

Bonding Polyethylene to Metals

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Synopsis

A process for adhering polyethylene to aluminum was developed which involves treating the aluminum substrate successively with chromic acid and then a selected organic acid. Certain organic acids utilized in this process appeared to produce a synergistic effect on the adhesion. This process, which required no modification or treatment of the polymer, resulted in peel strengths forty times greater than that obtained on untreated aluminum. Tensile shear values for the polyethylene-aluminum bond were greater than 2800 psi. The materials used for treating the metal in this system produced a maximum in the obtainable peel strength. Furthermore, minor changes in the etching acids resulted in drastic changes in the adhesion values.

INTRODUCTION

During the past few years there has been considerable interest in attempting to bond polyethylene to metal,¹ particularly aluminum.²⁻⁴ Although, recently some claims have been made for bonding unmodified polyethylene to aluminum,^{2,3,5} effort has been directed primarily toward modifying the polymer in some manner to enhance its adhesion to the metal.^{4,6,7} The commonest methods for obtaining polyethylene adhesion were through oxidation of the polymer such as the chromate etch developed by Picatinny Arsenal⁸ or flame treatment of the polymer.⁹

Suggestions were advanced⁴ that the reason for the difficulty in bonding polyethylene to metal was migration of low molecular weight material to the interface. More recently, adhesive bonding has been suggested to be intimately associated with the wetting of the substrate by the polymer. Both of these conditions are important, especially the necessity of having the polymer wet the substrate during joint formation. However, although wetting is a necessary condition for having good bonding, it may not be the only condition required. It will be shown in this work that a mild surface treatment of the metal was sufficient to promote bonding of polyethylene to aluminum. Furthermore, it will also be shown that minor modifications in the materials used for surface treating the metal resulted in a marked change in the bond strength of polyethylene to the metal.

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EXPERIMENTAL

Materials

The aluminum employed was soft annealed 4.5-mil foil. High-density polyethylene (Dow lot 3139, melt index 3.0) containing no lubricant or stabilizer was used without further modification. The polypropylene (Hercules Profax, lot no. 20805, formula 6501) appeared to contain a minor trace of a lubricant, since an extraction with diethyl ether was necessary before successful adhesion could be accomplished.

Two of the organic acids, maleic and citraconic, were prepared by dissolving appropriate quantities of the anhydride in water. The remaining materials employed in this work were used as received.

Preparation of Samples

The polyethylene film used for bonding to the treated aluminum surface was prepared in the following manner. High-density polyethylene (15 g.) was placed between Mylar slip sheets in a Pasadena hydraulic press under 110 psi and a temperature of 160°C. for 2 min. The sample was cooled in the press, removed, and tested according to ASTM D903-49 except that the aluminum foil was peeled from the polymer at a crosshead separation rate of 4 in./min.

The aluminum used for preparing the lap jointed samples was T3 2024 Alclad aluminum. Two samples 6 x 4 × 0.063 in. were treated by the process outlined in the procedure. These two samples were then overlapped 0.5 in. with a sample of polyethylene film placed between them and bonded in a bonding jig under a pressure of 60 psi and a temperature of 200°C. for 3 min. After cooling and removal from the press, the lapped joint thus produced was tested according to ASTM 1002-53T on the Instron testing machine. Polypropylene films were prepared and bonded in the same manner as described above except that a temperature of 215°C. and a pressure of 110 psi was used.

Procedure

The 6 × 8 × 0.0045 in. samples of soft annealed aluminum foil were treated by immersing them for the required length of time in 9 × 13 × 2 in. glass cake pans containing the selected acids. Prior to following the process, the aluminum foil was degreased by subjecting it to boiling perchloroethylene for 10 min. This degreasing step, while not essential to the process, was employed to ensure a grease-free surface.

In step 1, the metal foil was immersed for 5 min. in a 5% aqueous solution of CrO₃, prepared by dissolving 50 g. of CrO₃ in 1 liter of water. After the metal was removed from the bath in step 1, the adhering CrO₃ was rinsed off with running deionized water (step 2). This step may be omitted in the process with no adverse effects on the adhesion. However, the inclusion of this step prevents the adhering CrO₃ from contaminating

the solution in step 3. Following the water rinse in step 2, the metal was immersed for 2 min. in a 5% aqueous solution of a selected organic acid maintained at 80°C. The residual organic acid was rinsed from the surface with running deionized water (step 4). This step, similar to step 2, may be omitted with no detrimental effects on the adhesion. After the final water washing, the metal was allowed to air-dry for a short period until no further water was visible on the surface (step 5). Finally, in step 6 the polymer was placed with the treated metal between Mylar slip sheets and bonded in a Pasadena hydraulic press for 2 min. under 110 psi and 180°C.

In the subsequent data any reference to chromic acid alone implies the aluminum was treated by only steps 1, 2, 5, and 6 of the above process and aluminum treated with maleic acid alone refers only to steps 3, 4, 5, and 6.

RESULTS AND DISCUSSION

A plot of peel strength versus immersion bath temperature is shown in Figure 1. This graph reveals the combination of acids always produces adhesion superior to that with either individually. The line representing the adhesion due to maleic acid alone exhibits a linear increase in peel strength with temperature. Aluminum treated with chromic acid alone, on the other hand, shows an unexpected maximum in peel strength at 80°C. An examination of the polyethylene by x-ray fluorescence, after the bonded aluminum had been stripped from it, revealed that greater amounts of aluminum oxide were contained on the polymer stripped from aluminum treated at 100°C. than from aluminum treated at 80°C. This would indicate that aluminum treated at 100°C. produced a weak oxide

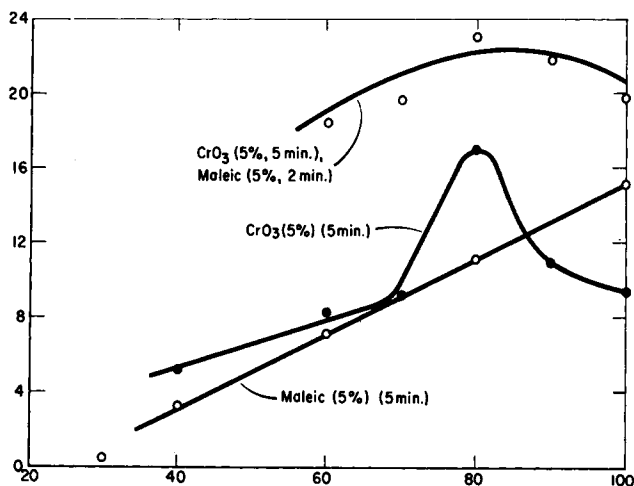


Fig. 1. Variation of peel strength (lb./in. width) with immersion bath temperatures (°C.).

layer, perhaps through too rapid an oxidation with chromic acid, which allowed the adhesive bond to break in this weak oxide layer. The linear increase in peel strength resulting from the maleic acid alone has been correlated with a linear increase in the concentration of ^{14}C maleic acid contained on the aluminum surface at different etching temperatures (Table I). Oddly, the concentration of maleic acid on the aluminum surface was lowest on the sample which had first been etched with CrO_3 before being treated with maleic acid, and yet this sample showed the greatest adhesion to polyethylene. This information suggests the possibility of a dual mechanism in this system for promoting the adhesion of polyethylene to aluminum. The following discussion indicates these mechanisms may be synergistic and not mutually destructive.

TABLE I
Maleic Acid (^{14}C) Remaining on Aluminum
Treated at Different Temperatures

Maleic acid solution temperature, °C.	Maleic acid, mg./in. ² of aluminum surface	Peel strength, lb./in. width
60	127	7.0
80	150	11.5
100	174	15.0
CrO_3 plus maleic at 80°C. (5% solutions)	27	22.7

At certain points along the curve in Figure 1, the combination of acids yielded a greater peel strength than the sum of the individual acids, i.e., at 60 and 70°C. This effect was not observed at all points along the curve, especially at 80°C. However, when the concentrations of the immersion baths were lowered from 5% used in Figure 1 to 0.1%, then from Table II the sum of the peel strengths from chromic acid alone (6.6 lb.) at 80°C. and maleic alone (5.8 lb.) at 60°C. is lower than the combination (14.0 lb.) at these concentrations and temperatures. Thus, the synergistic effect of maleic acid on chromic acid which is observed at 60 and 70°C. may also exist at 80°C. A possible explanation for the inability to observe this effect at the 5% concentration used in Figure 1 may involve some type of ceiling on the peel strength in this system. This maximum in peel strength, which is also mentioned below, is shown graphically in Figure 2.

The synergistic effect on peel strength of treating the metal with the organic acid after the inorganic acid was observed more clearly in the polypropylene system shown later. Thus, a weak boundary layer, the tensile strength of the polymer, or some other limiting factor may set a ceiling on the maximum peel strength that can be observed in this particular system.

TABLE II
Effect of Bath Concentration on HDPE-Al Adhesion

CrO ₃ concentration, wt.-% (immersion 5 min. at 80°C.)	Maleic acid concentration, wt.-% (immersion 5 min. at 60°C.)	Peel strength, lb./in. width
0.1	—	6.6
0.5	—	9.0
1.0	—	10.5
5.0	—	17.0
—	0.1	5.8
—	0.5	5.0
—	1.0	4.5
—	5.0	7.0
0.1	0.1	14.0
0.5	0.5	21.1
1.0	1.0	21.0
5.0	5.0	21.5

Acid concentrations higher than the 5% shown in Table II did not produce higher peel strengths. These latter results may also be related to the ceiling in peel strength mentioned earlier.

Other Acids

A number of inorganic acids were tested in step 1 of the previously outlined process. These acids (HCl, HNO₃, H₂SO₄, H₃PO₄, MoO₃, WO₃, and even the combination of Na₂Cr₂O₄ and H₂SO₄) failed to produce significant adhesion of polyethylene to aluminum. A combination of CrO₃ and H₃PO₄ successfully promoted the adhesion of polyethylene to aluminum; how-

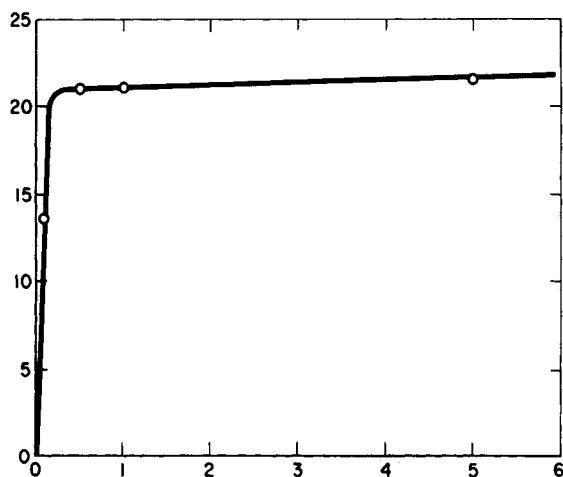


Fig. 2. Peel strength (lb./in. width) of HDPE on aluminum treated at various acid concentrations (wt.-%).

ever, the bond was unstable in a water-boil test. (The values obtained with this combination of acids may be found in water-boil test results of Table VIII.)

The organic acids which were substituted for maleic in the treatment are shown in Table III. This table is divided into two sections, those organic acids which promoted polyethylene adhesion to aluminum and those which were detrimental or had no effect.

TABLE III
Effect of Peel Strength of Aluminum Treated with
Various Organic Acids

Acids which promote adhesion			Acids which are detrimental to adhesion		
Acid	Peel strength, lb./in. width		Acid	Peel strength, lb./in. width	
	Alone	With CrO ₃		Alone	With CrO ₃
Maleic	11.5	22.7	Acetic		6.0
Citraconic	9.7	21.1	Propionic	1.8	9.2
Acrylic	9.1	20.8	Butyric	3.6	12.2
Polyacrylic	13.2	24.5	Oxalic	1.0	2.0
Methacrylic	2.0	17.7	Malonic	2.0	14.3
Crotonic	2.0	18.4	Succinic	1.2	13.3
Glutaric	2.0	19.0	Adipic	1.8	
Fumaric	13.0	19.0	Adipic	1.8	
			Pimelic		7.7
			Pyromellitic	1.0	9.8
			Lactic	1.8	9.1
			Tartaric	No adhesion	
			Chloromaleic		2.0

In considering Table III, it should be remembered that chromic acid alone resulted in a peel strength of 17 lb./in. width. Consequently, an organic acid used in conjunction with chromic acid, which produces a lower peel strength than this must be considered detrimental to the adhesion in this system.

Adhesion of Various Polymers to Aluminum

A variety of polymers were tested for possible adhesion to a treated aluminum surface. Polymeric materials such as polystyrene, poly(methyl methacrylate), Saran, poly(vinyl chloride) and several styrene-butadiene copolymers exhibited negligible adhesion to aluminum. However, a number of polyolefins were successfully bonded to a treated aluminum surface. These polymers and their peel strengths are listed in Table IV. The aluminum used for bonding to these polymers was treated according to the process outlined in the Procedure section.

TABLE IV
Adhesion of Various Polyolefins to Treated Aluminum

Polymer	Peel strength, lb./in. width
High-density polyethylene	22.7
Low-density polyethylene	15.5
Ethylene-propylene rubber	13.0
Ethylene-propylene copolymer	8.1
Polybutene-1	5.0
Polypropylene	17.5

The adhesion of polypropylene to aluminum treated under various immersion bath temperatures is shown in Table V. The aluminum used in these tests was treated by the previously described process, except that citraconic acid replaced the maleic acid in step 3. In general, it has been found that polypropylene does not yield as high a peel strength on aluminum as high-density polyethylene. The data shown in Table V also illustrate a significant point. Neither chromic acid nor citraconic acid, when used individually, has a great effect on the peel strength. However, aluminum treated by the combination of these acids exhibits greater adhesion than either alone or even the sum of the peel strengths from the individual acids. This effect, as mentioned previously, may also exist with polyethylene but due to the limiting value of the peel strength it may not be observed.

TABLE V
Polypropylene Adhesion to Aluminum

Temperature, °C.	Peel strength, lb./in. width		
	CrO ₃ (alone)	Citraconic acid (alone)	CrO ₃ + citraconic acid
60	1.5	No adhesion	2.0
80	1.0	1.0	12.0
100	3.0	1.0	8.5

Other Metallic Substrates

The metals which have been tested in this process are shown in Table VI.

TABLE VI
Polyethylene Adhesion to Various Metals

Metal	Peel strength, lb./in. width		
	CrO ₃ (alone)	Maleic acid (alone)	CrO ₃ + maleic acid
Aluminum	17.0	11.5	21.5
Nickel	7.5	2.0	12.0
Carbon steel	12.0	—	—
Tinplate	—	—	21.3

In addition to the above metals, galvanized steel has also been successfully bonded to polyethylene.

Lap Shear Tests

Another method of measuring adhesion is the use of a lap shear test (ASTM 1002-53T). Two samples of T3 Alclad aluminum were treated by the process and bonded as described in the Experimental section. The adhesion values obtained by this test are shown in Table VII. Also included in this table, as a means of comparison, are the lap shear values given by Schonhorn² and by Hart and Rieke.⁶ Table VII further indicates the improved adhesion resulting from the surface treatment of aluminum. These samples, similar to the peel specimens, usually revealed a thin film of polymer on each half of the broken lap bond.

TABLE VII
Lap Shear Values of Various Polymers and Surface
Treatments on Aluminum

Polymer	Treatment	Lap shear strength, psi
Polyethylene-acrylic acid graft copolymer		1576 ^a
High-density polyethylene	(H ₂ SO ₄ + Na ₂ CrO ₄)	1459 ^b
High-density polyethylene	(H ₂ SO ₄ + Na ₂ CrO ₄) + stearic acid monolayer	1561 ^b
High-density polyethylene	Maleic acid (alone)	2270
High-density polyethylene	CrO ₃ (alone)	2540
High-density polyethylene	CrO ₃ + maleic acid	2860

^a Data of Hart and Rieke.⁶

^b Data of Schonhorn.²

Environmental Tests

The effect on the adhesive bond of prolonged immersion in boiling water is shown in Table VIII. The results in this table again emphasize the superiority of the combination of acids over either individually.

TABLE VIII
Water-Boil Test of Aluminum-Polyethylene Adhesive Bond

Metal treatment	Bond strength, lb./in. width		
	Initial	After 16 hr. in 100°C. H ₂ O	Bond retention, %
CrO ₃ (alone)	15.0	11.3	75
Maleic acid (alone)	16.0	9.5	59
CrO ₃ + maleic acid	22.5	22.5	100
CrO ₃ + H ₃ PO ₄	20.0	4.5	22.5
(CrO ₃ + H ₃ PO ₄) + maleic acid	26.0	15.5	59.5

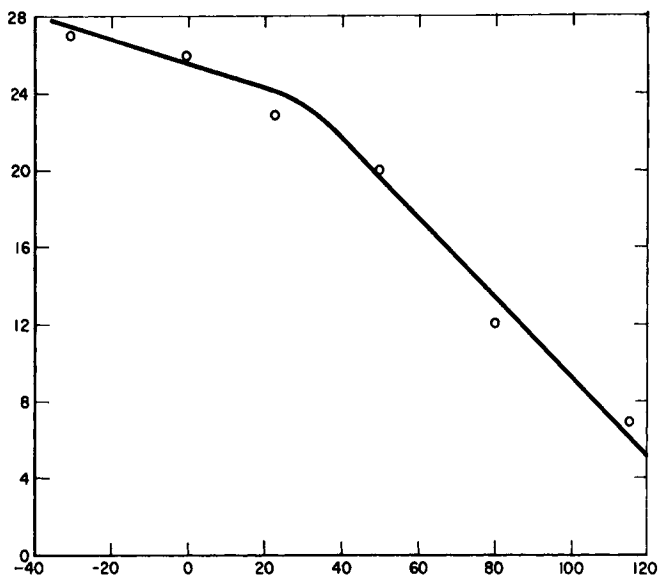


Fig. 3. Peel strength (lb./in. width) vs. peeling temperature (°C.) of aluminum-polyethylene bond.

The strength of the adhesive bond was measured at various temperatures by peeling the aluminum from the polymer at peeling temperatures from -35 to $+115^{\circ}\text{C}$. These data are shown graphically in Figure 3 and illustrate that, even at 115°C ., there is still a respectable peel strength of 7 lb./in. The shape of this curve is roughly similar to that obtained with a high-density polyethylene-acrylic acid graft copolymer on aluminum.⁶ However, in the case of the graft copolymer, the peel strength at -30°C . was 11 lb./in. width and at 115°C . was 2 lb./in. width. A comparison of the retention of bond strength in the two systems indicates 26% with high-density polyethylene on surface-treated metal and 18% with the graft copolymer.

CONCLUSION

A process was developed for bonding unmodified polyethylene to metals through the simple expedient of surface etching of the metal.

The organic acid used in conjunction with the inorganic acid appears to result in a synergistic effect on the adhesion.

High-density polyethylene reveals a ceiling in peel strength when the test was conducted in the manner described in this study.

Mild changes in the etching conditions both organic and inorganic created marked changes in the adhesion level.

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Résumé

Un processus pour faire adhérer le polyéthylène à l'aluminium a été développé; il comporte le traitement de substrats aluminiques successivement par l'acide chromique et ensuite par l'acide organique choisi. Certains acides organiques utilisés dans ce processus apparaissent produire des effets synergistiques en ce qui concerne l'adhésion. Ce processus, qui ne requiert pas de modification, ni de traitement du polymère, permet une force 40 fois plus élevée de résistance au pelage que celle obtenue par de l'aluminium non traité. Les valeurs de cisaillement à la tension pour le lien polyéthylène aluminium étaient plus grand que 2.100 psi des matériaux utilisés pour le traitement du métal dans ce système produisaient un maximum dans la force de résistance à la pelure. En outre, des changements faibles dans les acides d'attaque ont comme effet, des modifications drastiques dans les valeurs d'adhésion.

Zusammenfassung

Ein Verfahren zur Bindung von Polyäthylen an Aluminium mittels sukzessiver Behandlung des Aluminiumsubstrates mit Chromsäure und einer ausgewählten organischen Säure wurde entwickelt. Gewisse, bei diesem Prozess benützte organische Säuren scheinen einen synergistischen Adhäsionseffekt hervorzurufen. Der Prozess erfordert keine Modifizierung oder Behandlung des Polymeren und führt zu einer vierzig mal grösseren Abziehfestigkeit als sie bei unbehandeltem Aluminium erhalten wird. Die Schubfestigkeit bei Zug war für die Polyäthylen Aluminiumverbindung grösser als 2800 psi. Die zur Behandlung des Metalls in diesem System verwendeten Stoffe erzeugten die maximale erreichbare Abziehfestigkeit. Weiters führten kleinere Änderungen bei den zur Ätzung verwendeten Säuren zu drastischen Änderungen der Adhäsionswerte.

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