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High adhesion between aluminum and unsaturated polyester through hierarchical surface patterning

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Abstract

The main target in this study was to increase adhesion of unsaturated polyester (UP) adhesive to aluminum substrates by structuring the aluminum surface on the microscale and nanoscale as well as by functionalizing the surface with 3-methacryloxypropyltrimethoxysilane. The micrometer-level surface structures were produced with a micro-mesh printing technique and sandblasting, while a nanoscale pseudoboehmite surface structure was obtained with a boiling water treatment. These modifications were combined to form different hierarchical surface structures on the aluminum substrate. The adhesion strength of polyester to aluminum was assessed with a tensile-shear test. The mere micro-mesh printed pattern increased the tensile-shear strength of the joint from 2.3 MPa to 5.8 MPa, while the micro-micro-hierarchical joint specimen possessed a shear strength of as high as 14.5 MPa. Further, the adhesion of UP adhesive with the three-level hierarchical micro-micro-nanostructured specimens increased so high that the joints started to deform plastically during the shear strength measurement, preventing the evaluation of their maximum strength. The silane-treated specimens displayed also significantly higher shear strengths and more cohesive failure than the corresponding untreated specimens. Silanization was also observed to improve the interaction of the UP adhesive with the aluminum nanostructure. The results demonstrate that the adhesion of polyester to aluminum surface can be significantly enhanced utilizing readily available and environmentally friendly methods.

Keywords: Adhesion; Resins; Adhesive Joints; Fracture; Hierarchical surface patterning; Functionalization;

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Declaration of interests: None
1. Introduction

Organic polymer adhesives are increasingly replacing the conventional welding, bolt-nut, and rivet joints in aviation and automobile industries because of the various advantages of the adhesive joints. These include capability to join different material pairs, a more uniform load distribution over the joined area and a simpler and quicker manufacturing process [1–4]. Therefore, the desire to produce high performing adhesive joints is growing constantly.

Hierarchical micro-nanostructures are well known to have superior adhesion properties. The surface structures on feet of insects, spiders and geckos are one of the best known examples of natural hierarchical micro-nanostructures having high adhesion properties [5, 6]. In fact, the natural surface structures have inspired researchers to develop similar hierarchical micro-microstructured [7, 8] and and micro-nanostructured [9] polymer surfaces possessing enhanced adhesion features. These studies indicate that the hierarchical surface structures could also provide a new approach to develop more effective and robust metal-adhesive joints.

Aluminum substrates can be easily structured on microscale using grit blasting [10–12], mechanical abrasion, [13] milling [14, 15], and micro-working robot technique [16, 17]. Porous microscale and nanoscale structures can also be produced using wet etching [11, 18, 19] and anodizing pretreatment techniques [20, 21]. Moreover, a boiling water treatment has been studied as an environmentally friendly method to produce nanostructure on aluminum surfaces [11, 22–24]. The produced nanostructure provides a high surface area and numerous locking points, thus increasing adhesion between aluminum and adhesives [22, 24].

Unsaturated polyester (UP) adhesives are commonly used in high performance laminates due to their good fiber wetting and impregnation properties. As highly cross-linked polymers, unsaturated polyesters have e.g. a high strength and good resistance to chemicals [25, 26]. Unsaturated polyesters have high wetting and impregnation properties and therefore they are good adhesives to study the effect of nanostructuring on adhesion. Van der Brand et al. [24] have studied the effect of the pseudoboehmite nanostructure on adhesion of epoxy adhesive with aluminum. In order to get sufficient penetration into the nanostructure, epoxy resin had to be diluted to a high solvent content. Due to their low viscosity, unsaturated polyesters are expected to offer a better possibility to fill the nanostructures of nanopatterned aluminum substrates.
Chemical modification of the aluminum surface can improve the bonding strength of adhesive-bonded aluminum. [27] A well-known chemical method to improve adhesion between a substrate and adhesive is silanization. Silane binds onto the substrate surface and acts as a chemical bridge between the substrate and adhesive [28–31]. Methyltrimethoxysilane, 3-glycidoxytrimethoxysilane and 3-methacryloxypropyltrimethoxysilane (MPS) have been studied as coupling agents between UP adhesive and Al₂O₃-particles or aluminum substrate [25, 26]. The silane compound (MPS) having two types of functional groups can act as a chemical bridge between the polyester adhesive and the aluminum substrate. MPS has also been found to increase the adhesion between UV-curable polyester and antimony doped tin oxide nanoparticles [32]. These studies indicate that silanization of the aluminum substrate could also increase the strength of aluminum-UP adhesive joints.

The aim of this study is to improve the tensile-shear strength of aluminum–UP resin single-lap joints using new types of hierarchical surface structures (micro-microscale, micro-nanoscale and micro-micro-nanoscale). To achieve this, we utilize an easily accessible micro-mesh printing technique, which can produce regular ridge textures on polymer [33] and aluminum [34] substrates. The structures on smaller scale are prepared using sandblasting and hydration methods. Furthermore, the combined effect of the fabricated surface structures and functionalization with 3-methacryloxypropyltrimethoxysilane is studied. For the failure mode characterization, the adhesive distributions on the fractured surfaces of the single-lap joint specimens are examined using electron microscopy and a new optical method based on the photoluminescence property of unsaturated polyester resin. The different surface modifications approaches utilized in the study are presented in Fig. 1.
2. Materials and methods

2.1. Materials

Commercial Sea class EN AW-5754 aluminum alloy sheets (Impexmetal s.a. Aluminium Konin, Warszawa, Poland) were used as substrates. The composition of the alloy is given in Table 1. Styrene cross-linkable dicyclopentadiene based Synolite 8388-P-1 unsaturated polyester resin (UP) (DSM composite resins, Heerlen, Netherlands) was used as an adhesive and methyl ethyl ketone peroxide (Butanox M-50, S.A. AkzoNobel Chemicals N.V., Arnhem, Netherlands) was selected as a curing agent. The amount of the curing agent relative to that of the resin was 2 wt %. 3-Methacryloxypropyltrimethoxysilane (MPS, 98%) was utilized as a coupling agent and was purchased from Sigma Aldrich (Espoo, Finland). Stainless steel microscale meshes used in the micro-mesh printing procedure were purchased from Spinea Ltd (Helsinki, Finland).

Table 1. The composition of the EN AW-5754 aluminum alloy

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>Cr</th>
<th>Al</th>
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</thead>
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<tr>
<td>Amount (%)</td>
<td>0.40</td>
<td>0.40</td>
<td>0.10</td>
<td>2.6-3.6</td>
<td>0.50</td>
<td>0.20</td>
<td>0.30</td>
<td>rest</td>
</tr>
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</table>
2.2. Specimen preparation, shear strength measurement and fracture investigation

The aluminum alloy substrates (dimensions of 3 mm*25 mm*100 mm) were degreased with acetone in an ultrasonic bath for 15 minutes. This procedure was performed after the mechanical modifications (mesh printing or sandblasting) and before hydration and silanization. All substrates were cleaned with compressed air in order to remove possible dust particles before fabrication of the joints. The air line contained an oil-free compressor and an air dryer to remove any impurities from the air.

The UP resin was mixed with the curing agent at room temperature using a magnetic stirrer until the color of the viscose mixture changed from a pale color to yellow. Joining of the substrates was done in a special jig, that allowed an accurate control of the adhesive layer thickness, overlap length and alignment. The overlap length was set to 12.5 mm and the adhesive layer thickness to 0.1 mm. The joined specimens, illustrated in Fig. 2, were cured at room temperature for 5 hours followed by post curing at 75 °C for 17 hours. After the curing process, the spew fillets were cut alongside the joint using a blade and the specimens were stabilized in a desiccator for 4 hours.

![Figure 2](image)

Figure 2. A schematic picture of fabricated single-lap joint specimen. Aluminum substrate width 25 mm.

The tensile-shear properties of the adhesive single-lap joint of aluminum substrates were then measured with a Zwick Z010/TH2A material testing machine. The specimens were fastened using asymmetrical grips (Zwick/Roell Typ 8306) in order to align the specimens and to avoid bending and peeling in the shear testing. The cross head speed was set to 1 mm/s and was kept constant. At least 5 specimens were measured for each set of samples. The fracture surfaces were examined with a Hitachi S-4800 scanning electron microscope (SEM). The acceleration voltage was set to 3 kV. For the SEM examination, the specimens were coated with a 4 nm gold layer using a Cressington Sputter Coater 208HR applied with a Cressington thickness Controller MTM-20. A visual appearance of the fractured single-lap joints was captured with a Sony HDR-SR 11E camera under ultraviolet light (UV) (12W, peak wavelength 368 nm).
2.3. Physical modification with microstructuring

Microscale patterning of aluminum substrates was done with a micro-mesh printing technique and with sandblasting. The microstructured area was 25 mm×15 mm. The micro-mesh printing was performed with a hydraulic press using a constant pressing time of 1 minute. The mesh sizes of the metal sheets used were 100 µm, 200 µm, and 400 µm. Their wire gages were 65 µm, 125 µm, and 250 µm and the pressing forces applied were 35 kN, 33 kN, and 30 kN, respectively. A schematic presentation of the micro-mesh printing of the aluminum substrates is shown in Fig. 3.

![Figure 3](image1.png)

**Figure 3.** A schematic picture of micro-mesh printing technique.

A grain size of the quartz sand used in the sandblasting was less than 1 mm and the sandblasting pressure was set to 6 bars. Sandblasting was carried out till the structured surface of the aluminum substrate was visually entirely matt. The fabricated structures were illustrated with a MountainsMap SEM Topo 3D modelling program. The stereoimages for 3D models were taken with a Carl Zeiss Sigma HD/VP electron microscope using 10 kV acceleration voltage.
2.4. Physical modification with nanostructuring

A nanoscale surface pattern on aluminum was obtained via hydration. Degreased aluminum substrates were immersed in boiling deionized water for 5 minutes. After the hydration, the substrates were first air dried and then stabilized overnight in a desiccator or silanized. Specimens, whose last modification was hydration, were ultrasonicated in acetone before the joint fabrication to eliminate possible particles formed during the process. The pseudoboehmite nanostructure was characterized using a ThermoFischer Nicolet iS50 FTIR spectrometer and a Hitachi S-4800 scanning electron microscope.

2.5. Chemical modification with silanization

3-Methacryloxypropyltrimethoxysilane (MPS) was hydrolyzed in an ethanol solution containing 5 vol% of water. The solution was mixed with a magnetic stirrer (500 rpm) for 1 hour and the degreased aluminum substrates were immersed in the solution for 5 minutes. After the immersion, the silanized aluminum substrates were cured at 150 °C for 30 minutes followed by stabilization in a desiccator overnight before the joint fabrication. The summary of the utilized surface treatments and abbreviations of the microstructures are presented in Table 2.
Table 2. The utilized surface modifications and their combinations. Numbers in abbreviations indicate mesh size, e.g. M$^{100}$S equals to 100 µm mesh printing followed by sandblasting.

<table>
<thead>
<tr>
<th>Surface type</th>
<th>Abbreviation</th>
<th>1. treatment</th>
<th>2. treatment</th>
<th>3. treatment</th>
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<tr>
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<td>Micro-mesh</td>
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<td>M$^{400}$</td>
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<tr>
<td>Mesh printed and sandblasted</td>
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<td>Micro-mesh</td>
<td>Sandblasting</td>
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<td>Sandblasting</td>
<td>Hydration</td>
<td>Silanization</td>
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</table>
3. Results and discussion

3.1. Microstructuring

Three different microscale patterns on aluminum substrates were fabricated by using micro-mesh printing, sandblasting, and combined micro-mesh and sandblasting techniques. The aluminum specimens having smooth and sandblasted surface textures were used as references. The three-dimensional images of the fabricated structures are shown in Fig. 4. The side profiles were extracted from the 3D models to illustrate the height variation in the different surface structures.

![Figure 4. 3D images and side profiles of smooth, sandblasted, M-type and MS-type surface structures. The fabricated structures are illustrated using a Digital Surf MountainsMap SEM TOPO 3D modeling software.](image-url)
Figure 4 illustrates how sandblasting produces a random microstructure with sharp edges whereas micro-mesh printing generates a regular surface pattern. It is also evident that the larger mesh sizes produce higher microridges on M-type surfaces. In fact, the height of the microridges is almost the same as the wire gage of the mesh used. The 100 µm mesh produces approximately 50 µm tall ridges, while the corresponding values are ~100 µm and ~240 µm for the 200 µm and 400 µm meshes, respectively. When the micro-mesh printing and sandblasting are combined, the resulting surface structure is highly hierarchical with the larger micro-mesh structure covered with a smaller scale microstructure produced by sandblasting. However, sandblasting causes a notable decrease in the height of the microridges. The ridge height of M\textsuperscript{100} surface reduces more than 20 % and the residual structure barely differentiates from the S-type surface structure. In contrast, the larger 200 µm and especially 400 µm mesh structures retain their characteristic patterns and nearly their initial ridge height. The effect of the surface structures on the tensile-shear strength of the single-lap joint specimen is shown in Fig. 5.

![Figure 5](image_url)

**Figure 5.** Effect of microstructuring on the tensile-shear strength of the Al/UP/Al single-lap joints. The columns represent the average values and the error bars display the standard deviation.

The M-type surfaces have approximately 2-3 times higher shear strengths when compared to a smooth reference surface. It is also noteworthy how the decreasing mesh size results in a higher shear strength. This result is opposite to those obtained in our previous study with epoxy adhesive [34]. The different behavior is most probably due to the lower viscosity of the UP adhesive used compared to that of the epoxy adhesive. The UP adhesive can fill the small microstructures much more efficiently, and thus more effective interactions and locking points are obtained, and therefore the trend is reversed.
When compared to smooth and M-type surfaces, the sandblasted and MS-type surfaces give superior shear strengths. The sandblasted specimen exhibits a shear strength of 12.6 MPa, while the corresponding value for the M$^{400}$S sample is 14.5 MPa. The shear strength values of the MS-type substrates have a clear ascending trend compared to the descending values of the M-type substrates. In fact, the trend is similar to that found in our previous study [34]. According to Fig. 4, sandblasting enables formation of a significant surface hierarchy on the M$^{200}$ and M$^{400}$ substrates, observed as a notable increase in the shear strength. On the other hand, the surface structure of the M$^{100}$ substrate levels considerably during the sandblasting and the residual structure is only slightly hierarchical. This causes only a minor increase in shear strength. The results highly suggest that the multilevel surface hierarchy is required to increase the tensile-shear strength of the aluminum single-lap joints produced.

The fractured surfaces were examined with photographing under UV-light and SEM imaging to gain information of the fracture mechanisms on both macro- and microscale, respectively. Cured unsaturated polyester is known to have a strong fluorescence emission under UV-light [35, 36] which allows a more profound characterization of the fractured aluminum/UP-joints with photography. The photographs under UV-light and SEM images of the fractured single-lap joint specimens are depicted in Fig. 6.
Figure 6. Photographs under UV-light (1) and SEM images (2) of the fractured Al/UP/Al specimens. A) smooth reference, B) sandblasted reference, C) M^{100} and D) hierarchical M^{400}S samples. The white arrows indicate the direction of the stress. The light blue color indicates UP residues and the violet color indicates exposed aluminum surface.

The observed fracture types of the single-lap joints correlate well with the shear strength data. The smooth aluminum reference surface (shown with a violet color in the photograph) in Fig. 6A has poor adhesion to UP adhesive which has led to an almost complete adhesive failure. The M-type surfaces, depicted in Fig. 6C, tend to fracture cohesively along the mesh wire structure perpendicular to the stress. Fig. 6 1B exhibits how the sandblasted reference surface provides a much higher adhesion between the aluminum substrate and the UP adhesive, resulting in a more cohesive failure. The exposed sandblasted aluminum substrate is covered with numerous small UP residues. In comparison, Figure 6 1C illustrates how only a few UP residues are visible on the exposed M^{100} surface. However, the hierarchically patterned M^{400}S surface has the best adhesion to UP
adhesive (Fig. 6 D). The UP has fractured cohesively throughout the whole mesh wire structure and UP residues cover all the mesh wire depressions. These results along with the shear strength data demonstrate that the micro-micro hierarchy improves the interaction and hence the adhesion between the adhesive and the substrate. The specimens possessing the best microstructure, M$^{100}$, and the best hierarchical micro-microstructure, M$^{400S}$, were chosen for the nanostructuring study.

3.2. Nanostructuring

The hydration process to produce nanostructures was optimized using sandblasted Al-substrates with five different hydration times: 1, 5, 15, 30, and 60 minutes. The SEM images of the resulting nanostructures are presented in Fig 7. The dimensions of the formed pseudoboehmite nanograss are highly dependent on the hydration time used [23, 24]. The longer the aluminum substrates are immersed in the boiling water, the larger is the whisker diameter of the formed pseudoboehmite nanograss.

Figure 7. SEM images of sandblasted Al-substrates with A) 1 min, B) 5 min, C) 15 min, D) 30 min, and E) 60 min hydration times.
Fig. 8 presents the results of the tensile-shear strength and FTIR measurements of the hydrated samples. According to Fig. 8 A, the hydration time has only a minor effect on the shear strength properties of the Al/UP/Al single-lap joint specimens. The highest improvement is obtained with the 5-minute hydration, which increases adhesion by approximately 15% compared to a sandblasted aluminum reference sample. Based on the shear strength results, the 5-minute hydration time was chosen for the further nanostructuring studies.

![Image of Figure 8](image-url)

**Figure 8.** A) Effect of nanostructuring on the tensile-shear strength of the sandblasted Al/UP/Al single-lap joints and B) FTIR spectrum of the pseudoboehmite nanograss on a smooth substrate.

The FTIR spectrum of the pseudoboehmite shown in Fig. 8 B is consistent with the corresponding literature spectra. The bands at 3322, 3099, and 1080 cm\(^{-1}\) are assigned to Al-OH group vibrations [24, 37, 38] while the bands at 885, 760, and 625 cm\(^{-1}\) are due to the AlO\(_6\) vibrations [39, 40]. The three vibrational bands at 1650, 1516, and 1395 cm\(^{-1}\) originate from water molecules adsorbed in the pseudoboehmite structure [24, 38]. The hydration process was also applied to the M\(^{100}\) and M\(^{400}\) microstructures to evaluate the effect of nanostructuring on the shear strength of the single-lap joints. These results are presented in Fig. 9.
Figure 9. Effect of the 5 min hydration on the tensile-shear strength of the joints with different surface structures.

The hydration does not improve the shear strength of the smooth aluminum surface significantly. However, when the hydration is combined with the M\textsuperscript{100} micro-mesh or sandblasted aluminum substrates improvement in adhesion is evident. The shear strength value of the M\textsuperscript{100} specimen rises from 5.8 MPa to almost 10 MPa, while the corresponding change for the S-type surfaces is from 12.6 MPa to 14.6 MPa. These results indicate that a mere pseudoboehmite nanostructure is unable to improve the adhesion properties, but enhanced adhesion requires a superimposed micro-nanostructure. This is also easily observed when comparing Figs. 6 and 10. The hydrated M\textsuperscript{100} and sandblasted Al-substrates, depicted in Figs. 10 A and 10 B, have considerably larger UP residues on the exposed aluminum surfaces than the corresponding non-hydrated aluminum substrates illustrated in Figures 6 B and 6 C.

Figure 10. Photographs under UV-light (1) and SEM images (2) of fractured Al/UP/Al specimens: A) hydrated M\textsuperscript{100}, B) hydrated sandblasted reference, and C) hydrated hierarchical M\textsuperscript{400S} samples. The white arrows indicate the direction of the stress. Light blue color indicates UP residues and violet color indicates exposed aluminum surface.
According to Fig. 9, the nanostructure increases only slightly the shear strength of the M$^{400}$S specimen having a hierarchical micro-micro-nano surface structure. When nanostructuring is applied on a micro-patterned aluminum substrate, the chemical nature of the surface was found to change from hydrophobic (a surface energy around 40 mJ/m$^2$) to highly hydrophilic (a surface energy of 81 mJ/m$^2$) due to the presence of aluminum hydroxyl groups (AlOH) and water molecules on the nanopatterned aluminum surface [41, 42]. This results in an extremely high adhesion between the substrate and adhesive. In the case of the M$^{400}$S specimen, the adhesion became so high that it caused plastic bending of the single-lap joint specimen during the tensile-shear strength measurement. High peeling forces acted on the UP adhesive are evident in Fig. 10 1C, where most UP residues have concentrated on the opposite end of the joint area when compared to any other fractured single-lap joint specimen. In our previous study [34], a similar behavior was observed with the highly modified Al/epoxy/Al single-lap joint specimens. This phenomenon, illustrated in Fig. 11., is typical for single-lap joints under a heavy strain [43]. The out-of-plane deformation activates peeling forces at the end of the adherend, causing a change in the fracture mechanism [44]. Therefore, the shear strength of the hydrated M$^{400}$S specimen is lower than expected. According to Fig. 10 2C, all micromesh depressions of the hydrated M$^{400}$S substrate structure are filled with UP residues confirming the strong adhesion between the adhesive and aluminum substrate.

Figure 11. A) A specimen deforming during the shear strength test and B) the fracture mechanism change caused by the out-of-plane deformation.
3.3. Silanization

Five different contents (0.5-2.5 wt%) of 3-methacryloyloxypropyltrimethoxysilane (MPS) in the ethanol-water solution were studied to achieve optimal parameters for silanization. Smooth aluminum substrates were used for the silanization study. The tensile-shear strength results of the Al/UP/Al single-lap joints after silanization and the fracture surface of the specimen silanized with a 1.5 wt% MPS solution are presented in Fig. 12.

![Figure 12](image)

**Figure 12.** A) Effect of silanization with MPS on the tensile-shear strength of the Al/UP/Al single-lap joints and B) the fracture surface of the smooth Al/UP/Al single-lap joint specimen silanized with the 1.5 wt% MPS solution. A photograph of the aluminum substrates (1B) and a SEM image (2B) of the fractured UP surface. The white arrow indicates the direction of the stress. The light blue color represents UP residues and the violet color denotes the exposed aluminum surface.

Fig. 12 A shows that the silanization with MPS almost doubles the shear strength compared to the unmodified smooth reference. This result agrees with the previous study [25] where the treatment of Al₂O₃ with MPS was found to improve the fracture toughness of the formed Al₂O₃/UP composite by almost 100% compared to untreated Al₂O₃/UP composite. Fig. 12 A also indicates that the concentration of MPS solution has no influence on the shear strength values. The comparison of Figures 12 1B and 6 1A illustrates how the silanized smooth specimens tend to fracture similarly to the corresponding unmodified samples at macroscale. However, a closer look at microscale in Fig. 12 2B reveals that cured UP adhesive has numerous of shear cuts perpendicular to stress, indicating that silanization increases the covalent binding of the UP adhesive with the aluminum substrates. Based on these results, the 1.5 wt% MPS solution in ethanol-water was chosen, because it provided the lowest standard deviation in the tensile-shear strength measurements.
3.4. Combination of hierarchical surface structures and silanization

The adhesion of the UP adhesive with the aluminum substrates was further examined by combining the chemical modification with the microscale surface structuring and hydration. The smooth, M$^{100}$, sandblasted, and M$^{400}$S aluminum substrates were treated with 5-minute hydration and silanization with the 1.5 wt% MPS solution. Fig. 13 describes the effects of the combined modifications on the shear strength.

![Chart showing shear strength for different surface types: Smooth, M$^{100}$, Sandblasted, M$^{400}$S.](image)

**Figure 13.** A) Effect of the combined microstructuring, nanostructuring and silanization on the tensile-shear strength of the joints and B) the condensation reaction of the hydrolyzed 3-methacryloxypropyltrimethoxysilane with the aluminum substrate.

As expected, the combined hydration and silane modifications give significantly high shear strength values on every substrate studied. 3-Methacryloxypropyltrimethoxysilane (MPS) is grafted onto the surface of the hydrated aluminum substrate by a condensation reaction, illustrated in Fig. 13 B, of SiOH hydroxyl groups of hydrolyzed MPS with AlOH groups of the pseudoboehmite structure. The vinyl groups of MPS are utilized in coupling with the unsaturated polyester adhesive [45]. On the smooth and sandblasted substrates, the silane treatment results in a slightly higher shear strength compared to the hydration modification. The M$^{100}$ structured specimen, however, behaves differently giving a higher shear strength with the hydration than with the silane treatment. Interestingly, the hydrated and silanized sandblasted specimen has a higher shear strength than that of the M$^{400}$S substrate. This can be explained with observed deformation of the M$^{400}$S joint. In fact, the maximum tensile-shear strength measured in the study, over 16.5 MPa, was obtained with the hydrated and silanized sandblasted specimen. The photographs and SEM images of the fractured hydrated and silanized specimens are shown in Fig. 14.
Figure 14. Photographs under UV-light (1) and SEM images (2) of fractured hydrated and silanized Al/UP/Al specimens: A) smooth, B) M\(^{100}\), C) sandblasted, and D) M\(^{400}\)S specimens. The white arrow indicates the direction of the stress. The light blue color represents the UP residues and the violet color denotes the exposed aluminum surface.

The adhesive-adherend interface of the hydrated and silanized M\(^{400}\)S specimens in Fig. 14 D exhibits mostly a cohesive failure. In contrast, the hydrated and silanized sandblasted surface in Fig. 14 C displays a more adhesive failure. Moreover, the adhesive failure initiates from the lower end of the joint in the S-type specimen, whereas in the M\(^{400}\)S sample the failure starts from the upper end of the joint. This result indicates that the fracture in the M\(^{400}\)S specimen is caused by a different stress compared to other surfaces. It seems that the adhesive crack propagation from the lower end of the joint relieves the strain in the joint, restraining the deformation of the specimen. However, the adhesion in the hydrated and silanized M\(^{400}\)S specimen is so high that the failure starts after the deformation has begun. According to Sorohan et al. [46] the deformation
produces high peeling forces at the end of the joint and the failure starts where peeling is strongest. As a result, the M^{400}S specimen fractures prematurely and the shear strength values are lower than expected and inconsistent with the fracture appearance. This phenomenon is evident in Figs. 10 1C and 14 1D, where the highest adhesive failure is concentrated at the opposite end of the joint compared to any other fractured surfaces. The photographs indicate that the hydrated and silanized M^{400}S specimen has the best adhesion to the UP adhesive, even though, the bending of the joint prevents an accurate assessment of its actual tensile-shear strength.

The combined influence of the silanization and the pseudoboehmite nanostructure is evident in the high magnification SEM images of the two fractured sandblasted specimens displayed in Fig. 15. The UP-adhesive peels off the nanoglass structure of the hydrated sandblasted sample depicted in Fig. 15 A. As a result, the nanoglass pattern has been transferred on the peeled adhesive (Fig. 15 B). In the silanized, hydrated and sandblasted specimen (Fig. 15 C) UP adhesive has penetrated in the pseudoboehmite nanoglass and there is no fully exposed nanoglass unlike in the case of the unsilanized specimen (Fig. 15 A). This phenomenon along with the high shear strength values demonstrate that the interaction between the pseudoboehmite and UP adhesive has been significantly improved by silanization. In a previous study [22], silanization of a grit blasted, hydrated aluminum specimen has been found to improve adhesion between the aluminum substrate and epoxy adhesive up to 25% compared to a mere grit blasted, hydrated aluminum specimen. This finding is in accordance with our results.

**Figure 15.** SEM images of A) exposed nanoglass on unsilanized hydrated sandblasted surface, B) nanoglass pattern on peeled UP adhesive, and C) UP coated nanoglass on fractured sandblasted, hydrated and silanized Al/UP/Al specimen.
4. Conclusions

The target of this study was to increase adhesion between aluminum substrates and unsaturated polyester adhesive (UP) by using the micro and nanostructuring. The structuring methods were combined to form various superimposed surface structures composed of different level micro- and nanofeatures. For a chemical modification of the aluminum substrate surface, a treatment with 3-methacryloxypropyltrimethoxy-silane (MPS) was applied.

The results demonstrate that the micro-mesh structuring is a very effective and rapid method to increase the adhesion between UP and aluminum by a factor of 3. The UP adhesive penetrated into the small mesh wire structures, providing numerous locking points. When the micro-mesh structuring was combined with sandblasting to produce two-level hierarchical surface structures, the shear strength was improved even further with a factor of 7. In addition, the failure mode was found to be more cohesive in the hierarchically structured specimens.

The mere pseudobohemite nanostructure obtained with hydration did not increase the shear strength of smooth aluminum substrate notably. However, when the nanostructure was combined with microstructures or hierarchical micro-microstructures, the adhesion was found to increase further. This indicates that nanostructure must be combined with a microstructure in the form of the superimposed micro-nano or micro-micro-nanostructure.

The chemical modification with silanization was found to be an effective way to improve the adhesion of UP adhesive with the structured aluminum substrate. Combining the silane modification with nanostructuring affords substrates with very high tensile-shear strengths on every substrate studied.

Combination of different types of surface structuring methods provides new routes to produce extremely strong aluminum adhesive joints, important parts in the car and aviation industries.
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References


