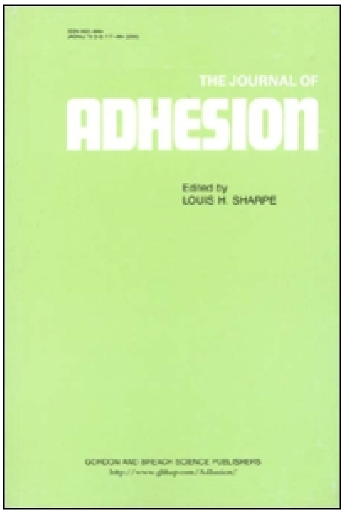

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Aluminum-Polyethylene Laminates Formed in High Vacuum†

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The bonding of LDPE to Al in high vacuum (10^{-5}Pa) was studied using a special apparatus that allowed the degassing at 200 C of each material prior to the application of mechanical pressure The results were compared with those obtained from samples bonded in air. Laminates formed from extruded LDPE and untreated Al in vacuum had higher initial peel strengths (13 Ncm^{-1}) than laminates formed in air (6 Ncm^{-1}) indicating the importance of volatiles, such as water, in the bonding process. Subsequent exposure to warm, moist air essentially negated the effect of the vacuum. The higher peel strengths generally obtained with extruded films when compared to samples made from other forms of the same LDPE resin, *i.e.*, as received pellets or pressed films, were attributed to the oxidized species produced during extrusion. Higher peel strengths were also obtained when the Al was boiled for 10 minutes in water prior to lamination to PE pellets, 10 Ncm^{-1} as contrasted to 1–2 Ncm^{-1} for untreated Al.

INTRODUCTION

In the literature on the bonding of polyethylene to aluminium,[1–9] almost all the studies which attempt to elucidate the mechanism of bond formation recognize the importance of oxygen and oxygenated species at the bonding surfaces. Some attempts have been made to exclude gaseous oxygen during the bonding process by flushing techniques with inert gas or by evacuation at moderate vacuum, but in each study there is reason to doubt that all traces of gaseous oxygen were removed. Other volatiles have also been postulated as interfering with bond formation by reason of the formation of a "weak boundary" layer.

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It was, therefore, decided to conduct a study in which both materials, low density polyethylene and aluminum foil, are held in high vacuum and then contacted with the application of mechanical pressure without breaking the vacuum. This paper reports on the design and construction of an apparatus to accomplish this and some initial results on the bonding of aluminum foil to polyethylene under high vacuum conditions.

EXPERIMENTAL

Vacuum Apparatus

The vacuum laminations were performed in a stainless steel press chamber (Figure 1) designed to fit inside an existing motorized hydraulic press with the mechanical pressure transmitted through the welded metal bellows. The chamber, which was connected to a 450 l/sec turbomolecular pump system containing a residual gas analyzer, was sealed with Cu gaskets. The polymer film or pellets used in the laminate were centered on an 11 cm Al foil pan placed on the bottom of the chamber. Above the pan an Al foil disc remained suspended on pins until the hydraulic press raised the chamber which applied pressure between the upper and lower platens. The chamber was heated by cartridge heaters at the bottom and a band heater at the top with the temperature monitored as shown.

Materials

The 76 μm Al foil (Alloy 1145, 99.5% Al, O temper) which was used had been cleaned by the manufacturer (Anaconda Aluminum Co.) by heating the Al rolls for ~ 20 hours at 400°C in a slightly reducing atmosphere. The advancing water contact angle of the neat Al surface was less than 5°, which indicated very little organic contamination. Surface analysis of the neat Al surface with X-ray photoelectron spectroscopy (XPS) also indicated a low level of C contamination. The Al2p to Cls peak height ratio observed was 2, whereas a ratio of 0.7 is reported by Briggs, *et al.*, for Al foil which had been cleaned by the frequently used chromic acid etch process.[2]

Table I shows a comparison of the melt index, density, and levels of 2,6-di-*tert*-butyl-*p*-cresol antioxidant (BHT) for the four lots of Dow 4005 extrusion grade low density polyethylene, and for the one lot of Chemplex 1014 low density polyethylene resin which were used in these experiments. These resins come in hemispherical pellets that are about 5 mm in diameter.

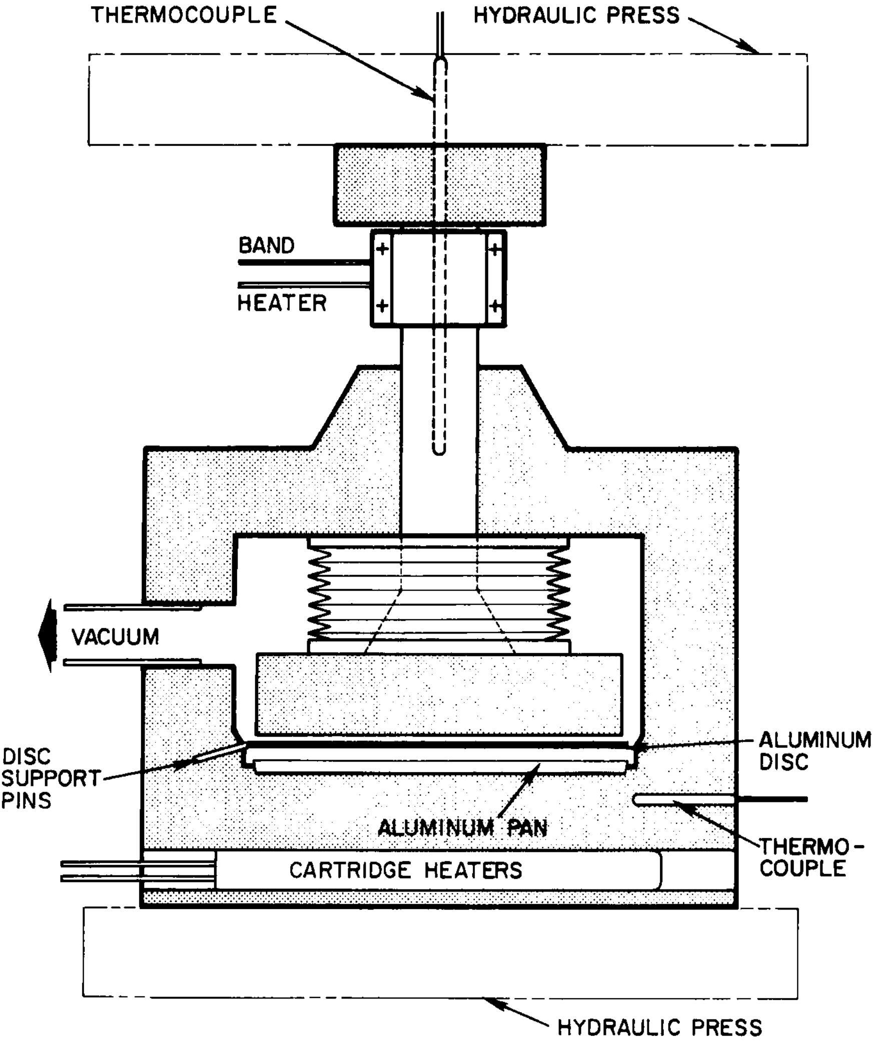

FIGURE 1 Vacuum laminating apparatus.

Pretreatments

In addition to using LDPE pellets and untreated Al foil to form laminates in vacuum, LDPE films (0.3 mm thick) prepared by extrusion of pellets in air

TABLE I

Analysis of LDPE pellets

Resin	Lot#	M.I.	Density[a]	BHT[b]
Dow 4005	A	5.4	0.916	71
	B	5.6	0.915	32
	C	5.7	0.916	64
	D	5.4	0.915	79
Chemplex 1014	A	6.0	0.918	0

[a] grams per cm^3 [b] parts per million by weight

using a Brabender Plasticorder at 290°C or by pressing either the pellets or ground pellets between Al foil in a hydraulic press at 125°C, 2 MPa or 10 MPa, for 15 or 60 seconds, were used.

For several experiments, the Al foil surface was oxidized to pseudoboehmite by boiling for 10 minutes in deionized water.

Lamination Conditions

The steps in a typical vacuum lamination were: (1) pump down to 10^{-5} Pa at room temperature, (2) heat to 200°C as determined by the bottom thermocouple (~15 minutes), (3) hold at 200°C until pressure drops to 10^{-5} Pa and the upper thermocouple reaches 175–200°C (~2 hours), (4) apply 2 MPa pressure for 15 or 60 seconds, (5) turn off heaters and cool under vacuum to ambient. (The temperature typically drops from 200°C to 110°C after one hour, to 90°C after 1½ hours.) The residual gas analyzer was used to measure pressure and monitor volatiles at all stages. When pellets were used as starting materials, the 2.5 gm used roughly covered the center 4.5 cm of the 11 cm Al pan.

Laminates made in air were normally heated 15 seconds (the residence time in the motorized, hydraulic press) and then allowed to cool to ambient on the laboratory bench.

Testing

Strips of the laminate (1.2 cm wide) were peeled in an Instron testing machine with a cross head speed of 13 cm/minute. Typically, the Al disc was first peeled from the PE at 180° using a rigid backing plate (ASTM D903–49), then the same sample was turned over, reattached to the backing plate with doublefaced tape, and the Al pan was peeled from the PE at the same angle. Error limits given are twice the standard deviation.

Laminates were tested within 24 hours after preparation; vacuum laminates were usually tested within a few hours after removal from vacuum.

EXPERIMENTAL RESULTS

The peel strengths obtained with untreated Al are divided into three groups according to the form of Dow 4005 used; the bonding conditions were essentially the same. For each form of Dow 4005, laminates were made in vacuum and in air. The peel strengths obtained by peeling the top sheet of the Al are distinguished from those obtained by peeling the bottom sheet of Al. In vacuum formed laminates the top foil sheet is called "disc" and the bottom foil sheet is called "pan".

Extruded Film

Table II shows that the peel strengths obtained with extruded film bonded in vacuum were twice as high as those bonded in air. After storage in a 40°C high humidity cabinet (90% relative humidity) for 4 days, all of the peel strengths (Table III) decreased. However, the value for the laminate bonded

TABLE II

Peel strength of Al/Dow 4005/Al laminates[a] prepared from extruded films

		Peel Strength (Ncm^{-1})[b] bonded in					
		Vacuum			Air		
Resin batch	Extrusion temp.	n^c	Pan	Disc	n	Bottom	Top
B	280°C	2	10±0	11±2	4	5 ±1	5 ±1
C[d]	290°C	8	14±2	13±2	6	5.9±0.3	6.3±0.3
C[d]	290°C	2	14±1	18±1	4	6.8±0.3	6.8±0.7

[a] Laminated at 200°C, 2MPa, for 15 seconds.
[b] 2σ limits based on peeling both sides of two 1.2 cm strips from each laminate.
[c] Number of Al-PE-Al test strips.
[d] Extruded on different dates.

TABLE III

Al/extruded PE/Al

Peel strengths after storage for 4 days at 90% relative humidity, 40°C

	Peel Strength (Ncm^{-1})[a]			
	Bonded in vacuum		Bonded in air	
	Pan	Disc	Bottom	Top
Original	13.7	12.8	6.0	6.3
Aged	6.0	3.0	4.2	4.4

[a] Average of two measurements

in vacuum decreased much more and closely approached the peel strength of the laminate bonded in air.

Pressed Film

Table IV compares the peel strengths obtained using pressed films. The peel strengths were weaker for laminates made in both air and vacuum than for the analogous laminates made with extruded film. The laminations in vacuum exhibited a definite asymmetry, the peel strength obtained with the Al pan being much higher than that obtained with the Al disc.

TABLE IV

Peel strength of Al/Dow 4005/Al laminates prepared for pressed films

	Peel Strength (Ncm^{-1})[a]					
	Laminated in vacuum			Laminated in air		
	n[b]	Pan	Disc	n	Bottom	Top
Film pressed from ground Dow 4005-A pellets at 125°C, 4MPa, 1 min dwell laminated to untreated Al foil at 200°C, 2MPa, 1 min dwell.	2	5.8 ± 0.5	0.3 ± 0.0	4	3.0 ± 1.0	2.8 ± 1.4
Film pressed from Dow 4005-A pellets (not ground) at 125°C, 10MPa, 15 sec dwell, laminated to untreated Al foil at 200°C, 2MPa, 15 second dwell[c]	2	3.5 ± 0.3	0.5 ± 0.5	4	0.3 ± 0.3	0.3 ± 0.2

[a] 2σ limits based on peeling both sides of two 1.2 cm strips from each laminate.

[b] Number of Al-PE-Al test strips.

[c] Other experiments with a 60-sec dwell time at 200°C in air did not result in laminates with different peel strengths.

Pellets

The peel strengths obtained with laminates made from pellets are given in Table V. Three different lots of Dow 4005 were used in these experiments—A, C, and D. The peel strengths for laminates made from A were different than those made from C and D regardless of whether they were formed in vacuum or in air. For laminates formed in vacuum with Dow 4005A, the pan peel strength was high only in the center region where the pellets were placed.

Ancillary Experiments

Additional (in vacuum) experiments which varied the bonding conditions using films pressed from Dow 4005A were performed. The type and results are as follows: (1) When the period of heating in vacuum at 200°C prior to

TABLE V

Peel strength of Al/LDPE/Al laminates[a] prepared from pellets

	Peel Strength (Ncm^{-1})[b]							
	Vacuum				Air			
Pellets	n[c]	Pan	Disc	Ratio[d]	n[c]	Bottom	Top	Ratio[d]
Dow 4005-A[e]	9	4.7±2.6[f]	1.0±1.0	5.2±2.3	4	0.7±0.5	0.3±0.2	2.0±0.8
Dow 4005-C	4	2.6±0.3	1.9±0.3	1.3±0.4	4	2.1±0.3	1.9±0.2	1.1±0.2
Dow 4005-D	2	2.4±0.0	1.9±0.5	1.3±0.4	4	2.1±0.0	1.7±0.3	1.1±0.2
Chemplex 1014[g]	2	4.2±0.5[f]	1.4±0.3	3.1±0.3	4	2.3±0.3	2.3±0.2	1.0±0.2

[a] Laminated at 200°C, 2MPa for 15 sec, except where noted.
[b] 2σ limits based on peeling both sides of two 2.2 cm strips from each laminate.
[c] Number of Al-PE-Al test strips.
[d] Average of ratios of peel strength of Pan/Disc or Bottom/Top.
[e] Vacuum experiment laminated for both 15 sec and 60 sec.
[f] Value for center 4.5 cm.
[g] Vacuum experiment laminated for 60 sec.

bonding was extended from 2 hours to 3 days, no change in peel strength was observed. (2) Maintaining the temperature at 200°C for two hours after bonding (usually the heaters were switched off after bonding) resulted in disc and pan peel strengths of 1.7 and 3.7 Ncm^{-1}, respectively. (3) A PE film was subjected to the standard heating cycle but the upper surface was not bonded as usual to the disc. The excess Al from the pan #1-PE laminate was trimmed, and this pan #1-PE laminate was reloaded in the vacuum press with the PE contracting a second pan (#2). The standard procedure was then followed, yielding a laminate with the least asymmetry and the following peel strengths: 2.8±0.3 and 2.5±0.2 Ncm^{-1} for pan #1 and pan #2, respectively.

Laminates made from pellets of a different LDPE, Chemplex 1014, and untreated Al (Table V) had an asymmetry between the disc-PE and pan-PE peel strengths like Dow 4005A, when formed in vacuum. The laminates formed in air had stronger peel strengths like those for Dow 4005C and Dow 4005D.

Water Treated Aluminum Foil

The data discussed above were for laminations made with as received Al foil. Boiling Al foil in deionized water for 10 minutes produces an irregular surface as seen in the scanning electron micrograph in Figure 2. The neat Al surface revealed no structure when examined with the SEM at comparable magnifications. Six vacuum formed laminates using Dow 4005A pellets and Al foil boiled 10 minutes in deionized water had pan-PE and disc-PE peel strengths of 10.3±1.0 and 10.2±0.7 Ncm^{-1}, respectively. Laminates formed in air had similar bond strengths. Insignificant changes in the peel strengths obtained in vacuum were found for variations such as (*a*) 5 sec bonding time, (*b*) 150°C bonding temperature, and (*c*) 122°C upper platen temperature.

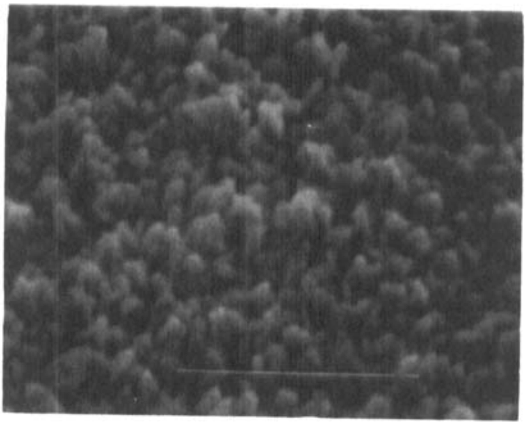

FIGURE 2 Scanning electron micrograph of the Al surface after boiling 10 minutes in deionized water. The long white line corresponds to 1 μm.

Gas Analysis

The residual gas analyzer was used to monitor the vacuum environment. Prior to heating, after the initial pumpdown the dominant species was water which is characteristic of an unbaked vacuum system without an air leak. On heating, the water signal increased and when the bottom thermocouple reached about 180°C, large N_2 and O_2 peaks were frequently observed and the pressure rose to 10^{-2} Pa; after several minutes the pressure decreased, the N_2 and O_2 peaks decreased more rapidly than the pressure. Typical hydrocarbon peaks at mass 27, 29, 41, 43, were also observed, and these decreased on prolonged heating. The pressure after two hours was usually 10^{-5} Pa.

The PE and Al foil were weighed prior to heating in vacuum and after removal. The weight losses observed corresponded to a PE weight loss of $\sim 0.3\,\%$, most likely due to volatiles initially present in the sample.

Surface Characterization

ATR-IR spectra were run on pressed and extruded films with a Perkin-Elmer Model 283B Infrared Spectrometer with computer data station, using a standard KRS-5 crystal (45°) which provided approximately 1 μm penetration of the sample at 1715 cm^{-1} (carbonyl band). Computer signal averaging of seventy-five and/or nine 12 minute scans were performed on all samples. Extruded Dow 435 which is an ethylene-acrylic acid copolymer with 3.5 % by weight acrylic acid was used as a standard for these measurements.

Contact angle measurements were made on pressed and extruded Dow 4005 films by the sessile drop method (drop diameter ~2 mm) using deionized distilled water at room temperature.

Table VI summarizes the surface characterization data on Dow 4005 films obtained from ATR-IR and water contact angle measurements. The extruded film exhibited a carbonyl peak not observed in the pressed film. No significant difference was observed with the water contact angle for any of the Dow 4005 films.

TABLE VI

ATR-IR and contact angle measurements on polymer films

Film	Absorbance 1715 cm^{-1}	Absorbance 1377 cm^{-1}	H_2O Contact[a] Angle (degrees)
Dow 4005-B, extruded	0.0090	0.25	98 ± 2
Dow 4005-C, extruded	0.0665	0.29	98 ± 3
Dow 435 (3.5 % EAA)	1.00[b]	0.24	85 ± 6
Dow 4005-A, pressed film[c]	not detectable	0.25	93 ± 5
Dow 4005-C, pressed film[c]	not detectable	0.25	95 ± 5

[a] 2σ limits based on 12 drops of each liquid.

[b] 1710 cm^{-1} peak.

[c] Pressed 125°C, 10MPa, 15 sec.

DISCUSSION

Good adhesion between polyethylene and smooth aluminum surfaces seems to be associated with the presence of oxygenated species on the polyethylene surface. Briggs, Brewis, and Konieczko correlated the adhesion of PE extrusion coated onto Al foil with the O/C ratio as observed by XPS.[1] In a second paper,[2] they again used XPS to show that melting PE in contact with Al in air at 150°C or 175°C for 10 minutes produced oxygenated species on the PE surface in contact with the Al.

The experimental data in Tables II, IV, and V show that the highest peel strength for PE/smooth Al laminates occurred with extruded PE film. The ATR-IR spectra of extruded PE had a carbonyl peak whereas no carbonyl peak was observed with pressed films. These facts support the importance of PE oxidation in PE/Al adhesion. However, the extruded film was more crosslinked as evidenced by a melt index of 3.5 compared with 5.5 for as received resin. This could have raised the cohesive strength of the extruded PE at the PE/Al interface and thereby increased the peel strength.[10]

The increased peel strength observed with extruded PE laminated to Al in vacuum compared with those laminates formed in air is attributed to moisture and absorbed gases interfering with bond formation. Exposure of laminates formed in vacuum or in air to high humidity (90% RH) at 40°C resulted in decreased peel strengths (Table III), especially for vacuum formed laminates. This suggests that two types of bonds are formed between the extruded PE and the Al surface; the additional one which forms in vacuum is unstable when exposed to humid, warm air for sufficient time to permit water and gases to permeate to the interface.

Laminates formed with LDPE which had not been subjected to extrusion temperatures exhibited high peel strengths only when the Al foil was pretreated in boiling deionized water, which produced the roughened pseudoboehmite structure (Figure 2). The formation of strong laminates did not depend on whether laminates were prepared in air or vacuum. Similar results have been reported by Packham, Bright and Malpass[6,7] who bonded LDPE to porous anodic films which are thick with large, clearly defined pores. Their explanation of mechanical forces determining the peel strength is also believed to apply to PE bonding to pseudoboehmite films produced by boiling Al.[11]

Earlier workers[7,12] have reported peel strengths of 2–3 $\mathrm{Ncm^{-1}}$ for PE/Al laminates formed by heating PE powder on nonporous Al in low vacuum (1 Pa) for times ranging from 100 seconds to 3 hours at 200°C. Peel strengths of laminates similarly bonded in air were 2–3 $\mathrm{Ncm^{-1}}$ when the heating period was 100 seconds, but 10–20 $\mathrm{Ncm^{-1}}$ when the heating time was 15–20 minutes. Considering the differences in starting materials and experimental arrangements, these peel strengths previously reported for the vacuum formed laminates and the laminates formed in air with a 100 second heating period agree reasonably well with the peel strength data in Tables IV and V.

The asymmetry between the disc-PE and the pan-PE peel strengths with Dow 4005A resin appear to be related to the different PE-Al contact time at 200°C. A recent model proposed by Owens[13] to explain the self-adhesion of corona-treated PE, attributes strong self-adhesion to hydrogen bonds formed between ketones and enolized ketones in adjacent surfaces and the decreased self-adhesion observed when corona-treated films were heated prior to laminating by intraphase hydrogen bond formation. It is possible that potential Al-bond formers in Dow 4005A became similarly bonded within the PE when heated out of contact with the Al. Another possible explanation for this asymmetry is that contact time of this PE with the Al surface resulted in chemical changes that increased the concentration of carboxylic acid groups, which are Al-bond formers.

XPS data recently published[14] showed that electrical discharge treatment of PE in "inert" gases produced oxidized moieties at the surface even though oxidized species in similarly treated films had not been observed by earlier workers using ATR-IR, presumably due to ATR-IR being less surface sensitive than XPS. It is postulated that small variations in the levels of oxidation and/or oxidized species undetected by ATR-IR (Table VI) existed in the different lots of Dow 4005 used in the experiments reported herein, and that these variations were a dominant factor in the PE to Al adhesion. These minor variations were overridden by further oxidation of the PE during extrusion, or by bonding the PE to an Al surface made porous by boiling. In the latter case, a mechanical effect contributed strongly to the peel strength.

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