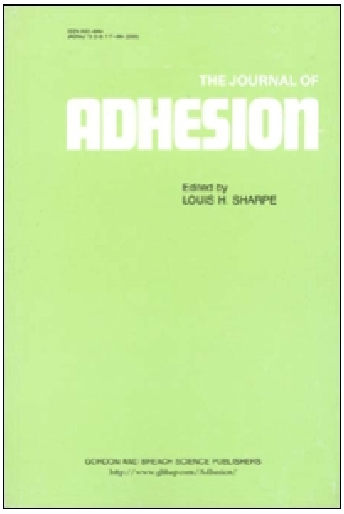

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Influence of Temperature on Aminosilane Thin Films Deposited on Aluminium Substrates: A Study by Surface Analysis

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Influence of Temperature on Aminosilane Thin Films Deposited on Aluminium Substrates: A Study by Surface Analysis

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Thin films of aminopropyltriethoxysilane (APS) have been deposited on grit-blasted aluminium and dried at four different temperatures: room temperature (RT), 50, 93, and 120°C. These specimens were prepared in order to assess the occurrence of the three important reactions known to take place when using silanes as films and/or primers: hydrolysis in the absence of water, condensation with the substrate, i.e., *covalent bond formation, and crosslinking or self-condensation.*

Analyses performed using X-ray photoelectron spectroscopy (XPS) indicate that the films reduce in thickness with temperature and that the type of silicon bonding changes mostly above 50°C. Time of flight secondary ion mass spectrometry (ToF-SIMS) reveals that covalent bonding of APS on aluminium occurs at all temperatures used in this study as well as showing that the films are close to being fully hydrolysed. It is also possible to assess the presence of crosslinking within the films.

Keywords: Aminosilane; Covalent bond; Crosslinking; Hydrolysis; Temperature; ToF-SIMS; XPS

1. INTRODUCTION

Adhesion promoters are employed in many applications, both as primers and within a formulated adhesive or coating system. These include environmentally friendly coatings as replacements for

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chromium (VI) surface treatments [1] and formulations such as adhesives, paints, or sealants. While such molecules may be found in formulated commercial products, the reactions they encounter are mostly described in solution [2] and although such work is of relevance, for example, to describe the deposition of a coating from a monomeric silane solution, it does not usually provide information as to whether the films deposited from solution have fully crosslinked or even whether hydrolysis has occurred in the absence of a stochiometric amount of water. More importantly, studying the reactions that occur within a pure film of silane can open horizons on the understanding of reactions involving the same molecules within a formulation.

Films of aminosilane were prepared by the simple dipping of grit-blasted aluminium into solutions of a commonly used aminosilane,

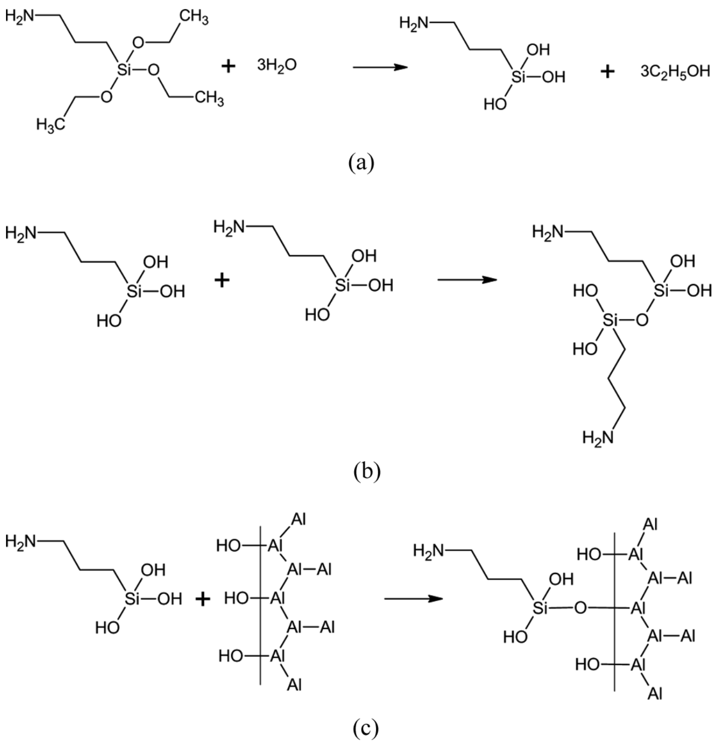


FIGURE 1 (a) Schematic of APS hydrolysis; (b) APS self-condensation (polymerization dimer formation); (c) APS condensation on aluminium surface (covalent bonding).

γ-aminopropyl triethoxy silane (APS), at dilute concentration and dried at various temperatures to induce variations in the amount of water present, the crosslinking, and the bonding at the interface. Analyses were performed using X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS). XPS was used to quantify the amount of organic material present at the surface following coating and drying at temperature as well as for the calculation of final state Auger parameters. ToF-SIMS was used to assess the presence of covalent bonds between the substrate and silane, the presence of fragments originating from the hydrolysed or partially hydrolysed molecule, as well as formation of silane oligomers within the thin film. Examples of reactions of hydrolysis and crosslinking of APS are shown in Figure 1. Until now it has not been possible to study the effect of temperature at high mass resolution (ToF-SIMS) and, therefore, provide a specific account of reactions that APS undergoes. Such work is also of importance when comparing the silane specific reactions if an adhesion promoter is incorporated within an adhesive.

2. EXPERIMENTAL

2.1. Film Preparation

Thin films were prepared using a 0.5% (v/v) concentration of γ-aminopropyltriethoxysilane in ethanolic solution which was left stirring for half an hour in order to obtain stabilization and partial hydrolysis of APS. The ethanol used in this work was not dried and it is, therefore, anticipated that a small amount of water, at trace level, will be present in the mixture. Small discs, of 10 mm diameter, were punched from a grit-blasted (alumina grit, ~60 μm size) sheet of commercially pure aluminium (Goodfellow, Cambridge, UK). It is anticipated that such a surface treatment will create a roughness within a range of 1.4 to 1.9 μm (Ra) [3]. These discs were then degreased in isopropanol and dipped (once dry) in the APS solution for 10 minutes. They were then tipped on their sides and left to drain the excess solution on a lint free tissue for thirty seconds. The relative humidity is expected to be at a level of 50% for the ambient and clearly significantly lower in the oven, hence allowing a certain amount of adsorbed water on the substrate. Three discs were prepared for each temperature used for drying and curing of the film: respectively room temperature (~20), 50, 93, and 120°C. Those temperatures were chosen as previous work from this laboratory [4] had indicated that durability of primer films prepared with another, epoxy functionalised silane, are considered to be optimum at 93°C. The samples were placed in the oven for an hour. In addition to the aluminium treated with APS, a blank sample of grit-blasted aluminium was also analysed for comparison and reference purposes.

2.2. XPS Experiments

XPS experiments were performed using a Thermo Electron Sigma Probe (East Grinstead, UK) using the MgKα anode of the twin anode; the analysis area was *ca.* 500 µm diameter. This X-ray source was employed as in AlKα radiation the Brehmstrahlung-induced Al*KLL* transition is at the same energy as Si2p, which is inconvenient and confuses spectral interpretation in this region. A survey spectrum, as well as high resolution spectra were recorded using pass energies of, respectively, 100 and 20 eV and step sizes of, respectively, 0.4 and 0.1 eV. Regions of interest were C1s, O1s, N1s, Al2p, Na1s, and Si2p. Additionally, Si*KLL* spectra induced by the Brehmstrahlung of the X-ray source were recorded in the so-called "negative" region of the binding energy scale (kinetic energy ~1610 eV) in order to calculate corresponding silicon Auger parameters. Quantification and peak-fitting were obtained using the manufacturer's software Avantage v*2.18*.

Auger parameters may provide information on whether specific bonds are established at an interface by one particular atom, in this context silicon. Various types are available but it is usually preferable to use core-core-core Auger transitions as they are more likely to reflect variations in electron transfer/polarisability. In this work, the Si2p binding energy and Si*KLL* kinetic energies were used to calculate α^*, the modified-Auger parameter as follows:

$$\alpha^* = \mathrm{BE(Si2p)} + \mathrm{KE(Si}\mathit{KLL}), \tag{1}$$

where BE and KE are the binding energy and the kinetic energy (in eV) of Si2p and Si*KLL*, respectively.

2.3. ToF-SIMS Experiments

ToF-SIMS experiments were performed using a TOF.SIMS 5 from ION-TOF GmbH (Münster, Germany). High mass resolution spectra were recorded from an area of $100 \times 100\,\mu m^2$ over a mass range of 0 to 800 u in both negative and positive mode of detection using the high current bunched mode at 8 kV. A primary Bi^+ beam was used with an energy of 25 keV. Time of acquisition was set at 150 seconds with a cycle time of 100 µs. Mass calibration was obtained using common hydrocarbon ions (H to $C_7H_7^+$ in positive polarity and H to C_6H^-

in negative polarity) and data examined using the manufacturer's software.

3. RESULTS

Table 1 presents the results of the XPS quantification (major components) and Figure 2 shows a comparison of survey spectra for two temperatures, respectively RT and 93°C. The as-received aluminium exhibits a very clean surface with a very small amount of adventitious carbon at less than 17 at %. The aluminium surface is mainly composed of aluminium oxide as indicated by the high amount of oxygen (56.3 at %). The grit-blasting process introduces a certain amount of sodium (11 at %) and also of fluorine (0.7 at %, not shown in Table 1); these are common surface impurities obtained through grit-blasting [5]. The peak-fitted carbon signal of the reference sample is presented in Figure 3 and exhibits four types of chemical species at: 285, 286.8, 289.9, and 291.8 eV with chemical shifts for the last three peaks of 1.8, 4.9, and 6.8 eV, respectively. The first component may be assigned to C-C, C-H type of carbon (label A), the second to C-OH (label B) from traces of solvent left after rinsing (isopropanol) or polar carbon adsorbed at the surface; the third may be assigned to carbonates which is consistent with a shift of 4.8 eV cited in the common literature; and the latter (the highest binding energy) may be due to small amounts of potassium [6]. The presence of potassium at 293 eV is indicated by the K2p3/2 peak. Alternative assignments for the third and fourth components (labels C and D, respectively) are carbons bound to fluorine.

Observation of the data obtained after adsorption indicates that organic material has been deposited on the surface of aluminium as indicated by the increase of carbon, the decrease of oxygen, and the silicon attributed to the presence of the organosilane at the surface of the samples (see Table 1). The heating of the films induces dramatic changes as indicated by the variation of concentrations of all elements:

TABLE 1 Surface Composition Obtained with XPS (at %)

Elements	Al	O	C	N	Si	Na
Al blank	16.8	56.3	14.9	0.0	0.3	11.0
APS RT	8.5	39.2	36.2	6.2	6.5	2.9
50	14.3	49.2	26.0	2.4	2.3	5.6
93	16.6	52.6	21.0	1.4	1.8	6.8
120	15.2	47.7	28.9	1.8	2.1	4.3

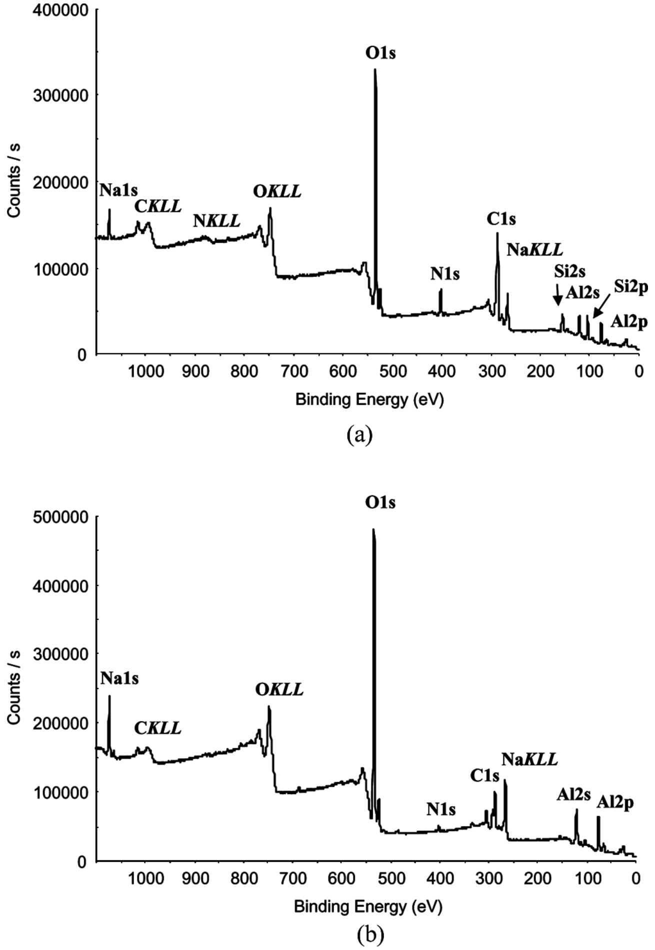


FIGURE 2 (a) Comparison of XPS survey spectra of APS films dried at room temperature and (b) at 93°C.

a reduction in the carbon, nitrogen, and silicon concentrations and an increase of aluminium and oxygen concentration. However, no further dramatic effect of temperature may be noticed on the surface composition upon drying at higher temperatures than 50°C, with a small further decrease in concentration of carbon, nitrogen, and silicon up to 120°C where this sample seems to exhibit more organic material than samples dried at other temperatures. It seems that it may have retained slightly more APS which is presumably due to a slight variability in the drainage of the excess material amongst samples. The

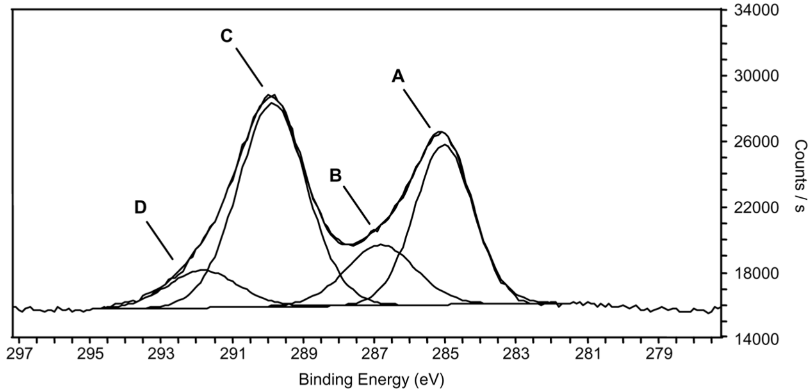


FIGURE 3 Peak-fit of C1s spectrum for reference (untreated) aluminium sample.

drop of concentration above 50°C may be partly assigned to the films' thickness decreasing as a result of drying/curing at temperature, while crosslinking and water evaporation occur at the same time. Through the drying phase a certain amount of silane evaporation is possible as has been shown by Mishra and Weimer [7] which would also result in a reduced amount of organic material on the surface. Another possibility is the formation of a composite phase consisting of both silane and aluminium oxide, hence, changing the anticipated stochiometry of the film resulting in an apparent thinning of the coating. It is also known by the authors that APS (studied in the same conditions) adsorbs according to Langmuir adsorption and, therefore, in a uniform film [8]. Performing peak-fitting of the carbon 1s spectrum may provide further insight within the overall transformation

TABLE 2 Peak-Fitting of Carbon Signal, Binding Energy (relative concentration in brackets)

Carbon	Total concentration (at %)	Carbon			
		A	B	C	D
Reference	14.9	285.0 (30.9)	286.8 (14.0)	289.9 (46.2)	291.8 (8.9)
APS RT	36.2	285.0 (70.8)	286.5 (15.2)	288.6 (9.0)	290.4 (5.0)
50	26.0	285.0 (53.7)	286.7 (17.9)	289.8 (22.5)	291.3 (6.0)
93	21.0	285.0 (46.9)	286.7 (19.8)	289.6 (21.9)	291.2 (11.5)
120	28.9	285.0 (64.5)	286.7 (17.0)	289.5 (12.5)	291.0 (6.1)

the films are undergoing with temperature (see Table 2). Similarly to the reference sample, the carbon signal may be peak-fitted with four components at the following binding energies: 285, 286.5, 288.6, and 290.4 eV for samples dried up at room temperature. However, once the drying temperature is increased at and above 50°C, the chemical shifts obtained for the four carbon components change and seem to shift back to those obtained for an untreated sample, albeit in different amounts. For a drying temperature of 120°C, the carbon signal also indicates a decrease in thickness of the film as the carbonate signal at a chemical shift of approximately 4.5 eV is visible again after heating up. Subtle effects may be seen in variation of the components, intensity as well as variation of the binding energy of the components. The most important effect is visible on the decrease of the C-C, C-H component which may be an indication of evaporation of the molecule as the molecule contains within its structure two carbons that may yield such a binding energy (propyl chain). Other features include a shift of the second carbon increasing from 1.5 to 1.7 eV. This may be partially explained by reorientation of the APS molecules as described by George *et al.* in their "flip-flop" model [9]. Such a model shows that the APS molecule may turn upside down under the effect of temperature and, therefore, if as low a temperature as 50°C may induce this movement, alkoxy functionalities still present in the film would be exposed more than any C-N type of bond, thus increasing the binding energy of the second component. This is because the carbon binding energy associated with nitrogen is lower than when it is bound to oxygen. Conversely, it could also be simply a thickness effect again when the binding energy is reverting to exhibit a surface composition close to that of the initial substrate. Another obvious conclusion to be drawn is that not all carbonaceous material originally present has been displaced by interaction of the silane with the aluminium substrate as indicated by the variations of concentrations of carbon components C and D.

TABLE 3 Peak-Fitting of Nitrogen Signal, Binding Energy (relative concentration in brackets)

Nitrogen	Total concentration (at %)	Nitrogen A	Nitrogen B
APS RT	6.2	399.6 (73.2)	401.1 (26.8)
50	2.3	399.7 (66.3)	401.4 (33.7)
93	1.8	399.9 (66.5)	401.5 (33.5)
120	2.1	399.8 (64.6)	401.3 (35.4)

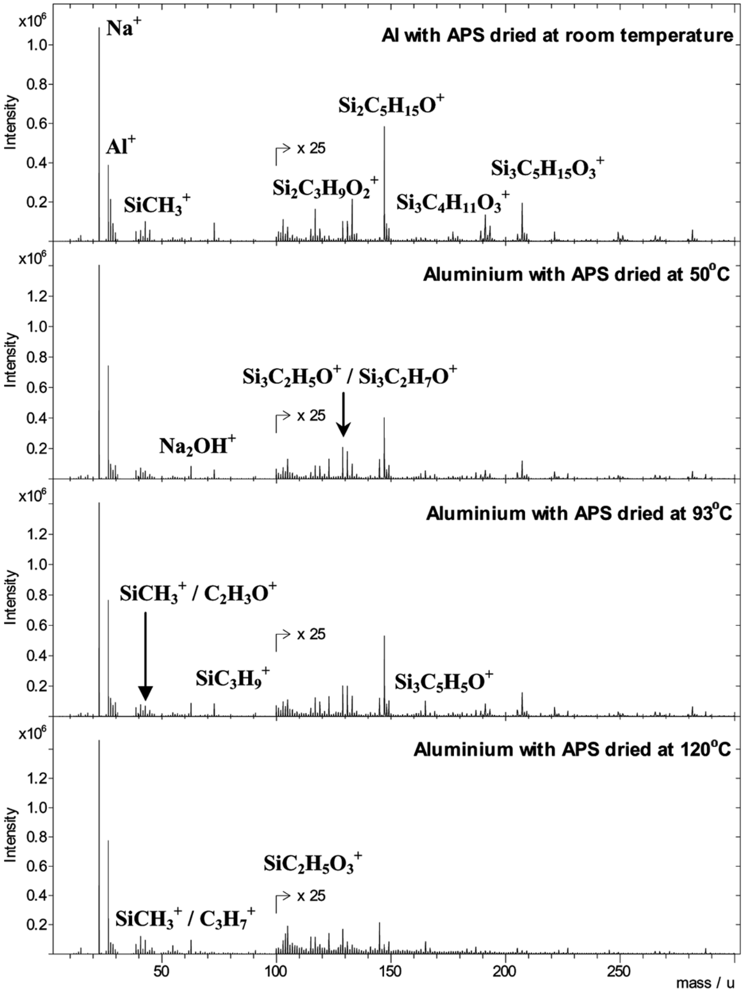
A similar fitting was performed on the nitrogen signal and the results are reported in Table 3. Two components are obtained and while the former corresponds to a "neutral", *i.e.*, non-charged nitrogen, the latter bears a partial positive charge as exhibiting a chemical shift comprised between 1.5 and 1.7 eV compared with the first, neutral nitrogen component. The contribution of the charged nitrogen varies as a function of temperature and increases up to 35.4% of the total N1s signal as a function of temperature. It is also observed that the chemical shift (reliable as obtained within 0.1 eV) of the second component of the nitrogen increases when the temperature is increased above 50°C, indicating an increase in the partial charge borne by this atom and, therefore, of strength of interaction of this nitrogen with other species *via* Lewis acid-base type of bonds like, for example, with the substrate, absorbed CO_2 within the film, or even with neighbouring molecules/species. Although it has been shown that CO_2 may desorb from, for example, aminosilane treated glass fibres when heated up to 100°C [10], hence indicating that an interaction between nitrogen and CO_2 is reduced at temperatures, other explanations are possible, including formation of internal chelate between with nitrogen and silanols functions [11]. Table 4 shows the values for the Auger parameters calculated according to Equation (1). Although small, a drop of 0.2 eV is a noticeable variation and will be considered further in the discussion section. These values are on the margin of error for Auger parameters considering that both binding energies and kinetic energies can be considered correct within a tenth of an eV. However, as these data were reproducible, the authors consider them reliable.

ToF-SIMS analysis was also performed for those samples and spectra are presented in Figure 4 as a function of temperature for both polarities. Peaks of note have been annotated on the spectra. They are, if only the most intense species of the nominal mass are considered: 23(Na^+), intense 27(Al^+) indicating that films are very thin which is consistent with the XPS data, as well as 63(Na_2OH^+) from the

TABLE 4 Silicon Auger Parameter α^* Values *versus* Temperature (eV)

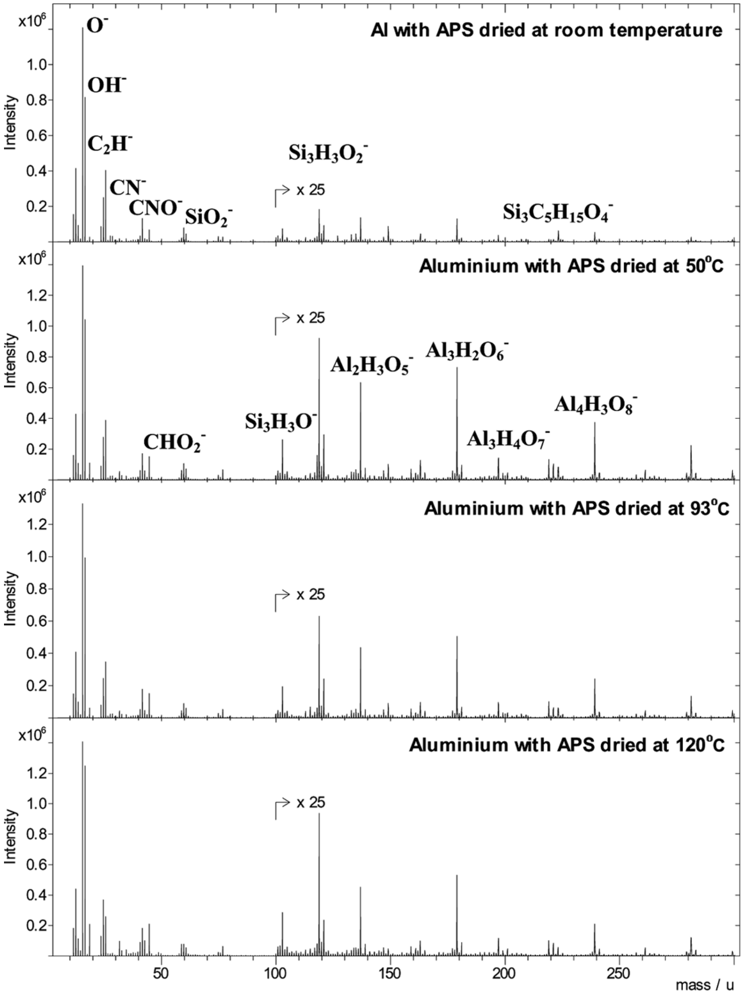
Drying temperature	α^*
APS RT	1712.4
50	1712.2
93	1712.2
120	1712.2

grit-blasting, C_xH_y type of fragments at 41($C_3H_5^+$), 43($C_3H_7^+$), 45($C_3H_9^+$), 55($C_4H_7^+$), and silane-related peaks at 45($SiHO^+$), 59($SiC_2H_7^+$), 91($Si_2H_3O_2^+$), 117($SiC_4H_9O_2^+$), 133($Si_2C_3H_9O_2^+$), and 177($Si_2C_7H_5O_2^+$). In the negative mode, the following corresponding peaks may be found: 26(CN^-), 42(CNO^-), 59($C_2H_3O_2^-$), 60(SiO_2^-), 61($SiHO_2^-$), 77($SiHO_3^-$), 89($SiC_3H_9O^-$), 103($Si_3H_3O^-$), 137($Al_2H_3O_5^-$), 163($Al_3H_2O_5^-$ and $C_{13}H_7^-$), 179($Al_3H_2O_6^-$), and 197($Al_3H_4O_7^-$). It is clear



(a)

FIGURE 4 (a) ToF-SIMS spectra for all temperatures in positive polarity and (b) negative polarity for masses 5 to 300 u.



(b)

FIGURE 4 Continued.

that above a certain mass the most noticeable peaks are aluminium oxide peaks. Also present are various peaks which are identical in mass to that of a common contaminant, poly(dimethylsiloxane) (PDMS) at masses such as 43($SiCH_3^+$), 73($SiC_3H_9^+$), 147($Si_2C_5H_{15}O^+$), 207($Si_3C_5H_{15}O_3^+$), and 221($Si_3C_7H_{21}O_2^+$); similar features are obtained in the negative polarity at 59($SiCH_3O^-$), 75($SiCH_3O_2^-$), 119($Si_2CH_3O_3^-$), 149($Si_2C_3H_9O_3^-$), and 223($Si_3C_5H_{15}O_4^-$) although it has been argued by the present authors that such structures may also originate from polymerization of APS [12]. However, if all spectra are compared as a function of temperature, certain peaks reduce in intensity and disappear seemingly to the benefit of a neighbouring ion. Examples are 73 to 77, 147 to 145, 207 to 205, 221 to 227 and finally 281 to 287 u. Several of these may be explained as the result of the overall film layer decreasing in thickness under the influence of temperature, as indicated by XPS experiments also. Good examples are the couples (207/205) and (221/227) where poly (dimethyl) siloxane-like (PDMS) peaks are "replaced" by aluminium oxide peaks, respectively, $Al_4HO_6^+$ and $Al_7O_2H_6^+$ for 205 and 227, with little variation of intensity above 50°C in agreement with the XPS data. A good indication of the effect of temperature on the film thickness may be obtained by examining the intensity of fragment 27($C_2H_3^+$) *versus* that of aluminium 27 (Al^+); the ratio of the former by the latter is the highest at RT (0.151) with, once again, very little variation above 50°C (ratios 0.048 to 0.051). This is illustrated in Figure 5.

Other effects of the cure temperature can be assessed by examining its effect on the two main reactions that silanes undergo: hydrolysis and crosslinking. Mass spectrometry not only allows assessment of the state of hydrolysis of the silane within the film but also whether it has crosslinked and to what extent. The silane may be present and not have undergone any hydrolysis, although this is unlikely, or hydrolysis of one or two functionalities, or have fully reacted as shown in Figure 1. The relevant hydrolysed and crosslinked structures are provided in Table 5. It shows the masses for various states of hydrolysis to be, respectively, 163 ($SiC_6H_{15}O_3^+$), 135 ($SiC_4H_{11}O_3^+$), 107 ($SiC_2H_7O_3^+$) and 79 u ($SiH_3O_3^+$) in increasing order of hydrolysed

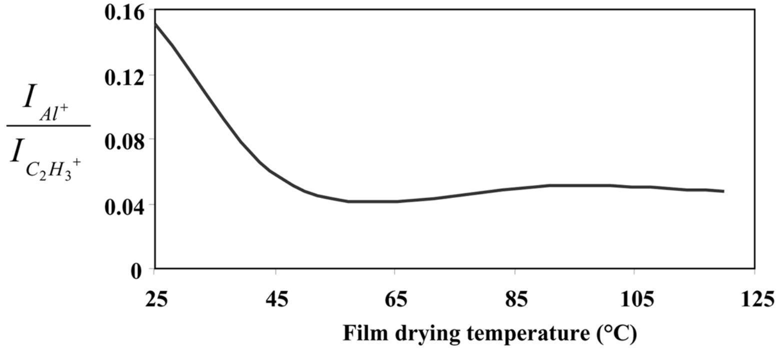
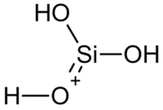
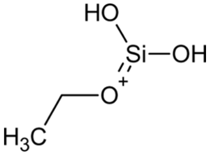
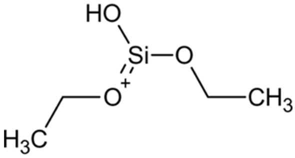
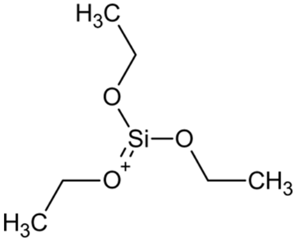
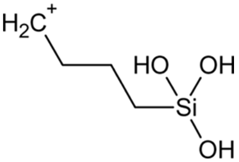


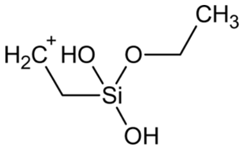
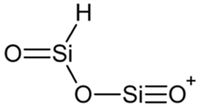
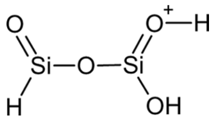
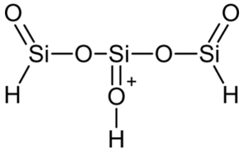
FIGURE 5 Plot of ratio of intensities of Al^+ to $C_2H_3^+$ versus drying temperature.

TABLE 5 Structures of Ions Relevant to Hydrolysis, Crosslinking, and Interaction Phenomena *Versus* Temperature

Bonding at interface APS/aluminium, m = 71 u	$AlOSi^+$
Full hydrolysis, of three alkoxy, m = 79 u	
Hydrolysis of two alkoxy, m = 107 u	
Hydrolysis of one alkoxy, m = 135 u	
No hydrolysis at all, m = 163 u	
Alternative assignment to 135: hydrolysed silane with remaining alkyl chain (n = 4)	

(*Continued*)

TABLE 5 Continued

Bonding at interface APS/aluminium, m = 71 u	$AlOSi^+$
Alternative assignment to 135: Two silanols with remaining alkyl chain (n = 2)	
Crosslinking, m = 105	
Crosslinking, m = 123	
Crosslinking, m = 167	

silanols, in the positive mode of detection. To illustrate the presence or absence of those peaks, an example of those masses is shown in Figure 6 representing room temperature. This figure indicates that mostly only the ions of mass 79 and 135 are present with an intense $SiH_3O_3^+$ indicating that APS must have reached full, or very close to full, hydrolysis in spite of the absence of water within the system. It may seem paradoxical that only fragments corresponding to full or only one hydrolysis may be present but this may be explained relatively easily: the structure corresponding to mass 135 u may be rearranged to be yielded by a fully hydrolysed silane bearing an extra CH_2 compared with the APS chain, probably originating from an impurity. Another possibility matches a structure for an ion yielded from a molecule having undergone hydrolysis and formed two silanols and still bearing part of the initial propyl chain of APS. Those two alternative structures are also presented in Table 5.

Crosslinking may be examined according to two types of reasoning, either by checking the relative amount of water present in the film as

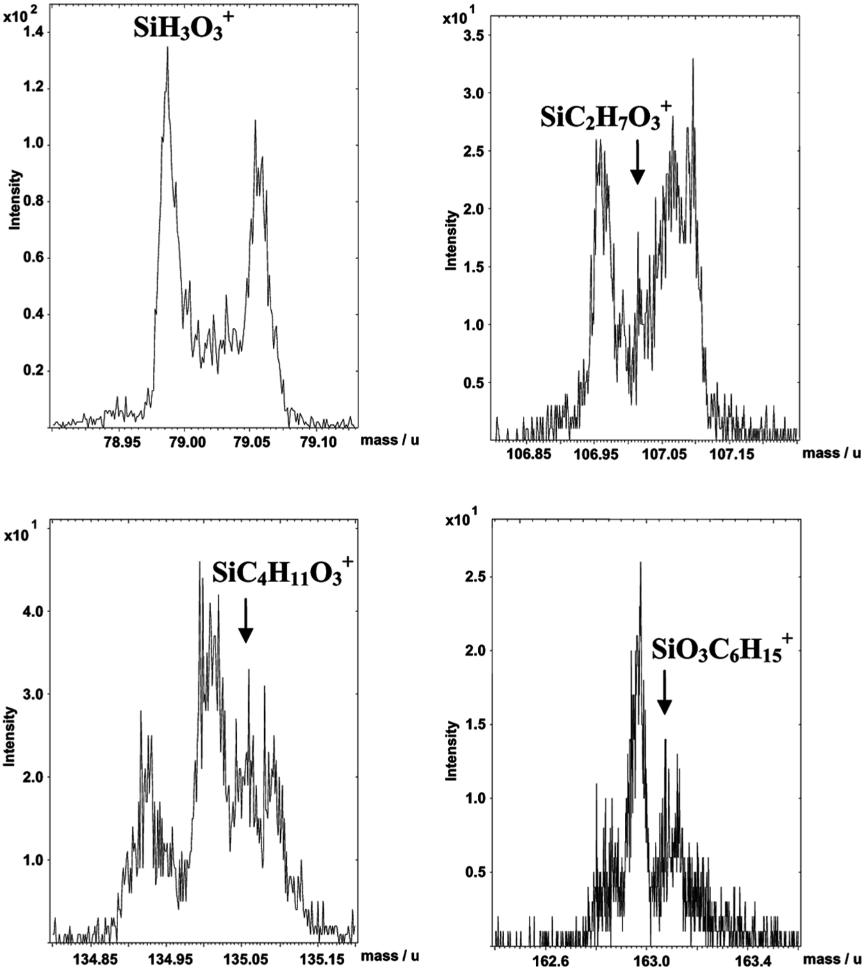


FIGURE 6 ToF-SIMS spectra at high mass resolution for mass 79, 107, 135, and 163 u for sample dried at RT.

it is produced through crosslinking or by examining the presence and relative intensity of ions containing at least two atoms of silicon, as this is only theoretically possible when oligomerization occurs between two (or more) molecules of APS. The latter is a more reliable diagnostic as water may be absorbed from the ambient atmosphere and also be partially pumped out within vacuum instruments. Therefore, in this work ions such as 105 ($Si_2HO_3^+$), 123 ($Si_2H_3O_4^+$), and 167 ($Si_3H_3O_5^+$) have been used as they contain more than one silicon; hence, they

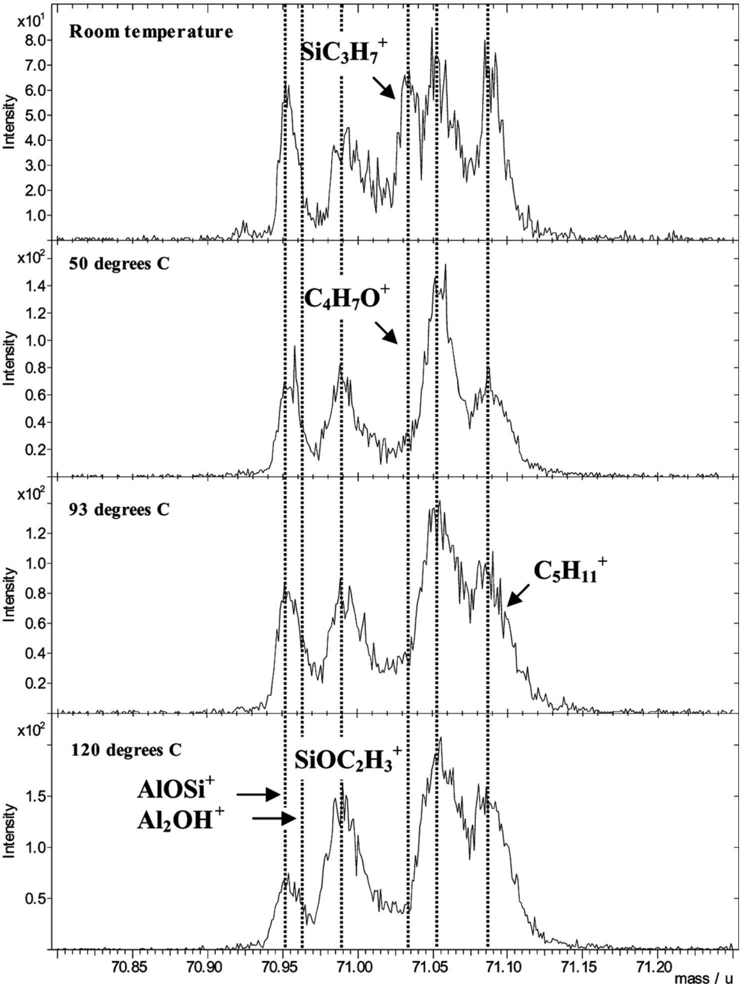


FIGURE 7 ToF-SIMS spectra at high mass resolution for nominal mass 71 for all temperatures used in this work.

illustrate crosslinking and are different from peaks that may be yielded from PDMS.

Mass spectrometry data may also be used for assessment of the bonding as shown in previous work [13]. The presence of covalent bonding may be assessed by checking the presence of the Al-O-Si$^+$ ion at nominal mass 71 u in the positive mode of detection. An example of the peaks obtained at this mass is given in Figure 7, for all temperatures considered in this work. The main difficulty in assessing the presence of this specific bond resides in obtaining a sufficient mass resolution so that $AlOSi^+$ may be separated from a neighbouring ion, Al_2OH^+. The difference in mass between those two ions is equal to 12.44 mu. Figure 7 shows the nominal mass 71 region with the position of these two ions for all samples of this study as well as other ions present in the same mass window. It also, incidentally, shows that bonding has occurred at all temperatures.

4. DISCUSSION

Various effects may be encountered while using temperature to dry a film of silane deposited on a substrate. First and foremost, evaporation of water may be anticipated if a temperature approaching 100°C is used. However, a solution of silane may contain several forms of the molecule from the unhydrolysed form through the three steps of hydrolysis and also probably some oligomeric forms. Hydrolysis of APS will produce some ethanol and condensation will produce some water. Besides, the solution itself was prepared in ethanol and one would also anticipate loss of ethanol if some has been retained after drying only at room temperature; the boiling point of ethanol is 78.4°C, which is below some of the temperatures used in this work.

It is also anticipated that the crosslinking will change as heating also brings energy for new bonds to form *via* condensation of silanols. It has been shown for γ-glycidoxy propyltrimethoxy silane (GPS) that the amount of Si-O-Si bonds increases with temperature when compared with room temperature which, in essence, indicates an increase of crosslinking density [14]. The effect of the temperature may also be damaging and inspection by RAIRS of the effect of drying a thin film of GPS has shown that the epoxy ring opens to form a carbonyl functionality when dried at 180°C [14]. Obviously, this is a deleterious effect on the capability of the silane film to act as a primer with an epoxy adhesive and such indications are noteworthy when connecting the parameters used to form the film with subsequent durability. It is not known if such an effect may be anticipated for APS, but this should be kept in mind. Fragment structures illustrating the state of hydrolysis of the organosilanes molecules are given in Table 5 together with those illustrating the presence of crosslinking of the silane. One of the main questions is concerned with the effect of the temperature on bonding of silane at the aluminium/film interface. Such bonding has been shown previously by several authors to lead to the $M\text{-}O\text{-}Si^+$ ion, where M corresponds to the metal used as substrate, be it iron ($Fe\text{-}O\text{-}Si^+$) [15,16], aluminium ($Al\text{-}O\text{-}Si^+$) [13,17] or zinc ($Zn\text{-}O\text{-}Si^+$) [17]. All those phenomena may occur to various degrees and this communication aims to bring, at least, partial answers to all these questions. To this effect, relative peak intensities using the total ion signal have been calculated and are reported in Table 5.

4.1. Assessment of Hydrolysis and Crosslinking

This may be achieved by looking at the presence, or absence of the peaks corresponding to the various states of hydrolysis. Figure 6 shows the peaks of interest for hydrolysis for the sample dried at RT. These peaks have been chosen on the basis that they represent fragments that correspond to states of hydrolysis. No full fragment of hydrolysed APS was detectable in the spectra, presumably because we are dealing with a structure containing extensive crosslinking. From the spectra it is obvious that the state of hydrolysis is advanced as no ion at nominal mass 163 and a very small ion at 135 u may be seen. It is well known that amino functionalised silanes are auto-catalysed both for hydrolysis and condensation (be it polymerization or bonding on the surface) and this is consistent with the absence of the ions cited above [18]. This is quite remarkable as no water was added to the system and that any water necessary for the hydrolysis would have to be found as traces on the substrate or being absorbed from ambient atmosphere around the sample (assuming that APS goes through hydrolysis before polymerising). The latter has certainly been shown to happen; for example, Kent and Yim have shown that unfunctionalised silane films prepared with bis(triethoxysilyl)ethane (BTSE) exhibit an increase of deuterium concentration near the inner portion of the film when exposed to an atmosphere of D_2O [19]. This work also shows that the variation occurs upon hydrolysis of the ethoxy and formation of Si-O-D. In this work, water incorporated will certainly not be in as high a concentration as for films conditioned in a humid environment. Nevertheless, this smaller effect will certainly be mitigated by the fact that the polarity will invariably be higher for an APS film compared with BTSE (apolar) and, hence, the films in this work should absorb water more easily. It is also possible that water was present at trace level within the solution.

Figure 8 shows the peak at 79 u at high mass resolution at all temperatures. On this figure the peak corresponding to the fully hydrolysed silane [$Si(OH)_3^+$; $m/z = 78.9872$ for the sample prepared at room temperature] is readily observed until a temperature of 93°C but is markedly reduced in intensity at 120°C. The presence of this peak at such intensity indicates that a fair amount of, to full, hydrolysis has occurred even with the deliberate absence of water within the solution. The disappearance of the peak at high temperature is likely to be connected to increased crosslinking within the film which, in turn, will consume lone molecules and, hence, prevent easy formation of this particular structure. One should also note that

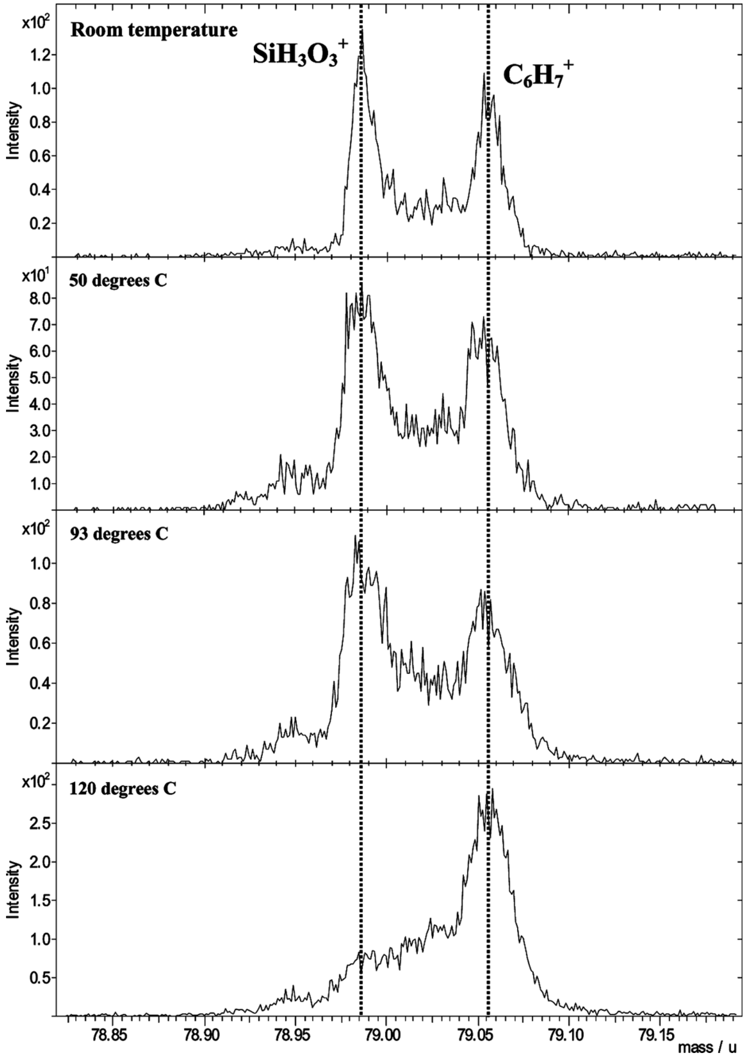


FIGURE 8 ToF-SIMS spectra at high mass resolution for nominal mass 79 for all temperatures used in this work.

the disappearance of this peak indicates a threshold for full cross-linking which seems to occur close to 120°C. The structure given in Table 5 at mass 163 u corresponds to the unhydrolysed specie and is shown in Figure 6 and its absence is clear in the ToF-SIMS spectrum. This indicates that there is not any of the first species left and that, at least within the depth of analysis available to ToF-SIMS no pure APS remains. A similar (very low intensity) situation is found for peaks representing one or two hydrolysed alkoxy functionalities and, hence, shows that close to a full hydrolysis has occurred within the film without any addition of water. This finding also removes any doubt as to whether the state of APS solution hydrolysis will have an effect on the film structure. Relative peak intensities (RPIs) were calculated for the peak at m/z = 79 u illustrating full hydrolysis as a function of the total ion signal by dividing the integrated (area below peak) intensity by that of the total ion signal. Those data are reported in Table 6. In agreement with the aspect of the spectra at nominal mass 79 as shown in Figure 8, the proportion of the peak representing $SiH_3O_3^+$ is reduced overall with increasing temperature.

It has also been shown that drying of silane films at temperature induces loss of water which, in turn, induces further crosslinking [14]. It is, therefore, anticipated that the intensity of ions originating from crosslinking should increase with temperature. This, of course, may be hindered by any change of the structure itself if it induces matrix effects which prevent formation of ions illustrating crosslinking formation within the silane film. Another possible consideration consists of the fact that a highly crosslinked system will be inherently very brittle, not only mechanically but also under the effect of an ion beam, resulting in a large amount of uninformative small fragments in the spectra. Table 6 exhibits the relative peak intensity of fragments believed to illustrate the amount of crosslinking present in the thin film, *i.e.*, containing more than one silicon (crosslinking will induce bonding of two molecules *via* silanols). The lowest possible mass is set at 105 u ($Si_2HO_3^+$), followed by 123 u ($Si_2H_3O_4^+$), and 167 u ($Si_3H_3O_5^+$). Similarly to RPIs calculated for hydrolysis reactions, all fragments exhibit an overall increase in intensity. Another type of

TABLE 6 Relative Peak Intensities for Peaks Illustrating Hydrolysis, Crosslinking, and Interaction Phenomena *Versus* Temperature (all *E-04)

	71		79		105		123		167	
RT	2.5	*40.8*	5.2	*85.9*	4.2	*70.7*	2.8	*47.1*	1.3	*21.7*
50	3.1	*132.9*	5.0	*212.9*	5.8	*248.5*	13.3	*569.9*	2.8	*117.8*
93	3.5	*134.5*	5.9	*230.6*	5.5	*215.4*	12.4	*481.7*	2.9	*114.0*
120	2.8	*158.3*	4.3	*243.7*	6.4	*359.7*	15.9	*898.9*	3.3	*187.4*
Trend	up ∼	up	down ∼	up ∼	up ∼	up ∼	up ∼	up ∼	up	up ∼

RPI = relative peak intensity, ions are reported: relative to the total ion counts for regular numbers, relative to silicon 28 for numbers in italics.

normalization consists of using the silicon signal. In this case, the intensity shows a marked first increase from RT to 50°C then another sharp increase at 120°C; this indicates that increasing the temperature from RT to 50°C induces an important onset of crosslinking within the material but there is another onset at 120°C, more noticeable on the ions at 123 and 167 nominal mass. This probably coincides with elimination of water which, in turn, induces reactions between silanols present in the film. One could argue that the matrix effect may be different according to the temperature of drying/curing but the fact that the same behaviour is obtained whether the calculation is obtained using the total ion signal or the silicon intensity is a counter argument to this assumption.

The values of Auger parameters are slightly more difficult to decipher as contributions of all possible variations in structure and chemistry may be reflected in α^*. However, the signal obtained by ToF-SIMS shows that the bond has already formed at room temperature. This is probably an indication that the Auger parameter decrease is an illustration of the effect of crosslinking within the film rather than interaction at the interface itself between the silane and aluminium. A definitive answer might be provided by coating a non-interacting metal, such as gold, to assess the value of the Auger parameter for a small interaction. This would mirror the approach of Kinloch *et al.* who have shown that interaction of silanes may be inferred from an Auger parameter obtained using the *KLL* transition and Si1s core-line [20]. It is important to stress, however, that although literature is available for Auger parameters using the *KLL* and Si1s core-line, the values of the Auger parameters defined with Si2s or S1s are very close as shown by Riviere *et al.* [21]. Assuming that variations should be identical whether Si2s or Si2p is used, the variation of the parameter calculated with Si1s changes by a maximum value of 0.25 eV, which is not a significant variation. It has also been shown that the Auger parameter may be used to determine coordination of silicon in silicates [22]. In this work, the values of 1712.2 and 1712.4 are consistent with the formation of structures close to solid silica and almandine (1712.2 and 1712.4 eV, respectively) [22]. The stochiometry of silica is of two oxygens for one silicon, whereas that of almandine ($Fe_3Al_2(SiO_4)_3$) is of four oxygens for one silicon. Once again, this reinforces the view that the variation of the Auger parameter is induced through crosslinking rather than bonding at the interface. Besides, it has been shown by Kinloch *et al.* that bonding through a silanol is illustrated by the increase of an Auger parameter rather than a decrease as shown in this work [20]. More general data obtained through XPS analysis and quantification do not provide further details concerning hydrolysis and crosslinking though a thinning of the film may be related to shrinking due to crosslinking and loss of volatiles such as water and ethanol.

4.2. Assessment of Bonding to Substrate and Interactions

The only definite proof that a silane has bonded that may be provided using surface analysis data is the presence of an Al-O-Si$^+$ fragment at nominal mass 71 in the ToF-SIMS spectra (see Figure 7). The accuracy is provided in ppm and is obtained by subtracting the experimental mass from the exact mass and dividing the result of this operation by the theoretical mass. Other peaks are visible and may be assigned as follows for the spectrum at RT: first peak: AlOSi$^+$, (−3.4 ppm); second peak: $SiC_2H_3O^+$, (−61.1 ppm); third peak: $SiC_3H_7^+$, (11.7 ppm), ppm), $C_4H_7O^+$, (7.8 ppm); fourth peak: $C_5H_{11}^+$, (12.9 ppm) for the sample prepared at room temperature. It is rather noticeable that the resolution decreases with increasing temperature and only four peaks are noticeable at and above 50°C. This may be attributed to the increase of relative roughness of the region examined; an increased effect of the roughness of the sample introduced either through grit-blasting or oxide growth is visible. The rougher the sample the smaller the observed mass resolution as the range of flight times for any secondary ion increases and, hence, a worse mass resolution is obtained. It is interesting to note that all samples exhibit the AlOSi$^+$ fragment and, therefore, indicate bond formation between APS and aluminium implying that no temperature threshold is necessary to induce bonding, this effect being probably due to the autocatalytic nature of the APS molecule. Table 6 shows the RPIs for this fragment for all samples and as a function of temperature. The RPI of AlOSi$^+$ may provide some insight on whether the intensity of this fragment changes with temperature. The RPI of AlOSi$^+$ increases as a function of temperature then decreases at 120°C. A similar calculation using the silicon (28) signal indicates a continuous increase. Overall, this seems to indicate that the number of bonds is increasing at the aluminium/APS interface. This may be partly attributed to the oxide growth through the organic film forming a composite structure. This is consistent with the concentration of aluminium and oxygen reaching surface concentration values which are almost equivalent to that of pure aluminium while the carbon never decreases totally. This is probably an indication of oxide growing through the organic layer while drying under temperature as has been demonstrated before using, for example, TEM experiments to view the structure of silane films deposited on aluminium [23].

It has been shown in previous literature that APS films easily absorb moisture and CO_2 from the surrounding atmosphere [9]. The presence of both molecules induces reaction of the nitrogen of the silane with formation of ammonium bicarbonate close to the interface with the air. It is not simple to determine the amount of bicarbonate induced through CO_2 absorption as we witness the simultaneous effect of film thinning and interaction with CO_2. If we assume that the amount interacting with CO_2 remains constant then any increase of charged nitrogen is the consequence of the NH_2 side of the silane interacting with the surface or within the film itself [11]. It is, however, known that CO_2, if present at the surface of glass fibres because of the presence of APS, can desorb when treated to a temperature above 100°C [10] which reinforces the above explanation. It has also been shown that if the silane first interacts at the substrate surface with the NH_2 functionality *via* hydrogen bonding ($-NH_3^+$), treatment with temperature decreases this functionality. Therefore, it is highly likely that we are dealing with a non-oriented film for which the temperature effect results in further interactions either at the surface or within itself. The intensity of the nitrogen signal is constant after 50°C but the amount of charged nitrogen rises from 26.8% at RT to 33.5 at 93°C then only slightly to 35.4 at 120°C. Although both interactions are probably present at any temperatures the film getting thinner with temperature renders more obvious that APS interacts with both sides, silanol and amine. There is also the possibility that some of the APS molecules have changed conformation, thus, inducing a different type of shift on the second component of the peak-fitted carbon as shown in the results section.

If all those results are put within the perspective of adding a silane to an adhesive formulation the following may be expected: it is anticipated that all necessary reactions (hydrolysis, condensation, bonding to substrate) will occur. A similar study using different temperatures for curing the adhesive will be performed to assess whether the crosslink density may be detrimental to durability. It is highly probable that there will be an optimum curing temperature for which the durability of a joint formulated with APS will also be optimum.

5. CONCLUSIONS

The effect of temperature on the hydrolysis, crosslinking, and bonding to substrate and possible interactions of thin films of APS on aluminium substrate has been studied using both XPS and ToF-SIMS. Analysis of the obtained data leads to the following conclusions:

- The films are thinning down with temperature with probable growth of an oxide within the organic material deposited on aluminium.
- Hydrolysis occurs without adding any water to the APS/ethanol mixture. The films absorb neighbouring water which, in turn, and with the help of the autocatalytic properties of APS induces close to a full hydrolysis reaction.
- There does not seem to be any temperature threshold for bonding of APS to the substrate. It occurs even at room temperature.
- There seems to be a threshold for full crosslinking of the APS films at 120°C.
- No APS monomer remains.
- The variations of the values of the final state Auger parameter are related to the crosslinking rather than to the bonding of APS to aluminium.

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