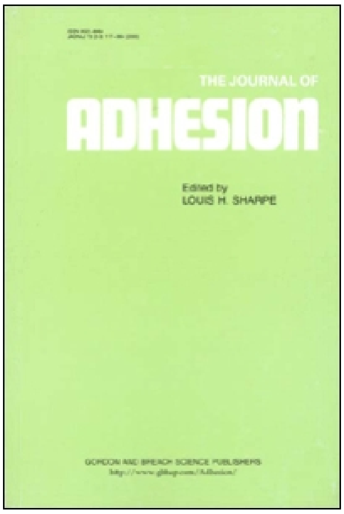

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The Effect of Silane Coupling Agents on the Durability of Titanium Alloy Joints†

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An aqueous solution of γ-glycidoxypropyltrimethoxysilane (GPS) applied to titanium alloy adherends greatly improved bond durabilities compared to alloy surfaces that were only abraded and solvent cleaned. γ-aminopropyltriethoxysilane (APS) also gave improved durability but was not so effective.

Three epoxy adhesives differed considerably in their responses to the five metal pretreatments that were compared. Overall, a sodium hydroxide anodise treatment gave the highest resistance to crack growth in the wedge test.

KEY WORDS Silane; epoxy adhesive; surface treatment; crack growth; durability; titanium; carbon fibre composite.

INTRODUCTION

Titanium alloy sheet can be used for surface bonded patch repairs to thin composite skin structures. The modulus of the metal is higher than that of typical carbon-fibre cross-ply laminates, and its low coefficient of thermal expansion keeps thermal stresses down. However, good long-term durability of the titanium-composite bond requires chemical pretreatment of the metal surface,[1] which may not be practicable in many field repair situations. The use of dilute

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aqueous silane coupling-agent solutions as simple and safe adhesion promotors has therefore been examined as an alternative.

Silanes are known to improve bond strength and durability with aluminium alloys and steels,[2–5] but less work has been done with titanium alloy adherends. Schrader and Cardamone[6] found that priming the adherends with a 1% aqueous solution of γ-aminopropyltriethoxysilane (APS) considerably increased both the initial dry lap shear strength of titanium/epoxide joints and the strength after exposure in boiling water, compared to surfaces that were either grit-blasted or pickled. Coury, *et al.*,[7] used another amino-functional silane in 0.5% aqueous solution and also found a considerable increase in wet lap shear strength retention, in this case after boiling in a saline solution; their unprimed adherends had been simply degreased. Boerio and Dillingham[8] also observed considerable increases in both dry and wet shear strength when 1% aqueous solutions of APS were applied to mechanically polished adherends. However, Cotter and Mahoon[9] found only a small increase in dry lap shear strength with 1% aqueous APS solutions applied to titanium adherends etched with alkaline hydrogen peroxide, and no improvement in durability. Naviroj, *et al.*,[10] studied the reaction of aqueous solutions of the mono-alkoxy counterpart of APS with TiO_2 powder using infra-red spectroscopic techniques. They tentatively assigned a band at 950 cm^{-1} to a Si—O—Ti bond formed by condensation of the hydrolysed, silanol form of the silane with TiOH groups on the surface of the powder. A hot water immersion test with the silane-treated powder showed that the silane was not easily displaced and this was confirmed by spectra of the powders.

Thus the potential of silane coupling-agents as adhesion promotors for titanium alloys was evident, and the aim of the work reported here was to establish their value more clearly for aerospace adhesive bonding. For this purpose five features of the work should be noted. (a) Silane treatments were compared with chemical treatments known to give good durability. (b) The well-established and severe wedge-cleavage test was used to assess joint durability. (c) Joints were exposed to the commonly-used and realistic condition of 50°C/96% RH. (d) APS was compared with GPS (γ-glycidoxypropyltrimethoxysilane), which has been widely and successfully used with aluminium alloys. (e) Three toughened aerospace structural adhesives were compared, curing at ambient temperature, 120°C and 175°C.

EXPERIMENTAL

Materials

The adherends were titanium alloy 6Al4V to specification BS 2TA10, 2 mm thick. Adhesive A was a 2-part, amine-cured toughened epoxide cured at room temperature. One to two per cent by weight of glass ballotini 0.1 mm dia were added to control glue line thickness. The joints were cured under a vacuum blanket at a differential pressure of about 65 kPa overnight at 20 ± 2°C and then kept at that temperature for at least 10 days prior to testing. Adhesive B was a supported, toughened epoxide film cured 0.5 h/120°C at 180 kPa in a press. Adhesive C was a supported, toughened epoxide film adhesive cured 1 h/175°C at 180 kPa in a press. The silanes were γ-glycidoxypropyltrimethoxy silane (GPS) supplied by Union Carbide UK Ltd as A187 and γ-aminopropyltriethoxysilane (APS), also from Union Carbide as A1100.

Pretreatments

(1) *Grit blast* (*GB*): Adherends were swabbed with methylethylketone, wet blasted with 180–220 grade alumina grit, rinsed with tap water, wiped dry, and finally again solvent swabbed. This treatment was also used prior to the other treatments (2)–(4) described below.

(2) *GPS treatment*: A 1% solution of GPS in deionised water (pH ≃ 4 to 5) was allowed to stand for 1–2 h before use. The adherends after GB treatment were kept wet with silane solution for 2 minutes using a brush. They were then placed vertically to drain off excess solution and allowed to air-dry for 2–3 h before use.

(3) *APS treatment*: APS was applied in the same way as GPS. It was reported that the natural pH of a 1% solution of APS is 10.4.[8]

(4) *Sodium hydroxide anodise* (*SHA*): The development of and earlier results using Adhesive B with this process are described

elsewhere.[1,11] The adherends were anodised at 10 V for 30 min at room temperature in a 5M solution of NaOH using stainless steel cathodes. The metal was then washed in tap water at room temperature, dried 15 min/60°C and bonded within 4 h.

(5) *Catalytic etch* (*CE*): This has also been described elsewhere.[1,11,12] The etch solution was 1 M NaOH, 0.001 M $MnSO_4 \cdot 4H_2O$ and 0.5 M H_2O_2 used at room temperature. The $MnSO_4$ was first added to the NaOH solution and the manganese hydroxide precipitate allowed to develop overnight. The adherends were then hung in the solution just before adding the H_2O_2. Etching was stopped when there appeared to be no further reaction and the metal was starting to acquire a brown smut (2.2–3.2 h). Any loose smut was wiped off and the metal then washed and dried as in Treatment (4).

Joint Type and Test Method

The wedge cleavage test (Boeing test) was carried out essentially as specified,[13] except that the joints were made separately instead of being cut from a panel; joint edges were polished and wedges were driven in slowly in a vice. Three replicates were used for each condition. The joints were left overnight over silica gel before measuring the initial crack length with a travelling microscope. They were then exposed at 50°C over a saturated solution of K_2SO_4 giving a relative humidity of 96%, and crack lengths were remeasured at intervals up to 312 h exposure. Fracture energies $\mathscr{G}$ were calculated from the equation

$$\mathscr{G} = \frac{Ew^2h^3[3(a+0.6h)^2+h^2]}{16[(a+0.6h)^3+ah^2]^2}$$

where: E = Young's modulus of adherends
w = displacement caused by the wedge
h = adherend thickness
a = crack length

Finally, the joints were split completely open and the fracture surfaces examined with a hand lens.

RESULTS AND DISCUSSION

The fracture energies at 0, 24 and 240 h exposure as a function of adhesive and pretreatment are shown in Table I and the full results are shown graphically in Figures 1–3. The initial values were plotted at a time of 0.1 h for convenience in presentation on a log (time) scale. This is physically reasonable and is not seriously misleading. Also, for each adhesive the average initial value of $\mathcal{G}$ calculated from all pretreatments was plotted rather than the separate values for each, because there was in general no significant difference between treatments; this was as expected because the initial cracks were almost entirely cohesive and reflected the properties of the adhesive rather than the metal-adhesive bond. In contrast, the crack growths at high humidity appeared to be almost entirely in adhesion, so that the fall in $\mathcal{G}$ with exposure time indicated the water-resistance of the bonds.

TABLE I

The effect of exposure duration and pretreatment type on the mean fracture energy $\mathcal{G}$ (kJ/m^2) of titanium alloy/epoxide joints exposed at 50°C/96% RH

		Exposure time (h)		
Adhesive	Pretreatment	0	24	240
A	GB	1.98 (0.26)	0.079 (0.044)	0.067 (0.031)
	GPS	2.13 (0.08)	0.470 (0.029)	0.232 (0.010)
	APS	2.17 (0.23)	0.190 (0.020)	0.090 (0.017)
	SHA	1.88 (0.28)	0.388 (0.031)	0.215 (0.018)
	CE	1.90 (0.33)	0.139 (0.016)	0.129 (0.014)
B	GB	2.37 (0.16)	0.052 (0.004)	0.051 (0.004)
	GPS	2.48 (0.21)	0.177 (0.056)	0.120 (0.002)
	APS	2.89 (0.41)	0.098 (0.014)	0.081 (0.007)
	SHA	2.66 (0.35)	0.982 (0.199)	0.581 (0.042)
	CE	2.48 (0.45)	0.764 (0.447)	0.414 (0.132)
C	GB	0.613 (0.027)	0.066 (0.001)	0.066 (0.003)
	GPS	0.803 (0.046)	0.647 (0.013)	0.397 (0.049)
	APS	0.789 (0.063)	0.177 (0.079)	0.163 (0.061)
	SHA	0.744 (0.144)	0.595 (0.093)	0.567 (0.113)
	CE	0.734 (0.065)	0.334 (0.214)	0.210 (0.051)

Figures in brackets are standard deviations (3 replicates). GB = grit blast only; GPS = epoxy-silane; APS = amino-silane; SHA = sodium hydroxide anodise; CE = catalytic hydrogen peroxide etch.

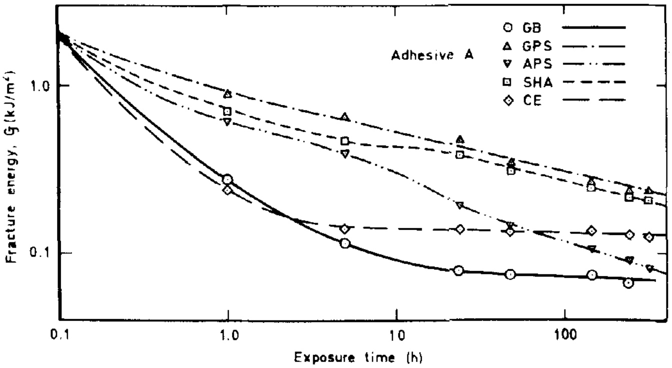

FIGURE 1 Fracture energies 𝒢 from the wedge test as a function of time of exposure at 50°C/96% RH for Adhesive A.

Table II shows the exposure times derived from these graphs for the fracture energy to fall to 0.5 kJ/m^2, which gives an indication of the relative durabilities of the various adhesive/treatment combinations.

Comparison of Pretreatments

As expected, the grit-blasted surfaces without further treatment gave very low durability for all three adhesives and both silanes considerably improved the water-resistance compared to grit-blast

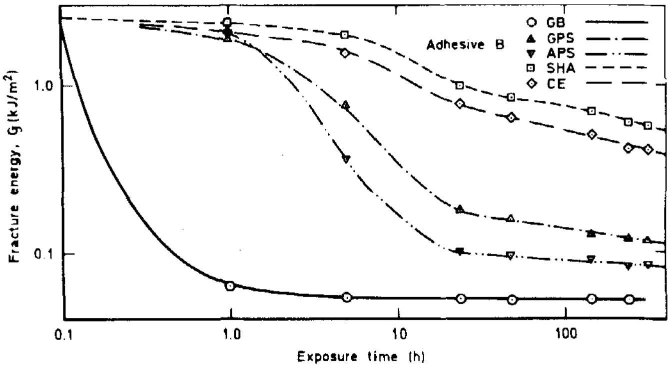

FIGURE 2 Fracture energies 𝒢 from the wedge test as a function of time of exposure at 50°C/96% RH for Adhesive B.

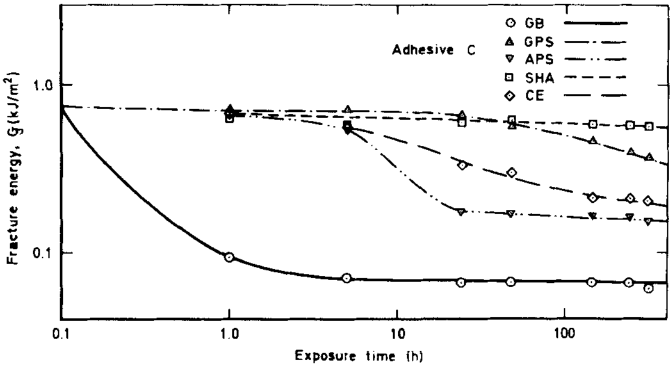

FIGURE 3 Fracture energies $\mathcal{G}$ from the wedge test as a function of time of exposure at 50°C/96% RH for Adhesive C.

TABLE II
Effect of adhesive and pretreatment types on exposure time for $\mathcal{G}$ to reach 0.5 kJ/m^2 in titanium alloy/epoxide joints exposed at 50°C/96% RH

Adhesive	Pretreatment (Note 1)	Exposure time for $\mathcal{G}$ = 0.5 kJ/m^2 (h)
A	GB	~0.5 (Note 2)
	GPS	13
	APS	2
	SHA	4
	CE	~0.5 (Note 2)
B	GB	~0.2 (Note 2)
	GPS	7
	APS	4
	SHA	~500
	CE	140
C	GB	~0.1 (Note 2)
	GPS	100
	APS	6
	SHA	≫400
	CE	8

Note 1: GB = grit blast only; GPS = epoxy-silane; APS = amino-silane; SHA = sodium hydroxide anodise; CE = catalytic hydrogen peroxide etch. Note 2: These times estimated from plots of log $\mathcal{G}$ *vs* t (not shown).

alone. GPS was more effective than APS with all three adhesives, although the difference was not large for Adhesive B. Also, with Adhesive A, GPS was at least as effective as the anodise treatment, and for exposures up to about 50 h this was so also for Adhesive C. These increases in water-resistance conferred by the silanes on surfaces that were not otherwise chemically treated are consistent with the previous evidence.[6-10] However, Coury *et al.*,[7] found that the amino-functional silane that they used was more effective than GPS, and it should not be concluded from the present work that epoxy-functional silanes give higher durability in general than the amino-functional type. Their performance relative to each other and to the other treatments will no doubt depend on the interaction between such factors as the particular chemical structure, the adhesive cure system and temperature, and the application conditions for the silane.

For example, on this last aspect, Schrader and Cardamone[6] found that rinsing the metal with water immediately after applying the silane lowered joint strengths slightly, whereas in contrast Coury, *et al.*,[7] observed a considerable increase in wet strength retention if the treated adherends were rinsed. Boerio and Dillingham[8] found that applying APS at a pH of 5.5 considerably reduced its effectiveness compared to application at pH 8.0 and 10.4. It should be noted that the conditions of silane application varied considerably among the studies cited, including the present work, and were not necessarily optimum in any of them. This aspect deserves much fuller study, to define optimum conditions and to determine the sensitivity of joint strength and durability to variations in application technique.

The anodise pretreatment gave overall the highest resistance to crack growth, although for Adhesive A there was little if any difference between SHA and GPS treatments. This superiority of anodising is consistent with previous findings and has been attributed to the microporous oxide layer that is formed.[1] The CE treatment, which also forms an oxide layer with some degree of microporosity,[1] gave considerably different results for the three adhesives. With Adhesive B the durability approached that given by the SHA treatment, in agreement with previous results for this adhesive.[1,11,12] In contrast, with Adhesive A the CE treatment was initially little better than grit-blasting alone, and with Adhesive C it took the middle position in the rank order of treatments. These differences cannot be explained at present, but may perhaps arise from the apparently smaller pore size given by the CE treatment compared to SHA with the 6Al4V alloy.[1] This may result in differences in penetration of the porous structures by adhesives of differing viscosities.

Comparison of Adhesives

The adhesives were typical of three types widely used in aerospace bonding with cure temperatures of ~20°C, 120°C and 175°C. As expected, the 175°C cure Adhesive C was less tough then the others as shown by the lower initial value of $\mathcal{G}$. However, after several hundred hours exposure the $\mathcal{G}$ values for Adhesive C were as high as or higher than for A and B, and at a $\mathcal{G}$ value of 0.5 kJ/m^2 the rate of decrease of $\mathcal{G}$ was lower. Conversely, the RT cure Adhesive A showed a generally lower durability than B and C.

These differences cannot be explained as yet. They are likely to be due in part to differing rates and equilibrium levels of water uptake affecting the water content near the interface just ahead of the advancing crack tip; to differing degrees of adhesive penetration into the porous oxide layers (for CE and SHA treatments); and to differing extents of reaction between adhesives and silanes. The elevated temperature cures for B and C may also cause additional reaction between the metal oxide surface and the polysiloxane layer formed by the hydrolysed silane, and further cross-linking within that layer. For example, recent evidence for an aluminium-PVC system suggests that there is an optimum silane curing temperature for maximum peel strength, with sharp decreases in strength at lower or higher temperatures.[14] The authors propose that a balance is required between adequate cross-linking in the polysiloxane layer and interdiffusion of polysiloxane with adhesive.

CONCLUSIONS

(1) Priming grit-blasted titanium alloy surfaces with epoxy- and aminofunctional silanes considerably increased the durability of

joints made with three epoxide adhesives, compared to metal surfaces that were only grit-blasted.

(2) For the particular silane application conditions and adhesives used in this work the epoxy-functional silane was more effective than the amino-functional.

(3) Treatment with the epoxy-functional silane was almost as effective as sodium hydroxide anodising for two adhesives.

(4) A 175°C cure adhesive, although less tough initially, gave the highest durability; a RT-cure adhesive gave the lowest durability.

(5) The conditions of application for the silanes need much more investigation in order to optimise joint durability and to identify unsuitable techniques.

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