THE EFFECT OF ALUMINIUM SURFACE TREATMENTS ON THE APPARENT SHEAR STRENGTH OF HYBRID EPOXY SINGLE-LAP JOINTS

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Abstract

Adhesive bonding in aluminium plates has been used for some time in aeronautical and automotive applications in order to replace rivets or welding. Surface preparation of aluminium prior to bonding is an important step that guarantees the strength of the joint. The use of silica micro-inclusions in the adhesive layers, and wash primers can improve the adhesion strength by some degree. In this study, an experimental characterisation was conducted in order to verify the influence of the surface treatment and silica micro-inclusions in the epoxy adhesive layers as well as the use of wash primer on the apparent shear strength of single-lap joints by tensile loading. Scanning electron microscopy (SEM), surface energy and *Ra* roughness measurements were conducted to characterize the aluminium surface. The results showed that the use of wash primer decreased the overall apparent shear strength of the joints in 55%. However, the inclusion of silica microparticles in the adhesive layers caused an increase of 24% in the shear strength. The surface treatment carried out with NaOH for one minute without the use of wash primer and with silica microinclusions provided the most resistant joint with mean apparent shear strength of 7.39 MPa. Cohesive break of the wash primer was the main cause of the decrease in strength. The joints without wash primer presented a mixture of cohesive and adhesive failure modes.

Keywords: Aluminium surface treatment, silica micro-inclusion, apparent shear strength.

1. INTRODUCTION

Aluminium is commonly used by numerous transportation industries for its durability, light weight, and cost-effectiveness. Bonding structural aluminium components with adhesives offer many advantages over conventional mechanical fasteners like lower structural weight and better appearance [1]. The surface of aluminium alloys contains a natural oxide layer that provides low quality bonding capabilities [2]. Surface pre-treatments such as mechanical abrasion and alkaline etching can be used to remove this natural layer and provide a more homogeneous surface, thereby increasing the strength of the bond. Furthermore, the relationship between roughness and adhesion strength is not very simple. Xu *et al.* [3] showed that the surface energy decreases with the increasing of surface roughness resulting in low wettability of the substrate.

Incorporating silica micro- or nanosized particles to adhesives is a simple and reliable method for increasing the bonding capabilities between adhesives and adherents [4]. Liu *et al.* [5] concluded that the incorporation of silica microparticles to the adhesive increases both the impact critical stress and strain of polymers. The use of surface treatments on aluminium adherents, along with the incorporation of silica micro or nanoparticles to the adhesive, has been used to increase the overall shear and fatigue strength of bonded joints [6].

The use of low viscosity wash primers usually increases the shear strength of the joint. This increase in strength is the result of better-filled aluminium surfaces, owing to a larger interface area between the adhesive and the wash primer. Also, wash primers have corrosion-inhibiting additives that further improve chances of providing long-term bonding strength in harsh environments [7].

In this study, the effects of surface treatments, silica microparticle enhanced epoxy, and the use of wash primer on the apparent shear strength of single-lap joints were analysed using a Full Factorial Design.

2. MATERIALS AND METHODS

2.1 Materials

Rectangular plates (178 x 103 x 0.5 mm) of the aluminium alloy AA 1200 were used in the experiments according to the standard ASTM D1002 [8]. The aluminium was supplied by Belmetal (Belo Horizonte – MG). The polymeric adhesive used was the epoxy Renlam® M-1 and hardener Ren® HY 956, both supplied by Huntsman®. The selected wash primer was the Lazzuril phosphate agent 045 along with the Lazzuril catalyst 051. The silica microparticles were classified in the mesh 325 - 400 US Tyler with size range between 37 and 44 μm.

2.2 Surface treatments

The aluminium plates were initially washed under tap water with soap and then paper wiped with acetone to remove remaining grease and oil. Degreasing is effective in removing contaminants from the surface and this process is normally used as reference condition. However, according to Xu *el al.* [3], it does not provide acceptable surface conditions for bonding adhesives and additional appropriate treatments are necessary.

Three different surface treatments were carried out. The first was mechanical abrasion using sandpaper (grit 600) followed by acetone cleaning. The second and third treatments were alkaline cleaning of the surface by immersing the plates in a solution of 100 g/l of NaOH for 1 and 5 minutes at 60°C respectively, followed by desmutting in a nitric acid solution of 50 % (v/v) for 30 seconds at room temperature (~23°C). After all the treatments, the plates were rinsed with tap water followed by hot blow drying.

2.3 Surface morphologies

The Hitachi model TM-3000 scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) model Quantax 70 was used to analyse the treated surfaces. The *Ra* roughness of the treated surfaces was measured using a Form Talysurf 50 profilometer (Taylor Honson®). The contact angle (θ) was measured with an optical microscope Easyover 800x using water and ethylene glycol drops (35 µl) as probe liquids. Since their surface energies components are known it is possible to calculate the surface energy of the treated surfaces, as follows. The work of adhesion (W_a) is calculated according to Equation 1, then Young's equation (Eq. 2) is used to get Equation 3, where γ_{SV}, γ_{LV}, γ_{SL} are the surface energies of the substrate, the liquid and the interface substrate/liquid respectively [3].

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{1}$$

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos\theta \tag{2}$$

$$W_a = \gamma_{LV}(1 + cos\theta) \tag{3}$$

The work of adhesion includes the polar component and the dispersion component (Eq. 4), where γ_{SV}^d and γ_{LV}^d are the dispersion components of the solid and the liquid surface energies respectively and γ_{SV}^p and γ_{LV}^p are the polar components of the solid and the liquid surface energies, respectively. Therefore, the apparent surface energy of the substrate is calculated according to the Equation 5 [3].

$$W_a = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2\sqrt{\gamma_{SV}^p \gamma_{LV}^p} \tag{4}$$

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \tag{5}$$

2.4 Fabrication of single-lap specimens

The plates were coated with epoxy modified and non-modified with silica microparticles. The wash primer was used in order to analyse its influence on the adhesion. According to Oosting [2], primers play an important function in protecting the aluminium substrate prior to the adhesive bonding. The wash primer was applied on the edges of the aluminium surface in an area of at least ten times the overlapping as showed in Figure 1a using an air coating applicator and the curing was held for 4 hours at room temperature.

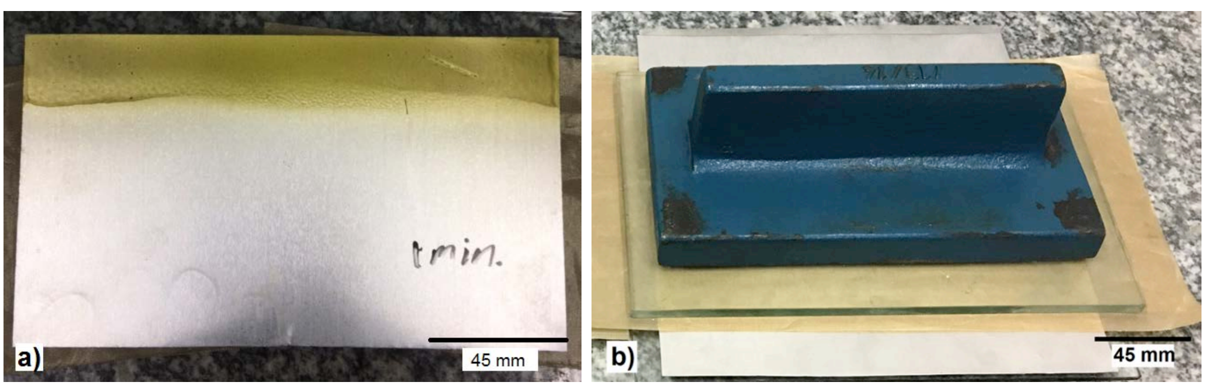

Figure 1: Plate with wash primer layer (a) and plates glued together (b).

The fabrication of the single-lap specimens was performed by pasting two plates with an overlapping area of 180 x 5 mm and subsequent compaction by a 3 kg weight for 24 hours as shown in Figure 1b. The total curing process (7 days at room temperature) followed the recommendations of the epoxy polymer manufacturer. After curing, the plates were cut into seven specimens (Figure 2a) according to the Figure 2b with a width of 25.4 mm, and the two specimens from the borders were discarded due to chance of adhesive failure as recommended by ASTM D1002 [8].

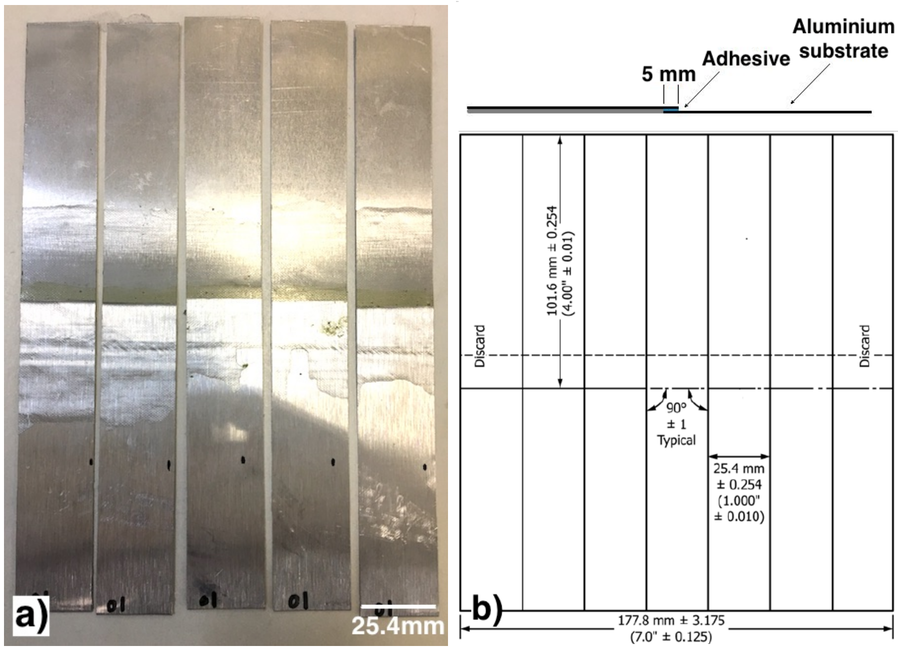

Figure 2: Single-lap test specimens (a) and standard panel (b) (Adapted from [8]).

2.5 Apparent shear strength of the single-lap joints

The apparent shear strength tensile tests were performed in a Shimadzu AG-X Plus testing machine with a testing speed of 1.3 mm/min according to ASTM D1002-10, (2010). Minitab v. 17 software was used to create the DoE scheme presented in Table 1, providing a $4^1 2^2$ Full Factorial Design, resulting in 16 conditions. The factors analysed were the surface treatment, the use of wash primer and the inclusion of silica microparticles in the adhesive layers.

Table 1: Experimental conditions.

Condition	Surface treatment	Wash primer	Silica inclusion (wt. %)
1	Degreased	With	0
2	Degreased	With	10
3	Degreased	Without	0
4	Degreased	Without	10
5	Mechanical Abrasion	With	0
6	Mechanical Abrasion	With	10
7	Mechanical Abrasion	Without	0
8	Mechanical Abrasion	Without	10
9	NaOH 1 min	With	0
10	NaOH 1 min	With	10
11	NaOH 1 min	Without	0
12	NaOH 1 min	Without	10
13	NaOH 5 min	With	0
14	NaOH 5 min	With	10

15	NaOH 5 min	Without	0
16	NaOH 5 min	Without	10

3. RESULTS AND DISCUSSION

3.1 Surface morphology

Figure 3 shows the SEM images of the different aluminium surfaces. Table 2 shows the EDS analysis of those surfaces. Figure 3a shows the degreased only aluminium surface, the red arrows indicate organic contaminants, degreasing is not effective in removing all contaminants. The surface treated with mechanical abrasion showed a common characteristic of grooves caused by sandpaper as shown in the Figure 3b. The mechanical abrasion enhances surface roughness and increases the contact area with the adhesive. promoting mechanical interlocking, which can improve the shear strength. The aluminium surfaces etched with sodium hydroxide presented characteristic pits (black dots in Figures 3c and 3d) generated by the alkaline solution. It can be noted that the number of pits in the sample treated for 5 minutes (Figure 3d) are higher than those treated for 1 minute, probably due to the longer immersion time in the alkaline solution. The small white dots in Figures 3c and 3d are intermetallic particles presented in the alloy, such as magnesium and iron that were revealed after the removal of the oxide layer by the sodium hydroxide.

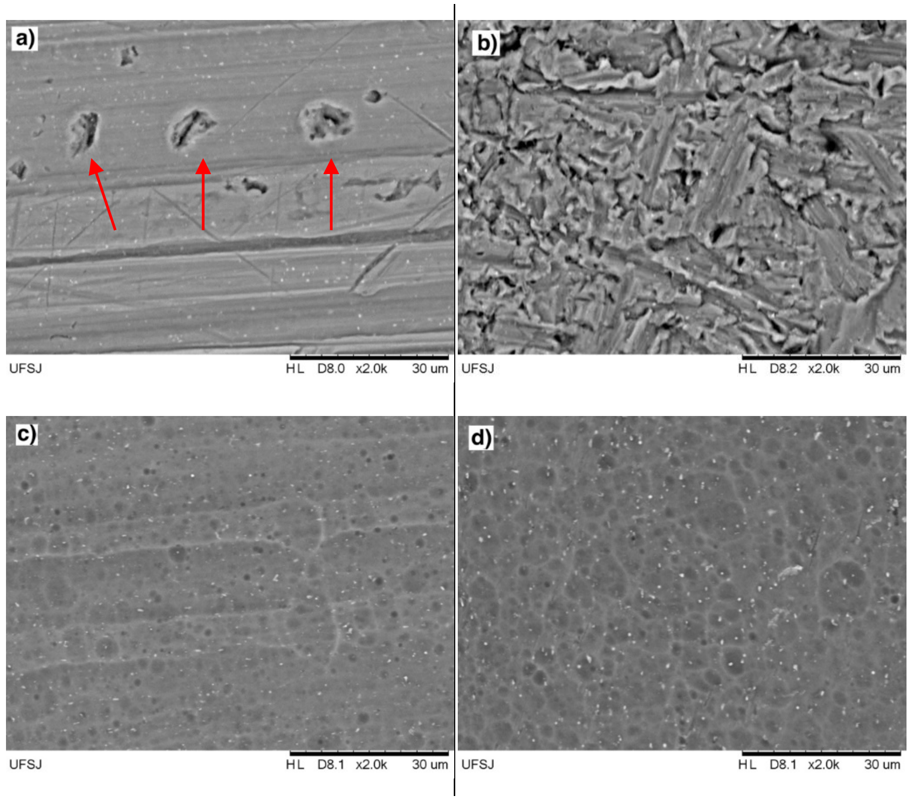

Figure 3: SEM images of aluminium surfaces degreased (a), pretreated by sandpaper (b), NaOH for 1 min (c) and NaOH for 5 min (d).

Table 2: Composition of the treated aluminium surfaces obtained from EDS.

Element (wt.%)	Al	C	O	Fe	Mg
Degreasing	92.78	4.76	1.81	0.10	0.11
Mechanical abrasion	83.76	7.46	8.00	0.11	0.17
NaOH for 1 min	94.48	3.65	0.97	0.28	0.62
NaOH for 5 min	94.44	4.04	0.77	0.43	0.32

Figure 4 shows the contact angles of the probe liquids for the degreased only aluminium surface. The contact angles of the surfaces subjected to the others treatments were measured the same way and the values of the their angles along with the calculated surface energies and *Ra* roughness are in the Table 3. The lower the contact angle of the drop with the surface, the greater the surface energy, indicating good wettability of the surface, which provides good adhesion properties [5].

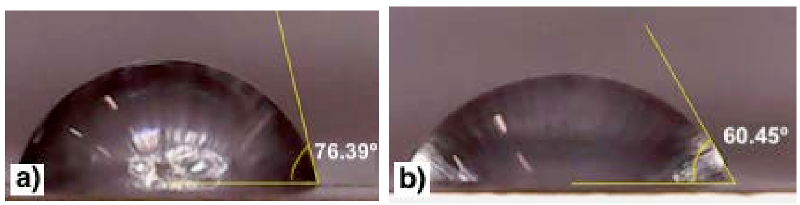

Figure 4: Contact angles for the water (a) and ethilete glycol (b) drops of the degreased sample.

Table 3: Contact angles, surface tension and roughness of the treated surfaces.

Condition	Contact angle (deg.)		Dispersive component (mJ/m^2)	Polar component (mJ/m^2)	Surface energy (mJ/m^2)	*Ra* Roughness (nm)
	Water	Ethylene Glycol				
1	76.39	60.45	11.30	16.80	28.10	398.4 ± 4,4
2	80.81	51.42	27.51	6.16	33.67	501.9 ± 8,9
3	73.36	41.79	28.06	9.57	37.63	358.9 ± 4,5
4	64.34	39.13	18.57	20.13	38.70	368.7 ± 3,2

Condition: Degreased (1), Mechanical abrasion (2), NaOH for 1 min (3) and NaOH for 5 min (4).

3.2 Apparent shear strength of the joints

Figure 5a shows the SEM image of the thickness layer of the adhesive in the joint, which had an average value of 0.126 mm. The apparent shear strength of the joints varied between 2.93 MPa and 7.39 MPa. Table 4 shows the analysis of variance (ANOVA) of the results. P-values lower or equal to a α-level of 0.05 imply significance of the factor effect on the variable response with a 95% of reliability [9]. The underlined P-values shown in Table 4 indicate the significant factors that affected the response. The adjusted R^2 value indicates whether the statistical model behaved appropriately. This means that the variance of the properties is explained by the variance of the factors analysed, the closer from 1 (100%) is the R^2, better is the predictive ability of the model. When one or more interaction effects are significant, the factors that interact should be considered together [10]. The R^2 value given in Table 4 is 86.60% showing good predictability of the model. The Anderson-Darling normality test was used to validate the ANOVA. In this case, the P-value must be equal or superior to 0.05 to follow a normal distribution configuration. The data followed a normal distribution with a P-value of 0.984 with the plot of residues shown in Figure 5b.

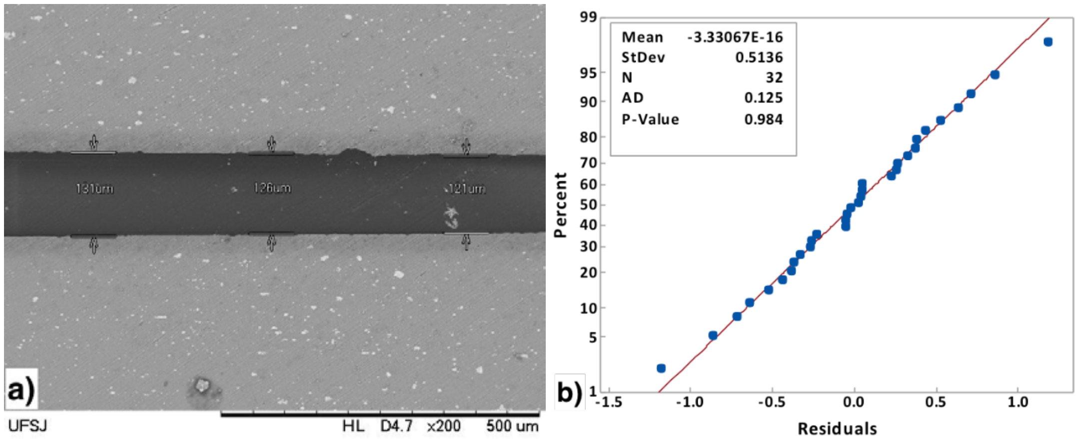

Figure 5: SEM image of the thickness layer of the adhesive (a), probability plot (b).

Table 4. P-values of the Analysis of variance

Experimental factor	**P-value**
Surface pre-treatment	0.385
Wash primer	**0.000**
Silica inclusion	**0.002**
Surface treat.*Wash primer	**0.004**
Surface treat.*Silica	0.783
Wash primer*Silica	0.163
Surface treat.*Wash primer*Silica	0.168
P-value And. Darling > 0.05	**0.984**
R^2-adjusted (%)	**86.60%**

Figure 6 shows the main effect plot for the use of wash primer and silica inclusion on the mean apparent shear strength. The wash primer decreased the apparent shear strength of the joints in 55%. According to Oosting [2], wash primer can improve the interface adhesion, but its cohesive strength is sometimes very weak, compromising the strength of the joint. Figure 7a shows a failure mode by wash primer cohesive break and Figure 7b a mixture of cohesive and adhesive failure modes of the conditions with neat epoxy. The silica inclusion improved the shear strength of the joints in 24%. Similar results were found by Liu *et al.* [6], who reported that silica inclusions may decrease crack growth rates increasing the apparent shear strength. Figure 8 shows the interaction plot between the factors of surface treatment and the use of wash primer. It can be noted that all conditions without wash primer presented better results of apparent shear strength, and the surface pre-treated by NaOH for 1 min provided the highest apparent shear strength, 45.9% higher compared to the mechanical abrasion condition. This is probably due to the better infiltration of the epoxy in the aluminium surface, owing to the higher surface energy compared to mechanical abrasion and degreased conditions. The mechanical abrasion condition showed the best result in the condition with wash primer, 32% higher than NaOH for 1 min condition. This is probably due the mechanical interlocking with the wash primer and the larger area of contact with the resin caused by the surface high roughness.

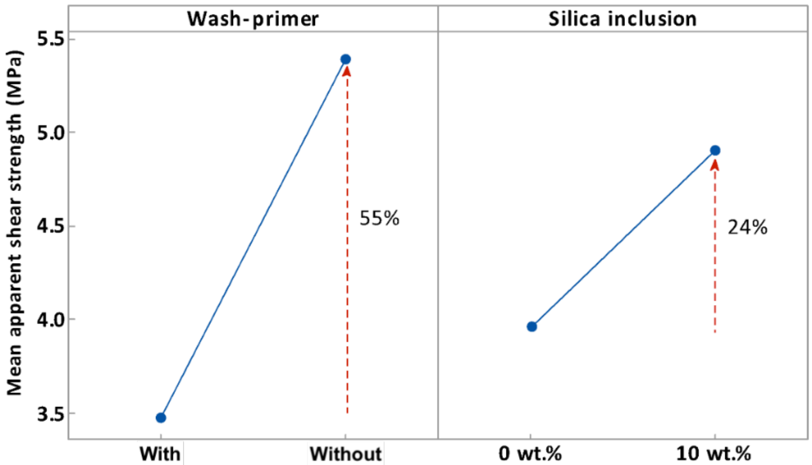

Figure 6: Main effect plot for the use of wash primer and micro-silica inclusion on the mean apparent shear strength.

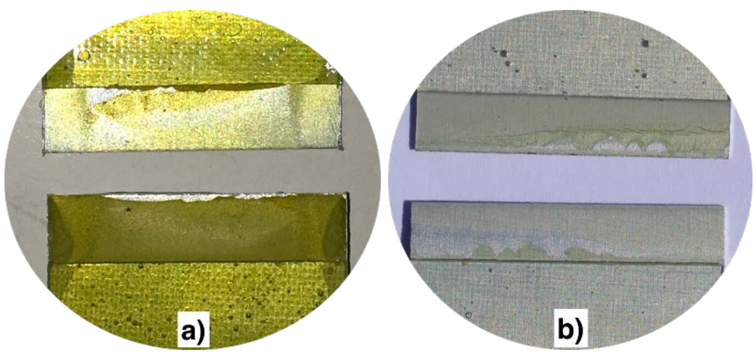

Figure 7: Failure mode by wash primer cohesive break (a), mixture of cohesive and adhesive failure mode of the epoxy adhesive (b).

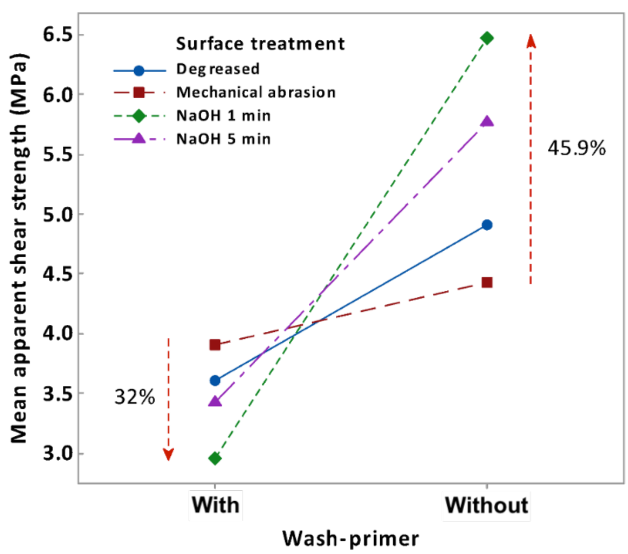

Figure 8: Interaction effect plot for the mean apparent shear strength.

4. CONCLUSION

This paper investigated the effect of aluminium surface treatment, micro-silica inclusion into epoxy polymer and the use of wash primer on the apparent shear strength of single-lap joints. A full factorial design was conducted to identify the effects of individual factors and interactions on the responses. The use of wash primer reduced the apparent shear strength of the joints in 55%. The micro silica inclusion was able to increase the overall shear strength of the joints in 24%. The failure mode of the joints with wash primer was mainly cohesive break and the failure mode of the joints without wash primer was a combination of cohesive break of the epoxy and adhesive break of the interface aluminium/epoxy. The use of accelerated aging of the joints by high humidity and temperature will be the scope of future works.

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