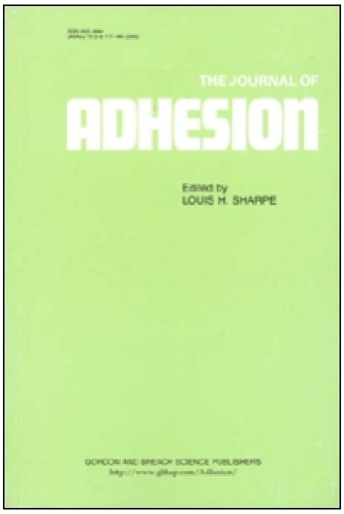

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Incorporation of an Adhesion Promoter in a Structural Adhesive: Aspects of Durability and Interface Chemistry

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Incorporation of an Adhesion Promoter in a Structural Adhesive: Aspects of Durability and Interface Chemistry

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The durability and interfacial chemistry of adhesively bonded joints fabricated from clad aluminium alloys (2024-T3) has been investigated using the Boeing wedge-test geometry and XPS analysis. A silane, γ-glycidoxypropyltrimethoxysilane (GPS), has been incorporated directly within the adhesive formulation, and the effect of four different silane concentrations, 0, 0.5, 1, and 2% w/w, have been studied. As expected, the durability of the aluminium joints depends on the silane concentration contained within the adhesive formulation. The mechanical tests carried out showed that a silane concentration lying between 0.5 and 1% w/w would be optimum for the aluminium joints investigated in this work. The failure mode was apparently interfacial but the XPS analysis showed that some fractures occurred partly within the adhesive. The calculations of the C/N ratios from small-area XPS analyses on the adhesive interfacial failure surfaces have provided an indication of the manner in which failure may occur. It has been found that a depletion of curing agent takes place at the region where failure subsequently occurs, leading to a reduction in the mechanical properties at this region within the bond line.

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INTRODUCTION

Aluminium alloys are widely used in the aerospace industry because of their good corrosion resistance and light weight; however, the pretreatments applied to the aluminium substrates are time consuming, expensive, and not environmentally friendly [1]. To replace the toxic chromium(VI)-containing solutions currently used in pretreatments of aluminium, organo-silane compounds molecules may be used. Silane molecules act as coupling agents and can be utilized as a primer, or directly incorporated within the adhesive formulation that is widely undertaken by many manufacturers of structural adhesives [2]. Although there are much data in the open literature relating to the durability and interfacial chemistry of silanes used as a primer layer, little published research has been carried out to investigate the mode of action of silanes used directly within the adhesive formulation. The work described in this article has been undertaken to gain insight into the effect of the incorporation of a silane within the adhesive. In the current work, the durability of the joints was tested at 90% relative humidity (RH) and at 50°C. For the four silane concentrations chosen, the durability was tested in triplicate at 90% relative humidity (RH) and 50°C, and duplicate joints of each silane concentration were also tested at ambient atmosphere (50% RH and 20°C), making a total of 20 mechanically tested joints. The main purpose of this work was to relate the durability results obtained from the mechanical tests to the interfacial chemistry of failure deduced from the surface analysis data.

EXPERIMENTAL PROCEDURES

Preparation of the Adhesives

Araldite 420™ is an epoxy adhesive manufactured under license at Huntsman Advanced Materials (Duxford, Cambridge, UK) and, therefore, not all details about the adhesive formulation (chemistry and concentration) may be described in this work. Nonetheless, it is possible to say that this adhesive is a two-part material, an epoxy partly based on diglycidyl ether of bisphenol A and a hardener (amine). It is known that the amine curing agent is a linear diamine containing an ether functionality that does not contain any conjugation. GPS is included in this adhesive but its optimum concentration is unknown to the present authors. This formulation also contains other components such as treated silica, pigments, additives, and toughening agents.

The adhesives studied in this work were prepared using a Moltini stirrer (Molteni AG, Rheinfelder, Switzerland) equipped with a vacuum system and planetary action to ensure that no air bubbles remain in the formulation and that the mixtures are homogeneous. To study the effect of the concentration of the GPS molecule within the formulation, its concentration was varied from 0 to 2% w/w GPS which was added to the epoxy part.

Fabrication of Adhesive Joints

The substrates of 2024-T3 clad aluminium were supplied in the following form: 15-cm length; 2.5-cm width, and 0.3-cm thickness. A chamfer was made on one end of each beam to aid the wedge insertion once the joint has been manufactured.

The aluminium beams were first degreased using a detergent solution, and then rinsed with 2-propanol. The degreased aluminium beams were then stored in aluminium foil to avoid any further contamination.

The mechanical treatment was by grit-blasting using dry white alumina 240 mesh ($\approx 60 - \mu$m diameter). After removal of the extraneous grit, the aluminium beams were paired and stored in aluminium foil prior to joint fabrication [3].

Araldite 420^{TM} adhesive was used and the range of silane concentrations investigated was as follows: 0, 0.5, 1, and 2% w/w of γ-glycidoxypropyltrimethoxysilane (GPS) incorporated directly in the adhesive formulation. The bond-line thickness of the joints was achieved using pieces of fishing line (200-μm diameter) at each end of the aluminium beams. A few layers of Teflon® tape were added at the end of each aluminium beam (where the chamfers were cut) to avoid interaction at the edge of the joint between the adhesive and aluminium to aid wedge insertion for mechanical testing. For each silane concentration, five joints were manufactured. Curing was achieved at ambient temperature overnight and, to make sure that a complete cross-linking was obtained, a postcure of 60°C for two hours was also used.

To study the chemical composition of bulk adhesives by XPS, it was necessary to obtain free handling adhesive samples to look at the center of the material. To achieve this, samples of the same adhesive compositions as described above were cured on a film of Teflon® wrapped on aluminium beams. After curing, the samples were embedded in a clear epoxy resin and microtomed until a depth of several hundreds of microns was reached within the depth of the material. The slices obtained at this level were then used to report the bulk analysis composition for each concentration of silane.

Durability Testing

The mechanical test used to assess the durability of the aluminium joints was the Boeing wedge-cleavage test, illustrated in Figure 1.

The Boeing wedge test [4] loads the joint as a result of the elastic-strain energy that is developed on forcing a wedge into the unadhered part of an adhesively bonded joint. Then, the test specimen is exposed to a specific environment and the crack growth is monitored using a traveling microscope to assess the durability of the joint.

In this work, the wedges were made of stainless steel because stainless steel has been found to work well with many adherends and is very durable and reusable. It is also harder than aluminium and relatively easy to process.

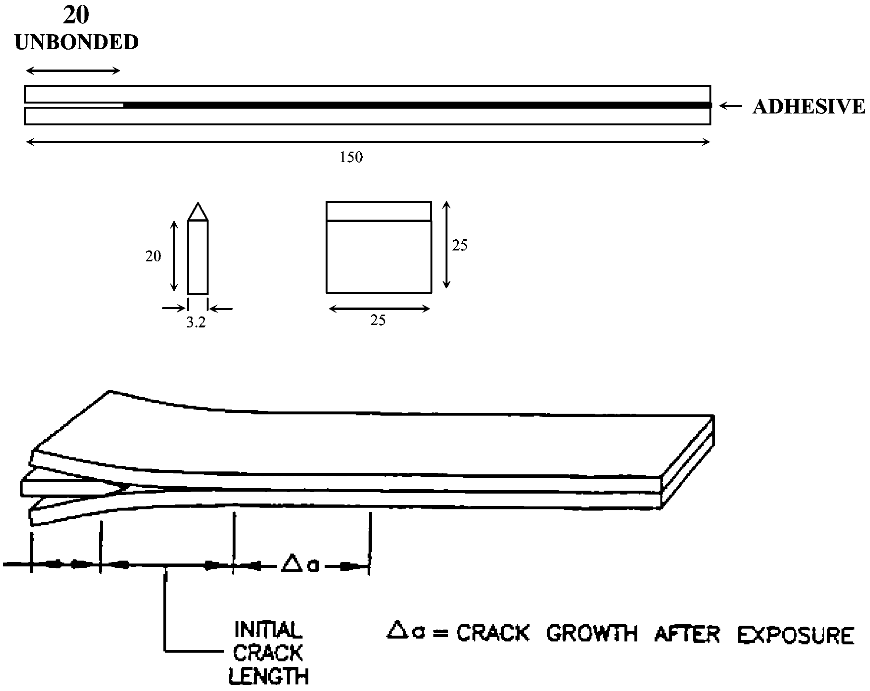

FIGURE 1 Boeing wedge test, showing dimensions of the test specimen and wedge (mm), and schematic of a test in progress with the crack extension specimen configuration.

Prior to wedge insertion, the sides of the joints were polished to make sure that no adhesive would hinder formation of the cracks and also that the stress is distributed in the same way for all the joints, because extraneous adhesive on the sides of the joint may prevent opening or induce asymmetric stress within the joint.

After the polishing step and subsequent drying, the sides of the joints were coated with white correction fluid (Tipp-ex) so that the crack propagation could be easily seen under the traveling microscope, as the adhesive is dark green and the crack would be difficult to observe against the polished aluminium beams [4].

The wedges were inserted into the unbonded ends of the joint using a screw-driven sash cramp[1] arrangement modified to ensure that both joint and wedge remained located along the axis of the applied load during wedge insertion.

After insertion of the wedges, the joints were left for 30 min in ambient atmosphere to allow the crack to stabilize. Then, the crack length at time $t = 0$ was measured with the traveling microscope. The joints to be tested under hot and wet environments were then introduced in the test chamber (90% RH) and placed in an oven (50°C), while the two other joints of each silane concentration tested at ambient atmosphere were left in ambient laboratory atmosphere. The 90% RH was obtained using an aqueous solution of sodium sulphate at saturation. The test chamber was made of a plastic box and the joints were supported above the sodium sulphate solution using cut-to-size smaller plastic boxes. The crack-length growth was monitored on either side of the joint using a traveling microscope. Figure 1 illustrates the measure of the crack length, Δa, of the joints. The measurements were made every 30 min for the first 9 h and then, when little crack growth was observed, every hour during the working day until about 50 h of testing for every joint was reached.

Surface Analysis

A Thermo VG Scientific Sigma Probe instrument (East Grinstead, UK) was used to perform the XPS analysis. A monochromatic AlKα source was used, at a power of 140 W. A spot size of 500 µm was chosen and a survey spectrum (150 eV pass energy) as well as high resolution spectra (50 eV pass energy) of the elements of interest were recorded:

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[1] British term referring to a device for holding parts of a frame in place during construction. It usually consists of a steel bar along which slide two brackets between which the work is fixed, with one of the brackets pegged into a hole in the bar while the other is adjusted by means of a screw, which applies the required load.

TABLE 1 Quantitative Surface Analyses for Interfacial Failure Surface for Joints Containing 0% Silane

Failure side	Position relative to crack front (Δx/mm)*	Al	C	O	N	Si	Cl	Na
Metal failure surface	–11.4	3.9	73.7	19.2	0.4	0.7	—	2.2
Adhesive mirror image of above	–11.4	0.4	77.5	18.0	1.7	2.5	<0.1	—
Metal failure surface	–20	12.8	39.9	43.0	0.6	0.3	0.1	3.4
Adhesive mirror image of above	–20	0.4	76.4	18.4	2.3	2.3	0.2	0.1
Metal failure surface	+12.9	6.7	67.3	21.7	0.5	0.4	0.1	3.2
Adhesive mirror image of above	+12.9	0.8	76.1	19.6	3.1	0.2	0.2	—
Metal failure surface	+12.9	9.7	55.5	28.7	1.2	0.8	0.2	4
Adhesive mirror image of above	+12.9	0.8	74.6	20.3	2.9	0.9	0.2	0.3

*Negative value indicates that the analysis was performed before the crack front limit, positive value indicates after.

C1s, O1s, N1s, Si2p, Na1s, and, whenever present, Cl2p, S2p, and F1s. The software used was Avantage *v1.85*. All samples were analyzed in duplicate or quadruplicate and, whenever relevant, a standard deviation value was added. Tables 1–6 report concentrations and ratios of interest.

At equilibrium crack growth, one joint of each silane concentration was opened and for the samples tested at room temperature the locus of failure was clearly cohesive within the adhesive itself. For the samples tested at elevated temperatures mirror image analyses on the interfacial failure surfaces were recorded by XPS.

TABLE 2 Quantitative Surface Analyses for Interfacial Failure Surface for Joints Containing 0.5% Silane

Failure side	Position relative to crack front (Δx/mm)*	Al	C	O	N	Si	Cl	Na
Metal failure surface	−33.6	10.3	34.0	43.8	0.8	0.5	0.2	10.4
Adhesive mirror image of above	−33.6	0.5	76.1	19.2	2.5	1.5	0.1	—
Metal failure surface	−36.7	10.6	33.2	44.5	0.9	0.2	—	10.2
Adhesive mirror image of above	−36.7	0.9	70.7	20.9	2.6	2.7	0.2	0.5
Metal failure surface	−40.9	11.4	37	44.9	0.9	—	—	5.9
Adhesive mirror image of above	−40.9	0.6	75.8	19.6	2.6	1.3	0.1	—
Metal failure surface	−43.0	10.4	43.1	41.9	1.0	1.1	0.1	2.5
Adhesive mirror image of above	−43.0	0.8	74.2	20.1	2.4	2.1	—	0.4

*Negative value indicates that the analysis was performed before the crack front limit; a positive value indicates after.

TABLE 3 Quantitative Surface Analyses for Interfacial Failure Surface for Joints Containing 1% Silane

Failure side	Position relative to crack front (Δx/mm)*	Al	C	O	N	Si	Cl	Na
Metal failure surface	–12.3	12.7	37.4	46.0	0.6	0.4	—	2.9
Adhesive mirror image of above	–12.3	0.5	76.0	19.7	2.9	0.6	0.2	0.3
Metal failure surface	–12.3	11.1	38.5	41.1	0.5	0.2	—	8.6
Adhesive mirror image of above	–12.3	0.5	73.0	21.9	2.6	1.4	0.2	0.4
Metal failure surface	–16.2	10.8	36.3	46.8	0.8	0.2	<0.1	5.0
Adhesive mirror image of above	–16.2	0.3	75.4	20.3	2.6	0.6	0.1	0.6
Metal failure surface	–16.2	10.2	37.6	42.0	0.6	0.2	—	9.4
Adhesive mirror image of above	–16.2	0.4	74.4	21.1	2.7	0.6	0.1	0.7

*Negative value indicates that the analysis was performed before the crack front limit; positive value indicates after.

Scanning electron microscopy (SEM) was performed using an Hitachi S4000 (Hitachi, Tokyo, Japan), with a range of magnifications and a beam energy of 5 keV. It was not necessary to coat the specimens prior to electron microscopy.

RESULTS

Durability

The crack growth of each joint measured as a function of time is reported in Tables 1–4. Figure 2 presents the results obtained for

TABLE 4 Quantitative Surface Analyses for Interfacial Failure Surface for joints Containing 2% Silane

Failure side	Position relative to crack front (Δx/mm)*	Al>	C	O	N	Si	Cl	Na
Metal failure surface	– 36.6	9.1	34.1	49.2	0.8	—	—	6.8
Adhesive mirror image of above	– 36.6	0.5	75.2	20.4	2.8	0.8	0.1	0.2
Metal failure surface	– 45.8	12.4	34.8	44.9	1.0	0.3	0.2	6.5
Adhesive mirror image of above	– 45.8	0.5	76.9	18.3	3.1	0.9	0.2	0.2
Metal failure surface	– 55.0	9.6	34.3	49.0	0.7	0.2	0.2	6.0
Adhesive mirror image of above	– 55.0	0.5	75.9	19.5	3.1	0.7	0.1	0.2
Metal failure surface	– 55.0	12.8	32.9	44.5	0.9	—	0.1	8.9
Adhesive mirror image of above	– 55.0	0.5	76.8	19.0	2.7	0.7	0.1	0.1

*Negative value indicates that the analysis was performed before the crack front limit; positive value indicates after.

TABLE 5 Comparison of the Amounts of Carbon Present on Different Aluminium Regions

Sample	Grit-blasted aluminium	Joint 0% w/w silane	Joint 0.5% w/w silane	Joint 1.5% w/w silane	Joint 2% w/w silane
Carbon concentration	15.7	40	36.9	37.5	34.1

the crack growth of joints tested at room temperature and those tested at 50°C and 90% RH. The same symbol is used to plot the curves in either plain or filled version (*e.g.*, • or ○) when the adhesive tested is a duplicate. However, for clarity of reading, the curves are also provided as average values in Figure 2b.

The crack growth obtained was then converted to fracture energy. The equation of the fracture energy has been derived using the Griffith theory in fracture mechanics and by considering the wedge test specimen as a double cantilever beam. The fracture energy G_{IC} (kJ m^{-2}) is then given by the equation [4,5,6]

$$G_{IC} = \frac{d^2 E h^3 \times [3(a + 0.6\,h)^2 + h^2]}{16 \times [(a + 0.6\,h)^3 + (a + 0.6\,h)h^2]^2} \qquad (1)$$

with G_{IC}, strain energy release rate or fracture energy in mode I loading (kJ m^{-1}); E, Young's modulus of the adherends (GPa); h,

TABLE 6 C/N Concentration Ratios of Polymer Points of the Joints and Bulk Adhesives

	Silane concentration			
Sample type	0	0.5	1	2
Failure	45.5 (−11.4)*	30.4 (−33.6)	26.2 (−12.3)	26.8 (−36.6)
Failure	33.2 (−20)	27.2 (−36.7)	28.1 (−12.3)	24.8 (−45.8)
Average	*39.4***	*N/A*	*N/A*	*N/A*
Failure	24.5 (+12.9)	29.2 (−40.9)	29.0 (−16.2)	24.5 (−55)
Failure	25.7 (+12.9)	30.9 (−43.0)	27.6 (−16.2)	28.4 (−55)
Average	*25.1*	*29.4*	*27.7*	*26.1*
Bulk adhesive	25.5	29.0	26.5	22.1
$\Delta_{C/N}$	13.9			
	0.4	0.4	1.2	4.0

*Values in brackets correspond to the position relative to the crack front in mm.

**Two average values are provided for the adhesive without silane because analyses were performed before and after the crack front. For all other concentrations, only one value is provided.

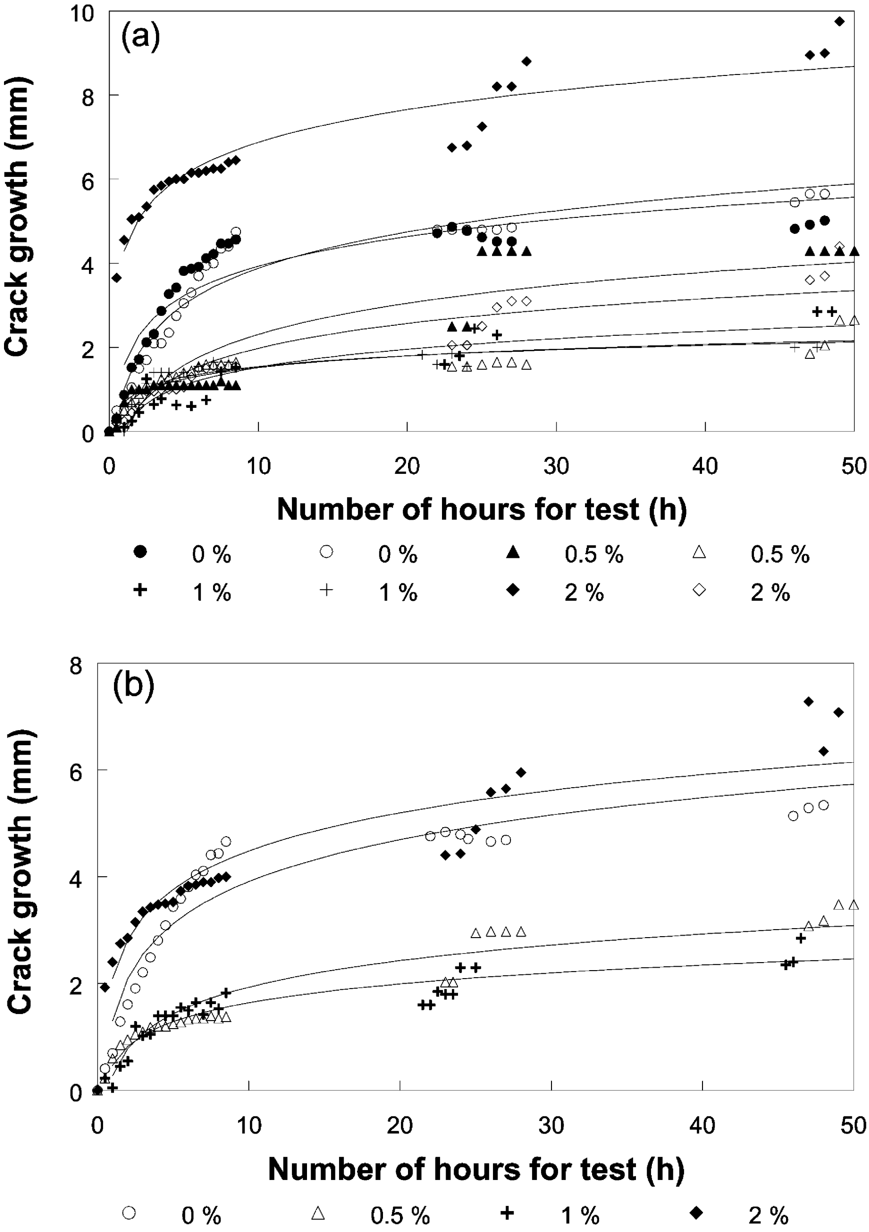

FIGURE 2 Comparison of the crack growth of (a) data for all joints tested at ambient atmosphere; (b) average values for joints tested at ambient atmosphere; and (c) joints tested at 50°C and 90% RH; for all silane concentrations. (Legend below each figure identifies silane concentration for the joints tested.)

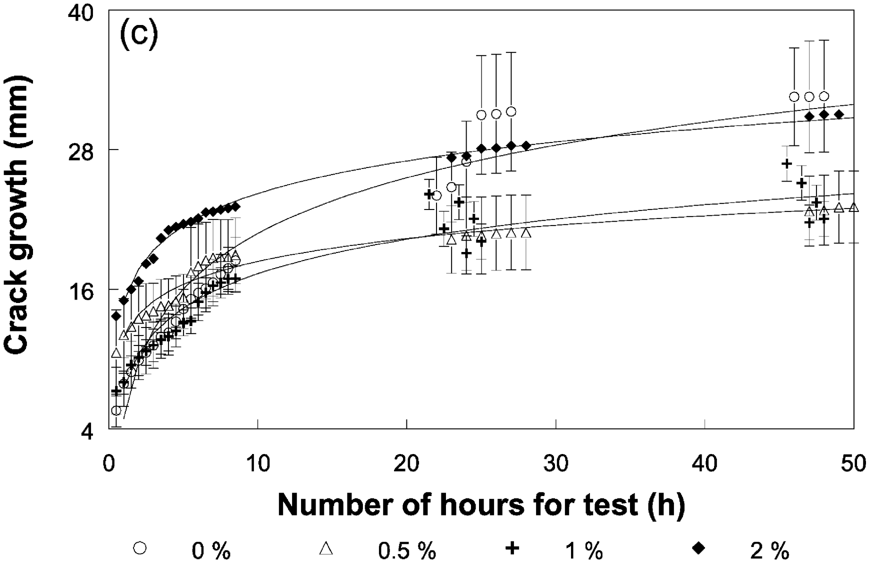

FIGURE 2 Continued.

adherend thickness (mm); *a*, crack length (mm); and *d*, displacement resulting from the wedge (mm).

The fracture energy of each joint was calculated as a function of time. Figure 3 illustrates the results obtained for the fracture energies calculated for joints tested at room temperature and those tested at 50°C and 90% RH. The procedure to report the results in Figure 3 is the same as that for Figure 2.

Figures 2 and 3 show that exposure of joints at 50°C and 90% RH reduces the mechanical properties of the joints. The average crack growths of joints tested in this environment are longer ($33\,\text{mm} < a < 5\,\text{mm}$) than those for joints tested at ambient atmosphere ($0\,\text{mm} < a < 10\,\text{mm}$). In the same way, the fracture energies of joints tested in the oven are lower ($0\,\text{kJ m}^{-2} < G_{IC} < 1.2\,\text{kJ m}^{-2}$) than those for joints tested at ambient atmosphere ($0.4\,\text{kJ m}^{-2} < G_{IC} < 2.6\,\text{kJ m}^{-2}$).

The curves of Figures 2 and 3 also allow one to provide a ranking of the adhesive durability as a function of silane content and, hence, adhesive performance and, thus, indicates which silane concentration provides the best durability among the joints.

For both the joints tested at ambient temperature and those at 90% RH and 50°C, the curves of Figures 2 and 3 show that the smallest crack lengths, and the highest fracture energies, are obtained when the adhesives contain a silane concentration of 0.5 or 1% w/w.

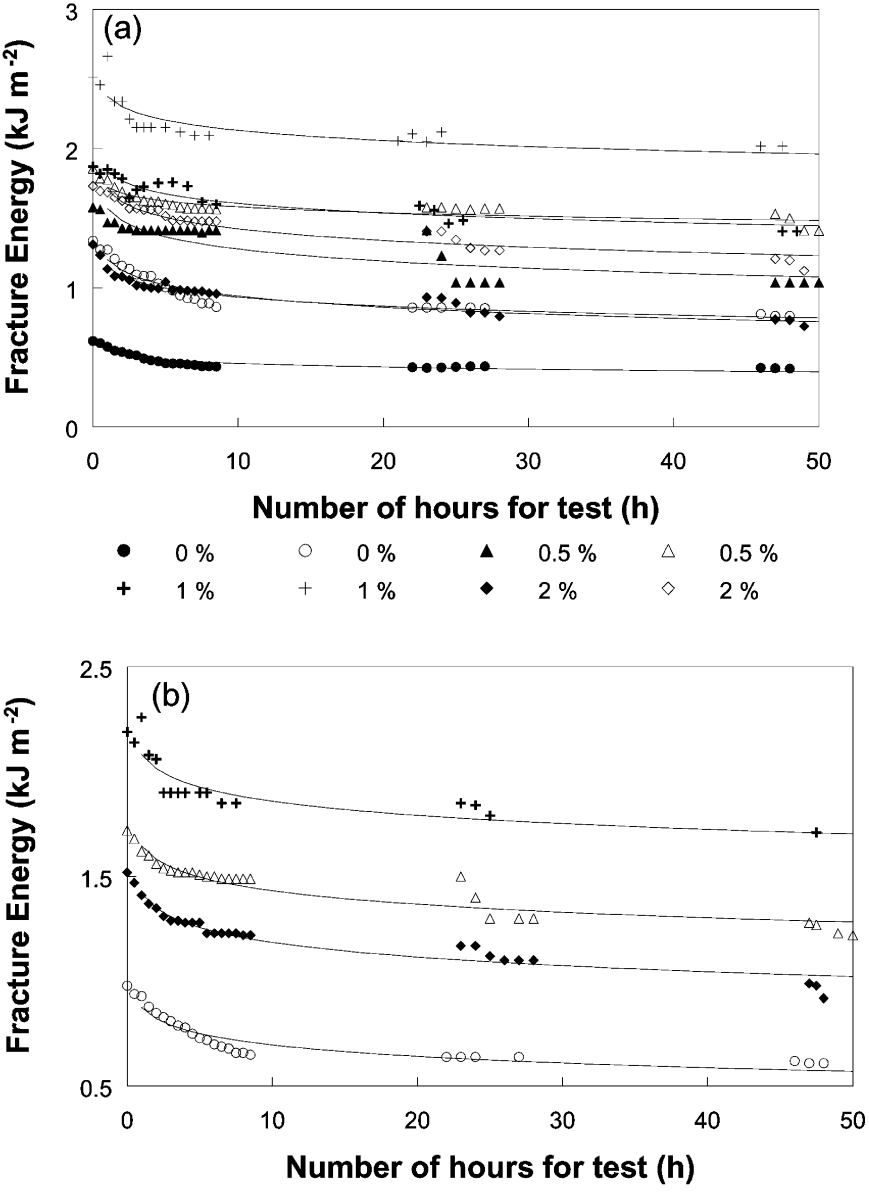

FIGURE 3 Comparison of the fracture energy of (a) joints tested at ambient atmosphere; (b) average values for joints tested at ambient atmosphere; and (c) joints tested at 50°C and 90% RH; for all silane concentrations. (Legend below each figure identifies silane concentration for the joints tested.)

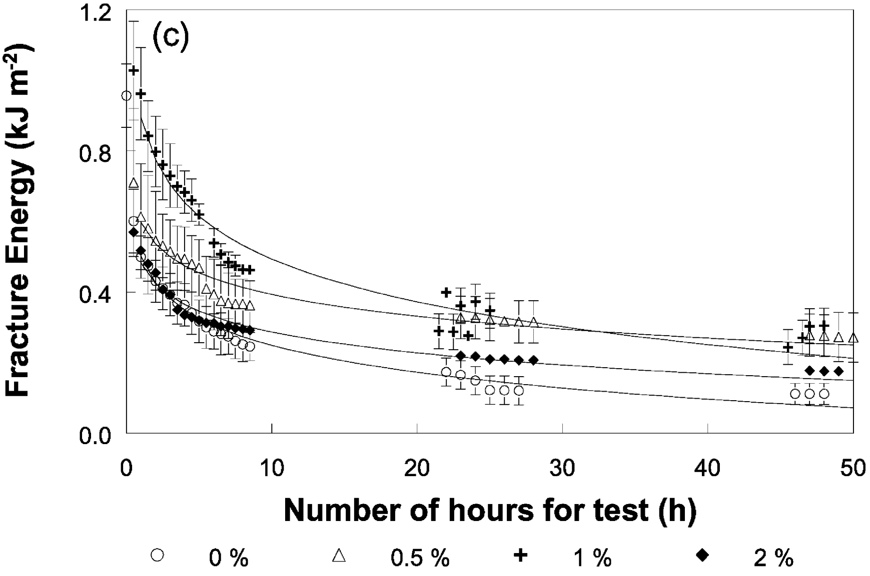

FIGURE 3 Continued.

Furthermore, for most of the curves, the behavior of adhesives containing 0 or 2% w/w silane concentration are similar. This indicates that, although incorporating silane into the formulation may be beneficial to the system, it may also prove to be detrimental to the performance if the concentration is too high.

It should be noted, however, that one of the curves obtained for the adhesive containing 2% w/w silane does not follow the general trend (symbol ◇). For tests performed at ambient atmosphere, this joint exhibits lower crack length than one of the joints containing 0.5% w/w silane (symbol ▲) and its fracture energy is higher than anticipated. A closer examination of this particular joint indicated that it contained slightly less adhesive at the edges, probably inducing reading errors (*i.e.*, with the Tipp-ex coating masking any cracks). Any data generated from this specific joint were, therefore, considered erroneous and not taken into account for any subsequent discussion. Another joint containing the adhesive formulated with 2% w/w GPS and tested at temperature (50°C) failed completely almost immediately and this explains why no error bars are reported for this concentration in Figures 2 and 3, as values were obtained for only two joints at either room temperature or 50°C.

Hence, the results obtained from Figures 2 and 3 allow us to conclude that in whichever atmosphere the joints are tested, for the commercial adhesive studied in this work, a silane concentration between 0.5 and 1% w/w provides optimum durability. However, it is important to point out that a silane concentration, x, within the ranges $0\% < x \leq 0.5\%$ or $1\% \leq x < 2\%$ could also be satisfactory. Some more tests at different silane concentrations within these ranges would be helpful to narrow down the best silane concentration range suitable for the adhesive used for the manufacture of the aluminium joints. Finally, the ranking order of the adhesives for joints tested at ambient atmosphere can be given as follows: $2\% < 0\% < 0.5\% < 1\%$ w/w silane concentration. In the same way, for the joints tested at 90% RH and 50°C, the adhesive ranking order can be given as follows: $0 \sim 2\% < 0.5 \sim 1\%$. In this case, a close examination does allow the exact ranking order of the adhesives to be defined but it does show that no silane at all or too much silane will be detrimental to the performance of the joint.

Visual Assessment of Failure Surfaces

After performing the mechanical tests, one joint of each silane concentration tested in damp and hot conditions was broken open for analysis of the failure surfaces. An example of the appearance of the opened joints for the adhesives containing 0 and 0.5% w/w silane is shown in Figure 4.

The majority of the parts of the joints examined exhibit gray (aluminium adherend) or green (adhesive) color, indicating, visually, a likely failure at the interface. It is also possible to detect areas of darker gray where failure probably occurred within the adhesive; these regions correspond to lighter green on the mirror image showing a thin layer of adhesive. However, some areas of light green (on the adhesive side) also point to some delamination of the adhesive below. Thus, visual assessment indicates that interfacial failure occurs, with the locus of failure passing from the adhesive–adherend interface at one side of the joints to the other, and that cohesive failure also occurs on some areas of the joint parts.

To define the locus of failure more precisely, the joints were analysed by XPS, by analyzing four aluminium points and their four respective mirror image points on the adhesive failure surface on the other failure beam. It is convenient that for the Sigma Probe spectrometer employed in this work, one entire beam can be loaded into the analysis chamber without the need for sectioning.

Surface Analysis

XPS analysis was carried out on one joint of each silane concentration tested at 50°C and at 90% RH. For each joint side, two polymer spots

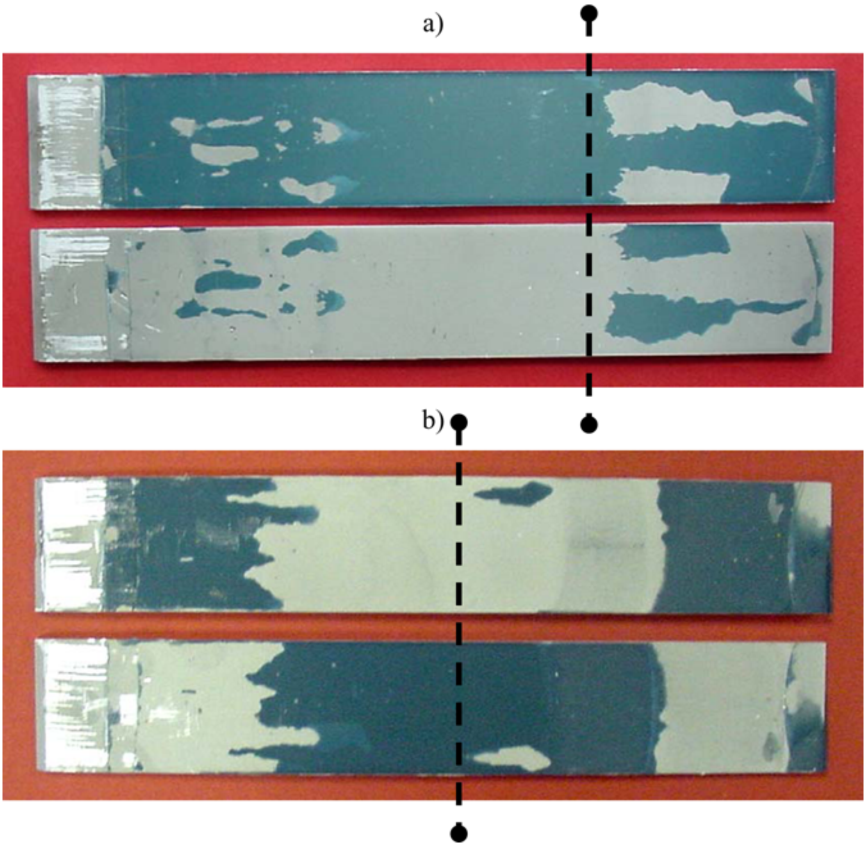

FIGURE 4 Separated wedge-test specimens at the completion of the mechanical tests: (a) complementary parts of joints containing 0% w/w silane concentration within the adhesive; (b) complementary parts of joints containing 0.5% w/w silane concentration within the adhesive. Crack propagation from left to right; dashed line indicates position of crack front at end of test (prior to opening of test pieces). The Δx identification of Tables 1 to 4 indicates the position of the small area XPS analysis, either before (*i.e.*, to the left of the line above, equivalent to –Δx mm) or after (+ Δx mm) the position of the crack front.

and two aluminium spots were analyzed as well as the mirror images of these points on the other side of the joint. The quantitative XPS analyses obtained from the metal and polymer regions of the four joint types are reported in Table 1 [7, 8]. Note that analyses obtained from mirror images are always provided in subsequent lines, so that the pair of analyses represent either side of the failure at that point.

The presence of sodium can be explained by the fact that the joints were tested in 90% RH and that the humidity was obtained using a sodium sulphate salt at saturation. Initial grit-blasting also induces the presence of sodium and the surface chemical composition of a fresh grit-blasted surface exhibits an amount of 7.1 at.%. The high-resolution chlorine 2p signals obtained in the spectra (not presented here) show that two binding energies can be peak-fitted: one at 198 eV providing evidence of the presence of chloride coming from contamination during grit-blasting and/or testing and another at 201 eV, indicating that both chloride and organic chlorine are present. No attempt was made to resolve the 2p peak into its component 2p3/2 and 2p1/2 parts. The organic chlorine within the polymer part originates from one of the components used to make the adhesive, (added in the expoxy part of the formulation to prevent crystallization of the polymer).

The only supply of nitrogen in the adhesive system originates from the curing agent used to cross-link the epoxy resin but may also be from an unspecified catalyst (such as a tertiary amine). The presence of nitrogen (up to 1 at.%), see Tables 1, 2, and 4, in the XPS analysis of the aluminium surfaces indicates that some organic phase has been retained on the substrate after failure. In the same way, the amount of carbon present on the analyzed aluminium beams indicates that some adhesive material remains on the adherend surfaces after fracture of the joints. Figure 5 shows the survey spectra of a 2024-T3 beam clad with pure aluminium after grit-blasting (a); together with those from aluminium sides of open joints containing the adhesive with no silane (b), 0.5% silane (c), 1% silane (d), and 2% silane (e). The spectra presented in Figure 5 indicate some significant differences between the failure surfaces, more specifically, in the relative C1s intensities between grit-blasted beams and the four tested joints. It should also be noted that some of them exhibit a well-defined N1s signal at *ca.* 400 eV. Table 5 shows a comparison of the average surface concentrations of carbon (before final crack front) present on different aluminium points. Note, for the joint containing 0% w/w silane, only one value of carbon concentration is included. It may be seen that for the four adhesively bonded aluminium beams, the amounts of carbon are higher (39.9, 37.0, 38.5, 34.3 at.%) on the aluminium failure side (see Tables 1,2,3, and 4, respectively) than on the unbonded grit-blasted aluminium beam (15.7 at.%). The amount of carbon on the grit-blasted aluminium sample may seem very low but is not atypical in our experience of this kind of material for which we obtain a range of carbon concentration usually below 20 at.% when freshly grit-blasted. It should also be noted that the grit-blasting cabinet used in those experiments is totally dedicated to “clean” surface analysis

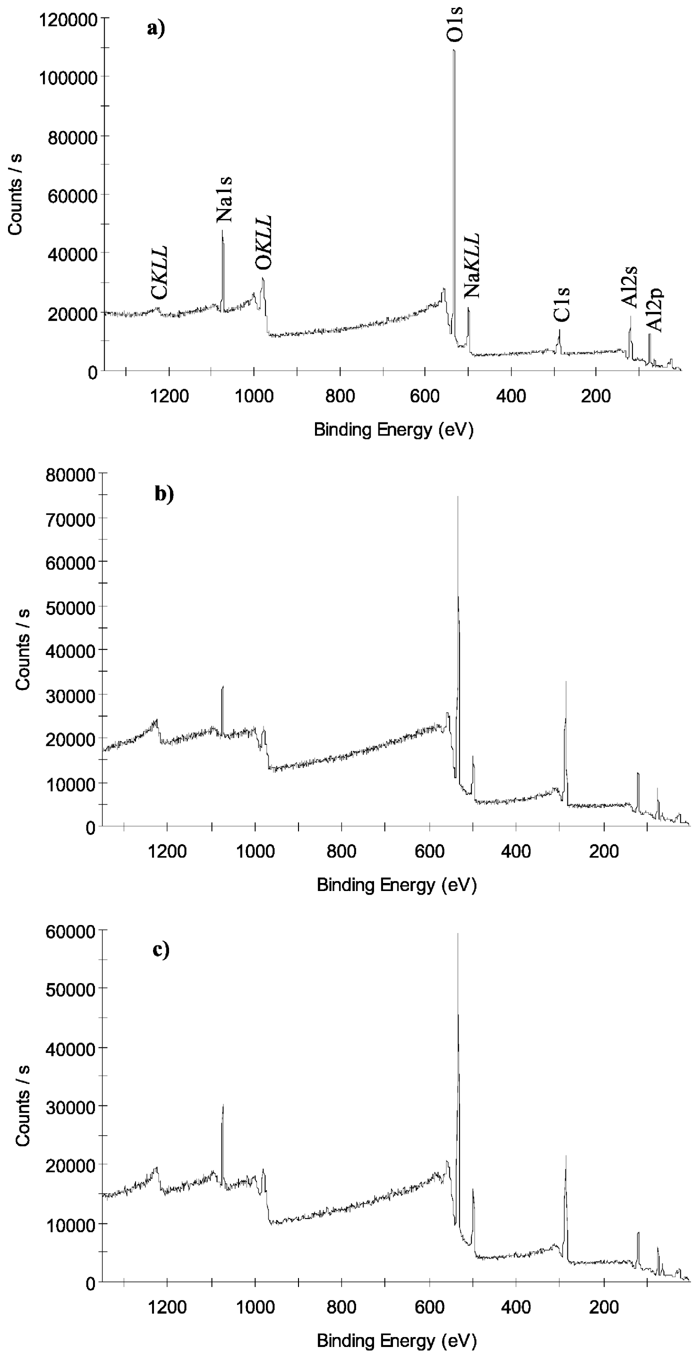

FIGURE 5 Survey spectra of (a) 2024-T3 beam clad with pure aluminium after grit-blasting; (b) aluminium points of joints bonded with adhesives containing 0% w/w; (c) 0.5% w/w; (d) 1% w/w, and (e) 2% w/w of silane.

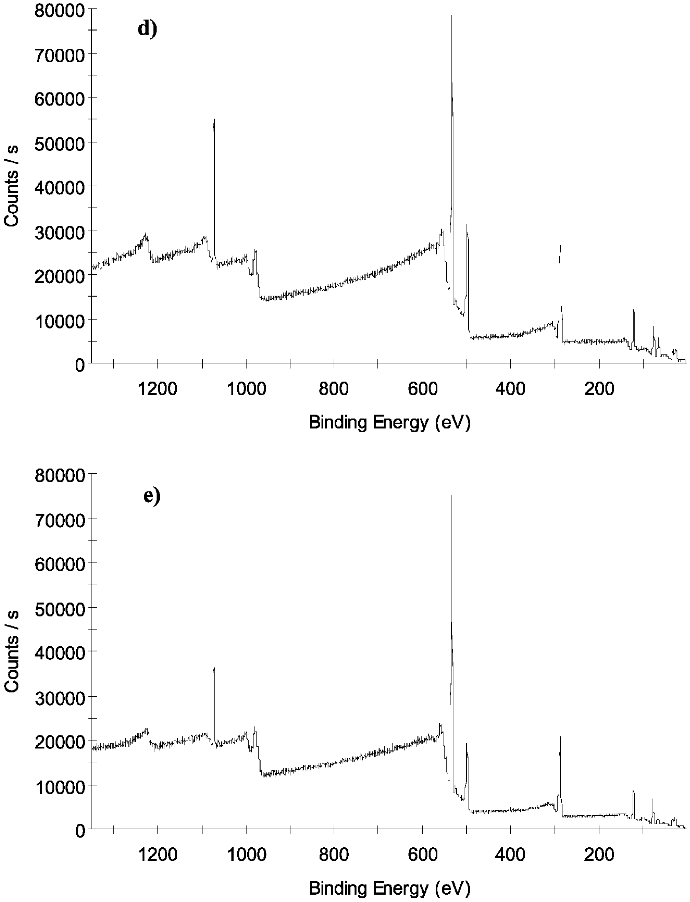

FIGURE 5 Continued.

experiments. On the four joints quoted above, the amount of carbon is, therefore, too high to be considered as originating from contamination only; hence, another explanation has to be suggested.

At failure, the amount of organic phase is about the same for the four silane concentrations. This means that the locus of failure is similar for all adhesive types. This surplus of carbon indicates that some polymer of the adhesive has been retained on the aluminium region that is analyzed by XPS. This means that the failure of the joints has occurred at least partly within the adhesive layer itself. Moreover, the variation in the mechanical performance must be a result of the subtle modification of the adhesive formulation with silane, in such a way as to make some of the formulations less susceptible to degradation from water molecules and heat than others.

For one type of adhesive only, 0% silane, an analysis was also performed after the final crack front, where the joint was forced open (see Table 1 with $\Delta x > 0$). The aluminium side of these spots exhibits a high amount of carbon, which is consistent with a fracture within the adhesive itself.

DISCUSSION

The investigation of the incorporation of silane within the adhesive formulation was undertaken to study the durability of adhesively bonded joints and to identify the locus of failure. The mechanical Boeing wedge tests have allowed us to provide data about the crack growth and the fracture energy. Both sets of data have shown that, for the commercial adhesive studied in this work, whichever atmosphere the joints are tested in, a concentration between 0.5 and 1% w/w of silane within the adhesive provides optimum formulation, in terms of durability. It was also shown that an excessive amount of silane in such an adhesive formulation may lead to a reduction of the performance of the adhesive in terms of strength and durability. This is demonstrated by the poor performance of the adhesive containing 2% of GPS, which exhibits performance comparable with that of an adhesive without any added silane.

Silanes are commonly incorporated in formulations and whenever an improvement is obtained, the general consensus is that these molecules migrate toward the interface to form bonds and improve the durability of the overall system. The mode of action of silanes is well known when these molecules are used as primers and it has actually been demonstrated that bonds, assumed to be of covalent nature, are formed between silane and the substrate [9, 10]. Indeed, these bonds are strong and have also been shown to provide good durability. However, in a system as in the present work, where silanes are incorporated in the adhesive, the formation of such bonds requires the migration of silane molecules toward the adhesive–aluminium interface and hydrolysis of these molecules prior to interaction with the substrate. This also requires that a monolayer of silane has been formed at the interface rather than a layer of polymerized silane that may induce early failure because of its presence as a weak boundary layer [11].

This work has shown that silicon is present on both sides of failed surfaces, aluminium substrate and adhesive, and a closer examination of the silicon signal (*via* peak-fitting) indicates that the Si2p signal exhibits a binding energy that is assigned to an organic silicon rather than to silica, for example (see Figure 6). However, this is only truly possible when the signal is of high enough intensity (~1 at.)% to allow for peak-fitting, *i.e.*, not for all samples examined in this work. It should also be noted that the silicon signal may originate from three different sources. One is the incorporated silane, GPS; another is the colloidal silica included within the formulation as a thixotrope; and the third is another silane, octyltrimethoxysilane used to treat the silica. Therefore, the silicon signal may be of mineral or organic origin, and because the concentration is invariably extremely low at the interfacial failure surfaces, it is sometimes difficult to tell whether the Si2p signal originates from an organic source or not. The situation is exacerbated by the fact that the Si2p (*ca.* 100 eV) and Si2s (*ca.* 150 eV) regions of the XPS spectrum are dominated by loss features associated with the Al2p (*ca.* 74 eV) and Al2s (*ca.* 124 eV) on the aluminium failure surfaces. In other words, one cannot conclude whether the GPS has migrated toward the aluminium–adhesive interface. Besides, the analysis was performed with a large sampling area (500 μm) and such a size is big enough to obtain a Si2p signal from small remaining fragments of the adhesive on the aluminium side of the failed surfaces. An

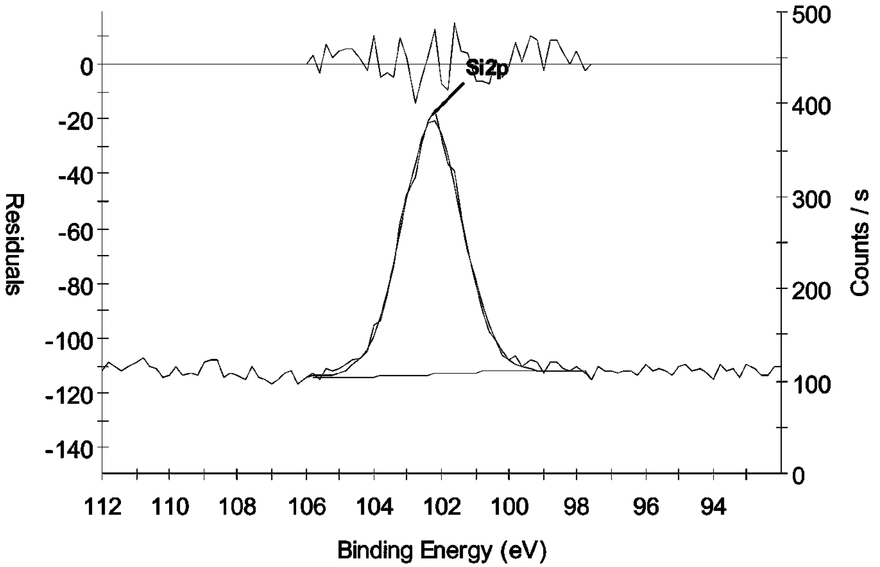

FIGURE 6 Peak-fitted spectrum of Si2p for the adhesive side of a joint containing 0.5% w/w silane. The binding energy obtained is 102.3 eV, characteristic of an organic silicon.

example of the presence of small fragments of adhesive is confirmed by using SEM imaging and is shown in Figure 7 for the aluminium side of an open joint that contained the adhesive formulated with 0.5% w/w GPS. Only in the case of the formulation without any GPS may an organic signal of Si2p be assigned: an organic silicon signal can then only originate from the octyltrimethoxysilane.

Examination of the XPS data in Tables 1–4 also indicates that there is no correlation between the crack growth (and/or the fracture energy) and the concentration of silicon present at the interface. Further work is needed and a number of experiments including the following are planned to resolve this dilemma: (a) record (using a non-monochromatized MgKα source) the Brehmstralung-induced Si*KLL* and combine with the Si2p to calculate Auger parameters, because these parameters may be correlated with particular organic species or chemical states, often in a much better way than binding energy shifts alone; the use of MgKα will also allow for a better signal-to-noise ratio of these signals because this X-ray source does not sample as deeply as AlKα and the intensity of the recorded signals is averaging to

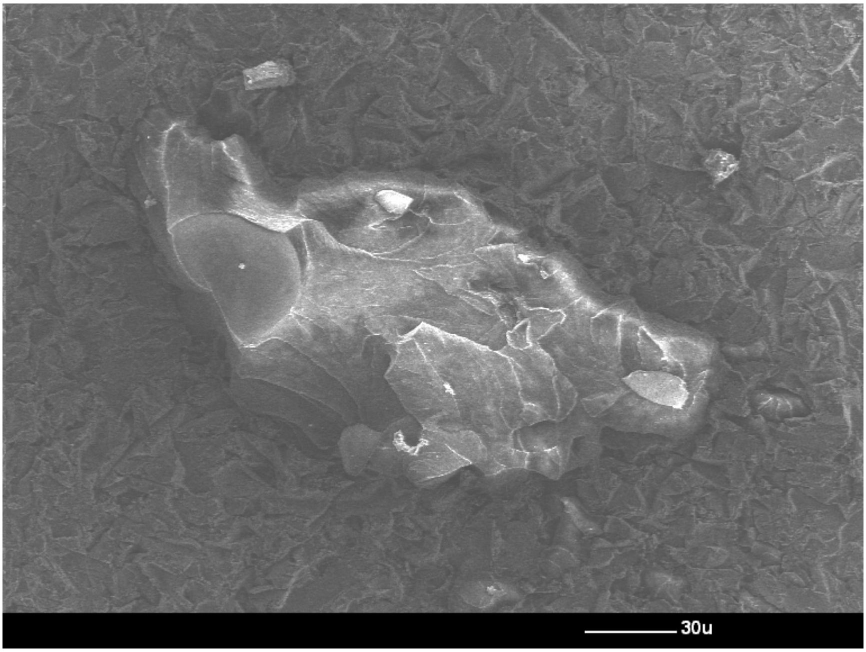

FIGURE 7 Fragment of adhesive on the surface of the aluminium side of a joint having contained the adhesive with 0.5% w/w GPS.

closer to the extreme surface of the sample; (b) perform the analysis of the same or similar samples by high mass resolution time of flight secondary ion mass spectrometry (ToF-SIMS), in particular mass $m/z = 71$ nominal mass, and see whether covalent bonds have been formed between any silane at the interface and the aluminium substrate [9].

Another possible effect induced by the presence of silanes in the formulation is a change in the density of the crosslinking of the adhesives. This may occur as a result of a reaction between molecules present in the adhesive and the silane. Both curing agent and epoxy resin exhibit chemical functionalities capable of reacting with GPS, such as amine and alcohol. This may be tested, for example, by finding out the values of toughness for each adhesive and ranking the data *versus* the concentration of silane. Again, this may explain why the adhesive formulation containing 2% w/w silane fails, apparently prematurely, as an excess of silane, if inducing excess crosslinking will render the material brittle.

Previous studies [12, 13] have also shown that other molecules, such as diluents or even a crosslinker, may migrate within a system. The curing agent used in this system is characterized by the fact that it contains nitrogen atoms. Although the complete formula is not available, it is known that it contains an ether functionality with a long carbon chain and no side branching. Apart from its reactivity, such a formula renders such a molecule relatively mobile and migration may be anticipated. Migration of the curing agent may be deduced by, for example, the amount of nitrogen present on the failed surfaces. Another way is the examination of the calculations of the C/N concentration ratios of the analyses performed on the polymer side of the failed surfaces; these can also provide interesting data about the way the failure occurs. Table 6 shows the C/N ratios of polymer point analyses of the joints and bulk adhesives (for comparison purposes) for the four silane concentrations. The $\Delta C/N$ data of Table 6 were obtained from replicate samples and the original data values are included in this table to indicate the reproducibility obtained. Because most analyses were obtained in duplicate, it is not possible to carry out any meaningful statistical analysis of the data, however desirable that might be. For the analyses carried out in quadruplicate, the values of standard deviation are very small (1–2%), indicating that these small variations of C/N are statistically significant. However by inspection of the original data values for all C/N values, a clear trend is observed.

It is important to point out that for some of the joints (containing adhesive formulations with 0 or 2% GPS), the C/N ratios calculated before the final crack front are, in general, larger than C/N ratios of the corresponding bulk adhesive material. It is also important to notice that the only known supply of nitrogen in the joint system originates from the curing agent used to cross-link the epoxy resin. Another possibility is an amine-based catalyst such as a tertiary amine. The differences between the values of C/N ratios for the bulk adhesives with the average values of C/N ratio of the joints before the crack front ranges from minimal values to larger ones. For the joint at 0% silane concentration, the difference between the C/N ratio of the bulk adhesive (25.5) and the average C/N ratio of 39.5 is 14. At 0.5 and 1% w/w silane concentrations, the $\Delta_{C/N}$ are 0.3 and 1.2 respectively, which is much lower than the $\Delta_{C/N}$ calculated for 0% w/w silane. When the 2% w/w silane concentration is reached, the $\Delta_{C/N}$ increases again to 4.2. If the C/N ratio increases, this may be interpreted as a decrease of nitrogen in the region that subsequently becomes the locus of failure. This means that the nitrogen depletion is higher when 0 or 2% w/w silane concentrations are used in the adhesive. This reduction in the N content means that there is a depletion of curing agent in the region where failure occurs, as explained in the schematic of Figure 8. The depletion of curing agent will lead to a localized reduction in cross-link density. The free volume of the resin in this region will, thus, be larger than that in the bulk of the adhesive. On exposure to water, the zones of large free volume will act as a preferential sink for water molecules (originating from the humid environment), which will condense in these zones and effectively apply an internal strain at these points. This, along with the potential to plasticize the resin, will lead to a reduction in mechanical performance compared with a “ideal, stoichiometric” adhesive with a uniform level of cross-link density. The greater the nitrogen depletion, the bigger the free volume available for introduction of water molecules. Hence, at silane concentrations of 0 and 2% w/w, more internal strains will be applied within the joints and the mechanical performance will be lowered. We can also conclude that too much silane (such as 2% w/w) should give better mechanical performance than the adhesive containing no silane at all because the nitrogen depletion is lower than when no silane is used in the adhesive. This is actually consistent with the results presented in this work.

Lastly, the C/N ratios of joints containing 0% w/w silane concentration for points localized after the final crack front have also been calculated. The values are not as high and are closer to the bulk values of C/N than those calculated before the crack tip. Thus, when the joints are opened mechanically, a cohesive failure within the adhesive is observed (data after crack tip), but when degradation occurs as a result of the conjoint action of stress at the crack tip and water vapor,

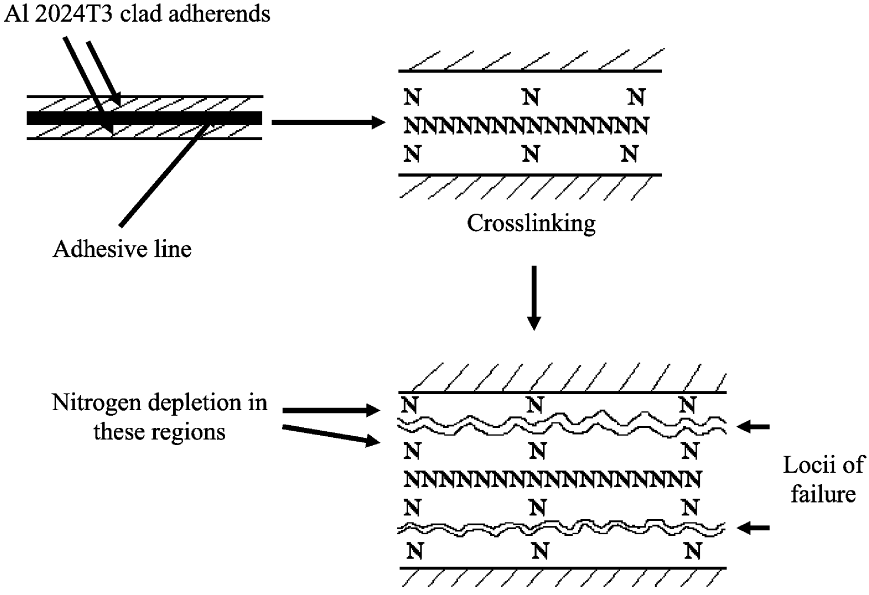

FIGURE 8 Model schematic for depletion of curing agent at the locus of failure.

the locus of failure is somewhat closer to the substrate–adhesive interface. The presence of silane has an influence on the behavior of the adhesive under stress. The presence of GPS is either beneficial or detrimental according to the concentration incorporated, which establishes that there is a higher threshold at which improvement (compared with a sample without any silane) is obtained and probably a lower threshold as well. It is highly likely that different phenomena induce either improvement of the system for low concentrations or have a detrimental effect for higher concentrations of GPS. There also seems to be a connection between the ability of the curing agent to migrate and create pockets of free volume within the adhesive and the amount of silane initially present in the formulation. The variation of the C/N values may indicate that the incorporation of silane within the formulation has an effect on the diffusion of curing agent within the system or at least its concentration throughout a hypothetic cross-section of the adhesive layer. The presence of this silane at concentrations of 0.5 and 1.0% w/w seems to enhance the uniformity of the crosslinking agent within the adhesive system, leading to improved durability. This assumption may be valid whether no silane or a higher concentration of silane is employed as indicated above. No silane may simply imply no control of molecular migration whereas too much may induce, for example, localized "pockets" of high concentration of silane with local polymerization and again no possibility for the control of migration of other mobile (*i.e.*, in the initial stages of crosslinking of the adhesive) molecules, such as the curing agent.

CONCLUSIONS

The effects of the incorporation of an organosilane (GPS) within an adhesive formulation on the durability of adhesively bonded aluminium joints have been investigated using the Boeing wedge test and surface analysis carried out by XPS.

The mechanical tests have shown that the durability of the aluminium joints was altered by exposure to a hot and humid environment. It has been noticed that, no matter what the silane concentration, the crack growths and fracture energy results are better for joints tested at ambient atmosphere than for joints studied at 50°C and 90% RH. The analysis of wedge-test data has also shown that the durability of the joints was affected by the silane concentration and the effect may be beneficial as well as detrimental if the concentration used is too high. It has been concluded that a silane concentration between 0.5 and 1% w/w was adequate with this particular commercial adhesive. However, the amount of mechanical testing performed during this work did not allow us to define the exact concentration that was optimum, and some further mechanical work should be carried out to establish which would give the best mechanical performance between the ranges $0\% < x \leq 0.5\%$ and $1\% \leq x < 2\%$ w/w. This corresponds to the concept of lower and higher threshold values of the amount of GPS to be used in such a system.

The surface analysis has allowed us to define the locus of failure of the joints. With only a visual assessment of the locus of failure, it seems that the failure occurs at the aluminium–adhesive interface. However, the XPS analyses and the study of the C/N ratios have shown that the locus of failure actually occurs within the adhesive for some of the points analyzed. Moreover, the analysis of a polymer point situated after final crack front (separation of the adherends by hand) and the C/N ratio values have shown that at the end of the wedge-test specimen, the failure occurs within the bulk of the adhesive.

The incorporation of silane at any concentration appears to have an effect on the concentration of the curing agent (or any molecule containing nitrogen) throughout the adhesive and could be correlated with a control of the migration of such molecules. It is postulated that for GPS concentrations of 0.5 and 1% w/w, the silane helps in controlling the migration of the curing agent, whereas for no GPS and higher concentrations the control is absent or hindered by formation of local polymerization pockets of GPS.

Finally, it was not possible to establish a correlation between either the fracture energy or the crack growth and the amount of silicon present at the interface, particularly on the aluminium side of the failed joint. Further work is needed to account for the possible migration of the GPS molecule at the interface, such as ToF-SIMS analyses of the failed surfaces.

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