Durability of Adhesive Bonds between Glass or Metal Substrates and a Polybutadiene–Polyurethane

FASI LIANG* and P. DREYFUSS, *Institute of Polymer Science, The University of Akron, Akron, Ohio 44325*

Synopsis

The durability of polybutadiene–polyurethane joints to glass or metals in water at elevated temperatures was studied. The effects of silane pretreatment of the surface and of surface morphology on adhesion were examined. The durability of the joint was related to the number of chemical bonds that could form between the polyurethane and the surface and to the type of surface treatment given to the surface. Proper treatment led to significant enhancement of durability of the joints.

INTRODUCTION

Adhesives are being used increasingly in engineering applications. One problem frequently encountered is that the mechanical properties of the bond component rapidly deteriorates upon exposure of the joint to its normal operating environment. Water (moisture) is one of the most hostile and common environments to which adhesive joints are exposed. This paper is concerned with the durability of polyurethane joints subjected to wet climate conditions. In order to accelerate such exposure, the joints were immersed in water at elevated temperature. The effect of silanes and surface morphology of etched substrates on joint durability was examined.

EXPERIMENTAL

Materials

The materials used were 3-aminopropyltriethoxysilane (AS), (γ-glycidoxypropyl) trimethoxysilane (GS), 3-chloropropyltrimethoxysilane (CS), and 3-mercaptopropyltrimethoxysilane (MS) from Petrarch Systems Inc.; TDI (80/20 mixture of 2,4- and 2,6-isomers of toluene diisocyanates) from BASF Wyandotte Corporation; Isonal-100 [N,N-bis(2-hydroxylpropylaniline)] from Upjohn Polymer Chemicals; MICRO laboratory cleaner from International Product Corp.; and hydroxy-terminated polybutadiene resin (R-45HT) from ARCO Chemical Co. The properties of R-45HT were listed in earlier studies.[1]

* Present address: Shanghai Rubber Products Research Institute, Shanghai 200030, The People's Republic of China.

Precleaned opticlear soda lime microscope slides (25 × 25 × 1.06 mm) were from KIMBLE. Mirror finish chrome ferro-type stainless steel places were from Appolo. The aluminum alloy was 300 3-H-14.

Preparation of Polyurethane

The polyurethane was prepared from hydroxyterminated polybutadiene (R-45HT), TDI, and N,N-bis (2-hydroxypropyl) aniline. The ratio [—NCO]/ total [—OH] was kept constant and equal to 1. Six percent excess [—NCO] to the hydroxyl number of R-45T was used. The equations for calculating the required amounts of diisocyanate and N,N-bis (2-hydroxypropyl) aniline and the procedure were the same as in previous studies.[1]

Surface Treatment of Substrates

All amounts are in parts by weight unless otherwise stated.

Glass. Unabraded glass slides were heated at 140°C for 1 h. and kept in a desiccator over $CaCl_2$ until treated with the desired reagent.

Surface abraded slides were ground with #600 aluminum oxide abrasive from Barnes Engineering Co., rinsed with distilled water, and immersed for 24 h at room temperature in a mixture of Micro laboratory cleaner with H_2O (50/50 by weight). The solultion was heated to 90°C for 1 h and then the slides were rinsed with distilled water, immersed in 90°C distilled water for 1 h, rinsed with cold distilled water, dried at 140°C for 1 h, and kept in a dessicator over $CaCl_2$.

Metals. Small plates (approximately 75 × 25 × 1 mm) cut from the ferro-type plates were treated by one of four different methods before applying the chemical and elastomer layers:

1. Cleaned with petroleum ether or acetone and dried at 60°C for 40 min.

2. Cleaned as in 1; immersed for 10 min at 90°C in a solution of concentrated hydrochloric acid (50 parts) and distilled water (50 parts); rinsed with cold distilled water; and dried at 60°C for 40 min.

3. Cleaned as in 1; immersed for 20 min at 80°C in a solution of oxalic acid (9 parts), sulfuric acid (1 part), and distilled water (80 parts); and rinsed and dried as in 2.

4. Cleaned as in 1; immersed at 70–75°C for 5 min in a solution of hydrochloric acid (83.3% by volume) and phosphoric acid (12.5% by volume); and rinsed and dried as in 2.

The surfaces of aluminum plates of similar size were prepared by one of four methods:

5. Cleaned with petroleum ether and dried at 60°C for 40 min.

6. Abraded with fine sandpaper, and cleaned and dried as in 5.

7. Cleaned as in 5; immersed for 10 min in a 70°C solution of distilled water (30 parts), sulfuric acid (10 parts), sodium dichromate (1 part); and cleaned and dried as in 2.

8. Cleaned as in 5; immersed in 15% NaOH at 40°C for 5 min; rinsed with distilled water; and then method 7 without the petroleum ether step.

Application of Silane Solution

The silanes were applied at room temperature by immersing the substrates for 5 min in a 0-5% by weight solution of the silane in a 50/50

mixture by volume of ethanol and water. Several drops of hydrochloric acid (pH≃4) as a catalyst for silane were added also except when the silane was AS. After removing the substrates from the silane solution, they were dried in air and then heated for 30 min at 100°C before applying the elastomer layer.

Application of Elastomer Layer and Curing

For adhesion studies appropriately treated substrates were placed in a Teflon-coated compression mold, and the prepolymer containing the glycol was poured on. The top plate of the mold was covered with a sheet of washed, dried, and pressed cotton cloth. The sample was cured at 100°C for 4 h at 25 psi/5-in. ram in a preheated PHI press. Rubber sheets were cured in a vertical mold in a Vacuum Oven at 100°C for 5h.

Measurement of Work of Adhesion

Peel tests at 180° were carried out on strips of cloth backed–elastomer layer after trimming them to a uniform width of 2 cm. on the substrate. The cloth-backed elastomer layer was peeled off the substrate at a constant rate of 0.5 cm/min. The work of adhesion per unit area of interface W_A was calculated from the time average of the peel force P per unit width w of the detaching layer $W_A = 2P/w$.

Tensile Tests

Tensile tests were carried out at room temperature and a cross head speed of 50 cm/min using dumbbell specimens. Breaking elongation was calculated from the ratio $(L_b\text{-}L_0)/L_0$, where L_0 and L_b were the initial length and the length at break, respectively.

Contact Angle Measurements

Contact angle meaurements were carried out at room temperature with a contact angle goniometer manufactured by Kernco Instrument Co. For each liquid, five drops were placed on a substrate, and contact angle readings were taken from both left and right sides of the liquid–air–solid interface. Readings were recorded at 10 and 20 min after the drops were placed on the substrate.
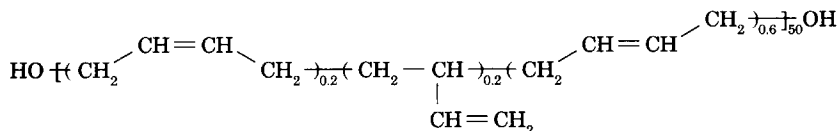
Electron Microscopy

The electron microscopy was carried out with scanning electron microscope Model JSM-U3.

RESULTS AND DISCUSSION

Effect of Water on Bulk Properties of Polyurethane

According to ARCO hydroxyl terminated polybutadiene resin, R-45HT has the following chemical structure[2,3].

$$HO \overset{}{\text{+}} (CH_2 \overset{CH=CH}{\diagup} CH_2 \overset{}{\text{+}}_{0.2} (CH_2 - \underset{\underset{CH=CH_2}{|}}{CH} \overset{}{\text{+}}_{0.2} (CH_2 \overset{CH=CH}{\diagup} \overset{CH_2 \text{+}_{0.6} \text{+}_{50}OH}{\diagup}$$

In contrast to the two principal classes of polyurethanes, from polyethers and from polyesters, the polyurethanes formed from Polybd resin display certain properties and performance characteristics attributable to the hydrocarbon backbone. The most outstanding of these characteristics are outstanding low temperature properties and good hydrolytic stability. The glass transition temperature of the polyurethane derived from a prepolymer containing 6% free NCO is about −65°C.[1] As shown in Figure 1, when this polyurethane was immersed in distilled water at 70°C, the ultimate tensile strength σ_b, and the elongation at break, e_b, decreased slightly with increasing immersion time. After soaking for 55 days at 70°C, σ_b decreased by about 30%, while e_b decreased by about 25%.

Adhesion of Polyurethane to Smooth Glass Surfaces

Warburg and Ihmori[4] recognized that glass surfaces, which have been exposed to room air, are covered by a water film. Infrared adsorption spectra of physically adsorbed water in porous silica show that the water is hydrogen-bonded both intermolecularly and to hydroxyl groups on the silica surface.[5] When the polyurethane elastomer of this study is applied to a glass surface, the tertiary amine groups from the N,N-bis (2-hydroxypropyl) aniline in the backbone of the polyurethane can react with the acidic silanol groups present in the glass surface or perhaps even with surface moisture to form an ionic bond.
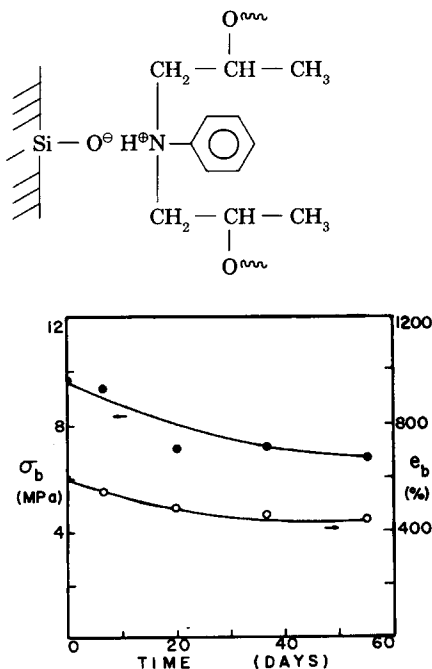
$$\begin{array}{c} O \text{\tiny ⌇} \\ | \\ CH_2 - CH - CH_3 \\ | \\ Si - O^{\ominus} \ H^{\oplus}N - \langle\bigcirc\rangle \\ | \\ CH_2 - CH - CH_3 \\ | \\ O \text{\tiny ⌇} \end{array}$$

Fig. 1. Effect of water on ultimate tensile strength (σ_b) and breaking elongation (e_b).

Our earlier studies indicated that high adhesion results. But as shown in Figure 2 the work of adhesion fell dramatically, when glass/polyurethane peel test specimens were immersed in distilled water at room temperature. In order to improve the wet adhesion, glass slides were treated with AS, GS, or MS before applying the polyurethane. The dry adhesion increased remarkedly. At equivalent concentrations of silanes the order of enhancement in the work of adhesion was AS > MS > GS. Cohesive failure was observed for glass slides pretreated with AS and MS. As in our earlier studies, results can be explained in terms of the different structures of silanes[1,6-9] AS has two reactive hydrogen atoms that can react with the —NCO group of the prepolymer, MS has just one reactive hydrogen atom, and GS has none. The degree of enhancement of adhesion is related to the number of bonds that can form between the silane and polyurethane.

$$\text{Glass} \quad -O-\underset{|}{\overset{|}{Si}}-CH_2-CH_2-CH_2-N\underset{\text{polyurethane}}{\overset{\text{polyurethane}}{<}}$$

$$\text{Glass} \quad -O-\underset{|}{\overset{|}{Si}}-CH_2-CH_2-CH_2-S-\text{polyurethane}$$

$$\text{Glass} \quad -O-\underset{|}{\overset{|}{Si}}-CH_2-CH_2-CH_2-\underset{\overset{\diagdown}{O}\diagup}{CH}-CH_2$$

The glycidoxy group might react with the hydrogen atom that is present in the polyurethane backbone by a ring opening reaction, but this reaction is much more difficult than the one between —NCO and —NH.

The wet adhesion was slightly improved for silane-treated glass surfaces, but the durability of the joints still decreased considerably after soaking for several days. At equivalent concentrations of silane, the order of decrease in the work of adhesion was AS > GS > MS.

The polyurethane based on Polybd resin R-45HT has good hydrolytic stability. Thus the losses in the work of adhesion after immersion in water must result from the adverse effect of water on the interface rather than

Fig. 2. Effect of different treatments of glass surface on work of adhesion, W_A: (◖) treated with AS; (●) treated with MS; (○) treated with GS; (▲) abraded and treated with AS; (□) abraded with No. 600 abrasive, + untreated.

on the bulk properties of the polyurethane. Thermodynamic calculations indicate that if only secondary forces are acting across a glass/adhesive interface, water will virtually always desorb an organic adhesive from the glass surface.[10] In our experiments the presence of ionic bonds can result in markedly reduced adhesion in the presence of water, which would solvate the ionic clusters.[11] Also according to Plueddeman,[12] a flexible polymerlike polybutadiene cannot form water resistant bonds to a hydrophilic mineral surface even with added silane coupling agents. As individual siloxane bonds are hydrolyzed, the silanols retract from the surface and are no longer available for new bond formation. Water gradually interposes itself throughout the interface until adhesion is completely lost.

From our observations, it seems that silane coupling agents do not exclude water from the interface but somehow function to retain adhesion in the presence of water. As shown in Figure 2 at equivalent concentrations of silane, the order of decrease in the work of adhesion was AS > GS > MS. With the GS- or MS-treated glass surface, a fully condensed polysiloxane has some polarity arising from the terminal epoxy or mercapto groups, but these groups do not usually take part in hydrogen bond formation. The cured material would not be expected to show highly polar interaction with water. In the case of AS, the terminal amine group has a strong tendency to absorb water by hydrogen bonding and that could lead to bond rupture and the poorer wet adhesion, compared to GS- or MS-pretreated glass surfaces, observed for AS-pretreated glass surfaces.

When AS-treated glass slide samples were prepeeled to some extent, a thin layer of elastomer was left on the glass surface due to cohesive failure. Upon immersion in distilled water for several days, the adhesion between the thin layer and the glass surface was completely lost, but the thin layer remained firmly attached to the elastomer. The initial W_A of AS-treated glass surfaces to the polyurethane was 1234 kN/M²; after soaking for 155 h in distilled water at room temperature, the W_A became 88 kN/M². When the specimens were dried in vacuum at room temperature for 4 days, the W_A increased to 1000 kN/M². Similar partial recovery in strength of adhesive joints after drying has been reported previously for bonds between polyethylene and glass or steel[12] and between epoxy adhesives and aluminum.[13] Permanent loss in bond strength has been ascribed to covalent bond rupture[13] whereas recoverable loss in bond strength is variously attributed to reforming of hydrogen bonds[13] and an equilibrium of bonding and debonding in the presence of water.[12] In the present case strength recovery can be attributed to reformation of ionic bonds.

Adhesion of Polyurethane to Abraded Glass Surfaces

The durability studies of Gledhill and Kinloch support the conclusions reached above.[14] They conclude that, in order to improve durability of adhesive joints to water, either the water must be prevented from reaching the interface or water-resistant interfacial bonds must be formed. Formation of such bonds requires that special care should be taken to prepare the surface prior to joint preparation. Abrading a surface could be advantageous in two ways. First, the surface area would be increased and provide more sites for formation of chemical bonds. Second, a suitably abraded
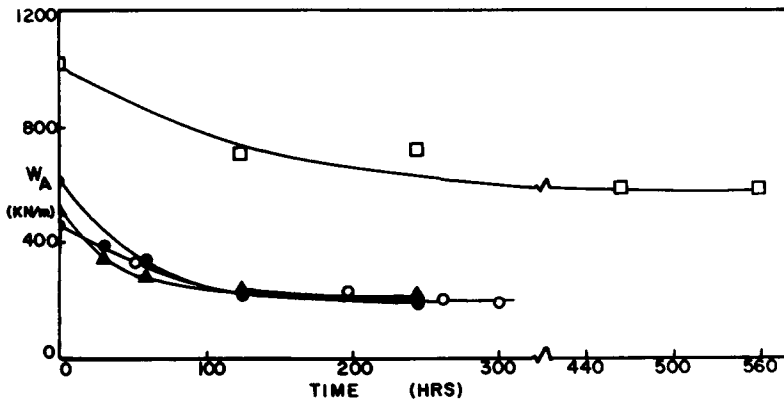
Fig. 3. Effect of silane treatment of chrome steel surfaces on W_A: (□) treated with AS; (●) treated with MS; (○) treated with GS; (▲) treated with CS.

surface could provide sites for mechanical interlocking of the adhesive to the substrate. In the present study, grinding a glass surface with #600 abrasive from Barnes Engineering Co., gave high dry adhesion but had no effect on improving wet adhesion (see Fig. 2). If the ground glass surface was treated with AS before applying the polyurethane, the durability of the joint in the presence of water was much improved. Anchoring of the organic polymer in a rough surface improved dry adhesion, but it was not effective at improving wet adhesion. When there were micropits along with an increased number of active chemical groups on the substrate surface as in the case of the AS-pretreated ground glass surface, the wet adhesion was much improved.

Adhesion of Chrome Steel to Polyurethane

Figures 3 and 4 show that, after immersion in distilled water for several days, the W_A of a petroleum ether cleaned chrome steel surface to polyurethane was decreased markedly. When the metal surface was pretreated with GS, CS, or MS, the treatments were similarly ineffective at improving the durability of the joints in water (see Fig. 3). Pretreatment with AS was
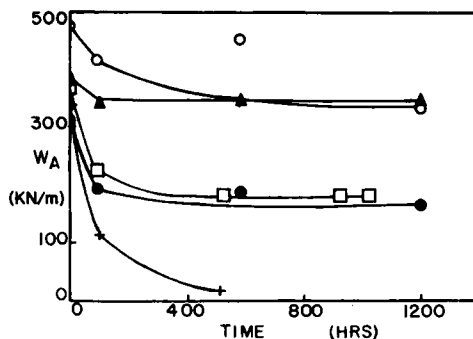
Fig. 4. Effect of acid etching of chrome steel surface on W_A: (○) etched with $HCl \cdot HF \cdot H_3PO_4$ (method 4); (▲) etched with $H_2C_2O_4 \cdot H_2SO_4 \cdot H_2O$ (method 3) and treated with prepolymer containing 0.5% GS; (□) etched with $H_2C_2O_4 \cdot H_2SO_4 \cdot H_2O$ (method 3); (●) etched with $HCl \cdot H_2O$ (method 2) + cleaned with petroleum ether (method 1).

very effective. The AS-treated chrome steel surface gave a high W_A, even after immersion in distilled water for 23 days; its W_A after 23 days was still higher than the initial W_A of surfaces pretreated with the other silanes, GS, MS, and CS, have less effect on the steel surface than AS. The amino group of the latter silane can be chemisorbed by metal oxide surfaces[15] and contribute to the high W_A observed.

The Influence of Chrome Steel Surface Preparation

Surface preparation of substrates for joining adhesively plays a dominant and most important part in the reliability of the finished product. The prime purpose for surface preparation is to develop a bonding surface that will result in an optimum bond and provide the best service protection possible in the expected service environment.

Etching. Chrome steel surfaces were subjected to surface treatments nos. 2–4 described in the experimental section. The effect of different surface treatment on the work of adhesion W_A of a chrome surface to polyurethane is shown in Figure 4. $HCl/HF/H_3PO_4$-treated chrome steel surface gave the highest W_A, HCl/H_2O and $H_2C_2O_4/H_2SO_4/H_2O$ treatment had similar effects on the W_A. Their wet adhesion was much improved compared to the unetched surface, probably as a result of mechanical interlocking of the surface and the adhesive. In addition, chemical treatment may have altered the surface to increase its free energy and make it more receptive to the adhesive. The usual result of chemical surface treatments of metals with acids in the presence of air is metal oxide formation.[16]

Experimental observations support the above conclusions. The morphology of the etched chrome steel surfaces is shown in Figure 5. As a result of acid etching, the surface profile was actually quite rough on a micro scale. $HCl/HF/H_3PO_4$ etching resulted in more micro etch pits than other treatments did. The $H_2C_2O_4/H_2SO_4/H_2O$-etched surface was smooth and micropit-free. Probably the etching condition was too mild.

Chemical surface treatment not only produces micro etching pits but also increases the chemical polarity of the surface. Contact angles for water and glycerol on the etched metal surfaces are shown in Table I. Chromium is resistant to the attack of a wide variety of chemicals at normal temperatures, but it can react with many of these at elevated temperature.[10,17]

When the $H_2C_2O_4/H_2SO_4/H_2O$-treated surface was pretreated with GS before applying the elastomer, the wet adhesion was enhanced significantly. The reasons for the improvement are probably similar to those given above in the section dealing with silane treatment of glass surfaces.

Etching of Chrome Steel plus Silane in the Resin Recipe. Silane coupling agents are usually applied to a substrate surface as a pretreatment from dilute aqueous solution. In this part of our study silane was added to the prepolymer at a concentration of 0.5 g silane/100 g prepolymer. The prepolymer containing silane and glycol was applied to a $HF/H_3PO_4/HCl$-etched chrome steel surface. The effect of different silanes on the work of adhesion is shown in Figure 6. The durability of the joint in the presence of water was much improved. Even after immersion in distilled water for over 2 months, there was only a slight decrease in W_A. The improved du-
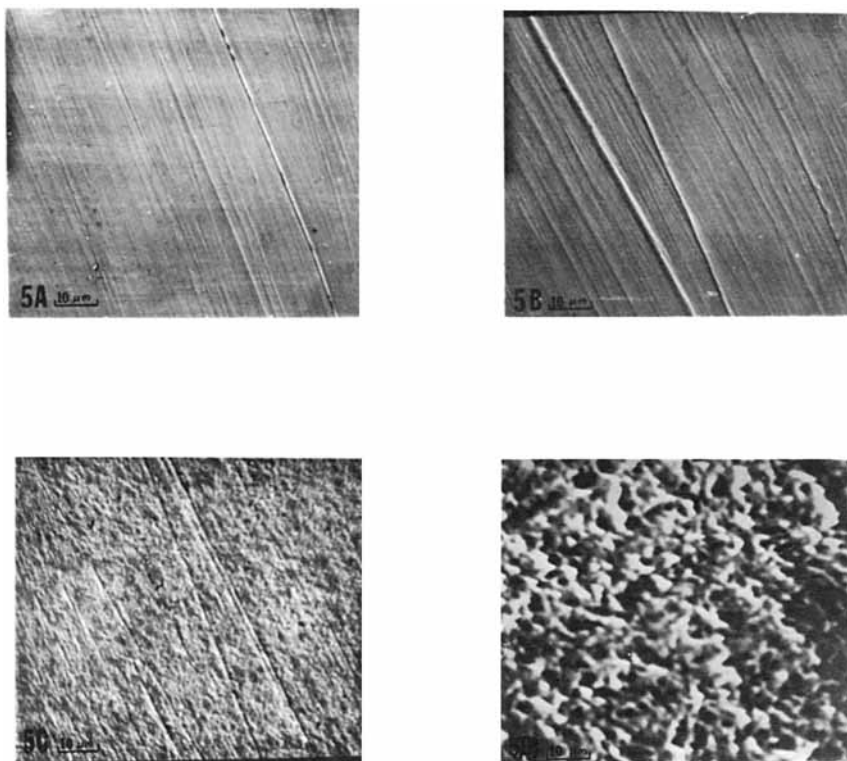
Fig. 5. Electronmicrographs of etched chrome steel surfaces.

rability is attributed to increasing the extent of covalent bond formation between silane- and acid-etched metal surfaces compared to unetched surfaces. Polyurethane containing 0.5% GS gave the highest W_A and that containing 0.5% MS provided the lowest W_A. Probably part of the MS was consumed by reaction of —SH with NCO. The $CH_2CH_2CH_2Cl$ group might to some extent form hydrogen bonds with the tertiary amine groups in the backbone of polyurethane, decrease the diffusion of GS into the interface, and result in the intermediate strength of adhesion.

TABLE I
Contact Angle on Metal Surfaces

Method of surface treatment	Contact angle	
	Water	Glycerol
Chrome steel		
Cleaned with petroleum ether	51	52
Etched with $HF \cdot HCl \cdot H_3PO_4$	31	55
Etched with $HCl \cdot H_2O$	28	54
Etched with $H_2C_2O_4 \cdot H_2SO_4 \cdot H_2O$	34	46
Aluminum		
Cleaned with petroleum ether	60	44
Etched with 15% NaOH	49	35
Etched with $Na_2CrO_4 \cdot H_2SO_4 \cdot H_2O$	50	28
Etched with 15% NaOH and $Na_2CrO_4 \cdot H_2SO_4 \cdot H_2O$	52	29
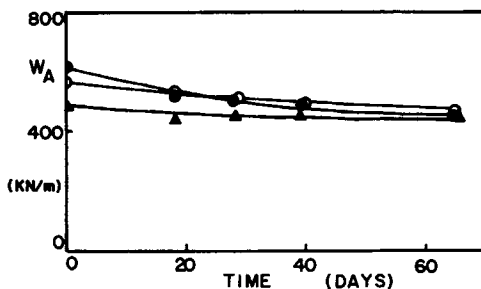
Fig. 6.   Effect of silane treatment of HF · HCl · H₃PO₄ etched chrome steel surfaces on W_A: (●) treated with GS; (○) treated with CS; (▲) treated with MS.

The Adhesion of Aluminum to Polyurethane

Aluminum is always covered with an oxide layer. The bonding interface of aluminum is not the metal itself but a variety of aluminum oxide structures whose physical and chemical constitution can be altered through a variety of chemical procedures.[10] Bondability depends on the structure of the oxide layer. Water is absorbed on the surface of nonhydroscopic oxides like (Al_2O_3) as hydroxyl groups (∼M—OH) and as molecular water held by H bonding to the surface hydroxyls.

Etching of Aluminum. One of the methods to assess the quality of a pretreated surface is to make an adhesive joint. The work of adhesion, W_A, of different pretreated aluminum surfaces to polyurethane is shown in Figure 7. Abraded aluminum surfaces gave high initial W_A, but during immersion in distilled water the rate of loss of W_A was similar to petroleum cleaned aluminum. Aluminum treated wtih aluminum surface treatment No. 8 gave much better wet adhesion than the others.

Figure 8 shows the change of morphology at different stages of pretreatment. The "as received" state of the aluminum surface is not structured, but it is contaminated. After cleaning with petroleum ether the "clean" surface still has some loose particles [Fig. 8(A)]. The alkaline degreased surface shows an irregular structure with pits and some loose particles on the surface [Fig. 8(B)]. An Na_2CrO_4/H_2SO_4-etched surface gave a smooth etched surface with micro pits [Fig. 8(C)] and the alkaline-cleaned–acid-
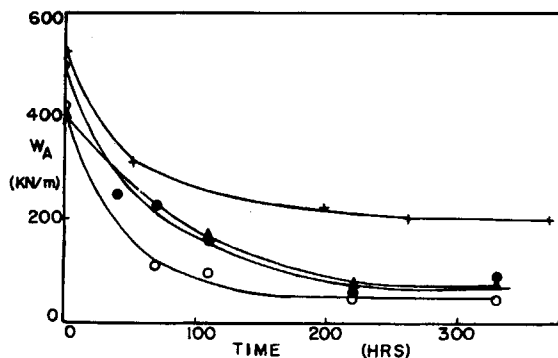

Fig. 7.   Effect of etching of aluminum on W_A + etched with 15% NaOH, Na_2CrO_4 · H_2SO_4 · H_2O (method 8); ▲ etched with $Na_2Cr_2O_4$ · H_2SO_4 · H_2O (method 7); (●) brushed with sand paper (method 6); (○) cleaned with petroleum ether (method 5).
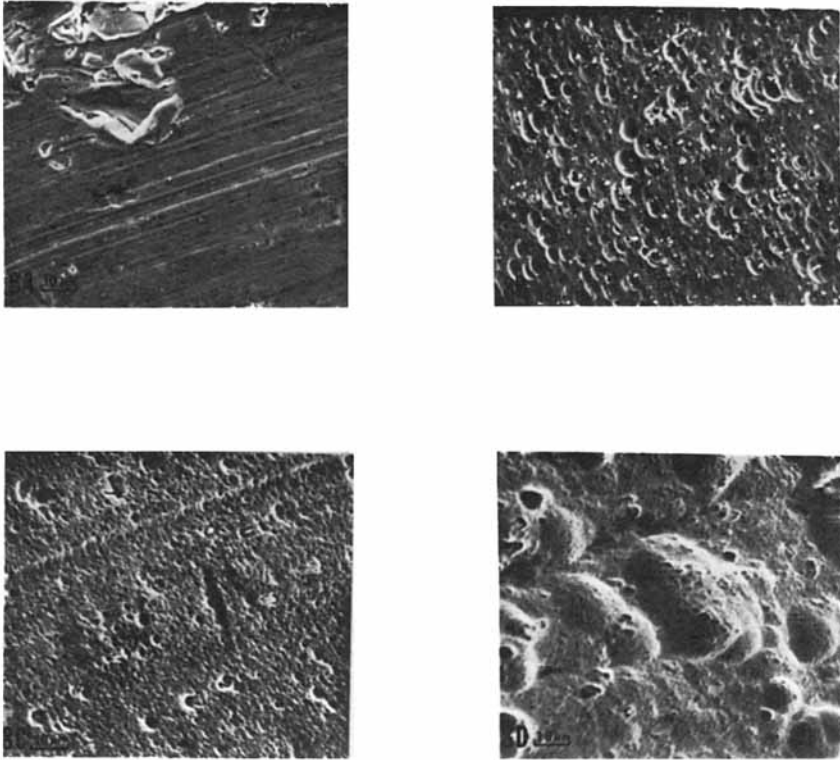
Fig. 8. Electronmicrographs of surface aluminum at different stages of pretreatment: (A) after cleaning with petroleum ether; (B) after alkali degreasing; (C) after etching with Na_2CrO_4/H_2SO_4; (D) after alkali degreasing and etching with $Na_2Cr_2O_4 \cdot H_2SO_4 \cdot H_2O$.

etched surface provided a concave, hilly micromorphology with oxide pits [Fig. 8(D)]. In our experiments acid etching was influenced by alkaline precleaning. A smooth surface gave a low peel strength while a microscopically rough surface provided high peel strength. It seems the anchoring of the adhesive plays an important role.

Acid Etching plus Silane Pretreatment. Bond failure in the presence of water is due to adsorption of water on the aluminum surface.[18] In order to improve the durability of bond strength, in the presence of water, acid-etched aluminum surfaces were treated with 0.5% silane. The effect of
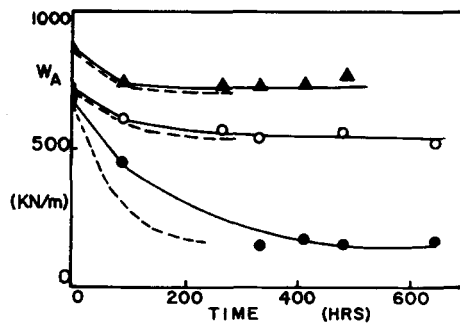

Fig. 9. Effect on W_A of silane treatment on acid etched aluminum surfaces: (▲) treated with AS; (○) treated wtih MS; (●) treated with GS; (——) 25°C; (---) 70°C.
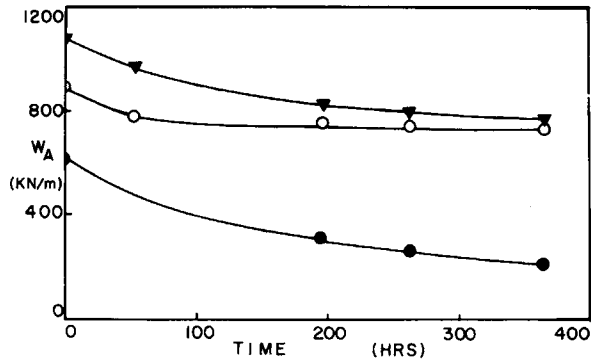
Fig. 10. Effect on W_A of silane treatment of NaOH cleaned and acid etched aluminum surfaces: (▲) treated with AS; (○) treated with MS; (●) treated with GS.

different silanes on the work of adhesion, W_A, of aluminum to polyurethane is shown in Figure 9. Their wet adhesion was much improved; even after immersion in 70°C distilled water for 264 h, W_A decreased just slightly. At equivalent concentrations of silane, the order of durability of bond strength in the presence of water was AS > MS > GS. Trialkoxysilane chemically bonds to polyurethane by reaction of the organic functional group such as —NH$_2$, —SH, etc., with an —NCO group of the prepolymer and may form metalosiloxane bonds to the aluminum surface. The degree of durability of the adhesion bond is related to the number of bonds that can form between the silane and polyurethane.

Base Cleaning plus Acid Etching plus Silane Pretreatment of Aluminum. The influence of alkaline cleaning in addition to acid etching is given in Figure 10. Alkaline-cleaned–acid-etched aluminum surfaces gave higher W_A's than just acid-etched surfaces. Durability was also better. As before, the reasons for the observed behavior probably include both improved mechanical interlocking and a greater number of interfacial covalent bonds.

CONCLUSION

The water durability of joints between glass or metal substrates and polyurethane can be greatly improved by proper surface preparation combined with the use of silane pretreatments. 3-Aminopropyltriethoxysilane is a very effective primer.

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