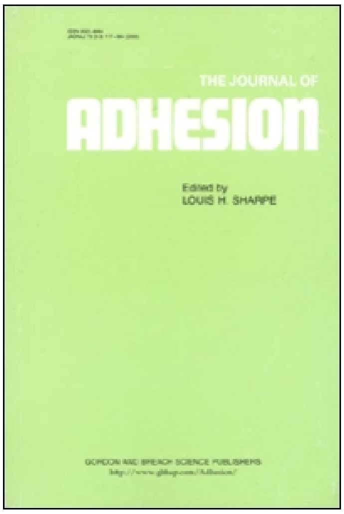

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W. Thiedmanu[a]; F. C. Tolan[a]; P. J. Pearce[a]; C. E. M. Morris[a]
[a] Materials Research Laboratories, Defence Science and Technology Organisation, Victoria, Australia

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Silane Coupling Agents as Adhesion Promoters for Aerospace Structural Film Adhesives†

W. THIEDMAN,‡ F. C. TOLAN, P. J. PEARCE and C. E. M. MORRIS

Materials Research Laboratories, Defence Science and Technology Organisation, Ascot Vale, Victoria 3032, Australia

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The performance of eight organofunctional silane coupling agents as adhesion promoters for the bonding of aluminium with two 121°C and two 177°C curing structural film adhesives was investigated and compared to the chromic acid (FPL) etch pre-treatment process and two non-chemical pretreatments. Aspects considered were shear strength of joints at ambient and elevated temperatures and durability, as judged by the wedge test.

The epoxy silane, γ-glycidoxypropyltrimethoxy silane, was found to be a very efficient adhesion promoter with all film adhesives evaluated. The cationic styryl silane, a neutral diamine monohydrochloride, showed promise with two adhesive systems. Four other neutral silanes were less effective.

Performance of amine functional silanes was mixed. Although the shear strength of joints with the primary amine silane at its natural pH of ~10.3 was relatively good, durability was poor. However, good durability was obtained if the primer was first adjusted to pH 8 with hydrochloric acid, but not if acetic or phosphoric acids were used. Diamine silane was not an effective adhesion promoter at either its natural pH or when acidified with hydrochloric acid.

KEY WORDS Silane coupling agents; Aerospace film adhesives; Aluminium; Durability; Lap shear tests; Wedge tests.

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‡ Present address: Chemistry Department, Deakin University, Geelong, Australia.

INTRODUCTION

It is well established that the surface treatment prior to bonding is of paramount importance in developing the optimum strength and durability of a structural adhesive assembly. Currently, the surface preparation applied to aluminium alloys in the aerospace industry involves alkali cleaning and vapour degreasing followed by the most important stage—an oxidising treatment, frequently a Chromic Acid Etch[1] or Phosphoric Acid Anodization (PAA)[2]. Although adhesive joints prepared using a chromic etch yield high lap shear strength at room and elevated temperatures, some systems have been shown to lack long term durability, particularly in a moist environment. The PAA treatment is considered superior in terms of durability,[3] but the process is lengthy and more complex than the chromic etch. Clearly, neither treatment is convenient in locations remote from ideal workshop conditions or when carrying out *in-situ* bonded aircraft repairs.

Organofunctional silanes, used originally for enhancing the bonding properties of glass fibres in reinforced plastics,[4] are now finding utility as primers or adhesion promoters for improving the hydrothermal stability of metal to metal adhesive bonds.[4] Silanes have the distinct advantage that their mode of application is simple (usually *via* immersing the parts to be bonded in 1% solutions), and the operation may be performed at room temperature.

Theories proposed to explain the mechanism by which silane coupling agents function are numerous but support for the presence of chemical bonding is well founded.[5–7] The structure is commonly $X_3Si(CH_2)_nY$, where X is a hydrolysable alkoxy group and Y an organofunctional group. Thus, the theory of chemical bonding suggests that Si—O bonds are formed by elimination of water between Si—OH groups of the hydrolysed silane and surface OH groups of the substrate, leaving the organic end of the molecule to interact with the matrix resin.

The commercial range of coupling agents includes a variety of silanes containing organofunctional groups tailored to be compatible with a wide range of polymers. Several have been suggested as suitable for epoxy systems.[4]

Previous studies undertaken to investigate the effectiveness of silane adhesion promoters for the bonding of metals with structural adhesives have been mostly concerned with the dry and wet strengths of aluminium, iron or titanium lap-shear or butt joints bonded with simple two-part epoxy systems and utilizing either γ-aminopropyltriethoxy silane or γ-glycidoxypropyltrimethoxy silane.[8-11] Work on two unspecified film adhesives is included in ref. 8.

This paper reports on an investigation of the efficiency of eight organofunctional silanes as adhesion promoters in the bonding of aircraft-grade aluminium with a range of epoxy based structural film adhesives. Joint strength is measured in terms of lap shear strength at both room and elevated temperature and durability is monitored using the Boeing wedge test. Results are compared with both degrease/sandblast and FPL etch surface pretreatments.

EXPERIMENTAL

Materials

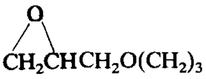
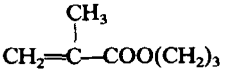
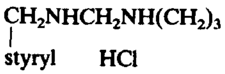
Details of the eight silanes and four structural film adhesives used in this work are given in Tables I and II, respectively. All materials were used as received. Aluminium used in the testing procedures was Alclad 2024-T3 of thickness 1.6 mm for lap-shear joints and 3.2 mm for wedge test specimens.

Surface treatments

Silane The adherends were solvent wiped with acetone, vapour degreased with 1,1,1-trichloroethane, grit blasted with <230 μ zircon sand, immersed for 20 mins in 1% silane solutions, drained and allowed to dry for 1 hour at 110°C.

Neutral silanes (Z6040, Z6030, Z6076, Z6075 and A172) were hydrolysed with aqueous 0.1% acetic acid (pH 4) and diluted with methanol to give a 95% methanolic solution. A1100 (primary amine) was used initially at its natural pH of 10.3 in 95% methanol. In further durability studies aqueous solutions were either used at pH 10.3 or adjusted to pH 8 with 1 M hydrochloric, phosphoric or acetic acids. Z6020 (diamine) was used at its natural pH of 10.3 in

TABLE I
Silane coupling agents

Trade name	Type	Name	Organofunctional group
Z6040[a]	Epoxy	γ-Glycidoxypropyltrimethoxy silane	
Z6030[a]	Methacrylate	γ-Methacryloxypropyltrimethoxy silane	 $CH_2{=}C(CH_3){-}COO(CH_2)_3$
Z6076[a]	Chloropropyl	γ-Chloropropyltrimethoxy silane	$Cl(CH_2)_3$
A1100[b]	Primary amine	γ-Aminopropyltriethoxy silane	$NH_2(CH_2)_3$
Z6020[a]	Diamine	N-(β-aminoethyl)-γ-aminopropyltrimethoxy silane	$NH_2(CH_2)_2NH(CH_2)_3$
Z6075[a]	Vinyl	Vinyltrimethoxy silane	$CH_2 = CH$
A172[b]	Vinyl	Vinyltriacetoxy silane	$CH_2 = CH$
Z6032[a]	Cationic styryl	N-β-(N-vinylbenzylamino)-ethyl-γ-aminopropyltrimethoxy silane monohydrochloride	 $CH_2NHCH_2NH(CH_2)_3$ (styryl) HCl

[a] Dow Chemical Co.
[b] Union Carbide.

95% methanol initially but in some later experiments aqueous solutions were adjusted to pH 8.0 with 1 M hydrochloric acid. Z6032 (cationic styryl) was used at its natural pH of ~7.0 as an aqueous solution.

Acid etching Adherends were solvent wiped and degreased as described previously and immersed in a chromic acid bath (FPL

TABLE II
Film adhesives

Name	Manufacturer	Type	Cure conditions
FM-73	American Cyanamid	Rubber modified epoxy	60 mins at 121°C
FM-300		Nitrile rubber modified epoxy	60 mins at 177°C
AF-130	3M	Unmodified epoxy	60 mins at 177°C
AF-163		Polyether rubber modified epoxy	60 mins at 121°C

etch composition—3750 g H_2O + 680 ml conc. H_2SO_4 + 500 g $K_2Cr_2O_7 . 2H_2O$) for 10 mins at 65°C ± 2°C. On removal from the bath the panels were washed with cold running tap water for approximately 10 mins, then dried at 65°C for 1 hour.

Adhesive joint testing

Joints were made in a heated platten press using the recommended cure cycle for the film adhesive (see Table II). For lap shear strength, joint geometry and test methods were conducted according to ASTM D1002–72. Strengths at ambient and elevated temperatures were assessed using an Instron 1185 Materials Testing Machine. Wedge tests were performed according to ASTM D3762–79. Specimens were exposed to a controlled environment of 96% RH at 50°C for periods of up to 350 hours. Crack growth was monitored at suitable intervals using a stereo microscope and plotted as a function of $time^{1/2}$.

Adhesive joint test results were generally based on the average of six replicates showing coefficients of variation of around 3%.

RESULTS

Shear strength

Using 121°C curing adhesive FM-73 (American Cyanamid), lap shear strength as a function of test temperature for aluminium joints primed with seven silanes was compared with the FPL etch and degrease or degrease/sandblast surface treatments. It can be seen from Table III and Figure 1 that the FPL treatment gave superior strength at all test temperatures and that most of the silane-primed joints were only marginally lower in strength at ambient. In contrast, joint performance at elevated temperatures showed significant differences with only the primary amine and epoxy types approaching the FPL values. Results obtained from the degrease and degrease/sandblast treatments were generally inferior to those obtained from primed joints.

Examination of the bonded surfaces after testing showed that all pretreatments resulted in >90% cohesive failure when tested at

TABLE III
Effect of pretreatment on lap shear strength of FM-73

Surface treatment	Lap shear strength (MPa)			
	Ambient	80°C	90°C	100°C
Chromic acid etch	38.7	26.3	24.7	22.1
Epoxy silane	36.8	23.8	21.8	17.2
Methacrylate silane	36.7	20.9	18.5	11.2
Chloropropyl silane	36.5	19.8	18.3	12.6
Amine silane	35.6	22.5	22.4	18.3
Diamine silane	35.4	23.1	20.6	13.8
Vinyltriacetoxy silane	34.4	20.5	18.1	12.5
Vinyltrimethoxy silane	31.1	19.6	16.3	12.5
Degrease	31.2	19.6	14.6	10.2
Degrease/sandblast	27.9	17.6	15.0	11.4

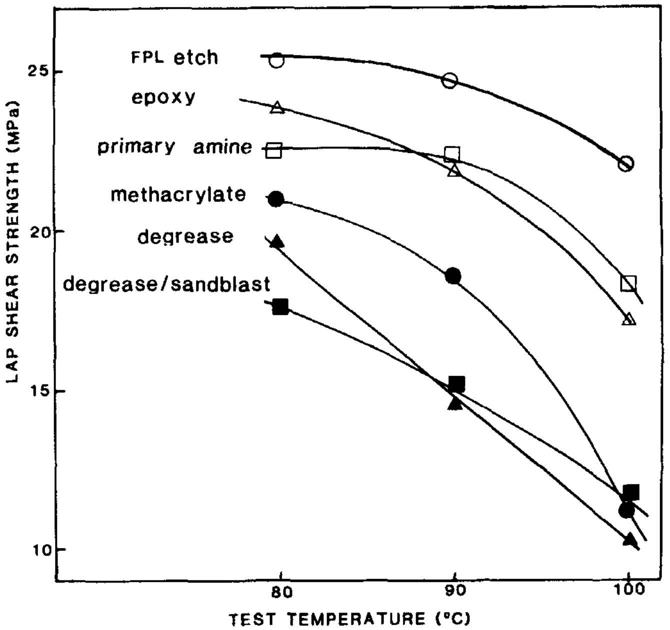


FIGURE 1 Effect of pretreatment on lap shear strength at elevated test temperatures—selected systems, FM-73 adhesive.

TABLE IV
Effect of pretreatment on lap shear strength of AF-130

	Lap shear strength (MPa)	
Surface treatment	Ambient	177°C
FPL Chromic etch	18.9	19.6
Epoxy silane	15.6	15.0

ambient but only the FPL etch maintained this performance at elevated temperatures. The degrease/sandblast and all silane treatments, with the exception of the diamine type, resulted in approximately 80%–90%, 60%–75% and 50%–60% cohesive failure at test temperatures 80°C, 90°C and 100°C respectively. The diamine silane and degrease-only treatments produced essentially adhesive (*i.e.*, interfacial) failures at the higher temperatures, particularly at 100°C.

Using the 177°C curing adhesive AF-130 (3 M Company), lap shear strength was determined at ambient and 177°C on joints primed with epoxy silane and compared with the performance of FPL-etched joints. The shear strengths obtained after the silane pretreatment were about 20% lower than FPL etched joints at both test temperatures (Table IV). All failures were cohesive.

Durability

Bond durability has been assessed in terms of crack propagation resistance during exposure to a hostile environment (50°C and 96% RH) using the wedge test. Although this relatively simple test simulates forces and effects at the metal-adhesive interface in a purely qualitative manner, results obtained have been shown to be more reliable than methods using lap shear or peel tests when predicting the environmental durability of adherend surface preparations.[12]

The qualitative nature of the wedge test is, to a large extent, the result of variation in initial crack length, and hence initial joint stress, due to the inherent fracture toughness of the adhesive under test. Thus, a comparison of crack propagation rates between different adhesive systems must be treated with caution. For any particular adhesive system, regardless of adherend surface pretreatment, the initial crack length remains fairly constant if cohesive failure occurs. The range of initial crack lengths observed in this work was AF-163 26.2–29.7 mm, FM-73 30.4–32.6 mm, FM-300 37.8–40.8 mm, AF-130 53.3–54.2 mm.

The crack propagation resistance of bonded joints made using four silane primers (primary amine, diamine, epoxy and methacrylate), the FPL etch and sandblast/degrease pretreatments is shown in Figure 2 for the 121°C curing adhesive FM-73. Results indicate a large variation in crack propagation rates between different adhesives.

To assess the potential of silane primers with a range of structural film adhesives, the durability of two 121°C and two 177°C curing systems was assessed from wedge specimens prepared using the

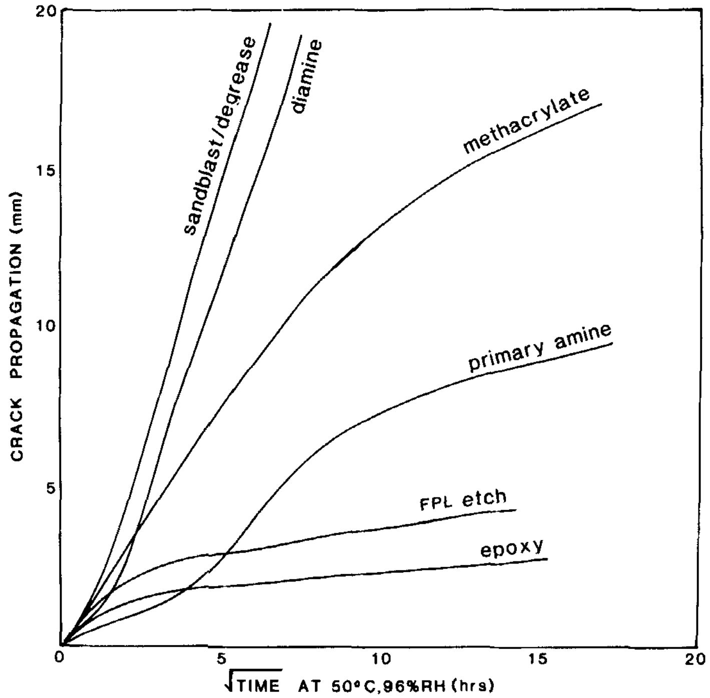


FIGURE 2 Effect of pretreatment on crack propagation, FM-73 adhesive.

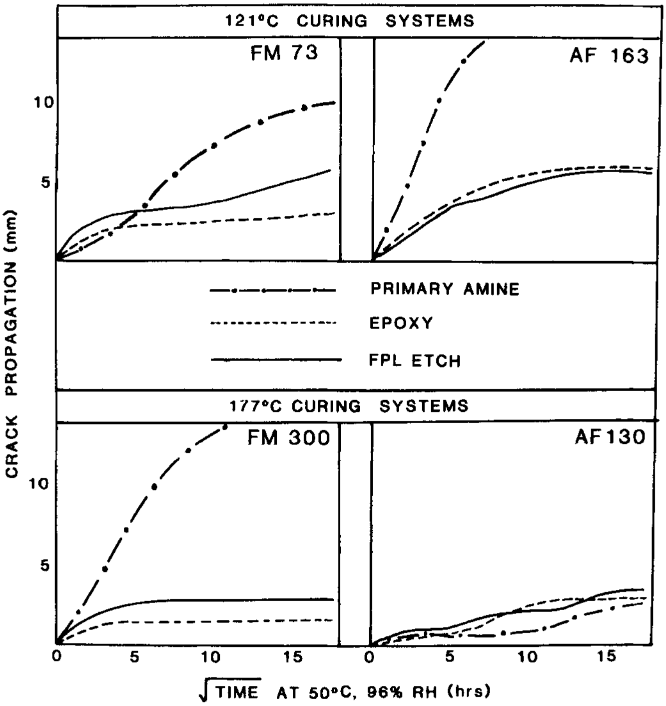


FIGURE 3 Effect of adhesive type on crack propagation—epoxy silane, primary amine silane and FPL etch pretreatments, four adhesives.

primary amine and epoxy silane. A comparison with FPL etched specimens is shown in Figure 3. With each of the four adhesives, the epoxy silane and FPL etch treatments produced good to excellent crack resistance in contrast to the primary amine treatment which was variable.

Further studies with primary amine silane

Drying time FM-300 bonded wedge specimens pretreated with primary amine silane and dried at 110°C for 16 hours under vacuum were compared with joints prepared using the normal drying schedule of 1 hour at 110°C. Only a small improvement in crack propagation resistance occurred after the extended drying period.

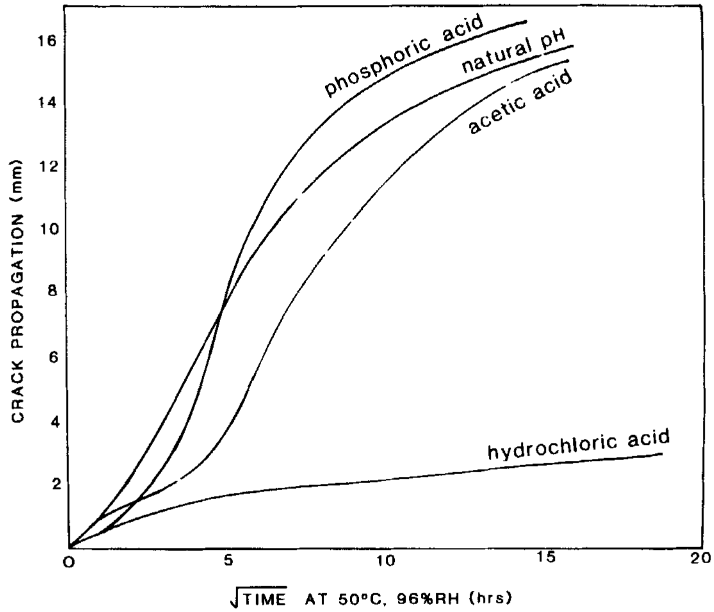


FIGURE 4 Effect of primer pH on crack propagation—primary amine silane adjusted to pH 8 with various acids, FM-300 adhesive.

pH effect Crack propagation rates of FM-300 bonded wedge specimens, pretreated with primary amine silane solutions adjusted to pH 8.0 with 1 M solutions of hydrochloric, phosphoric or acetic acids, were compared with joints prepared using the silane at its natural pH of ~10.3. As seen in Figure 4, the acetic and phosphoric acid modified solutions did not significantly improve the poor performance obtained with joints prepared at the natural pH but, in contrast, specimens obtained from the hydrochloric acid modified solution showed excellent crack resistance.

Hydrochloric acid modification of amino silanes

To assess the general effectiveness of the hydrochloric acid modification on amino silanes, FM-300 and FM-73 bonded wedge specimens were prepared after the following silane surface pretreatments: primary amine adjusted to pH 8, diamine adjusted to pH 8

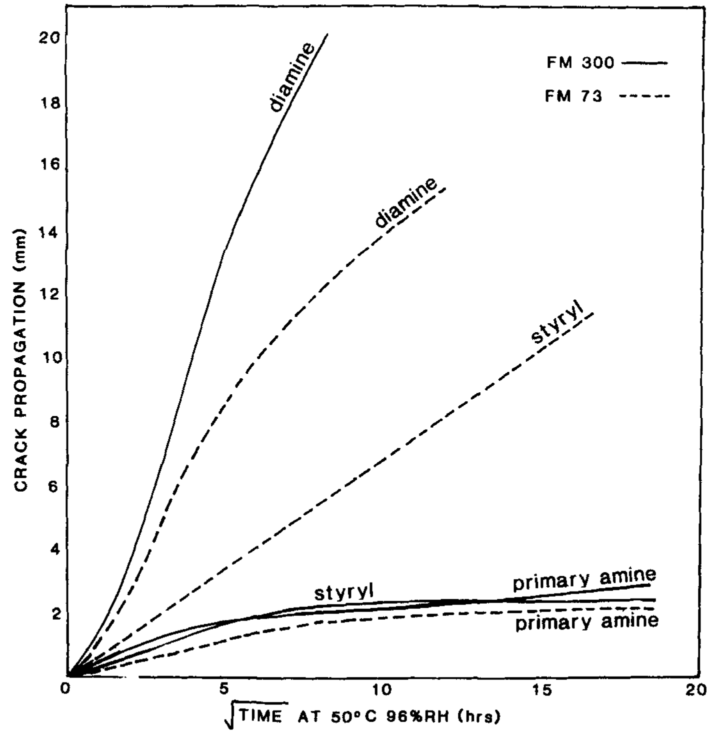


FIGURE 5 Effect of primer pH on crack propagation—primary amine and diamine silanes adjusted to pH 8 with HCl, cationic styryl silane at its natural pH, FM-73 and FM-300 adhesives.

and the cationic styryl (which is supplied as the monohydrochloride). Results, illustrated in Figure 5, indicate that joints primed with the primary amine silane and bonded with FM-73 gave excellent performance. The cationic styryl silane also performed well with FM-300 but was less successful with FM-73. In contrast, diamine silane treated joints showed poor crack resistance, particularly with FM-300.

DISCUSSION

Lap shear measurements on aluminium with the 121°C curing adhesive FM-73 highlighted the differences between a range of silane primers by showing that at the highest test temperatures only the amine and epoxy functionalities approached the values obtained using the FPL treatment (Table III). Since the strength differences between the silane and FPL treatments were much greater at elevated temperatures, and only the former treatments showed signs of adhesive failure, the possibility that the Tg of the polysiloxane network was a dominating influence was considered. Indeed, the literature has reported a Tg of around 108°C for the amine silane after prolonged drying.[13] However, joints primed with the epoxy silane and bonded with the 177°C curing adhesive AF-130 when tested at 177°C gave relatively good shear strength, compared with the FPL treatment, and failed cohesively (Table IV).

Durability studies showed a similar trend: in crack propagation experiments with a representative range of pretreatments on wedge test specimens bonded with FM-73, only the epoxy silane primed joints matched the durability exhibited by the FPL etch. Examination of the crack resistance of joints made from AF-163, AF-130 and FM-300 confirmed that treatment with epoxy silane matched the durability of the FPL treatment in all cases.

Since silanes containing an amino functionality should be chemically reactive in epoxy systems, it was felt that their relatively poor performance in terms of durability should be investigated further. Previous work, based on the dry and wet strengths of aluminium lap shear joints primed with primary amine silane and bonded with a simple, two-part epoxy system, showed that durability was a function of silane solution drying conditions[10] and pH[7]. Our study, using the primary amine silane with the 177°C curing adhesive FM-300, has shown that extended drying gives only a small improvement to the poor durability found using normal drying conditions. Experiments using the same system but with the amine silane adjusted to pH 8.0 produced a vast improvement in durability when hydrochloric acid was employed but no such improvement if either phosphoric or acetic acid was used to modify the pH. The reason for this is unclear and is being examined further.

Further experiments designed to investigate the general applicability of the HCl pH adjustment gave mixed results. The modified primary amine silane treatment produced good durability with both FM-73 and FM-300 but no improvement was noted with the diamine silane with either adhesive. The cationic styryl silane, which contains diamine functionality and is supplied as the monohydrochloride, gave encouraging results without further modification (Fig. 5).

CONCLUSIONS

1) The epoxy silane (γ-glycidoxypropyltrimethoxy silane) is versatile as an adhesion promoter for aluminium and confers acceptable lap shear strength and durability on a range of epoxy-based structural film adhesives.
2) The remaining neutral silanes evaluated (methacrylate, chloropropyl, vinyl triacetoxy and vinyl trimethoxy functionalities) are less effective.
3) The primary amine silane (γ-aminopropyltriethoxy silane) is a good adhesion promoter after treatment with hydrochloric acid. (Manufacture of this product as the hydrochloride, if feasible, might be beneficial).
4) The cationic styryl silane {N-β-(N-vinylbenzylamino)-ethyl-γ-aminopropyltrimethoxy silane monohydrochloride} shows considerable promise in the systems examined.
5) The diamino silane is not an effective adhesion promoter for epoxy film adhesives.

Acknowledgement

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