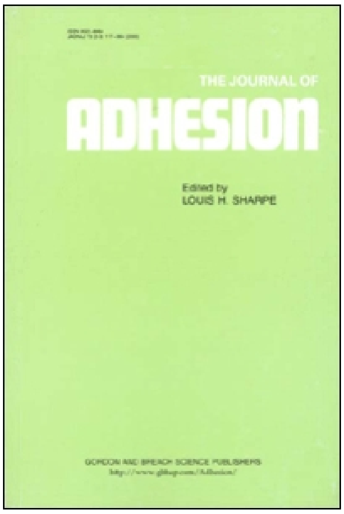

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The Effect of the Silane Deposition Conditions on the Durability of Aluminium Joints Pretreated using 3-Aminopropyltrimethoxysilane

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The Effect of the Silane Deposition Conditions on the Durability of Aluminium Joints Pretreated using 3-Aminopropyltrimethoxysilane

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The interfacial adhesive fracture energies and durabilities of aluminium/polyurethane joints pretreated with 3-aminopropyltrimethoxysilane using a range of deposition conditions has been investigated using the blister test. For substrates that were rinsed in order to remove the excess silane, the initial adhesive fracture energy was found to increase markedly compared with the unpretreated joints, but was not affected by changes in the pretreatment solvent (water and toluene), time (five and twenty minutes), or, for substrates pretreated from aqueous solutions, pH (6.8 and 10.4). However, the durability of these rinsed silane pretreated joints varied considerably with the silane pretreatment conditions. The most durable joints were formed when the aluminium was pretreated from aqueous solutions at pH 6.8 for five minutes. XPS analysis of the failed fracture surfaces revealed that the failure was associated with the very thin silane film, occurring at the metal/silane/polymer interface. When the excess silane was not removed by rinsing, the initial adhesive fracture energy was approximately half that obtained from the rinsed joints and the durability was also very poor. XPS analysis of the fracture surfaces showed that failure had occurred within a thick silane film.

KEY WORDS interfacial adhesive fracture energy; aluminium/polyurethane adhesive joints; effect of solvent, solution pH, time; blister test; XPS analysis; locus of failure.

1.0 INTRODUCTION

At present, aluminium substrates must undergo a series of chemical pretreatments in order to ensure that an adhesively bonded component possesses a high degree of durability. These chemical pretreatments usually involve anodizing the aluminium substrate. As this is an expensive and time-consuming process, bonded aluminium components cannot be used in mass-produced products requiring a high degree of durability (*i.e.*, the car industry).

The use of silanes to pretreat metallic components prior to bonding has been

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shown[1-5] to improve the durability of the joint. Silanes can be chemically represented by the general formula R—Si—(R′)$_3$. R is a short carbon chain containing some functionality usually capable of reacting with the adhesive resin. R′ is a group which can either react directly with the substrate hydroxyl groups (*e.g.*, Si—Cl$_3$) or which hydrolyses to form silanol groups (Si—(OH)$_3$). These silanol groups can then react with each other and any surface hydroxyl groups, eliminating water.

Considerable work has been directed at understanding the nature of the interaction between the substrate and the silane[6-12] and the adhesive and the silane.[13-15] However, to the authors' knowledge, surprisingly little work[16-17] has been performed directed at controlling the deposition conditions used during the pretreatment of the substrate and then assessing the subsequent effects on the durability of the adhesive joints.

Boerio and his co-workers[16,17] have studied the effect of pH on the durability of mild steel and titanium lap shear joints pretreated using a 1% aqueous 3-aminopropyltriethoxysilane solution (3-APES). The natural pH of a 1% 3-APES solution is approximately 10.4 and so in order to reduce the pH, the solutions were acidified using HCl. In the case of mild steel, they found that joints pretreated at pH 8.0 retained 75% of their initial strength, whereas joints pretreated at pH 10.4 retained only 50% of their initial strengths after immersion in water for 60 days at 60°C. In the case of titanium, these workers found that the use of the silanes resulted in both higher initial joint strengths and also improved durabilities. The joints pretreated at pH 8.0 and 10.4 possessed very similar durabilities; joints pretreated at pH 5.5 were less durable.

Boerio *et al.* proposed that the variation in the durabilities of the adhesive joints could be explained by the theory suggested by Bolger.[18] In this theory, a compound will remain strongly absorbed onto a metallic oxide if the pH of the water, used in the durability experiments, is between the isoelectric point (the pH at which the number of positive and negative species on the surface are equal) of the metal oxide and the dissociation constants of the functional groups. Boerio *et al.* assumed an isoelectric point of 10.0 for iron oxide and so at pH 10.4 roughly equal numbers of protonated $FeOH_2^+$ and unprotonated FeO^- groups would have been present. The effect of pH on the 3-APES can be described by the acidic dissociation constants (pK_a) of the amine and silanol groups. The pK_a of the amine group was about 10.0 and that of the silanol groups was about 3.0. Thus, during pretreatment at pH 10.4, the silane would adsorb onto the iron oxide surface *via* both the silanol and amine groups, whereas at pH 8.0 adsorption would primarily occur *via* the silanol groups. As the pH of the water was 6.2, using the theory developed by Bolger, the amino groups would be expected to be displaced, weakening the bond, whereas at both pH 8.0 and 10.4 the silanol groups would remain firmly adsorbed. Boerio *et al.* proposed that this may explain the increased durability of the joints pretreated at pH 8.0 compared with those pretreated at pH 10.4, because at pH 8.0 the silane primarily adsorbed onto the iron oxide surface *via* the silanol groups.

In the case of titanium, the isoelectric point is about 6.0 and so at both pH 10.4 and 8.0, the surface would consist largely of negatively charged TiO^- groups. Thus, at both of these pH values, the silane should adsorb primarily *via* the amino groups. The pH of the water was once more 6.2, thus, using the same argument as above, as the pH of the water is between the isoelectric point and the pK_a value of the amino groups, no difference in the durability of the adhesive joints would be expected. However, at a pretreatment pH of 5.5, adsorption would occur *via* both the amino and silanol groups and using water at pH 6.2 during the durability testing, the silanol groups should be displaced. This would be expected to reduce the durability of the adhesive joint and this was experimentally observed.

When Boerio *et al.* studied the adsorbed silane films deposited at pH 10.4 and 8.0 using reflection-adsorption FTIR spectroscopy, they found several interesting differences. At pH 8.0 they detected two bands at 1600 and 1500 cm^{-1}. As HCl was used to acidify the films, these bands appeared consistent with the formation of an amine hydrochloride. This assignment was supported by XPS analysis of the films which detected chlorine and also by the presence of two components in the nitrogen peak, indicating that both protonated and unprotonated nitrogen species were present. However, at pH 10.4, three bands were detected at 1600, 1500 and 1300 cm^{-1}. These bands were due to the reaction of the amine groups in the silane with atmospheric carbon dioxide and this assignment was confirmed, because when the films were prepared in a nitrogen atmosphere the three bands were no longer observed.

When adsorbed silane films on aluminium were studied slightly different results were obtained. These workers found that at pH 10.4, the silane etched the aluminium surface and it was only at pH 6.8 that spectra similar to those observed for iron and titanium were observed. Of particular interest was the observation that at pH 10.4 the Si—O—Si vibration was observed at 1080 cm^{-1} whereas at pH 6.8 it was present at 1120–1130 cm^{-1}. In view of the etching of the aluminium surface, these workers have proposed that an aluminosiloxane was formed. In addition, the observed etching was very time dependent with a film deposited at pH 10.4 for 1 minute being very similar to those formed on iron and titanium. However, at a pretreatment time of 15 minutes, the band at 1080 cm^{-1} appeared indicating that etching of the aluminium substrate had occurred. Analysis of the films using XPS, unfortunately, yielded no evidence to support the view that an aluminosiloxane was formed at the extended pretreatment times.

While Boerio *et al.* did study the effect of pH on the durability of mild steel and titanium lap shear joints pretreated using 3-APES, they did not present any similar data using aluminium as a substrate. However Thiedman *et al.*[19] have investigated the effect of pH on the durability of aluminium joints pretreated using 3-aminopropyltrimethoxysilane (3-APMS) bonded using aerospace epoxy film adhesives. The durability was evaluated using the well-known Boeing wedge test. These workers found that when the pH of the 3-APMS solution was controlled at 8.0 using 1M HCl, excellent joint durabilities were obtained, whereas at pH 10.3 the durability was relatively poor. However, when 1M phosphoric or acetic acid was used to acidify the solutions no improvement in the joint durability was obtained. One extremely interesting observation was that when a diaminosilane solution was acidified using HCl no comparable improvement in the joint durability was observed. One possible explanation for the poor durabilities of joints pretreated with 3-aminopropyltrimethoxysilane acidified using phosphoric or acetic acid is that these acids may react with the amine groups to form P—O—N and amide groups. These species may not be able to react with the adhesive resin, thus impairing the adhesion. The formation of a simple amine hydrochloride would still be able to attack the epoxy rings enabling the adhesive and the adsorbed silane film to cross-link and thus improve the durability. The failure of acidification to improve the durability of the joints pretreated using the diaminosilane is surprising and no explanation can be proposed at this time.

Clearly, the effect of the deposition conditions is extremely important. However the tests commonly used to evaluate the performance of silane pretreated joints only provide a measurement of the durability of the joint as a whole. The blister test, [20–23] however, is capable of providing quantitative data on the strength of the interface[21]. This test involves stressing an area of the joint by raising the pressure using a gas such as nitrogen until the joint fails, resulting in the formation of a blister. By plotting the failure pressure against the blister radius, corrected for specimen geometry effects, the adhesive fracture energy can be calculated. In addition, by replacing the pressurising gas with water at a constant pressure, the durability of the joint can be monitored by measuring the time taken for the crack to begin propagating. The blister test would appear to be ideal for testing the effectiveness of a silane primer and evaluating the effect of the silane deposition conditions on the interfacial fracture strength and the joint durability.

The current research has concentrated on evaluating the effect of the deposition conditions on the adhesive fracture energy and durability of aluminium joints pretreated with 3-aminopropyltrimethoxysilane. The deposition conditions varied included the solvent used, the deposition time, the thickness of the adsorbed silane film and the pH of the aqueous-based solutions. The effect of rinsing the pretreated substrates upon removal from the silane solutions with the solvent used during the pretreatment was also investigated.

2.0 Experimental

2.1 Substrate Preparation

British Standard (BS) 1200 aluminium alloy substrates (50 mm diameter; 6 mm thick with a 5 mm diameter hole drilled in the center of the disc) were etched for 10 minutes in 1.5M NaOH at 50°C, rinsed in distilled water, etched for a further minute in 10% nitric acid to remove any etch residues and then rinsed again in distilled water. The substrates were then rinsed using ethanol, followed by chloroform and were then rapidly dried using hot air. Analar grade solvents were used throughout this work. The use of the organic rinses ensured that the substrates dried rapidly and avoided any problems of unknown air-borne contaminants adsorbing onto the cleaned substrates prior to silane desposition. The above procedure yielded a surface that was fully wetted by water, indicating that a clean surface suitable for silane adsorption was produced. XPS analysis of the etched substrates also revealed that very low levels of nitrogen and silicon were present.

The prepared substrates were then immediately pretreated using 0.1M 3-aminopropyltrimethoxysilane (Fluka Chemical Ltd; used as received) solutions either in toluene or distilled water. The pretreatment times were either 5 or 20 minutes and in the case of the aqueous solutions the pH was either 6.8 or 10.4. The solutions at pH 6.8 were formed by adding 2M HCl to the 0.1M silane solutions, whose natural pH was 10.4. After pretreatment, the substrates were rinsed using the same solvent as the pretreatment medium (*i.e.* toluene or distilled water) and were then dried in a stream of hot air. In order to study the effect of rinsing, a series of substrates pretreated at pH 10.4 for 5 minutes which were not rinsed, but were simply dried in a stream of hot air, were also prepared.

In order to prepare the blister test joints after silane pretreatment of the aluminium substrates, 35g of a polyurethane resin (Solithane 113; Morton-Thiokol) was cast onto the substrates and the adhesive was allowed to cure for two days at 30°C before being removed from the mould. The prepared joints were then conditioned at 30°C for two weeks before being tested.

2.2 The Blister Test

In order to determine the initial adhesive fracture energy, G_c, the cured joints were then tested using the blister test with dry nitrogen as the pressurising medium. The equipment used has been recently described in detail by Fernando and Kinloch.[24] A constant nitrogen gas flow of 10 cc/min was used throughout this part of the work. The failure pressure at a range of blister radii was recorded and the adhesive fracture energy, G_c was calculated using Equations 1 and 2.[21]

$$P_c^2 a = EG_c f(h/a) \tag{1}$$

where P_c is the critical failure pressure, G_c is the adhesive fracture energy, E is the Young's modulus, h is the thickness of the polymer and a is the blister radius. $f(h/a)$ is a geometry factor which corrects for the change in the amount of energy dissipated in the polymer as the blister radius increases. $f(h/a)$ is expressed by

$$f(h/a) = \{1/(1-\nu^2)\}\{3/32[(a/h)^3 + 4/(1-\nu).(a/h)] + 2/\pi\}^{-1} \tag{2}$$

where ν is the Poisson's ratio (assumed to be 0.499 in this work).

The thickness of the joints was 17 mm and the Young's modulus of the polymer was 3.38×10^6 N/m^2. The pressure was then raised until blister radius increased and the pressure was recorded. After the blister radius increased, the pressure was then briefly raised to a much higher pressure than that required to cause blister growth. This caused rapid crack propagation and the pressure was then rapidly reduced to atmospheric pressure. This procedure ensured that the crack tip remained sharp. The new blister radius was then measured and the test repeated. A total of three joints were studied using the above procedure and typically five measurements were obtained from each joint.

The durability of the joints was obtained by pressurising the joints to 50% of their failure pressure for given initial blister radii (typically 8 mm) using water and then monitoring the time for the onset of crack propagation to occur. The time required for the joints to fail completely was also recorded. In order to assess the effect of the silane pretreatment, unpretreated aluminium joints were also studied. A total of three joints were tested for each set of deposition conditions.

To identify the locus of failure of the joints, 1 cm^2 samples were cut from the failed joints and the polymer and metal fracture surfaces were analysed using XPS. This work was performed using a "VG Scientific" ESCALAB spectrometer at the B. P. Research Center, Sunbury-on-Thames, Middlesex. AlKα x-rays at 280W (14 kV, 20mA) were used at a chamber pressure of between 10^{-8} and 10^{-9} Torr. An electron take-off angle of 70° was used to acquire the spectra using a 50 eV analyser energy. To allow the information from the failed surfaces to be more accurately interpreted, untested silane pretreated surfaces were also analysed.

3.0 Results and Discussion

3.1 XPS Analysis of the Adsorbed Silane Films

The results from the XPS analysis of the adsorbed silane films are presented in Table I. The analyses from the etched aluminium substrate have been included in order to allow easy comparison. The high level of oxygen detected on the etched-

TABLE I
XPS atomic concentrations for 1200 aluminium substrates pretreated using 3-aminopropyltrimethoxysilane under a range of conditions

Sample type			Atomic concentrations						
Solvent	Time/pH (mins/—)	Rinsed	Si	N	Cl	Na	Al	Al—O	O
etched only	n/a	n/a	—	0.1	0.4	—	14.5	16.2	43.5
Toluene	5/—	Yes	2.1	1.3	0.5	—	13.8	14.4	40.5
Toluene	20/—	Yes	3.7	4.3	0.8	—	6.4	9.6	32.9
Water	5/10.4	No	11.3	8.5	—	0.7	0.4	0.5	24.3
Water	5/10.4	Yes	0.9	0.8	1.1	—	6.7	7.2	44.8
Water	20/10.4	Yes	1.3	1.0	1.7	—	8.4	15.4	43.5
Water	5/6.8	Yes	0.8	0.4	1.3	—	8.1	17.4	45.1
Water	20/6.8	Yes	1.1	0.9	1.4	0.1	8.0	4.4	39.5

Solvent	Time/pH (mins/—)	Rinsed	C—C/H	C—O/N	C=O	O—C=O
etched only	n/a	n/a	16.5	1.2	0.5	1.9
Toluene	5/—	Yes	20.7	2.8	0.1	2.3
Toluene	20/—	Yes	22.3	11.9	1.3	0.8
Water	5/10.4	No	40.3	11.4	0.2	1.4
Water	5/10.4	Yes	23.1	2.4	—	1.0
Water	20/10.4	Yes	20.1	4.0	—	2.2
Water	5/6.8	Yes	19.3	3.8	—	1.8
Water	20/6.8	Yes	26.0	3.5	0.5	1.7

N.B. Al—O refers to Al bonded to an oxygen (*i.e.* the oxide); C—C/H refers to a carbon bonded to either another carbon and/or a hydrogen; C—O/N means carbon bonded to an oxygen or a nitrogen; C=O refers to a carbon with two carbon-to-oxygen bonds (*e.g.* a carbonyl group) and finally O—C=O refers to a carbon with three carbon-to-oxygen bonds (*e.g.* a carboxylate group). "—" means that the concentration of the species was below 0.05%. "n/a" means not applicable.

only sample was due to reduced attenuation of the oxygen signal present in the aluminium oxide by a thin hydrocarbon layer. This hydrocarbon is believed to have adsorbed onto all the samples during storage prior to XPS analysis. Similar oxygen intensities were detected from the majority of the substrates pretreated using silane films. The two exceptions to this are the films pretreated from water 5 mins/no rinse/pH 10.4 and the toluene/20 min. The high C—C/H signals in the case of the sample pretreated from water/5 mins no rinse/pH 10.4 indicate the presence of a thick silane film, a conclusion that is supported by the high silicon and nitrogen signals. This thick silane film severely attenuates the signal from the substrate, reducing both the oxygen and aluminium signals. The reduction in the case of the sample pretreated using toluene/20 mins is also due to the presence of a thick silane film as evidenced by the high C—O/N, silicon and nitrogen signals. However, the detection of aluminium (in the form of both the metal and oxide) shows that the film in this case is not as thick as the unrinsed silane film.

The results presented in Table I show an increase in the silicon and nitrogen levels for the silane pretreated substrates indicating that an adsorbed silane film was present on the surface. The nitrogen intensities are believed to be a better indication of the total concentration of silane present on the surfaces. This is because aluminium plasmon peaks interfered with the silicon peaks and so an estimate for the total silicon levels could only be made by curve fitting the plasmon peak on the etched aluminium surface, using this plasmon peak envelope to model the silicon peak and so to estimate the total silicon contribution. The relatively low levels of silicon present on the aluminium surfaces meant that noisy peaks were obtained and so some uncertainty regarding the silicon intensities exists. For this reason the nitrogen intensities are believed to be a more reliable indication regarding the thickness of the adsorbed silane films.

The carbon percentages of typically 20–25% cannot be explained by the adsorption of only the silane. The hydrolysed structure of the 3-APMS is $H_2N—(CH_2)—Si—(OH)_3$ and it can be seen that (assuming that the silane was fully hydrolysed in the pretreatment solution) the ratio of silicon, nitrogen and carbon should be 1:1:3. Thus, for a silicon concentration of 1%, a nitrogen intensity of 1% and total carbon percentage of 3% would be detected. From Table I, it can be seen that while the silicon to nitrogen ratios are in reasonable agreement, taking into account the interference of the aluminium plasmon with the silicon peaks, the carbon intensities are generally too high. The pretreated substrates were all wetted out by water just prior to immersion in the silane solutions and so cannot have been significantly contaminated. The detection of 16.5% of C—C/H on the unpretreated surfaces is believed to be due to adventitious hydrocarbons that adsorbed during storage of the samples prior to XPS analysis. Thus, the excess C—C/H carbon in the case of the silane pretreated substrates is believed to be due to adsorption of airborne contaminants onto the pretreated substrates. By considering the chemical formulation of the silane, curve resolution of the carbon peak should also have yielded two peaks: a carbon bonded to carbon or hydrogen (C—C/H) peak and carbon bonded to nitrogen (C—N) peak with a ratio of 2:1. This ratio was, however, not obtained and was once more due to the adsorption of the organic contaminants. The difference in the binding energies between the peaks due to carbon bonded to nitrogen (C—N) and carbon bonded to oxygen (C—O) is only about 0.5 eV. The curve resolution during this work was not able to separate these components reliably. Therefore, these components have been modelled as a single peak (C—O/N). Finally, the presence of low concentrations of two extra peaks in the carbon spectra indicative of carbonyl (C=O) and carboxylate (O=C—O) groups can also be attributed to contamination.

Substrates pretreated from toluene; toluene rinsed When the elemental concentrations of the films adsorbed from toluene at the different pretreatment times are compared, two interesting differences are apparent. Firstly, the nitrogen and also the silicon levels are higher for the films deposited for 20 minutes than those obtained from the film pretreated for 5 minutes. This indicates that a thicker silane film was formed at the longer pretreatment time. Secondly, the C—O/N value of approximately 12% for the films deposited for 20 minutes is much higher than can be explained by the presence of a single C—N species. The intensity of this peak would be expected to be similar to the nitrogen intensity, *i.e.* about 4%. The excess C—O/N intensity could be explained if unhydrolysed methoxy groups were present in the adsorbed silane film. The presence of these unhydrolysed methoxy groups would imply that the film adsorbed from toluene for 20 minutes was not completely crosslinked. This is because the trimethoxy groups must react with water to form silanol groups before condensation to form the polysiloxane (Si—O—Si) bonds can occur. Clearly, any reduction in the crosslink density of the silane film could weaken the strength of the film and also reduce its moisture resistance.

Substrates pretreated from water; unrinsed The results obtained from the unrinsed silane film adsorbed from water at pH 10.4 for 5 minutes are markedly different to those obtained from the silane film adsorbed under the same conditions, but which was subjected to a water rinse (see below). The very high silicon and nitrogen intensities, shown in Table I, indicate that this film was relatively thick and this conclusion is supported by the marked reduction in the aluminium intensity. Boerio *et al.*[16,17]) used ellipsometry to measure the thickness of unrinsed silane films adsorbed from water and found that typical film thicknesses were around 10 nm. The oxygen intensity has reduced compared with the rinsed film because the bulk of the oxygen detected is now associated with the silane which has a lower oxygen content than the aluminium oxide. The detection of a C—O/N ratio of 11% in this case is probably largely associated with the C—N species in the silane, as the intensity is similar to that obtained for nitrogen (8.5%) and also silicon (11.3%). The structure of APMS would predict a 1:1:1 ratio of N:Si:C—N. One point of interest is that a simple water or toluene rinse was able to remove such a high proportion of the initially adsorbed silane film. This indicates that the bulk of the silane film was only very weakly adsorbed, probably being only physisorbed. Bascom[25] has previously reported similar observations. Schrader[26] has concluded that an adsorbed silane film actually consists of an initially chemisorbed layer adjacent to the surface which cannot be removed even with boiling water and then a more weakly bound physisorbed layer. The above observations would appear to be consistent with the structure proposed by Schrader.

Substrates pretreated from water; water rinsed The results presented in Table I for the rinsed silane films adsorbed from water show that the nitrogen levels for the films deposited at pH 6.8 and 10.4 for 5 and 20 minutes are all very low compared with the results obtained from the unrinsed films discussed above. This indicates that very thin films were left after rinsing. The slightly higher nitrogen concentrations indicate that the silane films deposited for 20 minutes were slightly thicker than those deposited for 5 minutes. However, the low levels of nitrogen prevent any detailed interpretation of the nitrogen peaks and so it was not possible to confirm the observation made by Boerio *et al.*[16] that the silane films deposited at pH 6.8 contains both protonated and unprotonated nitrogen groups. The conclusion that the adsorbed films were extremely thin is reinforced by the strong signal from the aluminium substrate and by the strong oxygen peaks.

3.2 Mechanical Testing

3.2.1 Initial adhesive fracture energy studies A typical plot of the critical failure pressure (P_c) *versus* the blister radius corrected for the geometry effects ($(f(h/a)/a)^{1/2}$) is shown in Figure 1. Equation 1 predicts that the above relationship should be linear, the gradient equalling $(EG_c)^{1/2}$. The experimental points clearly obey Equation 1 and the fact that the plot goes through the origin is expected as the samples were cured at room temperature and so should not possess any significant levels of residual stresses. The adhesive fracture energy results are summarised in Table II. Clearly, for the rinsed samples, the adhesive fracture energies are very

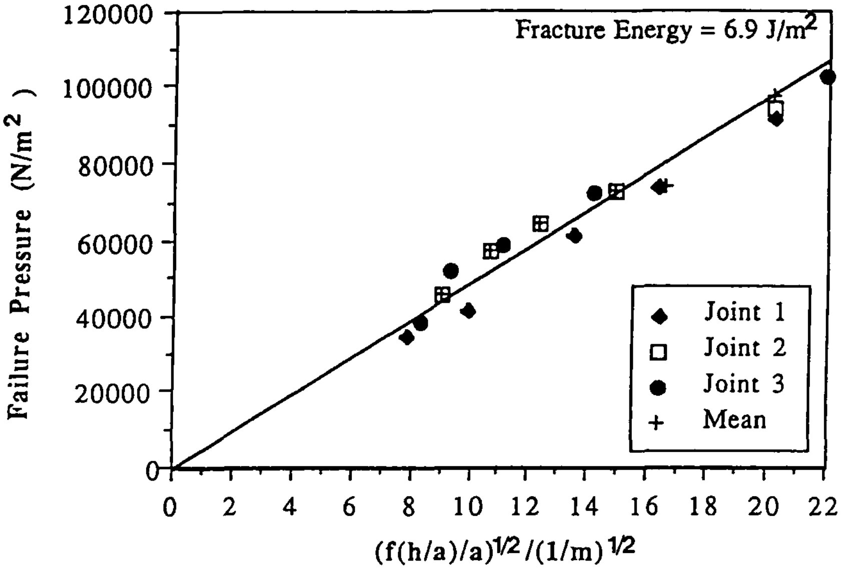

FIGURE 1 Plot of the critical failure pressure *versus* the corrected blister test radius for unpretreated BS 1200 aluminium/polyurethane joints. The plot shows the individual results obtained from a total of three joints and the line has been fitted to the mean of the individual results.

TABLE II
Table summarising the adhesive fracture energies G_c, for aluminium joints pretreated using 3-aminopropyltrimethoxysilane using a range of deposition conditions

Sample type				
Solvent	Time (mins)	pH	Rinsed	G_c (J/m^2)
	unpretreated		n/a	6.9
Toluene	5	n/a	Yes	12.9
Toluene	20	n/a	Yes	15.1
Water	5	10.4	No	7.6
Water	5	10.4	Yes	13.8
Water	20	10.4	Yes	13.9
Water	5	6.8	Yes	14.2
Water	20	6.8	Yes	14.5

N.B. "n/a" means not applicable.

similar and show a considerable improvement over the unpretreated joints. In the case of the unrinsed joints, little improvement in the strength of the joints was observed, compared with the strength of the unpretreated joint.

XPS analysis of the fracture surfaces was performed on the unpretreated joints, the joints pretreated for 20 minutes from both water and toluene and, finally, the unrinsed joint pretreated using water (5 minutes/pH 10.4).[27] The number of fracture surfaces precluded XPS analysis of the rinsed joints pretreated for 5 minutes. In the case of unpretreated joints, tested using both nitrogen and water, very low levels of nitrogen were detected on the metal surface, suggesting that the failure was interfacial. Analysis of the rinsed silane pretreated joints revealed that the failure using both media was associated with the thin, adsorbed silane films. The unrinsed joints tested, using both media, failed through the thick silane film as significant levels of silicon and nitrogen were detected on both failure surfaces. The low adhesive fracture energy of the unrinsed joints would appear to be due to the presence of the thick physisorbed silane film. Thus, the silane film in this case can be regarded as acting as a weak boundary layer, an observation that has been previously made by Gettings *et al.*[28]

3.2.2 Durability studies The durability data are summarised in Table III. In contrast to the adhesive fracture energy results, these results exhibit a marked dependency on the deposition conditions. In the case of the joints pretreated using 3-APMS from toluene, the measured times initially indicate that these joints were not as durable as the unpretreated joints. It should be remembered that the silane pretreated joints were tested using an applied fracture energy of 7.0 J/m^2 compared with only 3.5 J/m^2 for the unpretreated joints. For this reason, it can be concluded that all the silane pretreated joints are in fact more durable than the unpretreated joints.

TABLE III
Table summarising the durabilities of aluminium joints pretreated using 3-aminopropyltrimethoxysilane using a range of pretreatment conditions

Sample type					Measured times/s	
Solvent	Time	pH (mins)	Rinsed	Applied. Gc (J/m^2)	Onset	Failure
Unpretreated				3.5	360	3660
Toluene	5	n/a	Yes	7.0	360	2400
Toluene	20	n/a	Yes	7.0	120	1560
Water	5	10.4	No	3.8	<60	360
Water	5	10.4	Yes	7.0	600	4500
Water	20	10.4	Yes	7.0	480	2820
Water	5	6.8	Yes	7.0	1080	6780
Water	20	6.8	Yes	7.0	600	3900

N.B. "n/a" means not applicable; "Onset" means the time taken for crack propagation to be observed; "Failure" refers to the time required for complete failure of the specimen.

Joints pretreated from toluene; toluene rinsed In the case of the joints deposited from toluene, considerable improvements in both the initial joint strengths and durabilities compared with the unpretreated joints were observed. However, as can been seen from the increased time for both the onset of crack propagation and complete joint failure, all the joints pretreated from water (when also rinsed) were more durable than those pretreated from toluene. The locus of failure of joints pretreated from toluene occurred through the adsorbed silane layer near to the adhesive/silane interface. The lower durabilities of these joints may be due to the presence of unhydrolysed methoxy groups which would have reduced the crosslink density and so rendered it more susceptible to attack by moisture. The reduction in durability with pretreatment time could, therefore, be explained by an increase in the number of unhydrolysed methoxy groups. Indeed, evidence supporting the presence of these methoxy groups was obtained by XPS from the film adsorbed for 20 minutes whilst in the case of the film adsorbed for 5 minutes, increased levels of these groups was not detected.

Joints pretreated from water; unrinsed In the case of the unrinsed joints, the locus of failure occcurred in a thick silane layer. This layer would appear to be extremely susceptible to attack by moisture. In view of the poor durability of these joints, it is obviously advisable to rinse the silane pretreated surface before application of the adhesive. These results are in marked contrast to the results obtained by Boerio *et al.*[16,17] on mild steel and titanium and also those of Thiedman *et al*[19] on aluminium. These researchers obtained good durabilities for silane pretreated joints, any excess silane solution being simply removed with either dry nitrogen or allowed to drain away, before being heated at 110°C for one hour. However, the major difference between the work of these researchers and the current work is that in the previous work, the silane films were heated at some time during the preparation of the adhesive joints. Work by Phillips and Hercules[29] has shown that heating adsorbed silane films increases the resistance of the film to attack by water. The use of heat during the cure of the adhesives is suggested as the reason why these previous workers[16,17,19] obtained good joint durabilities.

In order to stabilise fully the adsorbed silane film against water, Hercules and Phillips found that the film needed to be heated to 200°C for two hours. This raises the possibility that the durability of silane pretreated joints may be influenced by the curing schedule of the adhesive. Thiedman *et al.* did briefly study the effect of drying the adsorbed silane film at 110°C for 16 hours under vacuum, rather than at 110°C for one hour, but were unable to detect any significant improvement in the durability of the adhesive joints. Nevertheless, it is interesting to note that these workers used various epoxy adhesives which cured at 121°C and 177°C for one hour, respectively. Generally, the joints cured at the higher temperature were more durable. The use of the different adhesives may account for the difference in the joint durabilities. However, the possibility exists that the use of the higher curing temperature may have increased the crosslink density of the adsorbed silane films and thus improved the durability of the adhesive joints. The effect of heat on the structure and moisture resistance of an adsorbed silane film would, therefore, appear to merit further study.

Joints pretreated from water; water rinsed Finally, the durability performance of the joints pretreated from water at pH 6.8 (water rinsed) was clearly the best of all, being superior to that achieved by joints pretreated at pH 10.4. XPS analysis of the fracture surfaces showed that failure had occurred close to the adhesive/silane or silane/aluminium interface. Analysis of the silane films prior to joint formation revealed no significant differences in the films. However, reflectance FTIR work by Boerio *et al.*[16,17] has indicated the 3-APMS deposited at pH 10.4 would etch the aluminium surface at pretreatment time of greater than one minute, possibly forming an aluminosiloxane. At pH 6.8, these researchers reported than no etching occurred. The formation of an aluminosiloxane at the adhesive/substrate interface may explain the dependence of the durability on the pretreatment conditions as the aluminosiloxane may be more soluble in water than the crosslinked silane film. As more aluminosiloxane would have been formed in the case of silane films deposited at pH 10.4 for 20 minutes compared with 5 minutes, the reduction in the durability of the 20 minutes films can also be explained.

The joints pretreated at pH 6.8 for 5 minutes were far more durable than those pretreated for 20 minutes. The XPS results detailed in Table I highlighted no major differences between these films, although the nitrogen intensities indicate that the 5 minute films may have been slightly thinner. This observation indicates that the durability improves as the thickness of the silane film decreases. However, the low levels of nitrogen detected on these surfaces prevents any detailed analysis of these results and further work is required to study this phenomenon.

4.0 CONCLUSIONS

1. The blister test is a rapid and effective method for testing adhesion promoters, as the crack propagates close to the interface. The test can be used to measure both the initial adhesive fracture energies and the durabilities of silane pretreated joints.
2. In the case of room-temperature-cured adhesive systems, the pretreated substrate should be rinsed prior to bonding in order to remove a thick, weakly adsorbed silane layer, which is extremely susceptible to attack by moisture. This procedure may also prove beneficial when heat-cured adhesives are used.
3. In order to form the strongest bonds on aluminium, the 3-aminopropyltrimethoxysilane should be applied from water at pH 6.8 and the substrate should then be rinsed prior to bonding. Pretreatment times in excess of five minutes would appear to be detrimental.

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