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Improvement in Strength of the Aluminium/Epoxy Bonding Joint by Modification of the Interphase

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Summary: This contribution describes the influence of different surface pre-treatments including self-assembly of phosphoric acid mono alkyl ester as adhesion promoter (AP) for adhesive bonding of aluminium alloy AlMg3. The investigations were performed using a cold hardening two components epoxy-adhesive. The pre-treated surfaces, the interphase structures and the joints were characterized by: SEM/EDX, surface tension, XPS, DMA and the determination of mechanical parameters. The results interestingly show that the test sample with three step pre-treatment (degreasing in acetone, then anodic oxidation in phosphoric acid and adsorption of AP) has the highest adhesive strength and durability.

Keywords: adhesion promoter; aluminium-bonding; epoxy-adhesive; interphase; pre-treatment

Introduction

Adhesive bonding of aluminium components is widely used in the aerospace industries and is becoming more common in the automotive and architectural sectors. When epoxy adhesives are applied onto aluminium substrates, an interphase between the coating part and the aluminium surface is created. Chemical, physical and mechanical properties of the formed interphase depend on the substrate nature and its surface treatment, the nature of the hardener and the curing cycle.

The impact mechanisms of surface pre-treatments like degreasing, etching, anodic oxidation are the elimination of organic contamination, the improving of the wetting behaviour, the decreasing of magnesium : aluminium ratios, the increasing of the surface roughness and the increasing of the oxide/hydroxide layer thickness. Some current pre-treatments offer an excellent durability but introduce toxic chemicals such as hexavalent chromium.

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Therefore, recent studies have used self-assembled molecules (SAMs) as AP to study how to replace the present chromated procedure on aluminium and how to improve the lacquer adhesion and corrosion inhibition [1]. The combination of different pre-treatments and SAMs application can be considered as an alternative for environmentally friendly surface treatments that bring not only a higher durability but also an improvement of the adhesive strength. Besides, the fracture behaviour has some changes due to the different surface treatments.

The aim of this work is to investigate the effect of different pre-treatments and AP application on the surface state of an aluminium substrate, and how these treated surfaces influence the formation of the polymer network structure in the interphase and the mechanical properties of the aluminium/epoxy joints.

Experimental

Materials and sample preparation

The substrates used in this study are sheets of the aluminium alloy AlMg3. The AlMg3 samples were pre-treated, using different methods (table 1). Phosphoric acid mono-(12-hydroxy-dodecyl) ester was used as AP. The pre-treated substrates were exposed to a 10^{-3}M solution of the AP in water. The exposure time was 5min at room temperature (RT). The substrates were rinsed with distilled water and dried in vacuum or in a stream of dry nitrogen. The adhesive was a two components cold curing epoxy resin (Delo-Duopox 1891). This adhesive does not contain fillers and primers.

Table 1: Surface pre-treatment procedures

Pre-treatment	Description
degreasing	degreased in aceton applying ultrasonic waves , 10min
etching 1	degreasing, alkaline degreased in NaOH 10%, 60°C, 2min
etching 2	degreasing, alkaline degreased in NaOH 10%, 60°C, 2min pickled in HNO_3 15%, RT, 2min
etching 3	degreasing, etched in 10g/l Bonder[a] V338M, 50°C, 20sec pickled in 5 g/l H_2SO_4, 11.7 g/l $Al_3(SO_3)_3$*H_3O+ 3.4g/l HF 40%, 50°C, 30sec
etching 4	degreasing, alkaline degreased in P3 almeco 20[b]: 30g/l, 60°C, 10min etched in P3 almeco 40[b]/NaOH: 15g/l P3 almeco 40, 50g/l NaOH, RT, 1 min pickled in HNO_3 15%, RT, 2min
PAA	degreasing, anodic oxidation in phosphoric acid 15%, 15V, 28°C, 23min
SAA	degreasing, anodic oxidation in sulphuric acid 15%, 15V, 28°C, 23min

[a] Bonder V338M is from Chemetal

[b] P3 almeco 20 und P3 almeco 40 are from Henkel

Test procedure:

The interphase aluminium surface/polymer, where the aluminium surface was differently pretreated was investigated by scanning electron microscopy (SEM), surface roughness, contact angle, X-ray photoelectron spectroscopy (XPS), dynamic mechanical analysis (DMA) and some strength tests.

- Scanning electron microscopy (SEM/EDX): Electron micrographs were obtained with a Zeiss DSM 982 Gemini SEM. The energy dispersive X-ray spectroscopy (EDX) was operated with the primary electron energy of 3keV. The element composition of the near–surface layer of the aluminium (information depth approx. 1µm) was investigated by the EDX which was coupled to the SEM. In addition, other SEM and EDX cross sections of samples, that were embedded into epoxy resin, polished and steamed with gold, were performed to measure the thickness of oxide/hydroxide layer.
- Contact angle measurements: Contact angles were measured by the sessile drop techniquewith DSA 10 from Krüss GmbH, Hamburg. Water was used as a test liquid.
- Roughness measurements: With a HOMMEL TESTER T8000 the roughness of different pretreated surfaces was measured.
- X -ray Photoelectron Spectroscopy (XPS): The very top surface region with information depth of 3–5 nm of the samples was studied by core level XPS. It was performed using a PHI 5702 spectrometer with a lateral resolution 30 µm, viewed samples diameter 800 µm area. The take-off angle was 45°.
- Dynamic Mechanical Analysis (DMA): The dynamic mechanical analyzer DMA 983 of the company TA instrument / USA was used under nitrogen atmosphere. The measurements were carried out in the resonance mode with an oscillation amplitude of 0.2 mm. For the dynamic measurements the heating rate was 3 K/min in the temperature range between –50°C and + 250°C. After mixing the adhesive it was applied between the aluminium substrates and clamped vertically into the oscillate system of the dynamic mechanical analyzer. The storage time represents the period between adhesive application (assembling) and time of the measurement. The glass transition temperature is definable by the maximum of the dynamic viscosity (the main

relaxation region of the mechanical damping) [2].

- Strength tests: The shear tension test according to the European standard test procedure (DIN EN 1465), the shear stress-shear strain-test (DIN 54451) and the floating roller peel test (DIN EN 1464) were performed with a shear tension machine AGS-G (Shimadzu). The strength of adhesive joints was measured after the curing and after the aging-test according to the standard procedures VDA 621-415. The VDA 621-415 consists of 10 cycles, in which one cycle is composed of the following segments:
    - 24h salt-spray-test DIN 50021
    - 96h condensation water alternating atmosphere DIN 50017
    - 48h RT DIN 50014

Results and discussion

Figures 1-3 show the results of the shear tension test, the floating roller peel test and the shear stress-shear strain-test after the VDA 621-415 relative to the initial strength depending on surface treatments.

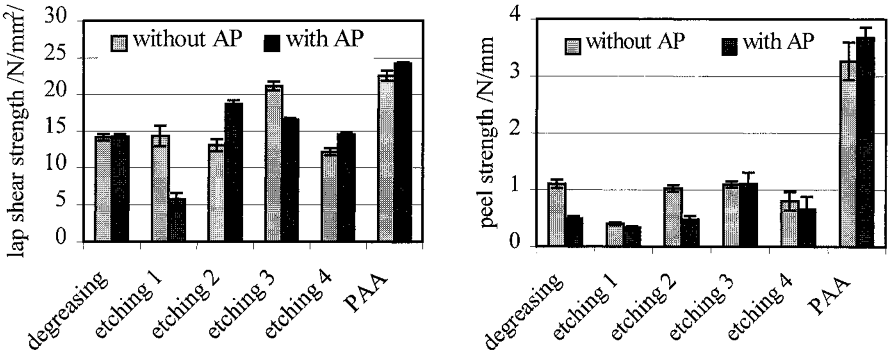

Figure 1. The initial adhesive strengths of different aluminium/epoxy-joints

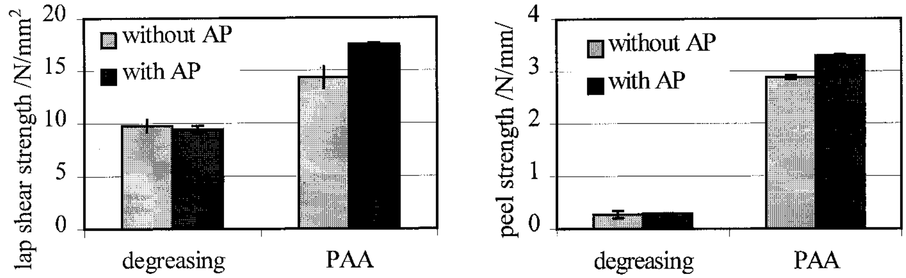

Figure 2. The durability of different aluminium/epoxy-joints after the VDA 621-415

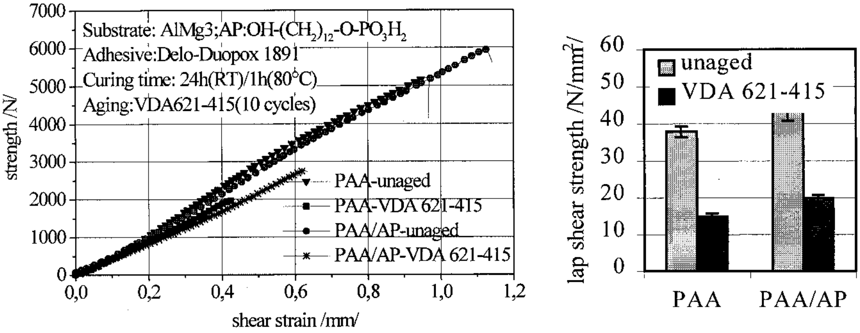

Figure 3. The shear stress-shear strain-diagrams of anodized aluminium/epoxy joints (PAA) and anodized with applied AP aluminium/epoxy-joint (PAA/AP) (DIN 54451)

It attracts attention that bonded specimens, which are degreased in acetone or alkaline- or acid-etched show clearly deteriorations of mechanical properties in comparison with PAA. The combination of those pre-treatments with AP have different effects on the adhesive strength of the joints. The highest improvement of the initial adhesive strength and the durability of the joints due to the impact of AP is achieved when the substrates were anodized. Therefore, PAA is considered as the preferable pre-treatment for applying AP to enhance the durability of the joints. This appeared to be interesting for further investigations concerning the influence of different surface pre-treatments and the role of the AP on the durability of aluminium/epoxy-joints.

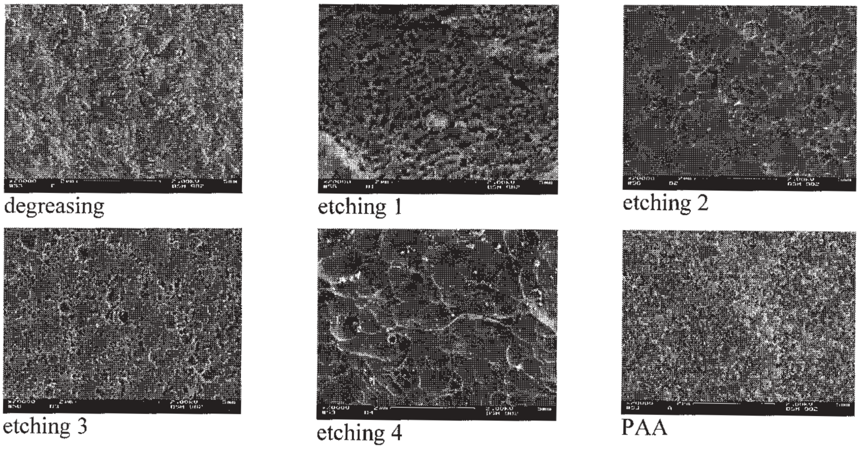

Figure 4. SEM images of the different pre-treated aluminium surfaces

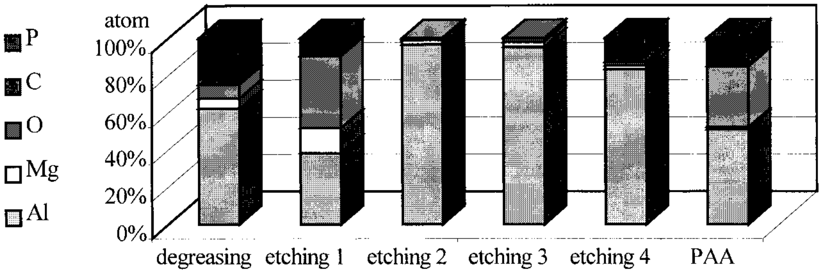

Figure 5. EDX linescans recorded from differently pre-treated aluminium surfaces

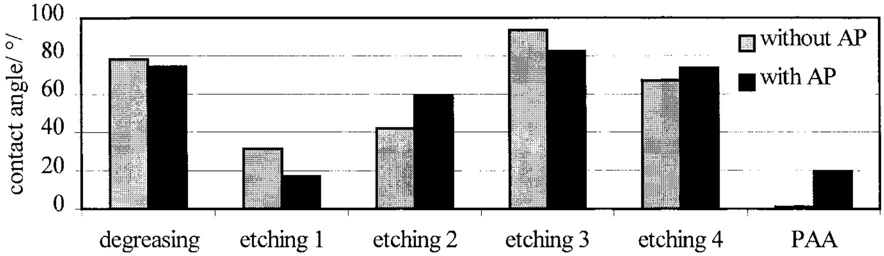

Figure 6. Water contact angles measured on pre-treated Al immersed in 10^{-3} M solution of AP

The effect of the various pre-treatments on the topography structures and the chemical state of aluminium surfaces was shown in Figs. 4 and 5, respectively. Degreasing in acetone can not completely eliminate the organic contamination and the roll texture that comes from the production process was found on degreased aluminum surfaces. Etch pits formations were seen on etched samples because etching dissolves some layers of the metal [3]. Alkaline etching (etching 1) removes the organic contamination and the original oxide layer but is unable to remove the magnesium. Other alkaline etchings and acid picklings eliminate the organic contamination, decrease the Mg : Al ratios, and form a very thin oxide/hydroxide structure. This oxide/hydroxide layer is at least three times smaller than the anodized oxide/hydroxide-layer (about 1 μm), shows poor corrosion resistance and a high degree of organic contaminations. PAA leads to columnar cell structure of the aluminium oxide/hydroxide layer [4].

The adsorption of AP on the aluminium surface was firstly investigated by the contact angle measurement (Fig. 6). If adsorption happens, the contact angle must be increased. It is evident that the degreasing, etching 1 and etching 3 are not suitable pre-treatments of aluminium surface for adsorption of AP. These pre-treatments induce the thin and unhomogeneous oxide layers, that contain high magnesium and organic contamination. It is supposed, that those surface properties prohibit the adsorption of AP on aluminium surfaces. The 2nd etched, 4th etched and anodized surfaces result in the increased contact angles after adsorption of AP. It proves that AP may adsorb on those pre-treated surfaces. Nevertheless, the contact angle measurements on those surfaces are not reproducible, because of the high surface roughness of the samples (Table 2), that significantly influences the water contact angle. This is the reason why the additional surface measurements were carried out to evaluate the ability of adsorption of AP on the different pre-treated aluminium surfaces.

Table 3 shows XPS results that represent the percentage of aluminium, oxygen, carbon and phosphorus atoms at the different pre-treated aluminium surfaces after an adsorption in AP solution. Highly curve fittings of the Al 2p core level yield an increase in hydroxyl group concentration from 64% to 70% on the anodized (PAA) and anodized/adsorbed AP (PAA/AP), respectively (Fig. 7). The curve fittings of the O 1s core level give the same information. In addition, the carbon concentration on anodized and applied AP surface was significantly increased and the atomic ratios, like [C]:[O], [P]:[O] or [Al]:[O], were changed after using AP. They confirmed the presence of AP molecules on the anodized sample. It suggests that the phosphoric acid was fixed on the AlMg3 surface after the PAA process. Hence, a small additional amount of phosphorus was only found after the adsorption of AP on those surfaces. It is supported by the appearance of phosphorus after applying AP of the SAA sample. That is a proof that AP is adsorbed on the anodized aluminium surface.

Table 2. Roughness measurements of the different pre-treated AlMg3 surfaces

	degreasing	etching 1	etching 2	etching 3	etching 4	PAA
arithmetical average roughness value /µm/	0.24	0.25	0.22	0.25	0.19	0.29
maximum roughness profile height /µm/	2.33	2.89	2.12	2.37	2.06	3.56

Table 3. XPS analyses of the AlMg3 surfaces depending on the different pre-treatments

Sample	C1s	O1s	P2p	Al2p	Mg2p	Rest	[C]:[O]	[P]:[O]	[Al]:[O]	[Mg]:[O]
degreasing	44.7	35.57	-	7.82	6.69	5.22	1.26	-	0.17	0.19
PAA	9.28	59.44	5.19	24.97	1.12	-	0.16	0.087	0.42	0.019
PAA/AP	24.4	50.17	5.02	20.42	-	-	0.49	0.1	0.40	-
SAA	23.41	51.98	-	20.64	-	3.44	0.45	-	0.39	-
SAA/AP	42.77	39.01	3.1	13.67	-	0.49	1.10	0.079	0.35	-

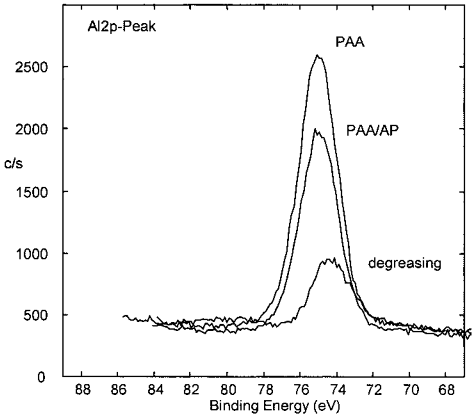

Figure 7. XPS Al 2p core level scan from degreased, anodized and anodized/adsorbed AP aluminium surfaces

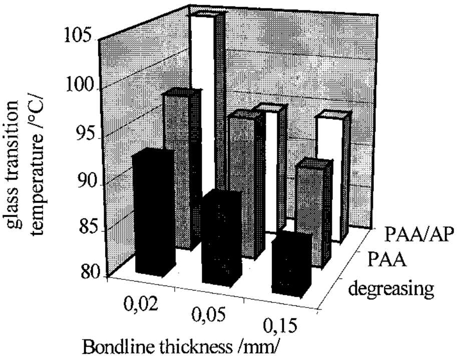

Figure 8. DMA results to determine the glass transition temperatures of the joints depending on the pre-treatment of the aluminium and bonded thickness

By the Dynamical Mechanical Analysis (DMA) several different glass transition temperatures of the joints depending on the surface treatment and the bondline thickness were found (Fig.8). The measured glass temperatures increase more especially in the substrate – near phase compared with the bulk phase of the polymer. The different temperature between those two phases is about 10 to 15 K. Thus, it may be concluded that the treated surface has a significant impact on the cross-linking of the epoxy resin. After adsorption of AP the anodized samples lead to the highest glass transition temperatures. It can be assumed that reactions between AP and oxirane of the adhesive can be considered as an initial reaction step in the curing process that causes to a formation of a epoxy network of higher density in the interphase of the aluminium/epoxy joints.

As a consequence, in the course of the curing process a continuous molecule growth takes place, oligomers and macromolecules are formed. This decreases the molecular mobility in the epoxy system which in turn results in an increasing glass transition temperature [5].

The differences of resulting surface properties in the scale of micrometers and nanometers and of resulting polymer network structures in the interphase due to different pre-treatments and the application of AP show a good correlation with the above presented strength and durability performances of aluminium/epoxy joints.

Conclusion

The adsorption of AP on differently pre-treated surfaces has been developed to improve adhesive strength and durability of the aluminium/epoxy-bonding joints. The results have proved that the AP has adsorbed better on the anodized surfaces than on other pre-treated surfaces. This treatment method leads changes both, the topography and more important, the chemical state of the aluminium surface. The PAA pre-treated aluminium oxide layers have more porous, thickness and hydroxyl group concentration than other pre-treated oxide layers. Hence, the phosphoric acid head-group of the AP was able to adsorb spontaneously onto the anodized surface, that has been proved by X-ray photoelectron spectroscopy. These induced chemical surface states influence the curing reaction of the epoxy system. Therefore the highest glass transition temperature is found for the near-interphase region on the anodized aluminium surfaces after adsorption of the AP by the DMA measurement. It is convincing that the different network structures in turn should influence the mechanical properties and the ageing behaviour of the epoxy/aluminium bonds. This has been confirmed by the industrial adhesion– and corrosion tests.

In conclusion, the idea using SAMs as adhesion promoter and corrosion protection layers for anodized aluminium surfaces appears to be promising. It is shown for the investigated systems that the effect of the anodic oxidation of aluminium in phosphoric acid and then adsorption of phosphoric acid mono-(12-hydroxy-dodecyl) ester as adhesion promoter on the interphase properties of the aluminium/epoxy joints has to be considered a very complex system. This interphase is characterised by a gradient of properties which vary from the pre-treatment ones to the bulk properties of the adhesive. The thickness, composition and structure of this surface treatment/adhesive system play a major role in the control of the adhesion performance and the joint durability.

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