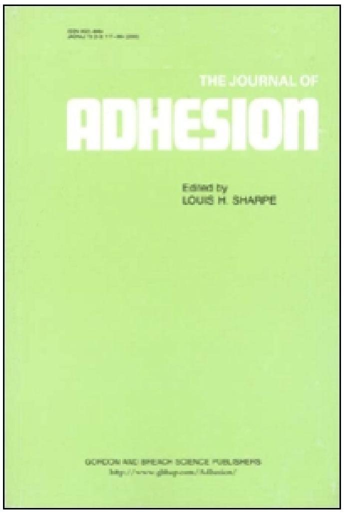

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An Environmentally-Friendly Process for Bonding Aluminum Using Aqueous Metasilicate Sol-Gel and Silane Adhesion Promoters*

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Bonding aluminum metal and its alloys with epoxy adhesives is sensitive to process variables, particularly surface contamination and moisture exposure. In the past, several surface modification schemes have been developed to improve the epoxy-bonding of aluminum. The present work describes a simple process that produces significant improvement in strength and durability of epoxy-bonded aluminum. In this process, aluminum surfaces are first rinsed with dilute sodium metasilicate solution followed by a dilute aqueous epoxysilane solution. The combination of the two materials exhibits a bond strength synergism as measured by bondline fracture toughness. The treated aluminum surface also exhibits a significant increase in bond strength tolerance to contamination and moisture exposure. The effect of epoxysilane chemical structure on bond durability was examined, as was the role of the silicate surface treatment.

Keywords: Aluminum adherends; aqueous surface treatment; environmentally-friendly; epoxy; metasilicate; silane; sol-gel

I. INTRODUCTION

The adhesive bonding of metal materials is important in the construction of light-weight, load-bearing structures. In many cases

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the adhesive and bonding surfaces are extremely sensitive to processing and environmental conditions of surface preparation and bond fabrication. The bonding of aluminum and aluminum alloys can be problematic because of the sensitivity of aluminum surfaces to moisture which can generate a mechanically-weak, hydrated oxide layer [1].

During the last twenty-five years significant efforts have been made to modify aluminum substrate surfaces to improve the strength and durability of aluminum-epoxy bonded interfaces [2]. These have included phosphoric acid anodization [2, 3], chromic acid anodization [2, 3], chromic–sulfuric acid etching [2, 4], sulfuric–boric acid [5], and silanes [6]. While some of these approaches have improved aluminum bonding and durability, they can be laborious and involve environmentally-hazardous materials.

The work reported here involves a two-step, aqueous-based surface preparation that significantly improves the bond line performance of aluminum and other metal/epoxy bond lines that is both simple and environmentally friendly [7, 8]. The process involves coating the bonding surface with an aqueous solution of sodium metasilicate followed by an aqueous organosilane rinse. This process uses an alkali or alkaline earth metal metasilicate salt which, when dissolved in water, buffers the pH of the solution at approximately pH 11.0–12.3. It is believed that exposure of the metal surface to this solution dissolves the surface oxide layer which is then replaced by a coating of silicate that spontaneously polymerizes on the metal surface due to the reduction in pH at the metal surface. The silane rinse following the metasilicate rinse provides a mechanism for incorporating an organofunctional silane into the polymerizing silicate gel on the metal surface. A similar process has been applied to galvanized steel by Van Ooji *et al.* [9] to enhance corrosion resistance. Van Ooji used aqueous alkaline water glass with $Ca(NO_3)_2$ followed by a silane rinse. He also observed enhanced paint adhesion on galvanized steel substrates. This paper attempts to show that sol-gel technology combined with silanes can help the processability of aluminum bond lines.

II. EXPERIMENTAL

To examine the range of applicability of the surface treatment, a variety of specimens, surface treatment variations, and process timelines were used. The adhesion specimens tested were tensile adhesion, tapered double cantilevered beam specimens (TDCB) [10], and the Boeing Wedge specimen [11]. Tensile adhesion testing used a "Poker Chip" specimen [12] of 7075-T73 grade aluminum with 3.2 cm (1.25 inch) diameter. The adhesive used was EA-946 epoxy (Dexter Hysol) with a bond gap of 0.127 cm (0.050 inch). The TDCB arms were also of 7075-T73 aluminum and used a 0.127 cm (0.050 inch) EA-946 bond gap. The specimens were tested on a Satec 60K high-load instrument.

Wedge specimens were made of 6061 aluminum. The initial unbond length for the wedge specimen was set for each specimen to 2.54 cm (1 inch) by the width of Teflon tape placed on the adherends prior to bonding. The test conditions for the wedge specimen tests was 49°C and 100% R.H. Crack lengths were periodically measured.

The surface treatment process allows for either treating precleaned surfaces with metasilicate followed by an aqueous silane rinse or simultaneous cleaning and surface preparation. For clarity, the former process will be referred to as the Metasilicate Silane Surface Treatment (MSST) while the later process will be referred to as the Insitu-Surface Preparation (ISP). Simultaneous cleaning and surface treatment (ISP) can be accomplished with solutions which employ aqueous metasilicate plus the appropriate concentration of detergents and/or terpenes (wash solution), followed by an aqueous silane rinse (rinse solution). Typical conditions for the surface preparation are shown in Tables I and II. Solution 1 contains water and metasilicates. These studies used a nominal sodium metasilicate concentration of 4 pph (parts per hundred) by weight. This step was immediately followed by a rinse using Solution 2 shown in Table II. All organofunctional silanes used were terminal epoxides. If mixed and used immediately, no buffer is required; however, there is a tendency for the aqueous silane to poly-

TABLE I Recommended wash solution concentrations for solution 1

Solution components	*Concentration ranges (pph)**
Alkali or Alkaline Earth Metal Metasilicate	0.05–0.40
Water	99.6–99.95
Cleaning Additives	Optional

* *Based on sodium metasilicate.*

TABLE II Recommended wash solution concentrations for solution 2

Solution components	*Concentration ranges (pph)*
Organo-Functional Silane	0.24 – 10.0
Water*	90.0 – 99.8
Acetic Acid	As Required**
Sodium Hydroxide	As Required**

* Or an organic solvent depending on silane solubility.
** To adjust the pH to ~ 5.0.

merize to polysiloxanols and precipitate in a few hours if left to stand. For this reason, a 0.1 M sodium acetate/acetic acid buffer was used to hold the pH near 5. Sodium hydroxide or some other suitable base can be used to adjust the pH.

When the MSST surface preparation was used, the surfaces were precleaned using 1,1,1-trichloroethane vapor degreasing and grit blasting using 100 – 200 micron zirconium silicate grit at a pressure of 0.62 MPa (90 psi). The bond surfaces were then sprayed with an aqueous solution of sodium metasilicate followed by application of the organofunctional silane. Unless otherwise stated, the metasilicate and silane were spray applied. The spraying apparatus was a Sure Shot (manufactured by Milwaukee Sprayer Manufacturing Company). After applying the silane rinse, the specimens were allowed to air dry for 1 hour. Ambient humidity was typically 10 – 15%.

When ISP was used, the specimens were generally soiled with ample amounts of HD-2 grease (manufactured by Conoco Oil Company). The wash solutions containing detergents and metasilicate was heated to between 57°C and 66°C and the contaminated specimens spray washed. The remaining steps for treating the surface are identical to the MSST procedure.

To evaluate the surface treatment, a process-sensitive adhesive was required. The transition from cohesive to interfacial failure is often associated with the glass transition temperature of an adhesive. For this reason it was decided to use a rubbery, two-part epoxy, EA946, to evaluate the effect of the surface treatments on bond strengths. The specimens were cured for 36 – 40 hours at 41°C (105°F). The glass transition of this material is near 25°C. When tested using Tapered Double Cantilever Beams (TDCB), the failure produces "islands" of mostly interfacially-failed adhesive on the failed joint surfaces. The size of the "islands" is sensitive to surface preparation.

Bond durability was measured using three organofunctional silanes with different chain lengths. In addition to A187, two aliphatic epoxy silanes were synthesized using hydrosilation of 9,10 epoxy-decylene and 3,4 epoxy-butene and an equimolar amount of trimethoxysilane in the presence of a Pt catalyst [13]. The reaction products were obtained by purifying with vacuum distillation. The boiling point of the 9,10-epoxydecyltrimethoxysilane was 120 – 122°C at 0.7 mm Hg. The boiling point of the 3,4-epoxybutyltrimethoxysilane was 64 – 67°C at 0.7 mm Hg. After work-up, the purity was determined to be > 95% by GC-MS for both aliphatic organofunctional silanes. The γ-glycidoxypropyltrimethoxysilane was purchased from Union Carbide under the name A187. Primer solutions were prepared using 40% toluene, 40% ethanol and equal parts *n*-butanol and 2-butoxyethanol. This mixture was used to prepare a 5 pph (wt/wt) organofunctional silane.

Plates of 5.08 cm × 5.08 cm × 0.635 cm (2 in × 2 in × 0.25 in) 7075 aluminum were prepared with the various surface treatments discussed above for use in surface energy measurements. This was accomplished by making contact angle measurements using a Rame – Hart Model A-100 goniometer with a series of liquids with different dispersive and non-dispersive components [14, 15]. The standard analysis was used to determine the surface parameters for the solid surface from a plot of the ratio $W_A/(\gamma^d_{\mathrm{liq}})^{1/2}$, the liquid – solid work of adhesion and the square root of the liquid dispersion component. The dispersive component of the metal surface energy, γ^d_s, was determined from the intercept, and a non-dispersive, or polar, component, γ^p_s from the slope of the plot.

III. RESULTS AND DISCUSSION

A. Sodium Metasilicate/Silane Synergism

To illustrate the synergistic effect of metasilicate and silane, several sets of TDCB specimens were first cleaned using 1,1,1-trichloromethane (TCA) vapor degrease followed by an aggressive grit blast (V.D./G.B.). The beams were then treated with aqueous sodium metasilicate at five concentrations, 0.0 (distilled water), 0.05, 0.12, 0.40, 4.0 pph. These specimens were then rinsed with buffered aqueous

A187 (γ-glycidoxypropyltriethoxysilane) at five concentrations 0.0 (distilled water), 0.10, 0.25, 0.50, 5.0 pph. After treating the bond surfaces, the specimen were held at 25°C and 90 percent relative humidity (%R.H.) for 24 hours. The conditioned bond specimens were then bonded and cured. The results of the study are shown in Table III and Figure 1. These results illustrate the enhanced fracture toughness of the rubbery epoxy/Al bond lines obtained by treating bond surfaces with increasing concentrations of sodium metasilicate and aqueous A187.

Additional studies were conducted to find the upper end of bond line fracture toughness with metasilicate concentration. This sensitivity is dramatically illustrated in photographic images of the failed bond surfaces in Figure 2. The image shows the failure modes of EA946 bonded to 7075 aluminum TDCB specimens with increasing concentration of sodium metasilicate. The concentration of γ-glycidoxypropyltriethoxysilane was held constant at 5 pph for each specimen. From the image, the failure mode changes from mostly interfacial with silane alone to increasingly more cohesive failure with increasing sodium metasilicate concentration. The failure mode begins to become more interfacial at 10 pph sodium metasilicate.

B. Post-treatment Contamination

A measure of a bond line's robustness is its ability to retain its strength with exposure to contamination and environmental factors. This is an especially important concern for bonding in a manufacturing environment. Despite efforts to avoid surface contamination prior to

TABLE III Fracture toughness values for surface-treated aluminum

Fracture toughness (kJ/M^2)	*A187 Silane level* (*pph*)				
Meta Silicate Level (pph)	0	0.1	0.25	0.5	5.0
0.0	1.6	1.8	2.6	3.6	4.5
0.05	1.0	1.8	2.6	4.3	5.7
0.12	1.2	2.0	2.8	4.0	5.3
0.40	1.2	2.0	2.8	5.4	5.9
4.0	1.2	2.8	4.4	4.4	5.4

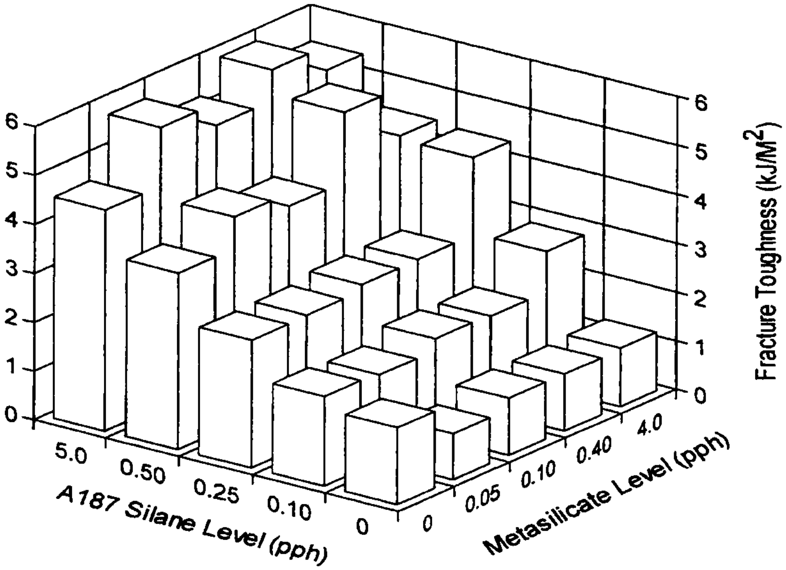

FIGURE 1 Sodium metasilicate–silane synergism on Mode I fracture toughness of EA-946 bonded aluminum.

bonding, it has to be assumed that bond surfaces will become contaminated. A robust bond surface preparation will provide a measure of tolerance for surface contamination in a manufacturing environment.

A series of experiments was performed using EA946 bonded to aluminum TDCB specimens. Three conditions were examined: (1) methyl chloroform vapor degreased and grit blast, (2) methyl chloroform vapor degrease followed by aqueous 5 pph A187 silane rinse, and (3) aqueous cleaning with 20% (wt/wt) metasilicate followed by 5 pph A187 aqueous silane rinse. Some of these specimens were then coated with a layer of HD-2 grease at 53–65 mg/m^2 (0.077–0.093 grains/ft^2) prior to bonding. The resulting fracture toughness of these specimens is summarized in Figure 3. These data show that even after post treatment contamination with 53 mg/m^2 of HD-2 grease, the ISP surface treatment has provided enough adhesive capability so as to yield fracture toughness values above those of uncontaminated surfaces treated with γ-glycidoxypropyltriethoxysilane alone.

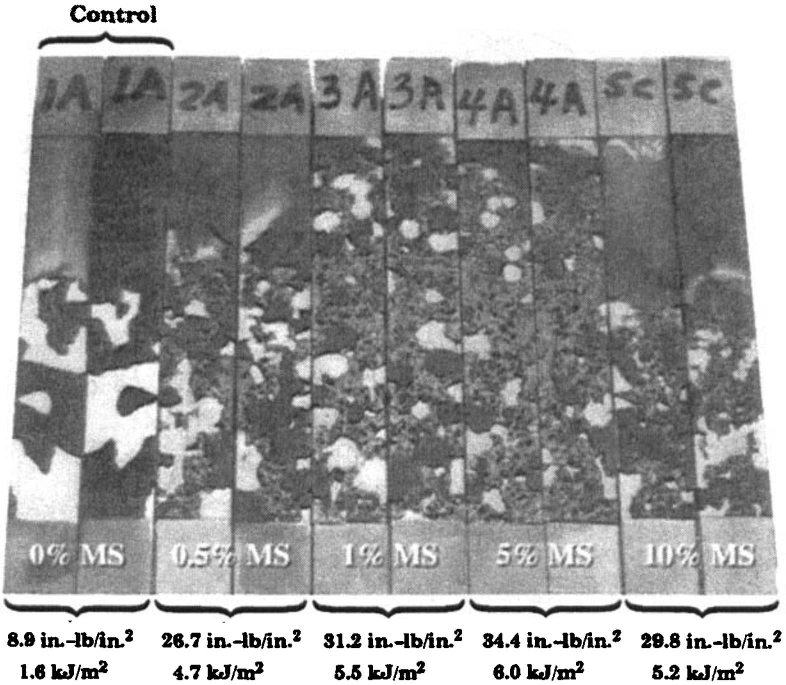

FIGURE 2 The effect of increasing sodium silicate concentration at constant silane level on TDCB specimen failure mode of EA-946 bonded to 7075 aluminum. (See Color Plate II).

C. Application Method

As mentioned above, the nominal method for MSST and ISP application was spraying. Often, there is a need to treat a metal surface that is surrounded by a material that should not or cannot be exposed to moisture (*e.g.*, phenolic materials). For this reason, hand application methods were investigated. The effect of various hand application methods are shown in Figure 4. The relative humidity of the room where the bond specimens were prepared was 10%R.H. Originally, there was concern that use of substances that possessed polar surfaces and/or large surface areas might deplete the concentration of the metasilicate solution. For this reason, polypropylene brushes were used and compared with Rymple cloth and nylon bristle

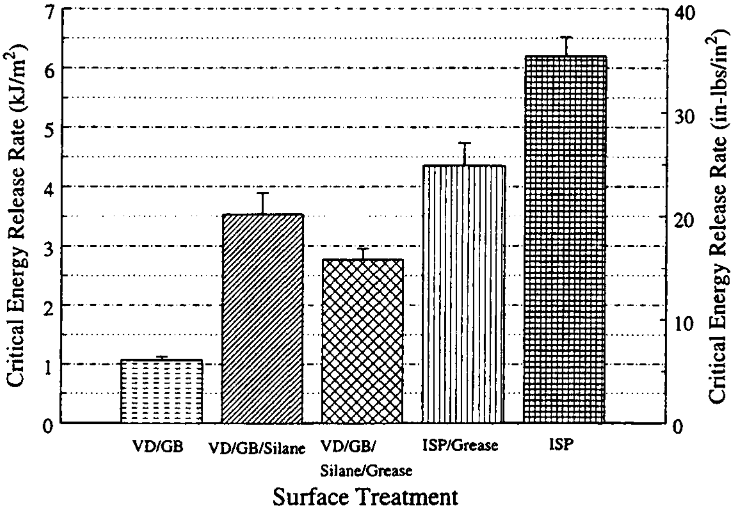

FIGURE 3 The effect of post treatment contamination of mode I fracture toughness of EA946 bonded to aluminum TDCB specimens.

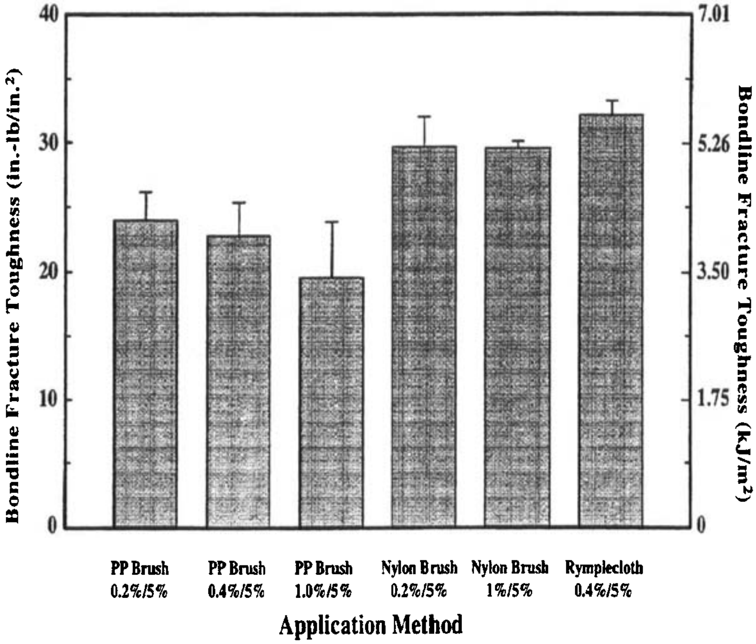

FIGURE 4 Illustrates the effect of different and application methods of MSST on Mode I fracture toughness of EA946 bonded to aluminum.

brushes. Both nylon bristle brush and Rymple cloth demonstrate mode I fracture toughness values that were equivalent to the spray process.

D. Process Timelines

Aluminum bond surfaces are sensitive to surface oxidation and hydration [1]. Often, in a manufacturing environment the surface bonding conditions can become uncontrolled and deteriorate with time. It would be desirable to use a surface preparation that will help a surface retain its "bondability" over an extended period of time until it can be bonded.

The process described in this paper has demonstrated an ability to retain a strong bonding surface significantly longer than untreated surfaces. This point is illustrated in Figures 5 and 6. Figure 5 shows the effect of aging bond surfaces at 100%R.H. on the tensile adhesion strength of EA946 bonded to aluminum tensile adhesion buttons, for both treated and untreated bond surfaces. These data clearly show that metasilicate has a stabilizing effect on the mechanical properties of the interphase. Furthermore, if the aluminum surface is aged 100 hours at 100%R.H., then rinsed, the bond surface becomes rejuvenated and the tensile adhesion strength is restored to that of the unaged specimens. The preservative nature of metasilicate is also illustrated in Figure 6 which shows the polar component of the surface energy, γ^p, as a function of %R.H. exposure. The metasilicate-washed surfaces maintained high γ^p values even after long term exposure to 100%R.H., while non-treated surfaces exhibited a steady decline. This behavior is similar to that observed in tensile adhesion strength shown in Figure 5.

E. Bondline Durability

An essential part of evaluating a new surface preparation is the long-term durability of the adhesive joint. It was postulated that bond line durability may be affected by the hydrophobic character of the silane coupling agent. To answer this question, a series of long-chain aliphatic organofunctional silanes was synthesized and applied to 7075

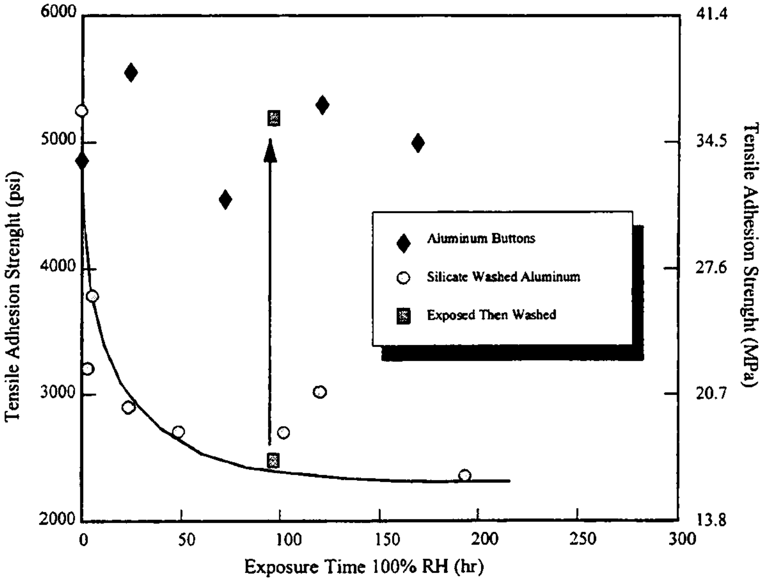

FIGURE 5 Effect on tensile strength of aging time at 100% R.H. of treated and untreated bond surfaces.

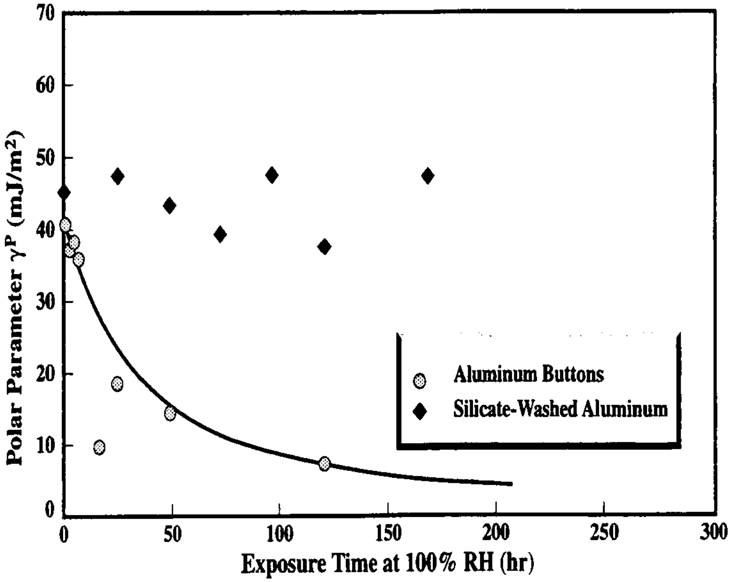

FIGURE 6 Effect of aging time at 100% R.H. on γ^{p} for treated and untreated bond surfaces.

aluminum TDCB specimens. The silanes were evaluated with and without metasilicate rinse and bonded with EA946. Witness coupons were prepared at the same time to measure the contact angle response of these prepared bonding surfaces. The average mode I fracture toughnesses of bond specimens prepared without metasilicate rinse are shown in Figure 7. The polar component of the surface energy is shown on the bars for each silane type. Surfaces with the aliphatic silanes possessed low surface energies. The ten-carbon silane had the lowest which suggested that the side chains were laying flat on the surface exposing their hydrophobic chains to the adhesive. The γ-glycidoxypropyltriethoxysilane possessed a relatively high surface energy. This may be due to the presence of the oxygen in the silane chain. It is interesting to note that the γ-glycidoxypropyltriethoxysilane (A187) also produced the highest average fracture toughness. The fracture toughnesses for the aliphatic silanes were approximately equal.

The effect of silane type with the addition of metasilicate rinse is also shown in Figure 7. The effect of pre-treating the aluminum substrates

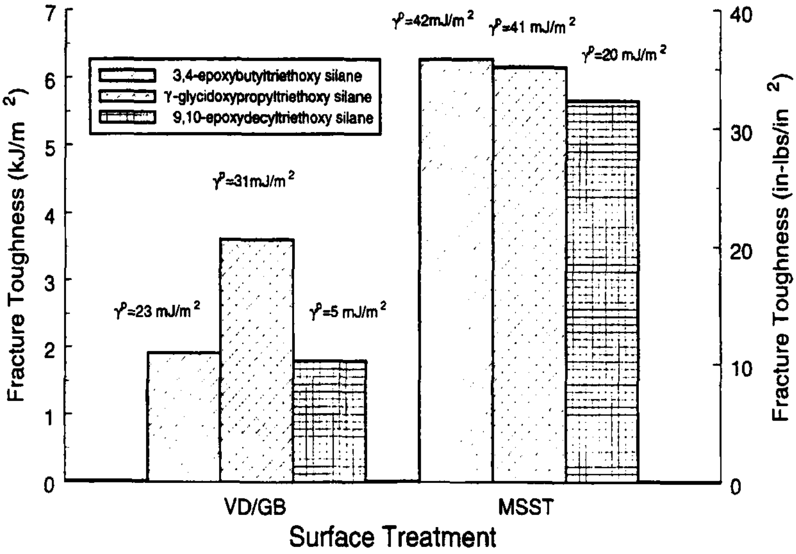

FIGURE 7 Effect of silane type on mode I fracture of EA946 bonded to 7075 aluminum; with and without a metasilicate rinse.

first with a 0.4% sodium metasilicate solution followed by a 5 pph solution of silane results in a dramatic increase in the mode I fracture toughness. Because of the relative immiscibility of the latter two silanes in water, it was decided to hydrolyze and dilute all three silanes in a solution consisting of a mixture of butanol, ethanol, water, and toluene. Metasilicate pretreatment dramatically enhanced the surface energy of the coupons treated with the aliphatic silane primers. This suggests that either less of the aliphatic silane is on the surface and the drop "sees" mostly silicate or the silane chains may be oriented normal to the surface exposing their polar functional groups. Time-of-flight SIMS [9c] and dynamic contact angle measurements [16] have indicated that alkyl chains of silane agents orient depending on chain length.

The Boeing wedge specimen [11] is a popular specimen for evaluating relative bond durability. In this investigation, several 6061 Al panels were prepared using the MSST method. To investigate the effect of silane chain length and polarity on bond durability, three organosilanes were evaluated. These were γ-glycidoxypropyltriethoxysilane (A187), 9,10-epoxydecyltriethoxysilane and 3,4-epoxybutyltriethoxysilane. After treating the surfaces, the panels were bonded with FM-73 film adhesive Cytec and tested. The average crack extension results of the wedge specimen testing are shown in Figure 8. In general, a crack growth that is less than 12.7 mm (0.5 inches) over seven days time at 49°C (120°F) and 95–100%R.H. is considered good for this particular adhesive. Prior experiments on these silanes and the EA-946 epoxy adhesive on aluminum TDCB specimens and dry conditions showed essentially equivalent enhanced fracture toughness. While previous experiments using metasilicate and 3,4-epoxybutyltriethoxysilane with EA-946 on aluminum TDCB specimens at dry conditions showed equivalent fracture toughness, this silane-treated surface was clearly more susceptible to moisture attack.

IV. CONCLUSIONS

A process has been described that provides a method of significantly enhancing mode I fracture toughness of certain types of epoxy

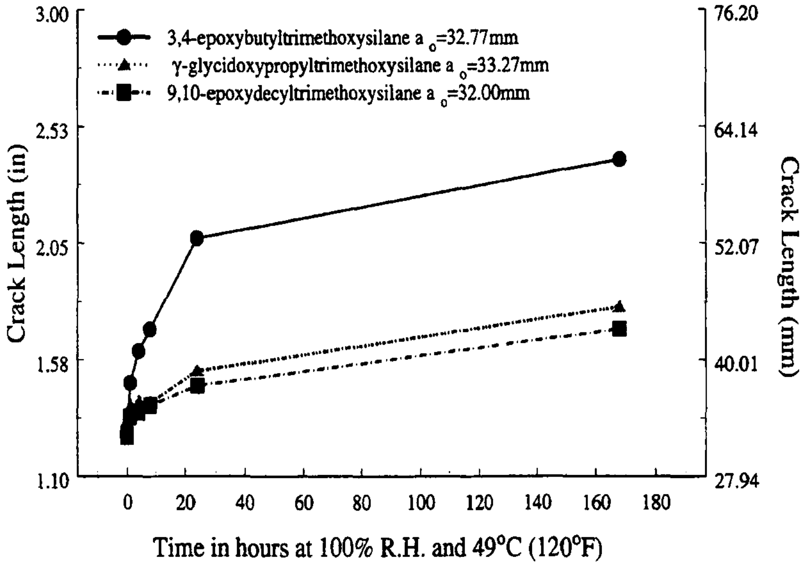

FIGURE 8 Effect of silane type on Boeing wedge crack extension at 100%R.H. and 49°C.

adhesives. The process is economical, uses few hazardous chemicals, and possesses minimal disposal costs. It can be applied using spraying, dipping or hand application. Sodium metasilicate pretreatment appears to provide a silicate rich surface that enhances the binding of organofunctional silanes. In addition, the gel left by the metasilicate solution appears to act as a preservative on aluminum surfaces to decrease moisture degradation. It also significantly enhances the surface energy of the treated surfaces. Silane chain length did not show a significant effect on mode I fracture toughness at zero time with metasilicate pretreatment. However, bond line durability, as measured by Boeing wedge tests at 100%R.H. and 49°C, was significantly reduced by the use of short chain silanes.

Acknowledgements

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