

# EFFECT OF SILANE SURFACE TREATMENT ON DURABILITY OF ACRYLIC-ALUMINIUM BONDS

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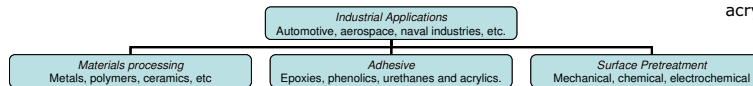
## 1.- General Abstract 2.- Technical Abstract

The use of adhesive bonding in the manufacture of load bearing structures can provide numerous benefits in comparison to more traditional joining techniques such as mechanical fastening or welding. Thus, for bonded aluminium structures, in order to promote long-term durability, surface treatment of the alloy prior to bonding has generally been regarded as a vital component of the manufacturing process.

Silane coupling agents are an environmental friendly alternative to other surface treatments which use toxic chemicals (hexavalent chromium compounds (VI), strong acids, etc), such as CAE, CAA or PAA. Due to the toxic and carcinogenic nature of hexavalent chromium [Cr(VI)] its use is limited or prohibited for environmental regulations in several countries [1]. Thus, the aim of this work was to investigate the effect of the organosilanes on the durability of aluminium joints bonded with toughened acrylic adhesives.

Typically, a silane coupling agent has a hydrolyzable alkoxy group such as methoxy (OCH<sub>3</sub>), ethoxy (OC<sub>2</sub>H<sub>5</sub>) and acetoxy (OCOCH<sub>3</sub>) and an organofunctional group. The alkoxy groups, OR, hydrolyze in the aqueous environment and form covalent bonds with hydroxyl groups on the surface, as well as with other hydrolyzed silane molecules. The organofunctional group, is expected to react with the organic polymer.

Silane coupling agents therefore have the possibility of working as adhesion promoters between the adhesive and the metal surface. Typically, silane coupling agents with amine, epoxy, methacrylic, or vinyl organofunctional groups are used for adhesion enhancement.



## 3.- Glossary

Term	Definition
Adhesive	Non-metallic substance capable of joining materials by surface bonding (adhesion), and the bond possessing adequate internal strength (cohesion)
Adhesion	The state in which the particles of the adhesive and the adherend are held together
Cohesion	The state in which the particles of the adhesive, or the adherend, are held together
Acrylic adhesive	An adhesive that is a solution of rubber-base polymers in methacrylate monomers. Acrylic adhesives bond quickly at room temperature, and can adhere to oily surfaces, as well as to many types of materials, including copper, most plastics, glass, and wood.
Epoxy adhesive	Synthetic resin containing epoxide groups usually used as structural adhesives or encapsulants
Durability	The ability of an adhesive to maintain an adequate bond under the conditions of service that the joint has to withstand
Bondability	Ability of a substrate to form a bond of specified properties with a specified adhesive under specified conditions.
P2 etch	Sulfo-ferric acid etch for surface treatment
CAA	Chromic acid anodising for surface treatment
CAE	Chromic acid etch for surface treatment (i.e. FPL: Forest Product Laboratory)
Grit blasting	Mechanical treatment in which a high-pressure airline projects grained grit onto the top surface of the metals producing a finish similar to cleft.

Table 1: Glossary

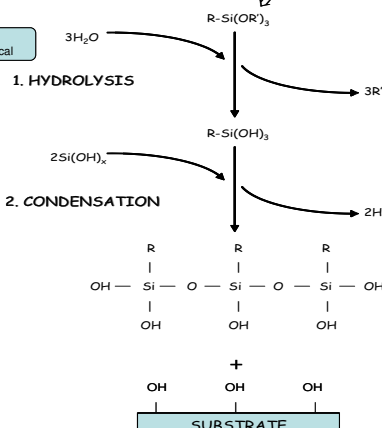


Figure 1: Organosilane hydrolysis and condensation reaction mechanisms

## 4.- Experimental Procedure

Silane coupling agents used in this study were supplied by Aldrich. Their chemical formulation and nomenclature are showed in Table 2.

Name	Abbrev.	Formulation
3-Glycidoxypropyltrimethoxysilane	γ-GPS	CH <sub>2</sub> CH(O)CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>
3-Aminopropyltrimethoxysilane	γ-APS	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>
3-Methacryloxypropyltrimethoxysilane	γ-MPS	CH <sub>2</sub> =C-COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>

Table 2: Silane coupling agents used in this study

The single-lap specimens were made according to the procedure described in UNE EN 1465 [2]. The single-lap joint specimens, schematically shown in Figure 2, were made from EN AW 6082-T6 aluminium alloy sheet.

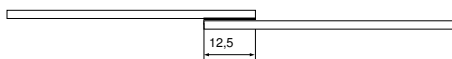


Figure 2: Schematic of single-lap joint

Wedge test specimens were prepared with some deviations to ASTM D3762 [3]. Dimensions are showed in Figure 3. Adherend thickness was 8 mm to avoid plastic deformation in specimens. The adhesive was spread so as to leave at one end of the joint a length of 19 mm bare and ready for the insertion of the wedge.

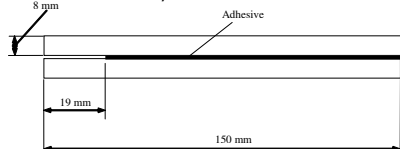


Figure 3: Schematic drawing of Wedge test specimen

Specimens were cured in a desiccator at room temperature for at least 7 days. When the joints were fully cured wedges were driven fully into place by with a tensile testing machine at a constant rate of 10 mm/min. Measurement of initial crack length and crack growth was carried out in both edges of each specimen.

The fracture energy,  $G_{IC}$ , was calculated from the mean value of the total crack length in each case.

$$G_{IC} = \frac{3E\Delta^2 h^3}{16(a+0,6h)^4}$$

Where:  
 $G_{IC}$  is the Mode I fracture energy,  
 $E$  is the Young's Modulus of the adherends (70.5 GPa for aluminium),  
 $\Delta$  is the displacement at the load point  
 $h$  is the adherend thickness

## 5.- Results and Discussion

Several results are shown and briefly discussed below, firstly single lap shear tests and secondly wedge tests.

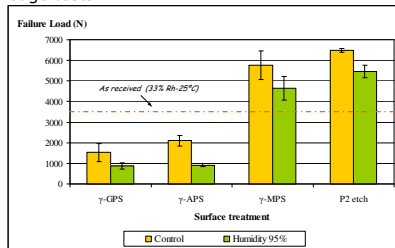


Figure 4: Failure load for lap shear specimens after 30 days of exposure at 95% HR and 50°C

Figures 4 and 5 show failure load data and fracture surfaces in single-lap shear tests with different surface treatments.

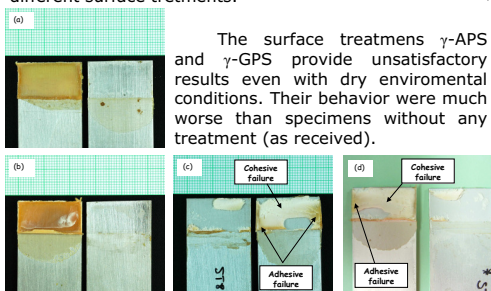


Figure 5: Fracture surfaces of test specimens after 30 days of cure at 95% HR and 50°C: a) γ-APS b) γ-GPS c) γ-MPS d) P2

## 6.- Conclusions

- γ-APS and γ-GPS behavior with the acrylic adhesive used is deficient. These pretreatments present unsatisfactory results even with dry environmental conditions.
- Durability obtained with test specimens treated with γ-Metacriloxipropiltrimetoxisilane are similar to those obtained with P2 etch treatment. γ-MPS enhances adhesion between aluminium and acrylic adhesives; and less environmental problems than hexavalent chromium based compounds.

## 7.- Acknowledgements

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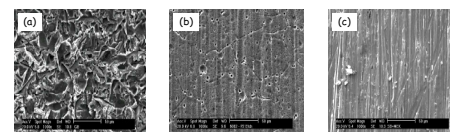


Figure 6: Images (SEM x 1000) of surfaces treated with: a) Grit blasting b) P2 etch c) Abrasion

Over these lines, surface characterization images are shown (Figure 6). These pictures are taken by SEM for different surface treatments.

Finally, Figures 7 and 8 show fracture surfaces and fracture energy evolution in wedge tests with different surface treatments.

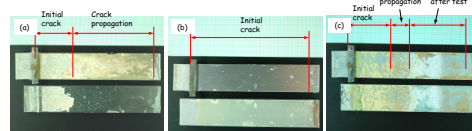


Figure 7: Fracture surfaces of test specimens after 30 days of exposure at 95% HR and 50°C: a) γ-APS b) γ-GPS c) γ-MPS

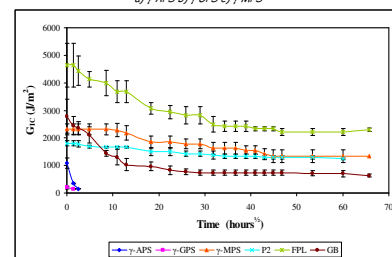


Figure 8: Fracture energy against exposure time for: γ-APS, γ-GPS, γ-MPS, P2 etch, FPL and Grit-blasting

Results of this test are analogous to the previous one, showing deficient results for γ-APS and γ-GPS. However, γ-MPS treatment present a satisfactory behaviour and, although FPL is slightly better, γ-MPS avoids environmental problems. The incompatibility of γ-APS and γ-GPS with the acrylic adhesive seems to be the reason for this bad behavior.

## 8.- References

- Directive 200/53/EC of the European Parliament and on the Council on end-of-life vehicles. Official J. Eur. Commun. L170, 81-84 (2002).
- UNE EN 1465:1996 Standard. Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies. (1996)
- ASTM D 3762:98 Standard Test Method for Adhesive-Bonded Surface Durability of Aluminum (Wedge Test).