



# The effect of silane incorporation on a metal adhesive interface: A study by electron energy loss spectroscopy<sup>☆</sup>

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## ABSTRACT

A silane-based adhesive formulation, used in the aerospace industry, was studied using sub-nanometre spatially resolved energy loss spectroscopy, as a function of the concentration of silane used in the adhesive. The changes in the relative oxygen concentration and the occupancy of p-type states in the oxygen density of states reveal the existence of a composite layer between the aluminium and the epoxy resin. This composite layer is prevalent in the 1% (w/w) organosilane sample, whilst it is smaller or absent for the 0.5% and 2% (w/w) silane concentration. These observations correlate well with the observed macroscopic durabilities observed when these adhesives are used for the structural adhesive bonding of aluminium aerospace alloys.

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## 1. Introduction

Adhesive bonding technology is of foremost importance for the aerospace industry. Light-weight alloys, usually based on aluminium, are used for this type of application and a pre-treatment is employed to prepare the surface in order to create the appropriate roughness and chemistry to allow adhesive bonding to be successful. However, some of the treatments involve the use of chromium containing solutions based on Cr(VI) (Bryson and Goodall, 1983) which is highly toxic and also necessitates specific and expensive recycling of the waste chemicals employed for the process. One alternative methodology consists of using organosilane-based adhesion promoters such as aminopropyl triethoxy silane (APS). When such a molecule is used as a primer (optimized process) on aluminium, the durability obtained is similar to that for chromic acid-anodizing pre-treatment and it has also been shown that a covalent bond is formed between aluminium and  $\gamma$ -glycidoxy propyl trimethoxy silane (GPS) as well as between an epoxy adhesive and GPS (Abel et al., 2000; Rattana et al., 2002).

The obvious next step is to incorporate the silane into a formulation rather than as a primer. Epoxy formulations of this type are already available as commercial products and it is proven

that the incorporation of silanes improves the strength but more importantly the durability of bonded joints (Sautrot et al., 2005; Sautrot, 2003; Makama, 2005). It has also been shown that silanes incorporated within the same system, as described here, migrate to the interface between the aluminium surface and the adhesive and that the concentration of silane present at the interface is similar for a typical range of concentrations employed (Abel et al., 2007). However, as the performance of a joint is also related to the amount of silane present in the adhesive, further study of the chemistry of the interface is necessary. In previous work, X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS) have been used to examine samples prepared by ultra-low angle microtomy but it is necessary to perform the analysis at a better spatial resolution than available with these methods (Abel et al., 2007). Hence, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) have been used in this work to examine the chemistry of oxygen in the aluminium oxide at an interface. Three concentrations of organosilane were employed and it was found that 0.5% and 1% (w/w) improve the performance and durability whereas a 2%-containing adhesive yields results close to an adhesive with no silane at all. In order to investigate the nature of the bonding across the extended aluminium–epoxy interface, we use sub-nanometre spatially resolved electron energy loss spectroscopy in a model system. In particular, we examine the empty density of states of oxygen across the interface and reveal the existence of a composite interfacial layer, which goes some way to explain the observed macroscopic durability tests.

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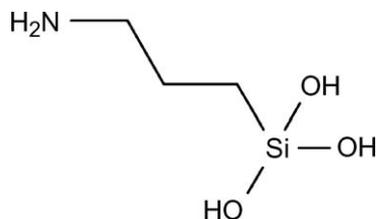


Fig. 1. APS formula in its hydrolysed state.

## 2. Experimental

### 2.1. Sample preparation

Model adhesive joints were prepared by encasing an aluminium foil within an organic resin adhesive. The resin, based on a toughened epoxy system and cured using a bifunctional amine, was prepared with three different concentrations of aminopropyl triethoxysilane (APS): 0.5%, 1% and 2% (w/w). A regular kitchen aluminium foil was used and no particular precautions were taken to minimise the formation of the native oxide. The structure of APS in its hydrolysed state is shown in Fig. 1.

The samples were then cured overnight at room temperature, followed by a post-cure of 2 h at 60 °C. To obtain electron transparent sections of the aluminium/adhesive interface, a small piece of the model joint was embedded in a mounting resin (Araldite Resin Agar CY212 premix kit hard, Agar Scientific) within a capsule (Beem capsules, G360-2, Agar Scientific) and cured at 60 °C for 48 h. The sample was then removed from the capsule and trimmed firstly with a freshly prepared glass knife and then thin slices were cut using an ultra-microtome (Reichert Om U3) equipped with a diamond knife, using a method described elsewhere (Furneaux et al., 1978; Toner, 2007). The cut was performed perpendicular to the surface of the aluminium foil. 70 nm-thick sections were collected on 200-mesh copper grids.

### 2.2. TEM and EELS analysis

The samples were examined in a Philips CM200 TEM (LaB<sub>6</sub> filament, 200 keV acceleration voltage), equipped with a Gatan imaging Filter (GIF 2001, 1 k × 1 k CCD). Spatially resolved EELS spectra were acquired on a Hitachi HD2300A scanning transmission electron microscope (STEM), with a 200 keV accelerating voltage and a probe diameter of ~2.5 Å. This instrument is equipped with a Schottky field emission gun (FEG) source and a Gatan Enfina electron spectrometer. In order to characterise the properties of the oxide layer present between the aluminium foil and the adhesive, spectra containing the oxygen K edge (~532 eV) were collected at a dispersion of 0.2 eV/channel and exposure of 2 s per spectrum, with the beam stepped across the interface every 8 Å, at a 14 mrad collection semi-angle. The beam was stepped at an angle of about 45° across the interface so as to limit the amount of damage to the oxide layer between successive points. The

oxygen profile of the oxide layer was recorded for samples with different concentrations of APS: 0.5%, 1% and 2% (w/w) in similar images. To do so, core loss spectra are acquired in a line scan conducted across the aluminium/adhesive interface, starting in the aluminium foil and ending in the epoxy adhesive. Such line scans are acquired over the interface recorded from a high angular dark field image of the interface cross-section.

## 3. Results

Fig. 2 shows a composite image of a section of an aluminium foil embedded within a resin containing 1% (w/w) of APS obtained from several TEM images. The extreme top left and bottom right hand side of the image correspond to the epoxy resin and as anticipated, exhibit a presence of nodules assigned to the second phase of toughening copolymerised additives (Kinloch and Young, 1983).

The composite image shows the embedded Al foil, with the polished side on the right and the rough side on the left of the image. Note that the rough side has only small voids, where the adhesive has detached from the Al, whilst on the polished side, the adhesive has become completely separated. This shows the role of the surface morphology in the resulting strength of the adhesive joint. The polished side is preferable for investigation in transmission electron microscopy as it has a well defined interface and it is unlikely that the chemistry of the bond is any different to the rough surface unless some chemical process was involved in the polishing process. Nevertheless, a region that is still bonded must be carefully chosen on the polished side of the Al joint.

On such a region of the specimen, spectra of the oxygen K edge were recorded in order to analyse possible variations of the aspect of the peak as well as quantifying the relative amount of oxygen along the thickness of the oxide layer. The silicon L edge was also of interest but attempts to record similar spectra in a limited time of exposure only produced noisy data because of the low concentration and the lower and broader cross-section of the silicon L-edge. Therefore further work concentrated on examining the oxygen K edge spectra and related data across the aluminium/adhesive interface, on the polished aluminium side.

Fig. 3 shows a typical core-loss EELS spectrum of the oxygen K edge for a section of the oxide layer between the aluminium foil and the epoxy adhesive, together with the windows of integration used for comparing the relative occupancies of the oxygen p-orbitals.

This spectrum is typical of the oxygen K edge peak for  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) (Brydson, 1996). If the sample were  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, a pre-peak would have been observed at 528 eV, even after an exposure time of 20 s per spectrum with a sub-nanometre focused probe (Jiang and Spence, 2006). In addition, other studies on aluminium oxide at the same experimental conditions (probe size, probe current) have demonstrated that a change of the alumina phase from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> occurs only after 60 s of exposure (Toner, 2007). Hence, care has been taken to record spectra in a limited exposure time (2 s/spectrum) so as to limit the damage to

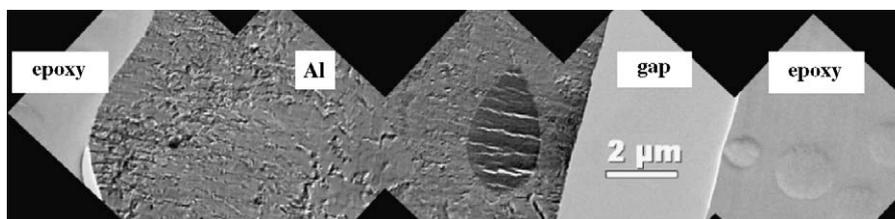
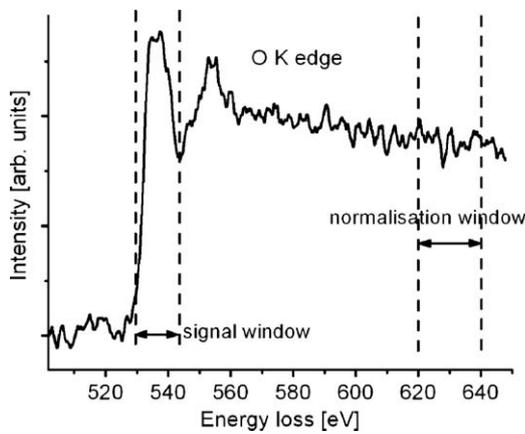
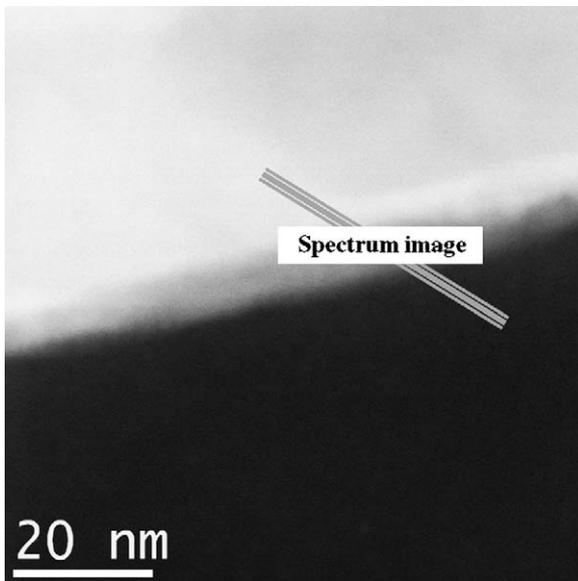


Fig. 2. Composite image of the cross-section of a sample containing 1% (w/w) of APS showing the aluminium/adhesive interface from several TEM images. The dark inclusion in the foil is likely to be an iron and silicon rich intermetallic, typical of those found in commercial alloys.



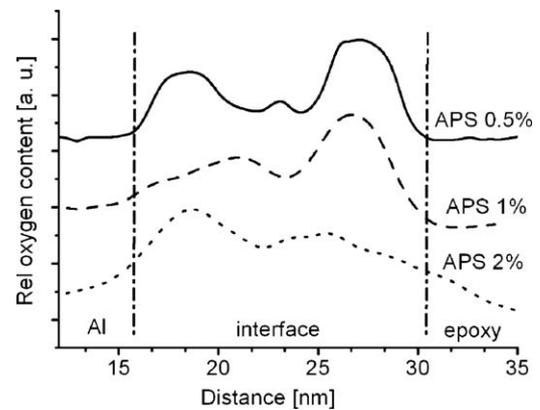
**Fig. 3.** EELS spectrum of the core loss region of the oxygen K edge along the aluminium oxide layer for a sample containing 0.5% (w/w) of APS. Also shown on the spectrum are the integration windows used for measuring the relative occupancy of the oxygen 2p orbital and for normalisation, respectively.



**Fig. 4.** High angle annular dark field (HAADF) image of the aluminium/adhesive interface for an adhesive containing 0.5% (w/w) of APS, with the line across which spectra are collected, typically running at an angle to the interface so that beam damage is reduced. Data extracted is presented on a position scale adjusted for the angle of the scanned line.

the sample. Fig. 4 shows a high angle annular dark field (HAADF) image recorded in the STEM of the aluminium/adhesive cross-section for an epoxy adhesive containing 0.5% (w/w) of APS. This figure indicates the respective regions as white for the aluminium foil, black for the epoxy adhesive and grey for the aluminium oxide layer.

The dark field (DF) core loss profile is recorded simultaneously with the core loss spectrum in the range [530–640 eV] where the oxygen K-edge signal appears. Then, the relative oxygen content over the oxide layer can be calculated from the area under the oxygen K-edge in the interval [532–548 eV] (the signal window as seen in Fig. 3), after background subtraction. The relative content of oxygen is then corrected for the thickness variations by dividing by the relative thickness measurements. To do so, low loss spectra are acquired to determine the relative thickness profile of cut sections, using the log-ratio method. The relative thickness ( $t/\lambda$ , where  $\lambda$  is



**Fig. 5.** Graph representing the relative oxygen content over the oxide layer for the various APS concentrations, obtained from EELS spectra. At 0.5% APS, the oxygen profile is bi-lobar, whilst at 1% and 2% the oxygen concentration has only one maximum, near the silane and near the Al respectively. The spectra are displaced for display purposes.

the inelastic mean free path) is a measure of the stopping power of the material:

$$\frac{t}{\lambda} = \ln\left(\frac{I_t}{I_{z1}}\right) \quad (1)$$

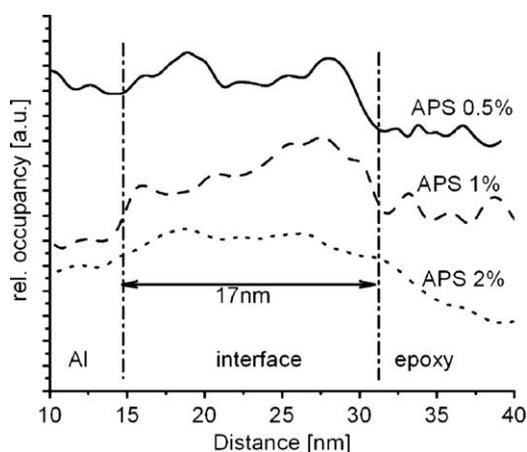
where  $t$  is the specimen thickness,  $\lambda$  the inelastic mean free path of the electron considered,  $I_t$  the total intensity below the energy loss spectrum (all incident electrons) and  $I_{z1}$  is the intensity below the zero-loss peak (all elastically scattered electrons) (Egerton, 1996). Both low loss and core loss spectra have been collected at the same location across the interface.

It is then possible to compare the relative oxygen contents at the interfaces prepared with different concentrations of silane. Fig. 5 shows a graph where relative concentrations of oxygen are plotted in increasing order of silane concentration.

The thickness of the oxide is evaluated as 17 nm overall, which is more than the thickness of an aluminium native oxide, usually of the order of a few nanometres (Uhlir and Winston Revie, 1985). The sample prepared with a resin containing 0.5% (w/w) of APS exhibits two distinct peaks, of similar intensities, with an oxygen deficiency in between, whereas the other two specimens exhibit a concentration of oxygen that either increases or decreases slightly from the aluminium foil to the epoxy for the sample prepared with 1% and 2% (w/w) of silane respectively. This implies that, according to the concentration of silane, the oxygen content varies: the amount of oxygen is higher close to the resin if 1% (w/w) of APS is used, whilst it is higher close to the aluminium metal if 2% (w/w) is used.

The graph of the relative occupancy of oxygen orbitals is shown in Fig. 6.

The relative occupancy is derived in a similar manner to the occupancy for 3d transition metals (Pearson et al., 1993): the scattering cross-section is proportional to the number of empty states in the valence band, therefore the area below the energy window [532–548 eV] is a measure of the occupancy of the valence band, when normalised to the theoretical (hydrogenic or Hartree-Slater) scattering cross-section far away from the edge onset (see Fig. 4 for the definition of the integration windows). This can be approximated to the area in an energy window far away from the edge [640–660 eV] (normalisation window as seen in Fig. 3) where the extended fine structure oscillations have dampened and where the theoretical and experimental cross-sections converge. As in Fig. 5, the sample prepared with 0.5% (w/w) of APS exhibits two peaks of similar intensity indicating a similar oxygen stoichio-



**Fig. 6.** Graph representing the relative occupancy of the oxygen orbitals for the various APS concentrations, obtained from EELS spectra. The behaviour is similar to that in Fig. 5. The plots are displaced for display purposes.

metry in those two regions with depletion in the centre. The other two specimens exhibit a different behaviour with an increasing relative occupancy for 1% (w/w) APS and a slowly decreasing relative occupancy albeit quasi-constant for a 2% (w/w) APS specimen. Once again this shows that both the oxide stoichiometry and/or chemistry can be altered according to the concentration of silane used in the formulation.

#### 4. Discussion

Fig. 5 shows the relative concentration of oxygen from aluminium through to the epoxy resin. The width of the first peak of the oxygen-concentration trace for the sample prepared with 0.5% (w/w) is estimated at 5 nm, which is consistent with the thickness of a native aluminium oxide (Uhlig and Winston Revie, 1985). However, the thickness of the oxide for all samples, is greater, at 17 nm. This implies that further growth occurred after treatment of the foil, probably when undergoing curing of the adhesive at temperature. The only difference in the treatment amongst the samples was the amount of silane incorporated within the adhesive and, according to Fig. 5 varying amounts of silane seem to have different effects on the oxide at the interface. At this stage, we compare only the relative variation of the oxygen concentration. Usually oxide growth occurs by cation diffusion, which means that it grows from bottom to top (Shrier et al., 1994), i.e. from the already existing oxide towards the adhesive deposited. Hence, the extra oxide thickness may result in the formation of a composite layer, with a mix of aluminium oxide and organic material present at the interface (Kinloch et al., 2000; Watts et al., 2004).

When a silane is added to a formulation, it is anticipated that it will migrate and form bonds at the interface with the chosen substrate, thus making the two materials more compatible and facilitate the bonding process, whilst increasing durability at the same time (Sautrot et al., 2005; Makama, 2005; Walker, 1992). It has been shown in previous work that APS indeed migrates to the interface and forms bonds at the interface with aluminium (Abel et al., 2007; Abel and Watts, 2009). However, and because of the inherent limitations of the spectroscopies previously employed, it has not been possible to report the aeric density of the bonds (number of bonds per surface area) formed between APS and aluminium at the interface of the joint, nor to assess the concentration of silicon present at the interface at the nanometre scale (Abel et al., 2007; Abel and Watts, 2009). These limitations mostly consist in a difficulty in quantification for ToF-SIMS or

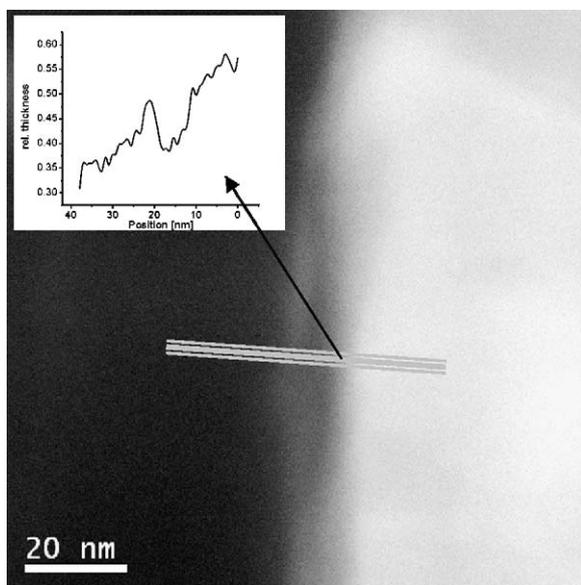
examining samples at a much larger scale with XPS, even though this can be improved using ULAM (Hinder et al., 2004, 2005). Therefore and even though the migration occurs towards aluminium, it is not clear whether the silane present at the interface actually bonds with the same aeric density according to the amount of silane initially present within the epoxy formulation. One should also consider the fact that APS appears to have migrated but may not be present in the same concentration at the interface when it is examined at the nanometre scale rather than micrometre, as has been done before.

Comparing the graphs for samples with 0.5% and 1% (w/w) of APS in Fig. 5, the difference in intensity in the second part of the graph (above 21 nm) may simply be assigned to a concentration effect, with less silane reaching the interface for the 0.5% (w/w) than for the 1% (w/w) sample and therefore only exhibiting a comparable amount of oxygen to the native oxide. The sample with 2% (w/w) of APS does not exhibit as much oxygen after 21 nm on the abscissa scale of Fig. 5 and this may be assigned to a lesser diffusion of APS, within this scale. One hindrance of a slightly higher concentration of this highly reactive silane may engender self-polymerisation, thus preventing diffusion.

Reprising Fig. 6, one can observe that the only sample showing an increase in the relative occupancy of the valence band of oxygen is the specimen prepared with 1% (w/w) of APS. This can be interpreted in a change in the cohesion energy (less anti-bonding states occupied) which, in turn, may be related with the formation of a different material at the interface: the exchanges and orbitals recombination will be different if silicon is involved in bonding with oxygen as opposed to only aluminium. It also follows that if the amount of silane is not sufficient at the interface, only a minor and/or negligible effect will be seen on the occupation of the valence band considering that aluminium and silicon are close in their electronic configuration. The increase is also seen without any discontinuity, as opposed to what is observed for the specimen prepared with 0.5% (w/w) silane. These observations are also consistent with the formation of a composite layer when enough silane is able to reach the interface between the adhesive and the aluminium foil. Besides, as the relative occupancy considered is that of the anti-bonding levels of energy, a decrease in those levels can be interpreted as an increase of the valence oxygen in the bonding state and hence a better bonding at the interface for this particular concentration. Incidentally, samples with 1% (w/w) were also the easiest to prepare, providing a clean “interface” and the least likely to separate during either preparation and/or analysis, suggesting it is mechanically the strongest bond. In comparison, the samples prepared with either 0.5% (w/w) or 2% (w/w) show very little variation in terms of orbital occupancy indicating that the presence of silane has little effect on the interface. In both cases it is likely that not enough adhesion promoter migrated to the interface either because the concentration is too small or because of self-condensation.

The study of the relative mass-thickness profile for the specimen containing 2% (w/w) of APS brings further data about the strength of the oxide layer. Indeed, as seen on the HAADF image of the aluminium/adhesive interface (Fig. 7), a black band about the oxide layer matches with the location of a dip in the relative mass-thickness profile of the section and the decrease of the relative oxygen content.

Notwithstanding, spectra recorded along the oxide layer have sometimes indicated the presence of only the first peak in the relative oxygen content graph, which consequently reduce the estimation of the oxide layer thickness to 6 nm. This implies that the region where a composite can be formed for other concentrations of silane (0.5% and 1% (w/w)), is weakened by the lack or the low formation of this composite layer in the case of a 2% (w/w) specimen.



**Fig. 7.** HAADF image of the aluminium/adhesive interface for a sample containing 2% (w/w) of APS, with, inset the measurement of the sample thickness across, as derived from Eq. (1). In places, the oxide comes apart from the Al metal layer.

To determine the durability of the model adhesive joint, wedge cleavage tests have been performed in previous studies, measuring the fracture energies and crack growth at the interface between the aluminium foil and the epoxy adhesive, in which various concentrations of APS have been incorporated (Makama, 2005). The results of these wedge tests establish an improved durability of the sample prepared with 1% (w/w) of APS as compared to the durability of samples with other silane concentrations (0%, 0.5%, 2% (w/w)). The existence of a composite layer at the interface between the aluminium native oxide and the adhesive is consistent with improved durability compared to a formulation where it cannot be found (no silane or 2% (w/w)). Indeed, if the formation of the composite layer leads to a higher aeric density of bonds between the aluminium foil and the epoxy adhesive, the joint strength should be increased and so should the durability; this is also implied by the findings shown in Fig. 6. Consequently, the APS concentration which brings the best joint performance is the one for which the potential/possible composite layer development is the most important, so the epoxy adhesive containing 1% (w/w) of APS in its formulation. It would seem that for concentrations of 0.5% and 2% (w/w) of APS, the composite growth does not exist or is not important enough to reach a good joint durability.

## 5. Conclusions

The interfaces of aluminium foil with several resins containing a range of aminopropyl triethoxysilane silane concentrations have been studied using TEM/STEM and EELS. The oxygen K edge was studied at sub-nanometre resolution and revealed that the oxygen relative content of the oxide does not exhibit the same profile according to the amount of silane incorporated within the original resin. Similarly, the occupancy of the empty states of the valence band varies according to the concentration of silane, with a highest occupancy for the sample prepared with 1% (w/w), which is also

the concentration exhibiting the best durability in other works. This suggests that a composite layer is present at the interface, composed of both silane and aluminium oxide grown through the silane layer at the curing stage of the samples' preparation. The amount of silane truly reaching and bonding at the interface between the aluminium foil and the resin varies with silane concentration. This results in a difference in aeric density of bonds between the silane and the foil and hence a difference in stoichiometry of the oxygen. This, in turn, is responsible for the correlation of durability with organosilane concentration.

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