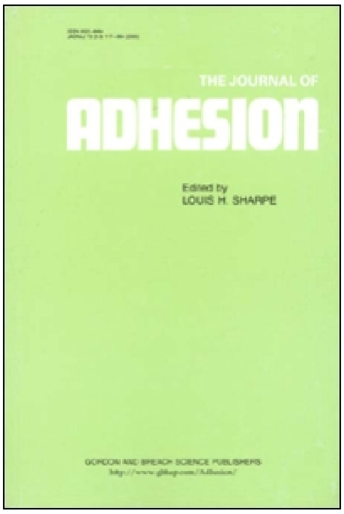

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Degradation of Interfacial Chemistry of Epoxy/Silane/Aluminium Interfaces as a Result of Aqueous Attack

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Degradation of Interfacial Chemistry of Epoxy/Silane/Aluminium Interfaces as a Result of Aqueous Attack

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The degradation of a thin layer of adhesive on a grit-blasted aluminium substrate, as a result of aqueous attack, was investigated and compared with the behavior of the adhesive on a grit-blasted aluminium substrate treated with γ-glycidoxypropyl trimethoxy silane (GPS). The degradation study was achieved by examining aluminium coupons treated with adhesive that had been immersed in water at 25°C and an elevated temperature (50°C) for various treatment times ranging between 10 min and 1 day. All samples were characterized using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). XPS and ToF-SIMS data indicated that the adhesive layer on both types of substrate was readily displaced by water. This is shown to be a two-stage process with bond rupture being identified by ToF-SIMS analysis and the displacement of the organic phase occurring at a later stage, as indicated by the XPS analysis, which showed a reduction in surface carbon concentration. When the substrates were directly in contact with water, a hydration process occurred and hydrated oxide species were formed on the surfaces. The results indicated that the hydration process was a postfailure event.

Keywords: Adhesive; Aluminium; Aqueous attack; Organosilane; Time-of-flight secondary ion mass spectrometry; X-ray photoelectron spectroscopy

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INTRODUCTION

In the use of adhesive bonding for structural purposes, one of the main concerns is the durability of such joints during their lifetime, particularly when exposed to an aggressive environment such as water in either the condensed or vapor phase. In recent years much progress has been made in the development of models to describe such behavior and provide numerical tools for the design of bonded structures [1, 2]. In such work, surface analysis is often used in a complementary manner to provide an accurate definition of the exact locus of failure. There is still a need to examine the interfacial chemistry associated with such degradation processes, and in this article preliminary results are provided toward this goal.

In previous work [3–6] extensive use has been made of a preparative approach known as the thin-film method. In essence a very thin (*ca.* 2 nm) film of the organic phase (resin, curing agent, or fully formulated adhesive) is deposited on the chosen substrate, and XPS and ToF-SIMS are then used to probe the interfacial chemistry of the interaction between the organic molecule(s) and the substrate. In this manner, we have investigated the interaction of epoxy resin, toluene diisocyanate (TDI) urone curing agent, and a fully formulated structural adhesive with bare aluminium and aluminium treated with γ-glycidoxypropyl trimethoxy silane (GPS). The aim of the work presented in this article is to investigate the manner in which such thin layers are degraded by exposure to an aqueous environment at ambient and elevated temperatures. In this way, we hope to identify the manner in which the interface chemistry of adhesion of the adhesive in question, which is known to interact *via* a covalent bond with GPS-treated aluminium [4], is attacked by water molecules.

In this work, the approach that was used is to take two aluminium substrates, one that has been treated by grit blasting and one that has been grit blasted followed by the addition of an organosilane treatment, cured in a manner known to give a durable (covalently bonded) interface [7, 8]. These substrates were then coated with an extremely thin layer of a commercial adhesive and exposed to liquid water for periods up to 1 day. XPS and ToF-SIMS were used to assess the extent to which the aqueous treatment had removed the adhesive. As the two major components of the epoxy adhesive are known, characteristic ions in the ToF-SIMS spectrum were used to compare the extent to which the epoxy component and the curing agent were retained on the bare aluminium surface compared with that treated with the organosilane.

EXPERIMENTAL

Aluminium Substrate

Aluminium sheets of commercial purity (99%) were supplied by Goodfellow Cambridge Ltd., Hundington, Cambridgeshire, UK. For the treatment by the GPS primer, samples were prepared by the same procedure, an industrial process, as employed in previous work [3, 6, 8]. Aluminium sheets were degreased in a detergent solution. They were rinsed with MilliQ water (reverse osmosis deionized and carbon filtered). Subsequently, they were degreased with acetone. After drying, aluminium samples were grit-blasted with fresh 50-µm alumina grit supplied by Abrasive Development Ltd., Solihull, West Midlands, UK.

Samples of 10 mm in diameter were punched from the aluminium sheet, followed by degreasing, which was achieved by flooding the specimen with acetone from a wash bottle and then draining onto a clean lens tissue.

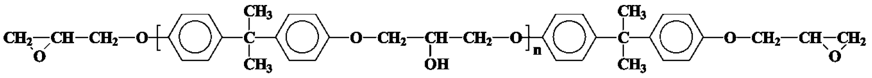
Silane Treatment

The samples were brushed for 2 min with a 1% (v/v) aqueous solution of GPS (OSi Silquest, Slough, Berkshire, UK, product designation A187) that had been hydrolyzed for 60 min to reach full hydrolysis in MilliQ water. The silane films were then cured in an oven at 93°C for 60 min.

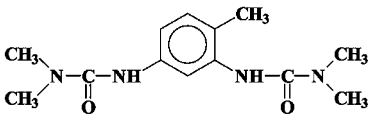
Treatment with Adhesive Solution

The commercial dry film adhesive was provided in its unsupported form, unlike in previous work [6] where the adhesive was supported by the inclusion of a knitted nylon mesh within the film. Because this is a commercial product the exact formulation is unknown. However, the two major components in the adhesive have been identified. The first component is the epoxy resin (DGEBA) (n between 0 and 1) and the other is a 2,4 toluene diisocynate urone curing agent (2,4 TDI urone). The molecular structures of these two components are shown in Figure 1. A 1% (w/w) solution of the adhesive was prepared by dissolving 2.168 g of the adhesive in fresh toluene in a 250-cm^3 volumetric flask.

The substrates were prepared in two sets: grit-blasted aluminium (GB) and GB aluminium treated with GPS, which were then immersed in the adhesive solution for 20 min. This time was adequate to reach the kinetic equilibrium of the adsorption for adhesive on the



the diglycidyl ether of bisphenol A (DGEBA)



2, 4 TDI urone curing agent

FIGURE 1 Molecular structure of DGEBA and the curing agent.

aluminium adherends [3, 4, 7]. The samples were then rinsed immediately with 40 cm^3 of toluene three times (2 min for each rinse). This procedure was to remove any weakly adsorbed material. This leaves a very thin layer of adhesive. Our previous work has shown that this is chemisorbed and of monolayer dimensions [4].

These samples were exposed to MilliQ water in a thermostated water bath with gentle stirring at 25°C ± 0.5°C and 50°C ± 0.5°C for various times. The 25°C temperature water was taken as representative of the room temperature (RT) behavior. The samples were removed periodically from the water bath and characterized by XPS and ToF-SIMS. The total set of samples prepared for this investigation is listed in Table 1. Two specimens were used as control samples: aluminium treated with the adhesive solution, and aluminium treated with GPS and then the adhesive solution, neither of these being exposed to water.

SURFACE ANALYSIS

XPS Analysis

XPS analyses were achieved using a Thermo VG Scientific Sigma-Probe spectrometer with monochromated AlK α radiation with a 400-μm spot size and a 100-W power (Thermo VG Scientific, East Grinstead, UK). Spectral processing was carried out using the manufacturer's computer software, Avantage *vl.85*. The pass energy was set up at 100 eV for the survey spectra and 20 eV for the high-resolution spectra of the core-level regions of interest: C1s, O1s, Al2p, Si2p, N1s, Ca2p, and Na1s.

TABLE 1 All Samples Prepared for the Degradation Study

Samples	Exposure time (min)
GB/adhesive, exposed to water at RT	0
	10
	30
	60 (1 h)
	1440 (l day)
GB/GPS/adhesive, exposed to water at RT	0
	10
	30
	60
	1440
GB/adhesive, exposed to water at 50°C	0
	10
	30
	60
	1440
GB/GPS/Adhesive, exposed to water at 50°C	0
	10
	30
	60
	1440

ToF-SIMS Analysis

ToF-SIMS analyses were achieved using a VG Scientific Type 23 system. This instrument is equipped with a double-stage reflectron time-of-flight analyzer and a gallium pulsed liquid-metal ion source. Static SIMS conditions with total ion dose less than 1×10^{13} ions cm^{-2} $analysis^{-1}$ were employed using a pulsed (10 kHz and *ca.* 30 ns) 20 keV $^{69}Ga^{+}$ primary ion beam rastered over an area of $500 \times 500\,\mu m^2$ at 50 frames s^{-1}. SIMS spectra were acquired over a mass range of 0 to 600 Daltons in both the positive and negative modes; analyses were recorded in (at least) triplicate from each sample.

RESULTS

XPS Characterization

XPS survey spectra, for the control samples and the samples immersed in water at RT and 50°C for various times, are shown in

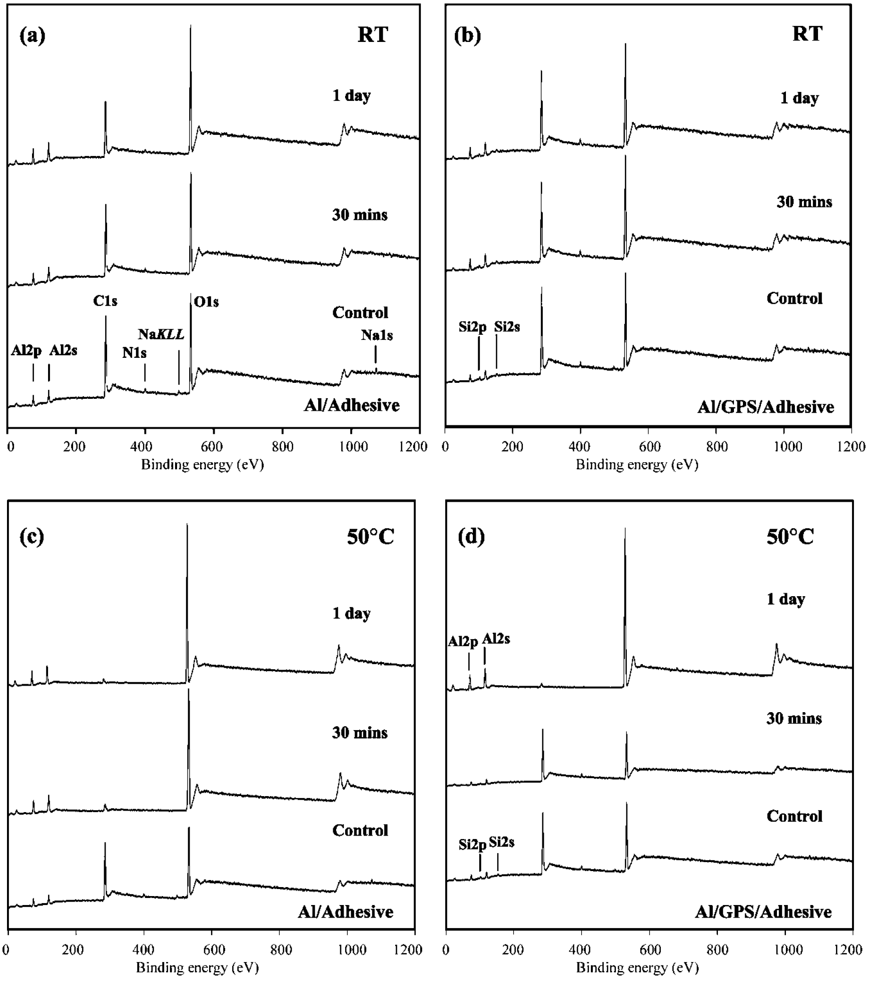


FIGURE 2 XPS survey spectra for GB samples (a) treated with the adhesive and then exposed to water at RT, (b) treated with GPS and the adhesive and then exposed to water at RT, (c) treated with the adhesive and then exposed to water at 50°C, and (d) treated with GPS and the adhesive and then exposed to water at 50°C, for 30 min and 1 day.

Figure 2. The spectrum of aluminium treated with adhesive shows the following signals: Al2p, Al2s, C1s, N1s, O1s, Na1s, O*KLL*, and Na*KLL*. These signals are also observed in the spectrum of aluminium treated with GPS and the adhesive solution, and Si2p and Si2s peaks are present as signals indicative of GPS. The nitrogen signal is indicative

TABLE 2 XPS Surface Composition for All Samples

Samples	Exposure time (min)	Surface composition (atomic %)				
		C	O	Al	Si	N
GB/adhesive, exposed to water at RT	0	58.6	30.8	9.0	N/A	1.2
	10	59.1	28.5	9.8	0.3	2.4
	30	55.4	32.7	10.8	N/A	1.1
	60	56.7	31.6	10.6	N/A	1.1
	1440	44.9	40.5	13.8	N/A	0.8
GB/GPS/adhesive, exposed to water at RT	0	64.3	26.4	5.9	1.3	1.7
	10	63.0	25.9	7.6	1.4	2.2
	30	58.9	28.7	8.9	1.4	2.1
	60	53.7	32.7	10.3	1.4	1.9
	1440	58.0	30.0	8.6	1.6	1.9
GB/adhesive, exposed to water at 50°C	0	58.6	30.8	9.0	N/A	1.2
	10	37.2	45.8	16.1	N/A	0.9
	30	11.4	67.6	21.0	N/A	N/A
	60	6.1	66.9	24.8	N/A	N/A
	1440	5.4	73.6	21.0	N/A	N/A
GB/GPS/adhesive, exposed to water at 50°C	0	64.3	26.4	5.9	1.3	1.7
	10	70.6	22.0	3.6	1.7	2.2
	30	66.9	23.7	5.2	1.5	2.8
	60	27.4	53.7	16.6	0.6	0.7
	1440	5.5	72.9	20.9	N/A	N/A

N/A: Not available; concentration is below the XPS detection limit.

of the 2,4 TDI urone curing agent from the adhesive. The surface compositions of the samples are listed in Table 2.

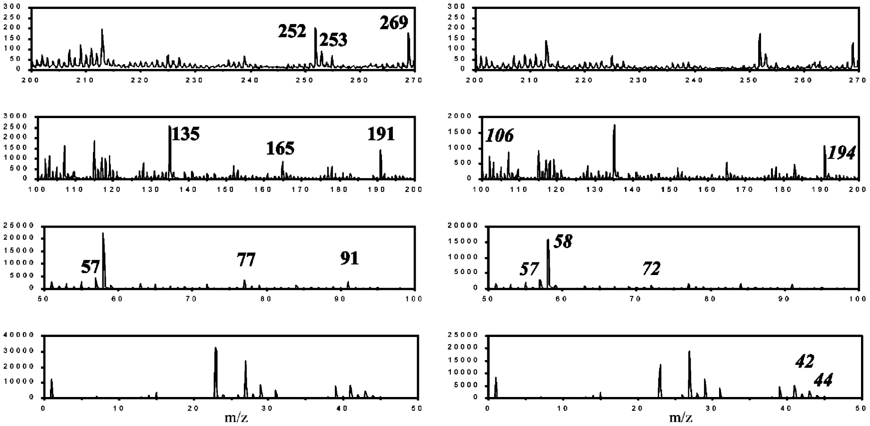
From Figure 2 and Table 2, it can be seen that when exposed to water at RT for a period between 10 min to 1 h, the carbon intensity is slightly decreased on both types of substrate. After prolonged exposure time (1 day), the adhesive-treated specimens show a dramatic decrease in intensity of carbon and an increase in intensity of aluminium and oxygen signals. Over the same full exposure period, the carbon intensity is slightly decreased when the sample is treated with the silane first.

The exposure to water at elevated temperature shows the following behavior: when there is no silane treatment, the carbon and nitrogen concentrations reduce rapidly after 10 min, whereas the intensities of these signals on GPS-coated substrates indicate little change at the same immersion time.

The reduction in intensity of carbon and nitrogen signals is apparent after 10 min for the bare substrate but only after 1 h if the substrate has been treated with the silane prior to the adhesive solution. The decreased intensity of both carbon and nitrogen indicates that the organic molecules (DGEBA, curing agent, and other adhesive components) adsorbed on the substrates were gradually displaced from the surface on water exposure. The increase of exposure temperature has a significant effect on the removal of the adhesive. It is clear that the adhesive is retained longer on the GPS-coated aluminium surfaces, than the bare, GB, substrates.

ToF-SIMS Characterization

Figure 3 shows positive ToF-SIMS spectra for the control samples (a) GB sample treated with adhesive and (b) GB sample treated with GPS and then the adhesive. Both spectra are very similar. Several positive fragments, such as 31, 57, 77, 83, 91, 135, 165, 252, 253, and 269 Da, are characteristic of the epoxy resin, DGEBA. Some of the positive fragments, including even mass ions, such as 42, 44, 58, 72, 89, 94, 107, 152, 177, and 194 Da, are characteristic of the



(a) Al/Adhesive

(b) Al/GPS/Adhesive

FIGURE 3 Positive ToF-SIMS spectra (m/z = 0–270 Da) for (a) GB aluminium treated with the adhesive, the DGEBA ions are labelled, and (b) GB aluminium treated with GPS and then the adhesive; ions from 2,4 TDI urone are italicized.

2,4 TDI urone curing agent. The structures of these fragments characteristic of both components have been described elsewhere [4]. Fragments of lower masses are 23 (Na^+), 27 ($C_2H_3^+$ and mostly Al^+), and 29 ($C_2H_5{}^+$). The fragments with masses greater than 30 are presented in Tables 3 and 4.

Positive ToF-SIMS spectra in the mass range $m/z = 275–280$ Da are shown in Figure 4 for aluminium a) GB only, b) GB and treated with the adhesive solution at 1% (w/w), c) GB and treated with GPS only, and d) GB and treated with GPS and then the adhesive solution at 1% (w/w), respectively. A particular feature at 277 Da was found only in the spectra for aluminium coated with the adhesive solution and for aluminium coated with GPS and then the adhesive solution. This particular fragment ($m/z = 277$ Da) indicates the interfacial interaction occurring on the substrates. The increased intensity of this mass on the GB aluminium substrate treated with GPS is associated with the interaction between the silane and the adhesive, as discussed at length elsewhere [4].

Figure 5 shows negative ToF-SIMS spectra in the mass range $m/z = 5–400$ Da for GB aluminium treated with the commercial adhesive exposed to water at 50°C for 1 h. Some fragments such as the ions at $m/z = 135$, 211, and 283 Da in the spectrum for the adhesive-treated surface are characteristic of the DGEBA molecule. After the sample has been exposed to water, these characteristic ions have a very low intensity. Some other fragments (*e.g.*, 119 Da) are present and intense. These fragments are indicative of hydroxide/oxide films.

DISCUSSION

Degradation of Interfacial Chemistry Studied by XPS

The interfacial degradation on both types of substrates by XPS can be studied by monitoring the surface compositions of carbon and nitrogen against water-exposure time, as carbon is indicative of all organic materials adsorbed and nitrogen of the curing agent. Figure 6 shows the relationship between the carbon concentration and the immersion time at RT and 50°C on both substrates. It is found that when the samples are exposed to water at RT, the carbon intensity on both substrates slightly decreases with increasing exposure time. However, there is little difference in intensity between the surfaces treated with GPS and bare substrates, although at the longest exposure time the carbon level on the bare substrate has started to fall. At higher water temperature, the carbon concentration for bare substrates dramatically

TABLE 3 Positive Ion Fragments Characteristic of DGEBA

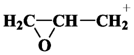
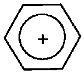
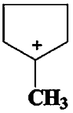
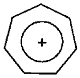
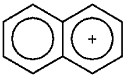
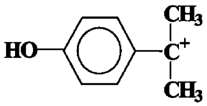
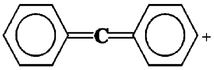
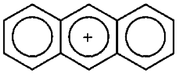
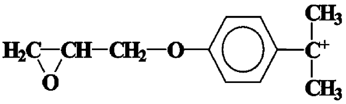
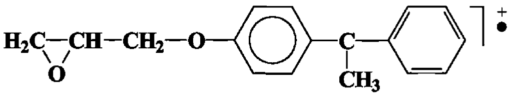
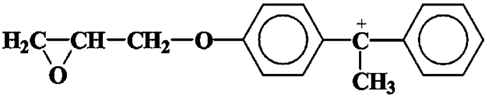
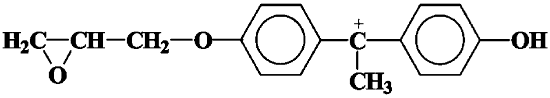
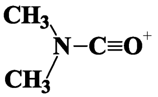
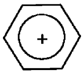
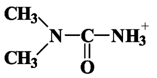
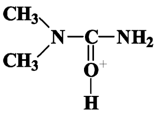
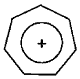
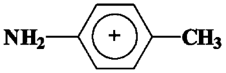
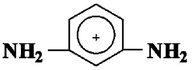
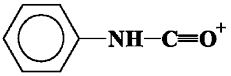
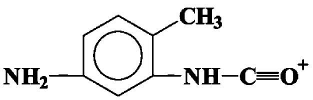
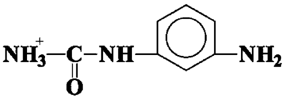
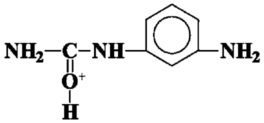
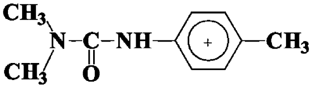
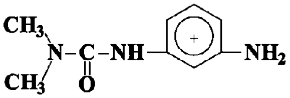
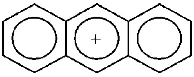
m/z	Formula	Structure
31	CH_2OH^+	$HO{-}CH_2^+$
57	$C_3H_5O^+$	
77	$C_6H_5^+$	
83	$C_6H_{11}^+$	
91	$C_7H_7^+$	
128	$C_{10}H_8^+$	
135	$C_9H_{11}O^+$	
165	$C_{13}H_9^+$	
178	$C_{14}H_{10}^+$	
191	$C_{12}H_{15}O_2^+$	
252	$C_{17}H_{16}O_2^+$	
253	$C_{17}H_{17}O_2^+$	
269	$C_{17}H_{17}O_2^+$	

TABLE 4 Positive Ion Fragments Characteristic of the Curing Agent

m/z	Formula	Structure
42	$C_2H_4N^+$	$CH_2=N^+CH_2$ $CH_2=N-CH_2^+$
44	$CH_2N_O^+$	$NH_2-C\equiv O^+$
58	$C_2H_4NO^+$	$CH_3-NH-C\equiv O^+$
72	$C_3H_6NO^+$	
77	$C_6H_5^+$	
89	$C_3H_9N_2O^+$	 
91	$C_7H_7^+$	
106	$C_7H_8N^+$	
107	$C_6H_7N_2^+$	
120	$C_7H_6NO^+$	
149	$C_8H_9N_2O^+$	
152	$C_7H_{10}N_3O^+$	 

(*Continued*)

TABLE 4 Continued

m/z	Formula	Structure
177	$C_{10}H_{13}N_2O^+$	
178	$C_9H_{12}N_3O^+$/ $C_{14}H_{10}^+$	 

decreases for the samples that were immersed in water for more than 10 min. After 30 min, the intensity is very low (less than 10%). However, at the same exposure time for the GPS-coated samples, the intensity slightly changes for 30 min and then declines rapidly with increasing exposure time.

Figure 7 shows the relationship of the nitrogen concentration to exposure time at the different water temperatures. It is shown that,

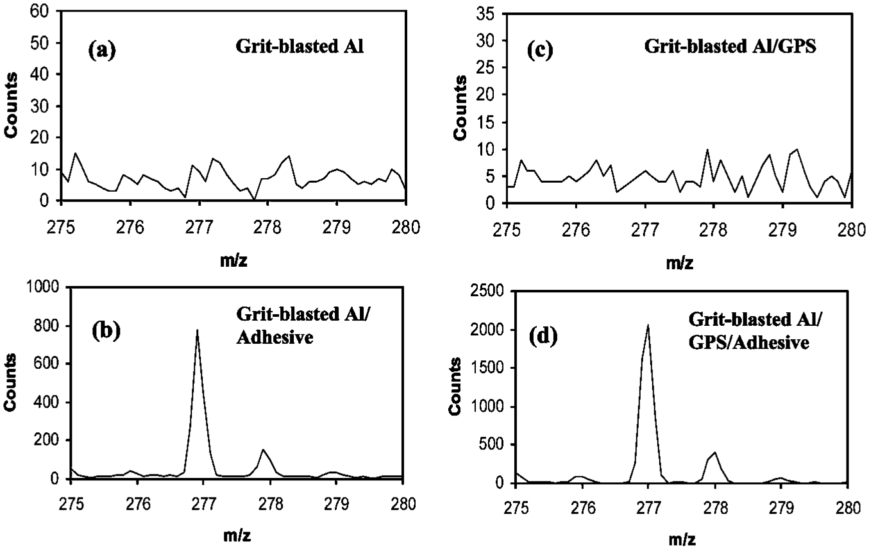


FIGURE 4 ToF-SIMS positive spectra (m/z = 275–280 Da) for aluminium (a) GB only, (b) GB and treated with the adhesive solution, (c) GB and treated with GPS only, and (d) GB and treated with GPS then the adhesive solution.

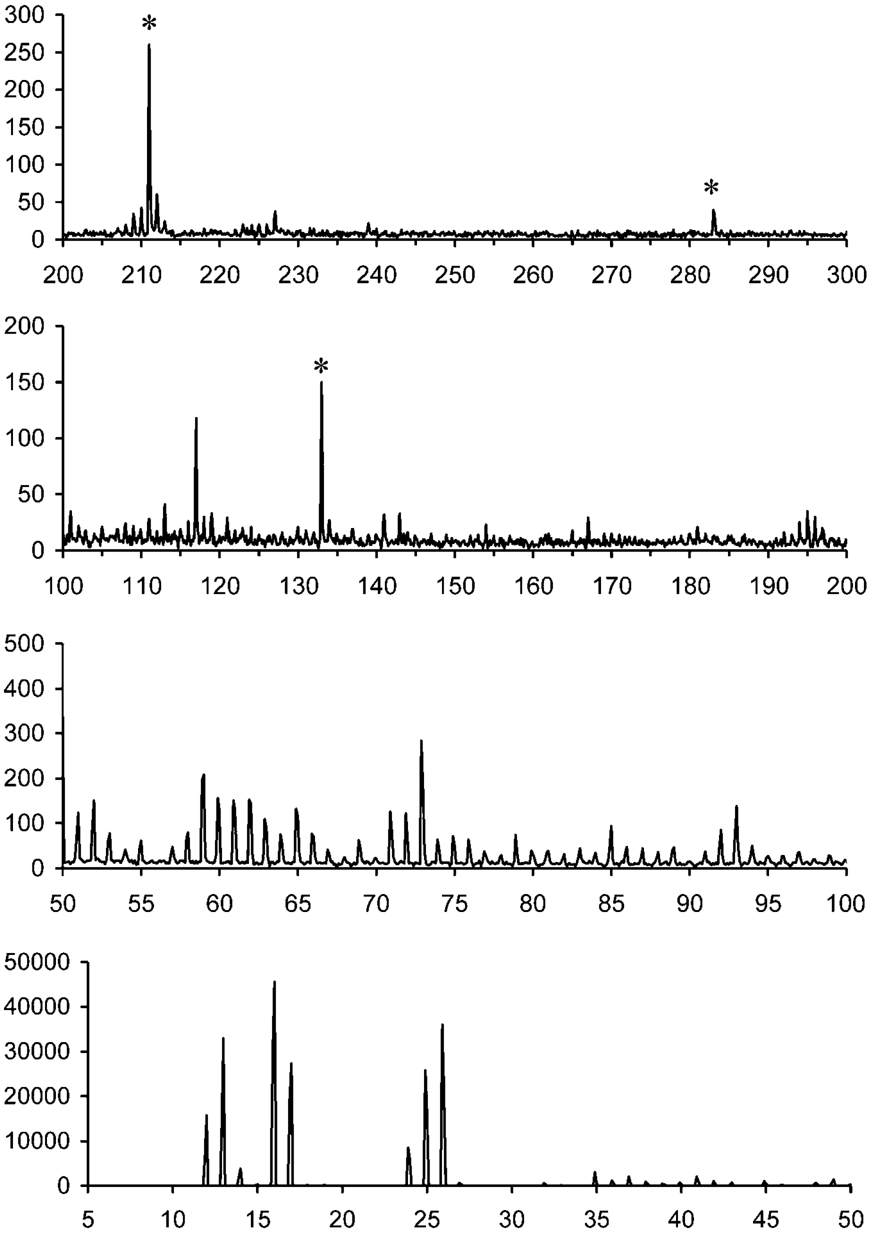


FIGURE 5 ToF-SIMS negative spectra (m/z = 5–300 Da) for GB aluminium treated with the adhesive solution (major DGEBA fragments identified by $*$).

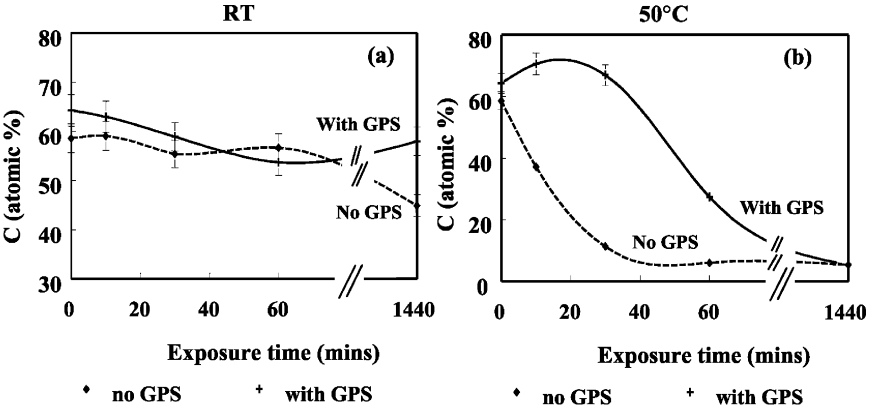


FIGURE 6 Plots of carbon concentration against exposure time for the samples left in water at (a) RT and (b) 50°C.

at RT, the nitrogen intensities on both substrates increase after 10 min and then decrease when the samples are left in water for longer times. However, the substrates treated with GPS provide a greater nitrogen concentration than the bare substrates at the same exposure time, perhaps indicating that the curing agent is more resistant to displacement on this substrate. At 50°C, there is a dramatic reduction of the nitrogen signal on bare substrates when immersed in water. The total loss of nitrogen intensity is observed for the samples left in water for

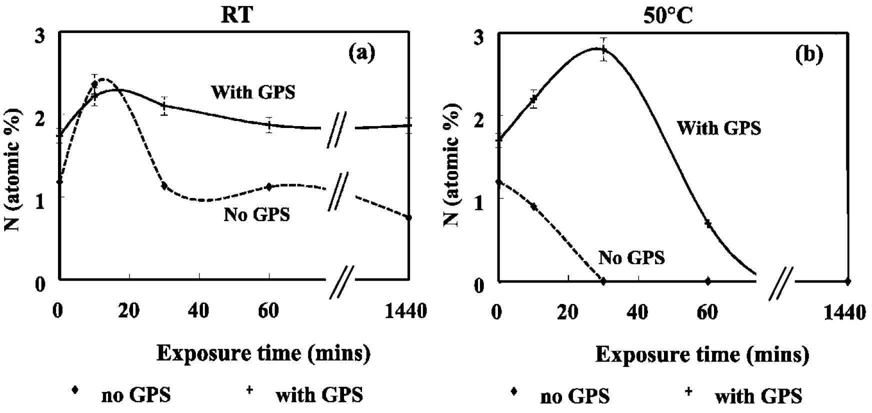


FIGURE 7 Plots of nitrogen concentration against exposure time for the samples left in water at (a) RT and (b) 50°C.

longer than 30 min. The GPS-treated substrates present a decrease in intensity after 60 min, and they have no nitrogen-containing species present on the surfaces after 1 day of exposure in water.

The results from the plots of carbon and nitrogen concentrations indicate that the increase of water-exposure time and water temperature have a significant effect on the degradation of interfacial chemistry of adhesion. However, the adhesive is removed from the bare surfaces more quickly than that from the GPS-coated substrates.

Degradation of Interfacial Chemistry Studied by ToF-SIMS

To study the adhesive degradation by ToF-SIMS, the ions at $m/z = 135\,\text{Da}$ (for DGEBA) and $m/z = 58\,\text{Da}$ (for the curing agent) were chosen to plot the relative peak intensity (*RPI*) against the exposure time. The *RPI* is expressed by

$$RPI = \frac{I_{\text{ads}}}{I_{\text{total counts}}} \qquad (1)$$

where I_{ads} is the intensity of an ion in the positive or negative ToF-SIMS spectrum characteristic of the adsorbate and $I_{\text{total counts}}$ is the intensity of all ions in the same spectrum in the mass range of 5–400 Da (mass veto = 0–5 Da).

The plots of the *RPI* of mass 135 Da (for DGEBA) and the exposure time are shown in Figure 8.

It is found that the intensity of mass 135 Da decreases gradually at RT. After 1 day (1440 min), little adhesive remains on both substrates

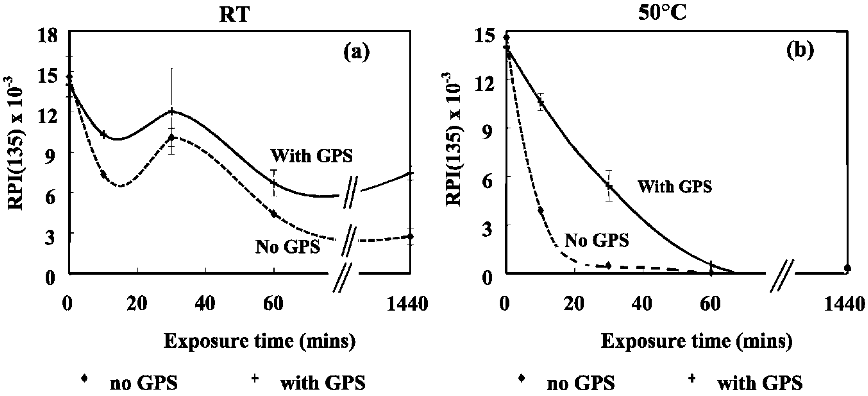


FIGURE 8 Plots of RPI of mass 135 Da against the exposure time for the sample immersed in water at (a) RT and (b) 50°C.

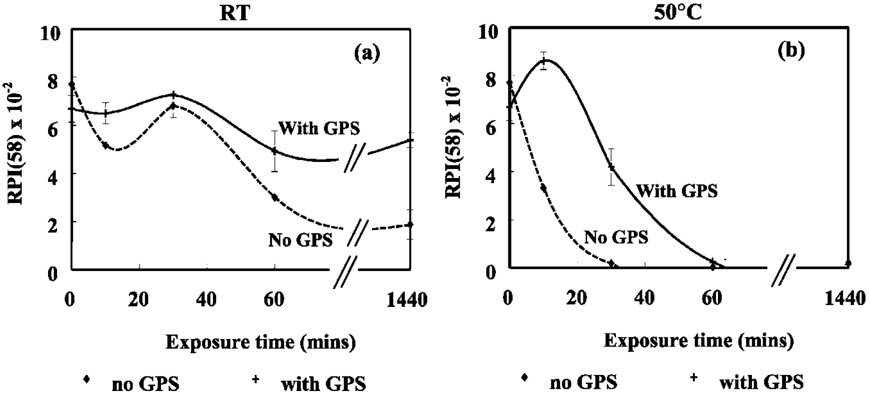


FIGURE 9 Plots of RPI of mass 58 against the exposure time for the sample immersed in water at (a) RT and (b) 50°C.

although the GPS-coated substrate has a slightly higher intensity. At 50°C, the intensity reduces more rapidly within 30 min. With the addition of the GPS treatment, the substrates can retain adhesive better than on the bare substrates at the same exposure time. However, the intensity almost reaches zero for both surfaces when exposure time for 1 h is reached. The results from the study of the degradation of interfacial chemistry using mass 135 Da are similar to the results using mass 58 Da (for the curing agent), as shown in Figure 9. This clearly indicates the removal of the adhesive from both substrates. The ToF-SIMS results are in good agreement with the XPS data for the 2,4 TDI urone curing agent, and for the DGEBA it provides a more concise picture, at rt, than the global carbon concentration determined by XPS.

Comparison of the Degradation of the Interfacial Chemistry Between XPS and ToF-SIMS Studies

The comparison between the nitrogen concentration from the XPS study (Figure 7) and the m/z = 58 Da intensity from ToF-SIMS study (Figure 9) is very informative. The consistency of the two data sets indicates a similar trend in the degradation of the interfacial chemistry of adhesion as a result of water exposure. In particular, the agreement between the Nls XPS data and the ToF-SIMS intensity of the cation m/z = 58 Da shows the XPS data provides a reliable indication of the surface concentration of the 2,4 TDI urone. Implicit in this observation is the absence of the any other nitrogen-containing components of the adhesive adsorbed on the substrate surface. The data show the reduction of the intensity of nitrogen and the characteristic ion of curing agent when exposed to an aqueous environment. This indicates the displacement of curing agent and/or adhesive by water. The adhesive is removed rapidly when the temperature of exposure water is increased from RT to 50°C. The exposure temperature is considered as a variable in which the kinetics of degradation of the interfacial chemistry on the substrate increase with temperature. This is probably indicative of an activated process, which can be described by an Arrhenius relationship. Because the covalent bond is formed on GPS-coated aluminium, the removal of the adhesive from the GPS-coated substrate occurs more slowly than that from the bare substrate.

Once the adhesive has been displaced, the degree of water attack of the original oxide surface is more extensive. This occurs at both temperatures. Hydration occurs and a hydrated oxide layer is formed. Negative ToF-SIMS spectra (not shown here) for samples exposed to water exhibit fragments such as $m/z = 43$ (AlO^-), 59 (AlO_2^-), 77 [$AlO(OH)_2^-$], and 119 [$Al_2O_3(OH)^-$] Da, which are characteristic of the hydrated forms of aluminium oxide. The intensity of these characteristic ions is plotted in Figures 10 and 11, for RT and 50°C treatments, respectively. The intensity of such ions increases as a function of exposure time and water temperature.

At RT, it is found that the yield of ions characteristic of the "oxide" produced from the bare substrate is slightly higher than that formed on the GPS-coated surface. However, when exposed to water for 1 day (1440 min), the intensity of the ion from the film on the bare substrate has increased rapidly and is higher, compared with the silane-coated surface. Both substrates show the effect of water at elevated temperature. The growth of oxide rapidly increases on the bare substrate compared with GPS-coated substrate. The current observation indicates that the development of the oxide films is related to the degradation of the interfacial chemistry at the interfaces as a result of water attack. When both substrates are attacked by water, the adhesive components are displaced from the substrate and growth and/or hydration of the oxide films occurs. This is an important point and provides the opportunity to comment on whether oxide hydration is a failure mode or a postfailure event.

A particular feature at 277 Da was found in both spectra for aluminium coated with the adhesive solution and for aluminium coated with GPS and then the adhesive solution. This fragment has been interpreted in terms of a specific interaction occurring when the adhesive is deposited on aluminium and on GPS coated aluminium(s).

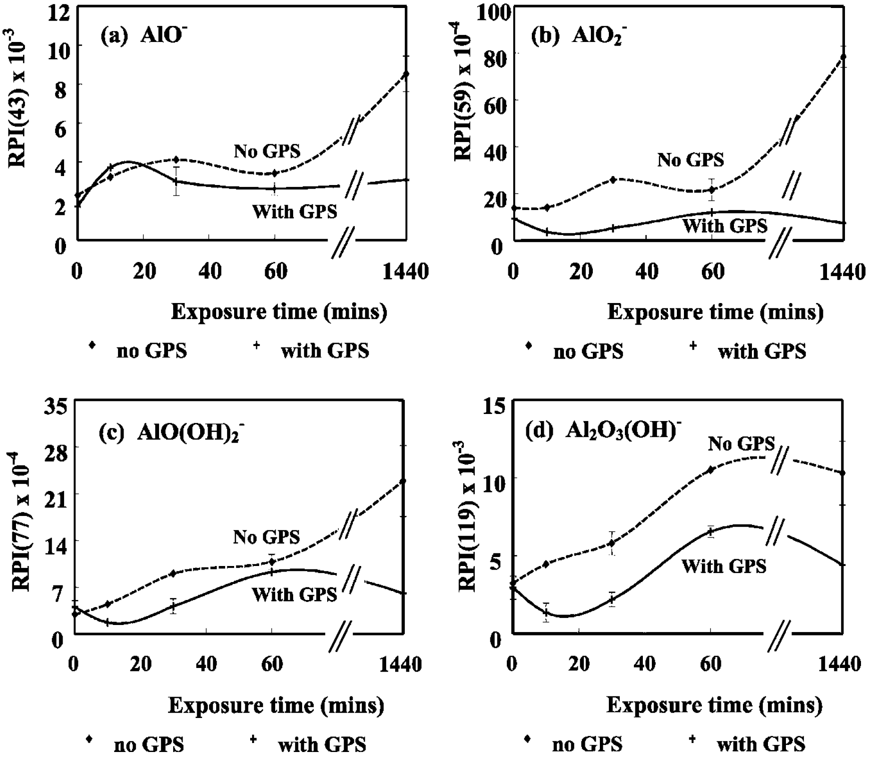


FIGURE 10 Plots of the intensity of the negative ToF-SIMS fragments characteristic of hydroxide/oxide films produced after immersion in water at RT, using the ions at (a) m/z = 43, (b) m/z = 59, (c) m/z = 77, and (d) m/z = 119 Da.

It is thought that in the case of bare aluminium, this mass is related to cross-linking within the adhesive, whereas, in the case of GPS-coated aluminium, it indicates as well the interaction between the adhesive and the oxirane ring of the GPS. The interaction occurring in the adhesive itself results from the reaction of DGEBA with the curing agent. This is a part of the reaction in the bulk of the adhesive, even though the samples were not cured at the usual curing temperature (usually greater than 100°C). The interaction between DGEBA and the curing agent is shown in Figure 12. The pattern of this reaction is also obtained in the interaction between the adhesive and GPS, which occurs *via* the curing agent existing in the adhesive. The interaction mechanism of the curing agent and GPS is shown in Figure 13.

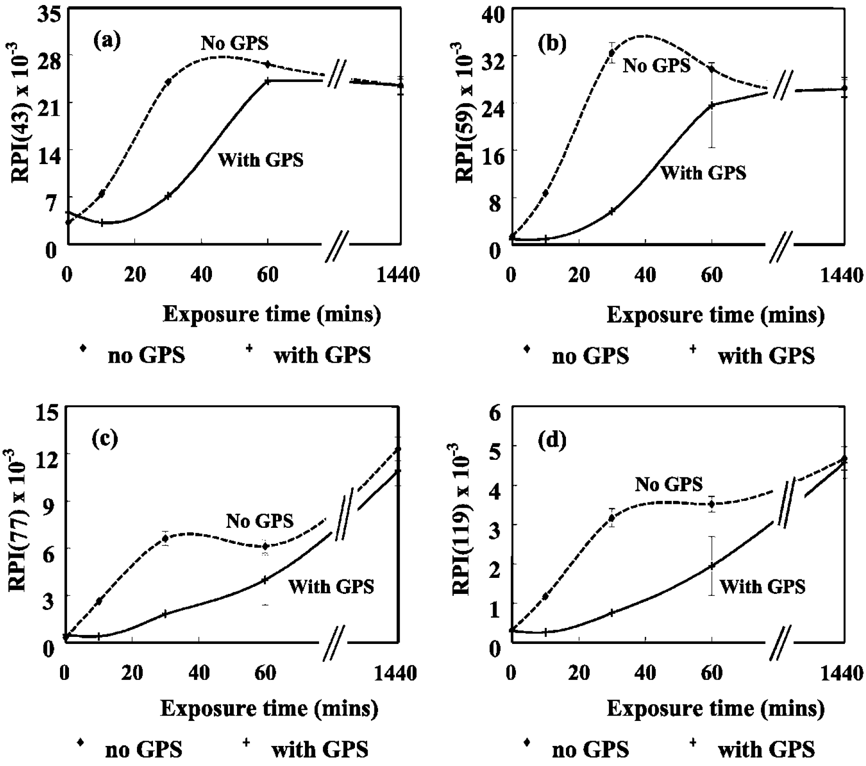


FIGURE 11 Plots of the intensity of the negative ToF-SIMS fragments characteristic of hydroxide/oxide films produced after immersion in water at 50°C, using the ions at (a) m/z = 43, (b) m/z = 59, (c) m/z = 77, and (d) m/z = 119 Da.

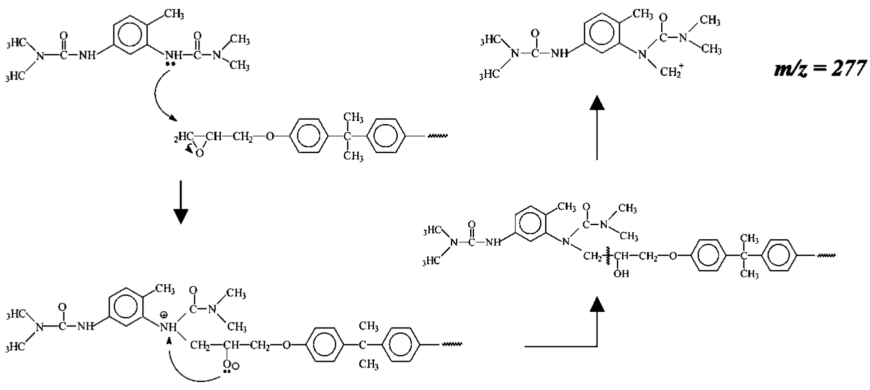


FIGURE 12 Interaction mechanism between the curing agent and DGEBA.

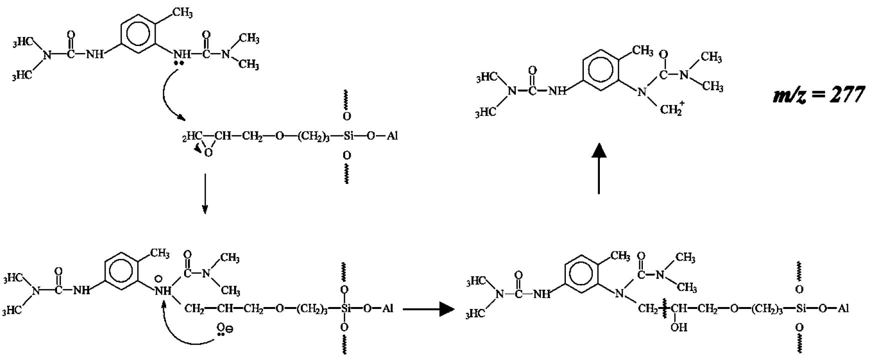


FIGURE 13 Interaction mechanism between the curing agent and hydrolyzed GPS.

Because mass 277 is a fragment indicating the specific interaction between the curing agent and GPS, the variation of this mass as a function of the water exposure time was evaluated, in order to study the effect of water on the bonding between the adhesive and the GPS. Figure 14 shows the relative peak intensity of mass 277 as a function of exposure time. It is found that at room temperature the intensity of this mass decreases rapidly for the sample immersed in water for 10 min. It remains stable until 60 min for the GPS-coated substrate before it declines dramatically at 1-day exposure time. At 50°C, the intensity decreases very quickly on both types of the substrates but it is higher when the GPS coating is used. However, after 30 min both substrates exhibit a very low intensity.

The temperature and time of exposure to water are significant factors in the interfacial degradation. The destruction of the covalent bond is observed after the samples are immersed in water. One should recall that the samples were examined following exposure to aggressive conditions (wet and hot), not in the mild conditions of normal ambient exposure. The elevated temperature, presumably following an Arrhenius relationship, will increase the degradation rate of the interfacial chemistry. The use of such an elevated temperature would help to discriminate rapidly among different surface treatments. However, sometimes the results obtained at elevated temperature do not discriminate among the surface treatments because the chemical change on the surface occurs too rapidly, as observed in the graph of intensity of mass 277 in Figure 14. In this case, the test conducted at RT shows that the treatment with GPS is important to reduce the rate of water attack at the interfaces. This indicates the

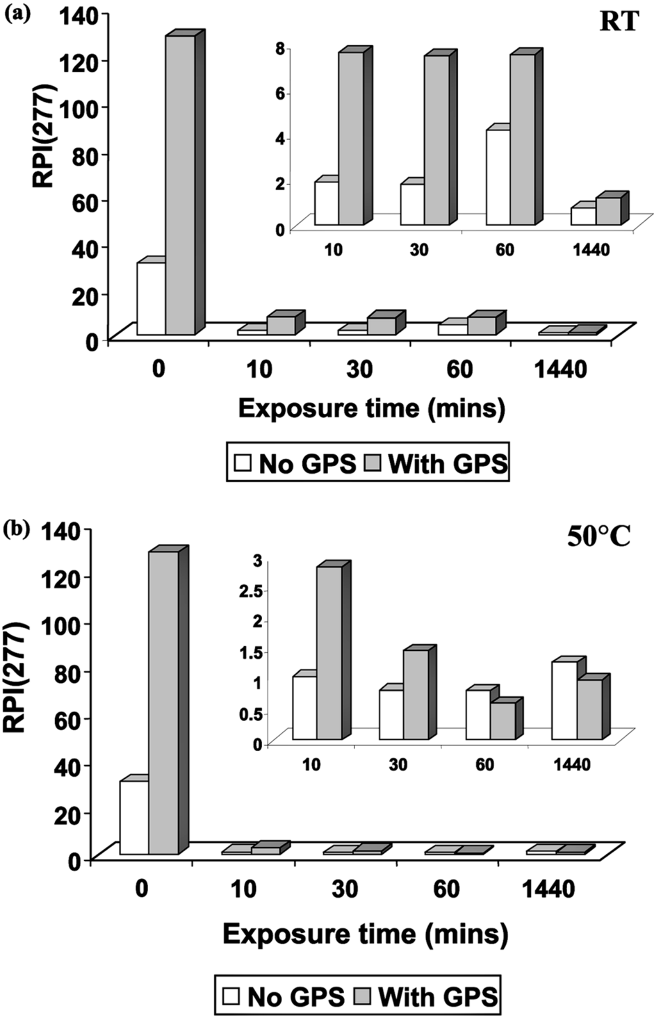


FIGURE 14 Graphs of the relative peak intensity of mass 277 against the exposure time at (a) RT and (b) 50°C.

influence of the GPS treatment on the durability of the joints. One must also recall that in the “normal” condition the diffusion of isolated water molecules through the adhesive will be the rate-controlling step in joint degradation. These molecules will aggregate close to the substrate/adhesive interface and degradation will then follow. In this work, we have removed, completely, the water transport step by using a very thin layer ($<5\,\text{nm}$) of adhesive.

Although the durability of the adhesive joints in aqueous media has been investigated for many years [9–13], this study has concentrated on the effect of water on the interfacial chemistry of a solution of the adhesive on the GB surfaces treated with silane compared with the bare GB surface. As described in our previous work [3], the adhesive components interact with the aluminium substrate *via* acid–base interaction, which, although generally considered to be a strong chemical bond, is weaker than a covalent bond. When water attacks the surface, the adhesive components, interacting with the substrate *via* acid–base interaction, are displaced, and they allow the water access to the interface and subsequent growth of the oxide film. The exposure to water results in bond breaking and the displacement of the organic material. Notably, the 50°C treatment temperature has caused more rapid interfacial degradation than the room temperature. The presence of water at the interfacial region in the bonded system is now proven to result in an increased probability of interfacial failure.

As described, the origin of the $m/z = 277$ ion may be assigned to either bonding of GPS to the curing agent or internal cross-linking within the polymer. Therefore, disappearance of the $m/z = 277$ ion for the untreated substrate may be explained in two different ways: either from removal of material or from a similar degradation to that of the bond formed between GPS and curing agent. If data for $m/z = 277$ are compared with that of carbon concentration (Table 2), the hypothesis of degradation seems more plausible for the tests performed at RT because the carbon concentration does not decrease significantly before a full day of immersion in water. However, the tests performed at 50°C indicate decrease of 277 by both removal of material and degradation of bonds.

Let us proceed to further examination of the XPS data in Table 2, at both RT and 50°C; careful inspection of the carbon assays for the bare and GPS-treated aluminium shows the expected trend; that is, for the longest exposure time the surface carbon concentration reduces from *ca*. 58% to 45%, indicating the eventual reduction in the quantity of organic material at the surface. In the presence of GPS this reduction of carbon concentration is not seen, even at 24 h of exposure for RT testing. As anticipated, the elevation of the test temperature enhances this effect, and removal of the organic phase is already seen at 10 min of exposure for the bare Al substrate. When the substrate is treated with GPS such a reduction in the organic phase is not seen until 60 min of exposure. Thus, the conclusion from these data would appear clear; at a critical exposure time, water has brought about the displacement of the adhesive layer, in the case of the untreated substrate presumably as a result of hydrodynamic displacement as predicted by surface thermodynamic considerations.

The ToF-SIMS data of Figure 14 are not consistent with such a model of simultaneous degradation and displacement and shows that the process may be more complex than the simple model described on the basis of XPS data. It should be recalled that the $m/z = 277$ peak represents a covalent interaction between an oxirane ring (on either GPS or DGEBA) and the TDI urone curing agent. On the briefest of exposures (10 min) at either ambient or elevated temperatures, the intensity of this fragment is significantly reduced for both bare and GPS-treated aluminium. It is proposed that this observation represents the initiation of the degradation, which compromises the adhesion of the organic phase to the metal oxide. Formation of the characteristic fragment is compromised by the hydrolysis of the adsorbed species but at this stage the organic phase is not completely displaced from the inorganic surface; this only occurs when the intensity of the fragment is vanishingly low (*ca.* $RPI = 1$). Thus, the ToF-SIMS data indicate the commencement of the degradation process, whereas the XPS data confirm that it is complete in certain areas by the reduction in global carbon assay.

Is hydration the cause of adhesive displacement from the substrate or is it merely a postfailure event? This is a question that has plagued the adhesion community for more than 30 years, and it is clear that there is no universal answer to this question. However, the data presented in this article go a long way to resolving the issue. Let us consider the data relating to the bare substrate at 50°C aqueous exposure. Fitting of the data set of Figure 8b indicates that the level of DGEBA has fallen to an inconsequential one by 20 min of exposure. The negative ToF-SIMS data of Figure 11 show that at this time ions, characteristic oxide and hydroxide species are still increasing and do not reach the knee of the curve until about 30 min of exposure. This provides powerful evidence that the hydration process is a postfailure event in the current investigation.

The SEM images of Figure 15 show the morphological changes after the samples were immersed in water at RT and 50°C for 1 h. The surfaces treated with the adhesive and the surfaces treated with GPS and then the adhesive, which are exposed to water at RT, exhibit a similar topography. At 50°C, the samples treated with the adhesive only (no GPS) exhibit the whisker-like structures across the surface, whereas, the samples treated with the silane and the adhesive show no such structure developing into whisker shapes. Such a morphology is formed when the samples were exposed to hot water and grown rapidly when the silane is not coated on the surface. The prebonding

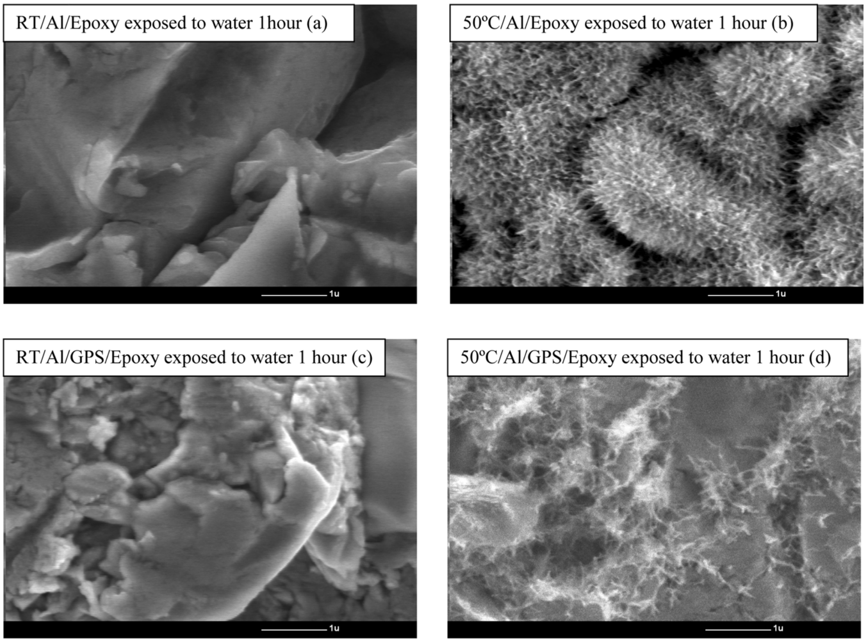


FIGURE 15 SEM images for samples (a) treated with the adhesive and then exposed to water at RT for 1 h, (b) treated with the adhesive and then exposed to water at 50°C for 1 h, (c) treated with GPS and the adhesive and then exposed to water at RT for 1 h, and (d) treated with GPS and the adhesive and then exposed to water at 50°C for 1 h, respectively.

hydration of aluminium at 100°C in pure water is known to be a beneficial pretreatment prior to the application of a GPS layer and provides a similar morphology [14, 15], These results indicate that the treatment with GPS improves the hydrodynamic stability and resists the aqueous attack. These results are in good agreement with ToF-SIMS data, which show an increase in the hydrated oxide films with temperature in Figure 11.

As expected, the GPS treatment on aluminium provides far better durability than the substrate that has no GPS treatment. Once again, the results obtained from ToF-SIMS spectra, showing the fragment at $m/z = 277$ Da, indicating a covalent bond formed at the silane/curing agent interface. The intensity of $m/z = 277$ Da for the GPS-coated substrate shows a slower degradation of interfacial bonds as a result of water than that for the bare substrate. Aluminium is a metal that can give rise to hydrolytically unstable oxides. The hydrolyzable oxides of aluminium substrate easily react with water. The treatment with GPS can improve the hydrodynamic stability on the substrates as the covalent bond is formed at the silane/aluminium interface and at the adhesive/silane interface, in the case of a deposition of the adhesive. As can be seen, this type of bond is formed from the aluminium surface through the bulk of the adhesive, providing a cross-linked network in the bonded system. Therefore, the displacement of the adhesive from the GPS-coated substrate by water is not as likely to occur. This study is a confirmation that the GPS treatment enhances the interfacial chemistry of adhesion and durability (resistance to environmental attack by water) compared with the results for the bare substrate.

CONCLUSIONS

XPS and ToF-SIMS were used to study the interfacial chemistry of the adhesive adsorbed on both GB aluminium and GPS-coated GB aluminium as a result of aqueous environmental attack (at RT and elevated temperature). The following conclusions can be drawn from this investigation:

- The adhesive adsorbed on the GB aluminium surface is displaced by water more rapidly than that on the GPS-coated substrate. This is a result of the formation of strong secondary bonds (donor–acceptor interactions) at adhesive/aluminium oxide interface compared with covalent bonding at the adhesive/silane/aluminium interface. The displacement of the adhesive is shown to be a two-stage process with bond rupture being identified by ToF-SIMS analysis and the displacement of the organic phase occurring at a later stage, as indicated by the reduction in surface carbon concentration of the XPS analysis. This has shown that the nature of covalent bond, required for good adhesion and durability, provides an improvement of hydrodynamic stability. One should stress, however, that the positive effect of silane, used in the same conditions, may not be automatically obtained if applied to another adhesive system.
- An increased temperature is an accelerating factor for the destruction of the interfacial chemistry on the substrate, leading to a rapid displacement of the adhesive by water. The displacement is not as rapid when GPS is used as a primer on the adhesive substrate. Although this type of result is known and anticipated, it shows that GPS adhesion promoter improves durability even when submitted to temperature and moisture.

- After the displacement of the adhesive from both types of substrates, the water directly attacked the original oxide layer. This hydration process leads to the growth of the oxide and hydrated oxide species. It is likely that the hydration process is a postfailure occurrence.
- Finally, this work shows that using a thin layer of adhesive as a model to study degradation of an adhesive layer under the combined stress of water and temperature is a valid and sound approach.

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