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Influence of the composite surface structure on the peel strength of metallized carbon fibre-reinforced epoxy ☆

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ABSTRACT

In this work, the effect of mechanical pre-treatment on the surface structure of carbon fibre-reinforced epoxy composites and on its peel strength of electroless/electroplated copper was investigated. Sandblasting with Al_2O_3 was used to pre-treat the composite surface. The parameters investigated were blasting time (3 s, 6 s and 9 s) and nozzle distance to substrate (300 mm and 500 mm). A two-step metallization process was used for depositing copper coatings on the pre-treated composite surface. First, an eletroless plating process was used to deposit a thin layer on the surface. Second, an electroplating process was used to reinforce the thickness of the coating. Increased blasting intensity leads to a significant increase in surface roughness, which promotes mechanical anchoring effects of the coating. Scanning electron microscopy images and contact angle measurements confirm the results of the surface roughness. The adhesion of sandblasted composites, characterized by measuring the peel strength, is 10 times higher compared to untreated specimens. In addition to the mechanical anchoring mechanism the exposure of carbon fibres on the surface due to the blasting process promoted a stronger bonding to copper, due to the higher, electrical conductivity of the fibres in comparison to the matrix.

1. Introduction

The usage of carbon fibre-reinforced polymers (CFRP) within the automotive and aerospace industry is continuously growing in the last decades to replace traditional materials and achieve weight reduction. Currently, this is not only the case for structural parts, but also for storage systems for cryogenic liquid hydrogen, which is gaining attention from both academic and industrial communities.

Liquid hydrogen as an energy carrier is of special interest because of the much higher gravimetric energy density compared to gaseous and solid stored hydrogen as well as compared to conventional fuel systems. Prototypes and technology demonstrators using liquid hydrogen can be found in automobile and aerospace industries [1]. Traditionally made of stainless steel, the cryogenic storage systems can alternatively be manufactured with CFRP leading to a weight reduction of approximately 60% [1].

However, standard epoxy composites are not sufficiently tight for the storage of liquid hydrogen because of the higher permeation and outgassing rates compared to stainless steel. A metal coating on the surface of the polymer composite is therefore required as permeation barrier in order to fulfill the requirements [1].

Suitable coating processes of CFRP are vacuum-metallization (e.g. PVD or CVD), indirect metallization (e.g. hot foil stamping) and plating processes (e.g. electroless/electrolytic plating) [1–3]. Hot foil stamping is a suitable and economically viable method for relatively simple 2D geometries [2]. However, it cannot be employed for the manufacture of cryogenic storage systems. In the case of these complex-shaped 3D parts manufactured with CFRP, plating process is the most suitable coating process mainly because of faster deposition rates, higher ductility of the coatings and lower process temperatures compared to PVD or CVD processes [4].

Regardless which of the above-mentioned processes is selected to coat the CFRP with a metallic layer for permeation barrier purposes, it is generally very difficult to create consistently high adhesive strength levels between the composite and the coating materials [5]. This is due to the much lower polarity of the polymer surface in comparison to the coating material [6]. As consequence of the weak adhesion, the coating can detach from the CFRP surface leading to a significant permeability increase. This process is further accelerated due to the fact that storage systems are subjected to dynamic loadings [7]. One reason for

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this arises due to the difference of the outer temperature (room temperature, e.g. 23 °C) and inner temperature (−253 °C, liquid hydrogen). Furthermore, such storage systems are subjected during their lifecycle to a number of predictable and unpredictable mechanical loadings, especially considering that these systems are employed in the transport sector. For instance, considering the promising use of cryogenic hydrogen as energy carrier for satellites, the storage system and the CFRP/coating interface must remain intact during and after the rocket launch.

To increase the adhesion of the polymer substrate with the coating layer, surfaces are often treated in a way to: a) increase the surface roughness for mechanical adhesion, or b) modify the surface energy to increase the wettability and adsorption [2,8].

In both cases the surface is modified by pre-treatment processes, which can be generally classified as mechanical, chemical or electrical pre-treatments. Mechanical processes are grinding and sandblasting whereas etching and wet-chemical surface modification are typical examples for chemical processes. Electrical pre-treatment processes include atmospheric and low-pressure plasma treatment [9].

Regarding thermoplastics, examples for chemical pre-treatment can be found in case of acrylonitrile butadiene styrene (ABS), the most widely electroless plated plastic. In this case chromic acid has two effects on the surface, which results in an improved adhesion. It increases the surface energy and wettability by oxidizing the surface and it dissolves the polybutadiene nodes in ABS, which increases the surface roughness and significantly improves the mechanical adhesion [10]. In case of polyetherimide etching with permanganate, the imide ring of the molecule is opened and allows the copper ions to be incorporated into the system, which results in a high adhesion of the cooper coating to the polymer substrate [11].

Examples for electrical pre-treatment are found in case of plasma treatment of polycarbonate surfaces for palladium chemisorption prior to electroless deposition. Charbonnier et al. showed that after plasma treatment a high efficiency in grafting chemical functions could be achieved [12]. Direct palladium chemisorption onto nitrogenated groups is highlighted. However no influence on the adhesion was presented.

Chemical pre-treatment of epoxy resins is very difficult due to the narrow processing window and the high chemical resistance of this thermoset to most etching media. This leads to difficulties achieving a structured surface, as either too long times or too aggressive media will lead to its destruction [13]. Effect of alkaline etching on the surface roughness of a fibre-reinforced epoxy composite has been studied by Roizard et al. [14]. It has been shown that a small change in the topography could be achieved but the effect of the adhesion of a metal coating was not investigated. Kirmann et al. [15] studied the effects of the alkaline permanganate etching of epoxy on the peel adhesion of electrolessly plated copper on a fibre-reinforced epoxy composite. In this study the adhesion could be controlled by chemical etching with alkaline permanganate. An extra epoxy layer was applied to the composite surface to avoid fibre damage during etching.

Electrical pre-treatment of epoxy-based composites can also be found in the literature, for instance in case of plasma surface treatment of carbon fibre-reinforced epoxy composites [16–18]. Zaldivar et al. [16] studied the effect of atmospheric plasma treatment on the chemistry, morphology and resultant bonding behavior. The bonding strength after plasma treatment could be increased as much as approximately 50%. In a further study, Zaldivar et al. [17] continued the investigation of how plasma treatment process parameters affect the surface chemistry and the bonding behavior. The changes in the surface chemistry after the plasma treatment could be correlated with the adhesive bond strength. These studies looked at epoxy bonding but did not investigate metallized surfaces.

Sandblasting and its parameters as mechanical pre-treatment have been mainly investigated on metal substrates [19,20]. It has been shown that adhesion of a coating is strongly dependent on the surface roughness of the metal substrate, which can be regulated by blasting parameters. Generally speaking, higher blasting intensity (e.g. higher blasting pressure, lower distance, higher times) leads to a higher surface roughness [21].

For epoxy composites the influence of blasting angle on the adhesion of metal coatings was studied by Menningen et al. [5]. Advantages of this pre-treatment include higher adhesion strengths in comparison to grinding and easier processing in comparison to chemical etching [2,21]. Fracture mechanics was applied to the adhesion and a change from 30° to 90° blasting angle led to an increase in energy release rate of approximately 40%. But in this study no quantitative analysis of the surface structure was presented. In a further study Menningen et al. [22] investigated the effect of micro roughening on the adhesion strength of a nickel coating on a CFRP surface. It has been shown that an increase in blasting pressure leads to higher surface roughness but not necessarily to higher adhesion strength. However the influence of further blasting parameters, such as blasting time and distance, on the surface structure and adhesion strength is surprisingly still not investigated.

There is therefore a lack of knowledge in the literature in the field of copper-plated carbon fibre-reinforced epoxy composites, which we cover with this manuscript. This study focuses on the effect of the surface structure, generated with a mechanical pre-treatment method (sandblasting), on the peel strength of copper electroless-/electroplated fibre-reinforced epoxy composites. The topography and the wettability of the surface of the composite are heavily dependent on the selected pre-treatment process and its parameters [2]. This study presents a correlation between the surface properties of the substrates and the peel strength of the metallized material as well as the parameters of the pre-treatment process.

2. Experimental

2.1. Substrate material

In this study CFRP material consisting of carbon fibres (non-woven 0°/90° biaxial NCF HS Carbon from WELA) with an areal weight of 300 g/m^2 and a toughened epoxy resin as matrix (XU3508/XB3486 from Huntsman) were used. The CFRP laminates were manufactured by VARTM-process in a 1-part machine setup with a two-sided hard mould. The application of release agent Loctite Frekote 770-NC was done thoroughly on the mould surfaces as mould preparation before injection. The laminate thickness of 2 mm corresponds to a fibre volume content of approximately 50%. The laminates were cured at 100 °C for 5 h according to the resin manufacturer's datasheet.

2.2. Surface pre-treatment

The CFRP surface must be pre-treated prior to metallization of the material. The method investigated in this study is sandblasting with aluminum oxide and 200 – 300 μm grit size and a mohs hardness of 10. The parameters investigated are blasting time (3 s, 6 s and 9 s) and nozzle distance to substrate (300 mm and 500 mm). The depth of abrasion is dependent on the blasting time whereas the nozzle distance influences the blasting medium velocity and thus the kinetic energy of a blasting particle. The sandblasting machine ST 1200 ID-Z-SB with a die diameter of 10 mm is used to perform the tests. Constant parameters are blasting pressure of 2 bars and a blasting angle of 90°. All plates including the reference laminate were cleaned using an ultrasonic bath with equal parts of ethanol and water for 30 min at 25 °C prior to the coating process.

2.3. Mechanical properties of the untreated and pre-treated composite

The mechanical properties of the untreated and sandblasted composites were investigated under quasi-static 3-point bending using a universal testing machine Zwick Z2.5. For the sandblasted composites flexural properties of specimens exposed to the highest blasting