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Influence of hierarchical micro-micro patterning and chemical modifications on adhesion between aluminum and epoxy

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ABSTRACT

The main target in the study of aluminum-epoxy resin joints was to enhance adhesion by increasing the surface area of aluminum substrates and by chemical functionalizing the aluminum surface to provide coupling points for epoxy resin. The surface area of the aluminum substrates was increased by fabricating microscale structures and hierarchical micro-microstructures by utilizing a micro-mesh printing technique and sandblasting. The effects of silanization with 3-glycidoxypropyltrimethoxysilane (GPTMS) and of oxygen plasma treatment were also investigated. Compared to a smooth surface, the micro-mesh structures improved shear strength by 33% and the hierarchical micro-microstructures by 116%. The utilization of the oxygen plasma treatment and especially the silane modification of the aluminum substrates were found to be effective in promoting adhesion. The specimens modified by combining the chemical or energetic modification method with surface texturing tended to fracture more cohesively than the specimens having a single modification. The hierarchically patterned and plasma and silane modified specimens had so high adhesion that the aluminum substrates started to deflect during the shear strength measurements, thus preventing the evaluation of their maximum strength.

1. Introduction

Adhesive joints are widely used in the automotive and aerospace industries instead of conventional welding and mechanical joints [1,2]. Adhesive joints have many advantages such as flexibility of design, lightness, fast and easy fabrication process, uniform load distribution over the whole bonded area and capability to join dissimilar materials [3–5]. As with any other method, adhesive jointing methods have their disadvantages which are for example environmental stress caused by the use of chemicals, limited shelf life of the adhesives and, frequently, a requirement for heat curing [6]. Moreover, adhesive joints do not have a high strength towards peeling forces and thus require pretreatment of adherend surfaces to achieve good bonding [6,7]. When improving adhesion between the adhesive and the substrate, it is important to know the factors having an influence on adhesion. Various adhesion theories have been developed and one of the most commonly referred to are mechanical interlocking, adsorption and chemical bonding theories.[2,8]

The pretreatment of adherend surfaces can be roughly classified into mechanical, chemical and energetic modifications. Mechanical pretreatments to increase surface area of the metal substrate include for example grit blasting [9,10], mechanical abrasion with sandpaper [11] and groove fabrication [12]. Acid etching [1,7,13], anodizing [14,15] and the use of coupling agents [16–18] are the most commonly used methods to functionalize metal substrate surfaces. Especially silanization has been proven to be an effective way to improve adhesion in metal–polymer resin joints. Use of adhesion promoters requires careful selection of the silane. The silane has to have suitable chemical groups to form chemical bonds both to the substrate and the adhesive. For polymer composites, energetic modifications such as plasma [19–21] and flame treatments [22,23] have been studied as more environmentally friendly adhesion enhancing methods. The plasma treatment of metal surfaces has been presented as a suitable adhesion promoting technique for metal–polymer resin interfaces [24–28]. Plasma treatment has also improved the wetting of an aluminum substrate with a silane solution [29]. This suggests that silanes could bind to the aluminum surface more effectively and therefore improve adhesion in aluminum–polymer resin interfaces.

The main target in our study of aluminum-epoxy resin joints was to improve adhesion by increasing the surface area of aluminum substrates and by functionalizing the aluminum surface to provide coupling points for epoxy resin. In the automotive and aerospace industries, epoxy resins are one of the most commonly used adhesives for aluminum [30]. The epoxy adhesive adsorbs

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onto the aluminum surface mainly with hydrogen bonds. The functionalization of the aluminum surface by coupling agents could provide an environment where covalent chemical bonding is possible, hence improving adhesion [17,31]. The use of hierarchical surface structures should also improve the robustness of the adhesive joints because it provides more mechanical interlocking points and larger surface area compared to the corresponding unstructured surface. In nature, hierarchical surface structures have been proven to have good adhesion properties. Probably the most well-known example of nature's hierarchical adhesion promoting structure is the feet of geckos [32–34].

In the present paper, new types of microscale and hierarchical micro-microscale surface structures were fabricated on aluminum substrates in order to increase their surface area. The adhesion promoting properties of the surface patternings were investigated with epoxy resin in single lap joints. In addition, the adhesion improvement by using 3-glycidoxypropyltrimethoxysilane and oxygen plasma treatment was studied. The effects of different combinations of the mechanical, chemical and energetic modifications on the adhesion properties of aluminum-epoxy joints were also investigated. The different approaches for improving adhesion between the aluminum substrate and the epoxy adhesive are summarized in Scheme 1.

2. Materials and methods

2.1. Materials

Commercial EN AW-5754-aluminum was selected as a substrate and Araldite GY 285 Bisphenol F epoxy (Huntsman) resin as an adhesive. Epoxy resin was cured with isophorondiamine (IPDA) curing agent and its relative amount to epoxy was 24.8 wt%. 3-Glycidoxypropyltrimethoxysilane (GPTMS) was used as an adhesion promoter. Curing agent and adhesion promoter were both purchased from Sigma Aldrich and their purities were $\geq$ 99% and $\geq$ 98%, respectively. Microscale stainless steel metal meshes, used in the microstructuring of substrates, were purchased from Spinea Ltd.

2.2. Specimen preparation, shear strength measurement and fracture investigation

The aluminum substrates (dimensions $3 \times 25 \times 100$ mm^3) were used as received. They were degreased with acetone in an ultrasonic bath for 15 min. Mesh printed and sandblasted substrates were degreased after the modification and silanized or plasma treated substrates were degreased before the modification. Epoxy resin was preheated and mixed with a magnetic stirrer at 70 °C and 500 rpm followed by the addition of the diamine curing agent. After the diamine was added, the mixture was further mixed for 3 min. Substrates and the diamine/epoxy-mixture were then joined together with a special jig, where adhesive layer thickness, overlap and alignment could be controlled. The adhesive layer thickness was set to 0.2 mm and overlap to 12.5 mm. A schematic representation of the manufactured single lap joint can be seen in Fig. 1. The joined specimens were cured with a curing sequence: 82 °C for 90 min and 150 °C for 90 min. After curing, the specimens were stabilized overnight in a desiccator followed by shear strength measurement.

Shear strength measurement using a single lap joint configuration was chosen for the adhesion measurements, because it provided a test system where the effects of different surface structures could be reproducibly measured on a laboratory scale. At least 5 specimens were measured to ensure repeatability. All shear strength measurements were carried out with a Zwick Z010/TH2A material testing machine. The test specimens were fastened by using asymmetrical grips (Zwick/Roell Typ 8306) in order to align the specimens and hence minimize bending and peeling during the test. The crosshead speed was set to 1 mm/min and kept constant. Shear strength P was calculated by using Eq. (1).

$$P = \frac{Fmax}{A} = \frac{Fmax}{l * w} \quad (1)$$

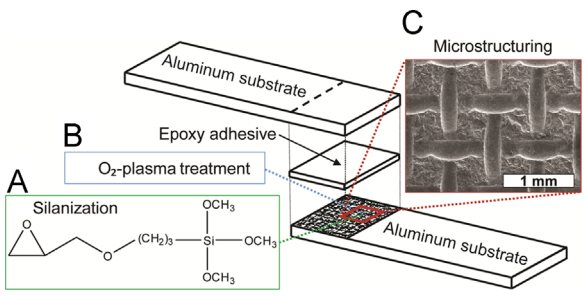
where F_{max} is the maximum force applied before total failure, A is the overlap area of the single lap joint specimen, l is the length and w is the width of the overlap area.

The fractured surfaces of single lap joint specimens were examined with an Hitachi S-4800 scanning electron microscope (SEM) and the acceleration voltage was set to 3 kV. All SEM samples were coated with a 4 nm gold layer using a Cressington Sputter Coater 208HR applied with Cressington thickness Controller MTM-20. A visual appearance of the fractured single lap joint specimens was captured with a camera (Sony HDR-SR 11E).

2.3. Physical modification with microstructuring

A mesh-type microstructuring was introduced onto aluminum substrates by the micro-mesh printing technique. The dimensions of the microstructured area were 25×15 mm^2. Mesh sizes of 100 μm, 200 μm and 400 μm were used in the study. The ratio between the mesh size and the diameter of the mesh wire was approximately the same with all the meshes used in the experiments (See Appendix A, Table A1). Micro-mesh printing was performed with a hydraulic press with a constant pressing time of 1 min. A supportive stainless steel plate (dimensions $10 \times 40 \times 130$ mm^3) was used in micro-mesh printing to prevent the deformation of specimens. Micro-mesh printing parameters are shown in Table 1 and a schematic picture of the micro-mesh printing set-up is presented in Fig. 2.

Sandblasting was used as a reference technique for microstructuring. The sandblasting pressure was set to 6 bars. The particle size of the quartz sand used in sandblasting was < 1 mm.



Scheme 1. (A) Chemical, (B) energetic and (C) physical modifications of an aluminum substrate.

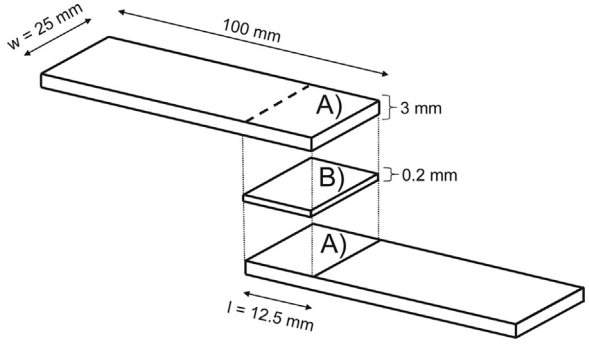


Fig. 1. A schematic picture of single lap joint specimen: (A) aluminum substrate and (B) adhesive layer.