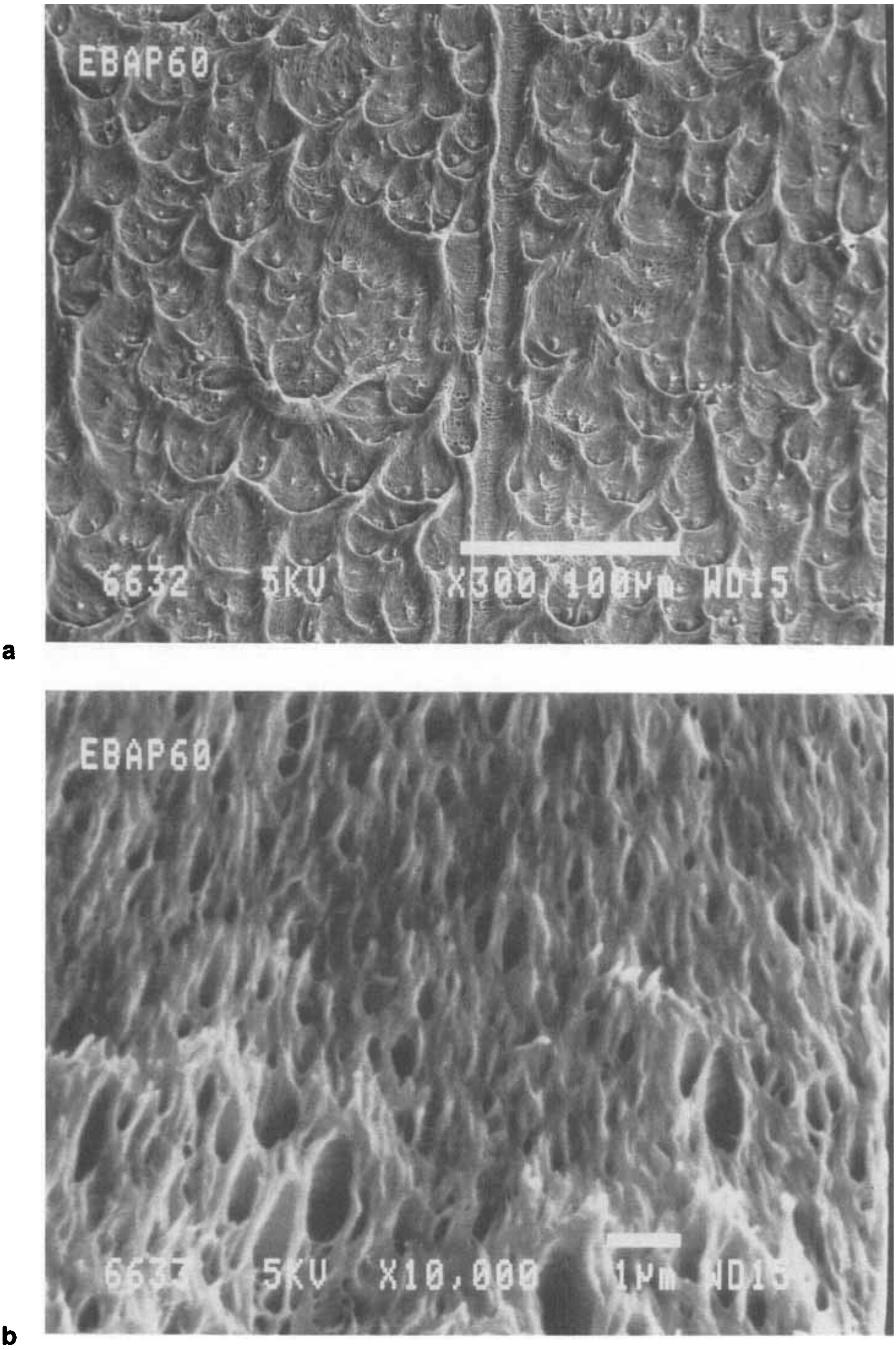


FIGURE 10 Fracture surface of the polymer side for an EBA laminate pressed at 150°C to aluminium hydrated for 60 seconds: a) original magnified 300×; b) original magnified 10000×.

side crackled flakes were found, see Figure 9b. By means of EDX (energy dispersive analysis of X-ray) a strong aluminium signal was obtained on this structure, which established that the flakes originated from the hydrated surface. The hydrated structure dominated the peeled aluminium surface, but at the higher temperatures the delamination of the pseudoboehmite layer may have an influence on the peel strength. Delamination of the hydrated film for the laminates pressed at 150°C was not found (see Figure 6b). This indicates that the polymer is more strongly bonded against the hydrated surface at 250°C as compared with 150°C. This may be attributed to the carboxylate formation, that most likely takes place more readily at the higher temperature. The penetration of polymer into the pores may also be increased at the higher temperature, due to lower melt viscosity. This can probably also explain the partial delamination observed at 250°C.

SEM analysis of the peeled aluminium side revealed no polymer layer for the magnification shown in Figure 6b. In the SEM micrographs of the corresponding polymer side a rough surface with torn-out ridges can be seen at low magnification, Figure 10a. At a higher magnification both a fine fibrillar structure and pores into the polymer can be observed, see Figure 10b. This observation indicates that EBA has been torn out from the pseudoboehmite layer and that it is strongly bonded to the hydrated surface. The IR analysis of the peeled hydrated aluminium sides indicates that a considerable amount of polymer is left on the aluminium surface. To evaluate the fracture on the hydrated aluminium side a greater magnification then

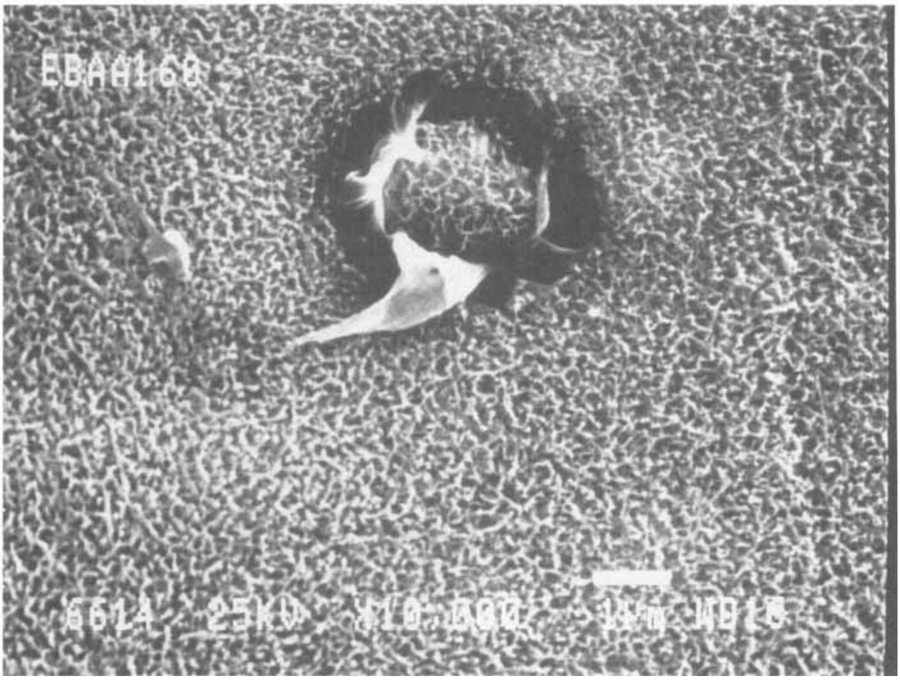
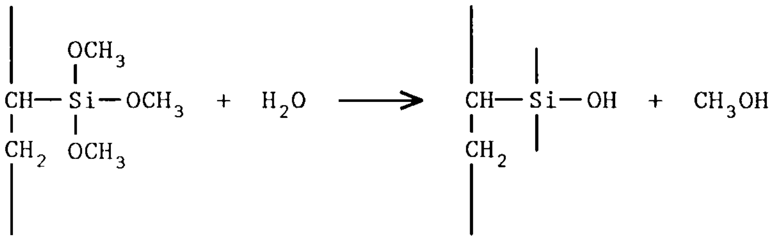


FIGURE 11 Fracture surface of the aluminium side for an EBA laminate pressed at 150°C to aluminium, with 60 seconds hydration time.

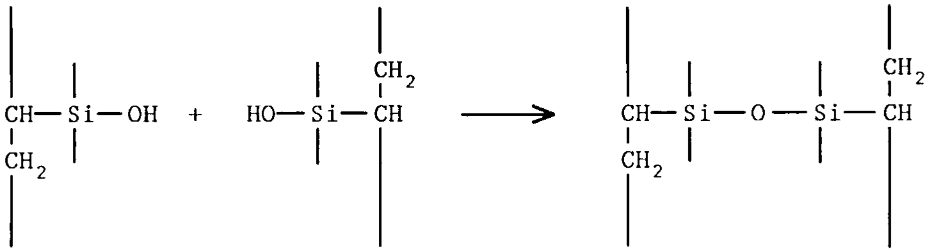
that in Figure 6b has to be used. A somewhat rougher structure appears in Figure 11 compared with that found after hydration, Figure 8c, and the polymer can in fact be seen as fine threads spread over the surface. This observation was somewhat more obvious for hydrated aluminium laminated at 250°C, where a thicker layer of polymer remained on the aluminium side. Based on these observations and the IR analysis, we suggest that the fracture of the hydrated laminates is cohesive for EBA. The low crystallinity for EBA (21%) implies that the interfacial region is more homogeneous. The stress will, therefore, be more evenly distributed than in the case of LDPE, which explains the failure close to the surface.

Methoxy Silane Groups

The methoxy silane groups in EVS and EVSBA can participate in several chemical reactions. The first is hydrolysis of the methoxy group leading to silanol which, thereafter, can take part in a condensation reaction:



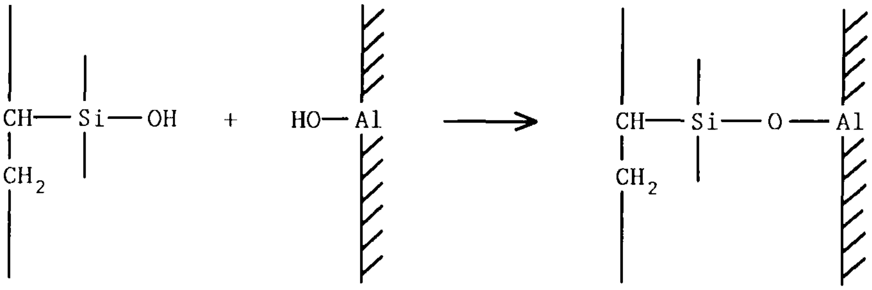
$$\mathrm{-CH(CH_2-)-Si(OCH_3)_2-OCH_3 + H_2O \longrightarrow -CH(CH_2-)-Si{\scriptstyle(-)(-)}-OH + CH_3OH}$$



$$\mathrm{-CH(CH_2-)-Si{\scriptstyle(-)(-)}-OH + HO-Si{\scriptstyle(-)(-)}-CH(CH_2-)- \longrightarrow -CH(CH_2-)-Si{\scriptstyle(-)(-)}-O-Si{\scriptstyle(-)(-)}-CH(CH_2-)-}$$

The latter reaction is mainly an intermolecular reaction and will lead to molecular enlargement and finally crosslinking. In fact, the main purpose in producing these copolymers is to introduce the crosslinking capability. The maximum gel content that can be obtained with the content of silane groups used in these samples is 70–75%.[33] The normal crosslinking conditions are 80–90°C in water or 90–100% relative humidity. To achieve reasonable crosslinking rates catalysts must be used, *e.g.* a Lewis acid such as dibutyl tin dilaurate or a Brönstedt acid such as stearic acid.[34]

At the interface to the aluminium oxide other reactions may occur as well. The most obvious is condensation between silanol and Al—OH groups:



Another possibility would, of course, be a direct reaction between methoxy and Al—OH groups. In both cases interfacial covalent bonds would be formed, which should give a significant contribution to the adhesion strength. In an earlier work we did indeed find indications of Si—O—Al bonds in RAS FTIR spectra of the interface between EVS and the aluminium oxide overlayer of ordinary aluminium foil, *i.e.* without hydration.[6] In contrast to laminates between LDPE and aluminium, laminates with EVS did not lose their peel strength when stored in water, which further supports the formation of interfacial bonds. This might explain the difference in peel strength between LDPE and EVS observed for untreated Al-foil after pressing at 250°C, 110 and 1180 N/m, respectively.

The content of hydroxyl groups in the aluminium oxide formed after the ordinary heat treatment used to remove rolling oil is, however, quite low. This is, *e.g.*, demonstrated by very low absorptions due to Al—OH groups in the RAS FTIR spectra of the untreated foil. With decreased temperatures, the reaction rate for both the hydrolysis reaction and the reaction forming interfacial bonds will, of course, decrease. Obviously, the low concentration of Al—OH groups makes the reaction rate a crucial factor below 200°C as judged from the drastic decrease in peel strength for the laminates between EVS and untreated aluminium. The FTIR data, Table II, of the aluminium side of the peeled laminates also indicate that the obvious cohesive failure observed in the laminates obtained at 250°C is changed to an adhesive failure for the laminates obtained at 150°C.

The hydration should favour these reactions in several ways. The content of hydroxyl groups at the aluminium oxide increases which also increases the acidity of the surface. The latter will lead to increased catalytic activity where the reactions preferably should take place. Furthermore, the pseudoboehmite formed contains a lot of physically adsorbed water, which will be deadsorbed at the temperature used when the laminates are pressed.[20] This will, of course, favour the initial hydrolysis reaction of the methoxy groups into silanols which subsequently may form both interfacial bonds and crosslink the interphasial region of the polymer. A higher content of Si—O—Al should *per se* be easier to detect, but the low content of vinyl silane comonomer in EVS and EVSBA (0.3–0.4 mol%) makes it difficult to observe any possible interfacial bonds. This is even more pronounced for the hydrated aluminium as the strong absorption band of Al—OH is found in the same region as the expected band of Si—O—Al bonds. Small changes in the oxide layer, which occur under the conditions used for pressing the laminates, thus mask the weak absorption band expected from the rare interfacial bonds. The observed changes in adhesion strength does, however, support the assumption of an increased reactivity after hydration.

EVS

For the EVS laminates pressed at 175°C a distinct increase in peel strength was observed when the aluminium had been treated with boiling water for times longer than the induction time for the pseudoboehmite rection, see Figure 2. Longer treatments did not lead to further improvements in peel strength. Both the FTIR data, Table II, and the SEM micrographs, Figure 3, of the aluminium side of the peeled laminates showed clearly that the increased peel force was accompanied with a change in the failure mechanism from adhesive to cohesive. When the cause for the increased strength is discussed both the increased probability to form interfacial bonds and the effects of the increased contact area as well as the possibility for mechanical keying in a porous oxide layer must be considered. In this respect, the steep increase observed for EVS between 10 and 20 s treatment time, in comparison with the moderate increase for LDPE, is important. After 20 s hydration there is some increase in the content of Al—OH groups, Figure 7, while the surface topography of the aluminium only has changed from a flat to a somewhat roughened surface. To form a porous pseudoboehmite layer as shown in Figure 8 longer hydration times are needed. Taking into account the expected increased reactivity of the aluminium surface due to the introduced Al—OH groups, we therefore consider the step in peel strength observed for EVS after 20 s hydration time mainly to be due to the formation of interfacial bonds. For longer treatments mechanical keying could be a contributing factor as well, but this can not be observed as the failure becomes cohesive in the polymer.

It should be noticed that both LDPE and EVS show cohesive failure in laminates made from hydrated Al-foil, although the level of peel strength is quite different, see Figure 2. The amount of polymer remaining at the aluminium side of the peeled laminates is, however, much larger in the case of EVS, see Table II and Figures 3b and d. One important reason for this difference may be formation of a transcrystalline layer which may result in a weak layer in the transition to the ordinary spherulite crystalline structure in the bulk as discussed above. The lower melt viscosity of the LDPE sample, MI = 4.5, should favour transcrystallisation in comparison with the EVS sample, MI = 0.8. Furthermore, the cohesive strength of the interfacial region of EVS can be improved due to the crosslinking capability of the methoxy silane groups. Crosslinking of EVS has already been reported to occur after lamination at 250°C to ordinary Al-foil.[13] The release of water during the pressing of the laminates and the potential catalytic effect of the oxide would indeed favour this reaction in the case of the hydrated aluminium. Figure 12 shows the relevant part of ATR spectra of EVS film before lamination and EVS remaining on the aluminium side after peeling (60 s hydration time). The spectra are plotted to give the same absorbance of the —CH_2— band at 1465 cm^{-1}. In the spectrum of the original film the Si—OCH_3 groups have bands[35] at 1190 cm^{-1} (—CH_3 rocking) and 1090 cm^{-1} (Si—O—C stretching), which have decreased considerably in the spectrum of the

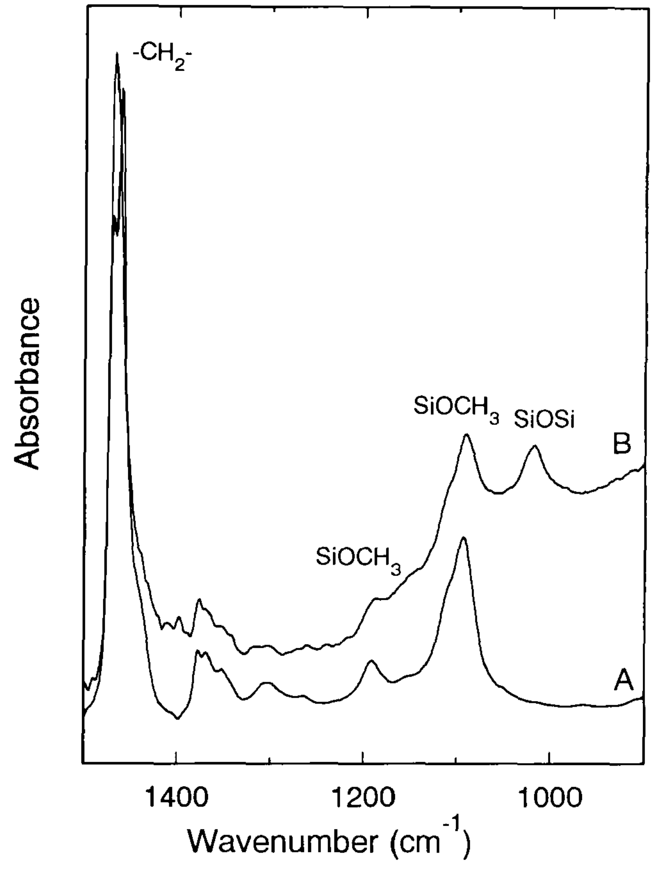


FIGURE 12 FTIR spectrum of EVS obtained by means of ATR: A) reference spectrum of film used for lamination, $\Delta A = 0.52$; B) fracture surface of the aluminium side, with 60 seconds hydration time, for an EVS laminate pressed at 250°C, $\Delta A = 0.10$.

material on the aluminium. In addition, a new band appears at 1030 cm^{-1} which can be assigned to Si—O—Si,[35] *i.e.* intermolecular crosslinks. Similar changes were observed in all spectra recorded from the aluminium side, but the underlying pseudoboehmite layer influenced the slope of the baseline in this region, which complicated a quantitative evaluation of the degree of crosslinking.

EVSBA

In the case of EVSBA both the presence of methoxy silane and ester groups should contribute to the adhesion strength. Compared with the polymer containing only the silane comonomer, EVS, the use of EVSBA in the laminates gives some significant differences. It should first be noticed that the peel strength obtained with the untreated aluminium does not decrease drastically with decreasing temperature. Using 150°C as press temperature, peel strengths of 1210 and 140 N/m were obtained for EVSBA and EVS, respectively, while the relative difference was considerably smaller for 250°C. In another study we have observed that EVSBA crosslinks much faster than EVS,[34] which can be related to a catalytic effect due to the Lewis base properties of the ester carbonyl. It is also reasonable that such a catalytic activity would also influence the reactions leading to interfacial bonds, which would explain the lower temperature sensitivity observed for the combination of EVSBA and untreated aluminium.

The high peel force obtained for the laminate between EVSBA and untreated aluminium does indeed indicate the presence of interfacial bonds, but in the SEM micrographs it is difficult to observe any polymer on the aluminium side, Figure 6. The absorbance of —CH_2—, Table II, however indicates the presence of *ca.* 400 Å of polymer. A similar result has been reported earlier based on XPS measurements after etching.[13] The conclusion is that the failure must have been cohesive. For the laminates pressed at 150°C short hydration times did not change this behaviour, but the peel force remained almost constant. Although the peel force was about the same for the corresponding laminates with EVS, the amount of remaining polymer was at least ten times larger in the latter case, *i.e.* the failure occurred deeper into the bulk of the polymer in the case of EVS. One reasonable explanation to this difference in the locus of the failure is the different levels of crystallinity, Table I. The low crystallinity of EVSBA, 15%, implies that the interphasial region is more homogenous. In fact, we have earlier observed that this layer is more or less totally amorphous in the case of EVSBA.[13] The stress will, therefore, be evenly distributed which explains the failure close to the surface. For EVS, on the other hand, the interphasial region is much more crystalline which leads to an inhomogenous stress distribution. The thickness of the polymer layer remaining on the aluminium side (as estimated from the FTIR data in Table II) is of the order of 1 μm, *i.e.* in the same range as the size of the spherulites observed in the interphase of polyethylene crystallized from the melt against aluminium.[13]

For hydration times longer than 40 s the EVSBA laminates gave increasing peel forces, see Figure 4. As the failure is cohesive this could imply an increased cohesive strength of the polymer. Considering the crosslinking capability of the silane groups, and the catalytic effect of the butyl acrylate comonomer, increased cohesive strength due to crosslinking is reasonable. In the case of the 60 s hydration time the increased cohesive strength of the polymer, and possibly increased density of interfacial bonds, has even resulted in partial delamination of the pseudoboehmite layer, see Figure 3. This is demonstrated more clearly with a larger magnification in Figure 13. In the areas where the oxide layer still is intact, it is easy to observe a thin and uneven overlayer of polymer.

For the longest hydration time used, 120 s, EVSBA showed extremely high peel forces, about 5000 N/m for laminates with failure in the interphasial region. The SEM micrograph of the aluminium side after peeling shows that the oxide layer has not delaminated, but it contains cracks perpendicular to the direction of peeling, Figure 13. This indicates that the cohesive strength of the pseudoboehmite layer probably has increased compared with that obtained after 60 s hydration. Such strengthening of pseudoboehmite layers at longer hydration times has also been reported earlier.[36] To obtain the high peel force the cohesive strength of the polymer must have increased still more. As the pseudoboehmite layer increases with treat-

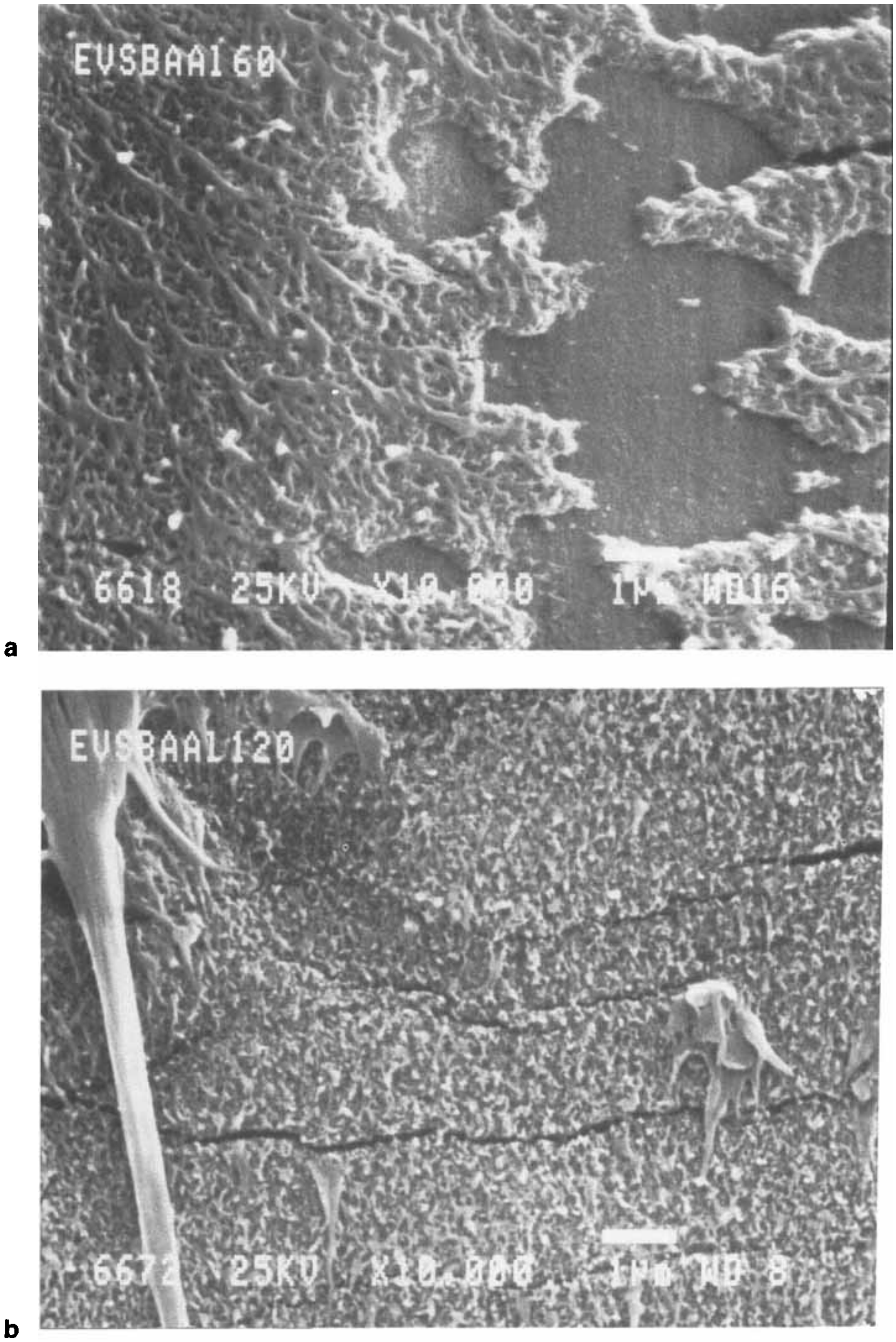


FIGURE 13 Fracture surfaces of the aluminium sides for EVSBA laminates pressed at 150°C to aluminium hydrated at 100°C for: a) 60 seconds; b) 120 seconds.

TABLE III
Absorbance at 2920 cm^{-1} of remaining polymer layer on the peeled untreated aluminium sides before and after 2 h extraction in boiling xylene. The press temperature used for lamination was 250°C

Polymer	Before extraction	After extraction
LDPE	0.010	—
EVS	>0.25	0.015
EBA	0.0038	—
EVSBA	0.018	0.0070

ment time, the amount of water that can be released in pressing the laminates also increases, which is consistent with an increased degree of crosslinking.

There are thus many evidences that the increased peel strength observed for the two polymers containing methoxy silane, EVS and EVSBA, compared with their non-silane counterparts, LDPE and EBA, to a large extent can be attributed to interfacial reactions between Si—OH (or Si—OCH_3) and Al—OH. The expected increased reactivity of the hydrated surfaces is also demonstrated. It has, however, not been possible to obtain direct spectroscopic evidences of possible Si—O—Al bonds. To demonstate further the strength of these bonds an extraction of the aluminium side of peeled laminates were done. To make the IR analysis more clearcut untreated aluminium was chosen, and 250°C was used as press temperature to ensure reaction. The aluminium strips were extracted for 2 h with boiling xylene which should remove all polymer unless it is strongly bonded. As seen in Table III the polymer layer disappeared completely in the case of LDPE and EBA, but for EVS and EVSBA a substantial layer was found even after the extraction. The measured absorbances of the —CH_2— band correspond to thicknesses of about 400 and 200 Å, respectively. This clearly shows the possibility of the methoxy silane groups to form strong bonds with aluminium oxide. As discussed above the interphasial layer is partly crosslinked, which may explain the relatively thick layers, corresponding to several monolayers, found after extraction.

SUMMARY

The hydration of aluminium leads to the formation of a porous pseudoboehmite layer with high content of Al—OH groups, which increases the peel strength for laminates with the investigated ethylene copolymers. For the polymers and/or lamination conditions which give adhesive failure against the untreated aluminium, the failure mode is changed to cohesive. To summarise, the porosity contributes with mechanical keying, and the effect of this is demonstrated isolated for the LDPE laminates. The increased content of Al—OH groups increases the possibilities for specific interactions. In the case of the ester group of the acrylate comonomer (EBA and EVSBA) Lewis acid-base interaction can occur, and at higher lamination temperatures hydrolysis of the ester may also lead to interfacial carboxylate formation. The most obvious increase in peel strength is, however, observed for the copolymers with methoxy silane groups (EVS and EVSBA). The most reasonable

explanation is that the silane group reacts with Al—OH and forms interfacial covalent bonds, Si—O—Al. In addition, intermolecular crosslinking between the silane groups increases the cohesive strength of the interphasial region leading to still higher peel forces. The increased reactivity of hydrated aluminium surfaces toward silane groups could thus open a possibility to obtain high peel strength with EVS also in laminates obtained in fast processes, such as extrusion coating.

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