METALLIZATION OF FIBER-REINFORCED EPOXY COMPOSITES - EFFECT OF SURFACE STRUCTURE ON THE PEEL STRENGTH

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1 General Introduction

The percentage of carbon fiber reinforced polymers (CFRP) within the automotive industry as well as within the aerospace industry is constantly growing. Not only the mechanical performance of the composite has to be taken into account, but also its surface properties with respect to post coating processes.

In the aerospace industry CFRP can be used as a material for cryogenic storage systems, which is of special interest because of the lightweight potential of the component and the storage of liquid hydrogen as an energy carrier.

However, their surfaces are not sufficiently tight for the storage of liquid hydrogen, so that CFRP often requires the application of a metal coating as a permeation barrier. Suitable coating processes are PVD, thermal spraying or electroless / electrolytic plating. Regardless of which coating process is selected to generate a coating or coating system on CFRP for permeation barrier purposes, it is very difficult to create consistently high adhesive strength levels of the CFRP coating system [1]. The knowledge about the surface structures of composite materials is essential for all parts, which are coated afterwards. To achieve high adhesion with this secondary layer surfaces are often treated in a way to increase the roughness or the surface energy [2]. Not only the interaction with other materials is affected by the surface structure but also the optical quality of the final component.

This study focuses on the effect of the surface structure, generated with a mechanical pretreatment method, on the peel strength of copper electroplated fiber-reinforced epoxy composites. The topography of the composite is heavily dependent on the selected pretreatment process and its parameters. The surface properties of the substrates are correlated to the peel strength of the metalized material and the parameters of the pretreatment process. Furthermore, a brief evaluation of the pretreatment method is presented.

2 Experimental

2.1 Substrate Material

In this study CFRP material consisting of carbon fibers (non-woven 0°/90° biaxial NCF HS Carbon from WELA) with an areal weight of 300 g/m^2 and an epoxy resin as a matrix (XU3508 / XB3486 from Huntsman) was used. The CFRP laminates were manufactured by VARTM-process in a 1-part setup. The laminate thickness of 2 mm corresponded to a fiber volume content of approximately 50 %. The laminates were cured at 100 °C for 5 h according to the resin datasheet.

2.2 Surface pretreatment

The CFRP surface must be pretreated in order to metalize the material. The method investigated in this study is sandblasting. Aluminum oxide with 200 – 300 µm grit size and a mohs hardness of 10 was used as a blasting medium. The parameters investigated are blasting time (3 s, 6 s and 9 s) and distance (300 mm and 500 mm) respectively impact energy. 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°.

2.3 Coating Process

The CFRP substrates were coated by the electroless/

electrolytical plating process. Direct electrolytical plating of CFRP is impossible because of the electrical nonconductivity of the polymer matrix. On account of this, a thin adherent conductive layer was chemically deposited on the CFRP surface. For this activation, a one step catalyst (a stabilized Pd-Sn colloid) was used. After this activating process, a 1 µm thick copper coating was deposited electrolessly on the surface and finally electrolytically plated with the same coating material. The final coating thickness was approximately 40 µm.

2.4 Surface Structure

Surface Roughness

The pretreatment process will influence the surface structure of the composite and consequently the topography of the substrates. Especially the surface roughness is an important aspect in correlating the adhesion strength to the topography of the substrates. The roughness measurements were carried out with the Universal Surface Tester (UST) as shown in fig. 1.

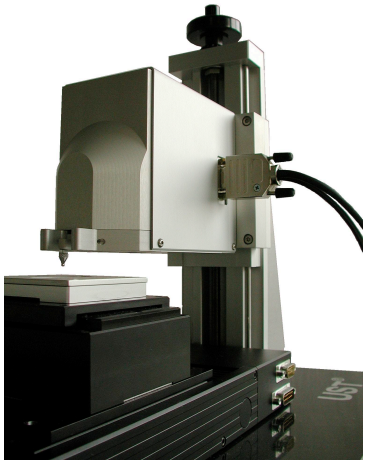

Fig. 1: Universal Surface Tester 100, Innowep GmbH

A 60° steel cone with a radius of curvature of 30 µm was used as a tip to measure the surface profile and roughness of the pretreated samples. A constant tip force of 1 mN and a tip speed of 0,1 mm/min were set to ensure reproducible roughness measurements according to DIN EN ISO 4287 [4] and ASTM D 7127 – 05 [5]. The surface of the samples were measured by 10 lines with a parallel distance of 2 mm and a measuring length of 20 mm to have representative information about the surface structure.

Microscopy

The microscopical surface investigations of the CFRP substrates were carried out by light and electron microscopy.

An optical microscope, Keyence VHX 100, was used, to show the deposits on the interfacial side of the coatings and on the substrates after the mechanical testing of the adhesion strength.

A scanning electron microscope (SEM), Jeol JSM-IC 848, was used to inspect the topography of the untreated and pretreated CFRP surfaces.

Contact angle

In measuring the contact angle the surface tension of pretreated samples and consequently the degree of wettability shall be determined. A drop of fluid with a defined volume and known surface tension γ_l is applied on the sample surface. The contact angle θ is then measured in the three-phase system solid (S), liquid (L) and gaseous (G) (fig.2) [2].

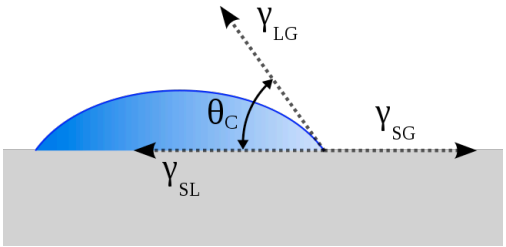

Fig. 2: Contact angle between a fluid and a solid

Contact angles of test liquids were recorded using a goniometer. The liquids tested were distilled water, and diiodomethane. Five droplets of each liquid, 2 μl in volume, were measured on each samples surface, and a software program quickly measured the contact angles. For each sample, the mean and standard deviation were calculated. Using the Owens, Wendt, Rabel, and Kaelble method, surface energy values were calculated as follows [6]:

$$\frac{(1+\cos\theta)\cdot\gamma_L}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p}\cdot\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d}$$

θ is the static contact angle of the liquid on the surface of the polymer, γ_l is the surface energy of liquid and is taken from the literature [7] and γ_s is the surface energy of the polymer. Superscripts *d* and *p* represent the dispersive and polar components of the surface energy accordingly. It should be noted that the total surface energy of a liquid or solid is equal to the sum of the dispersive and polar components.

2.5 Peel strength

The force required to separate a metallic coating from its plastic substrate is determined by the interaction of several factors: the generic type and quality of the plastic molding compound, the molding process, the process used to prepare the substrate for electroplating, and the thickness and mechanical properties of the metallic coating. By holding all others constant, the effect on the peel strength by a change in any one of the above listed factors may be noted. Routine use of the test in a production operation can detect changes in any of the above listed factors. The Peel-Test was carried out according to ASTM B 533-85 [3] by using a universal testing machine, Zwick Z2.5. Therefore, a 25 mm wide metal stripe was cut out of the substrate, using a paper knife, torn off at one end and peeled off at a velocity of 25 mm/min. The force was recorded as a function of the measuring path by software. To calculate the peel strength the mean of the recorded force was used and divided by the width of the peeled stripes.

3 Results and Discussion

3.1 Surface structure after pretreatment

Due to the manufacturing process, the CFRP laminates exhibited a closed epoxy matrix layer at the surfaces. Therefore, it is possible to pretreat the samples within the epoxy matrix layer on the one hand and on the other hand to remove the outer while carbon fibers become exposed to some extend. The variation of the blasting parameters time and distance results in a significant increase in surface roughness. Fig. 3 shows the mean roughness index over the blasting time while fig. 4 shows the roughness depth over the blasting time. In addition the effect of the blasting distance on the surface roughness is shown as well. It is clearly visible that on the one hand surface roughness is increased at higher blasting times but on the other hand the dncrease at a distance of 500 mm compared to 300 mm is not that significant.

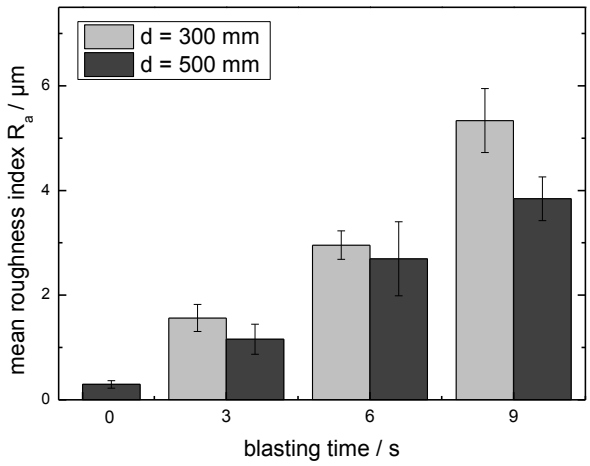

Fig. 3: Mean roughness index as a function of blasting time and distance d

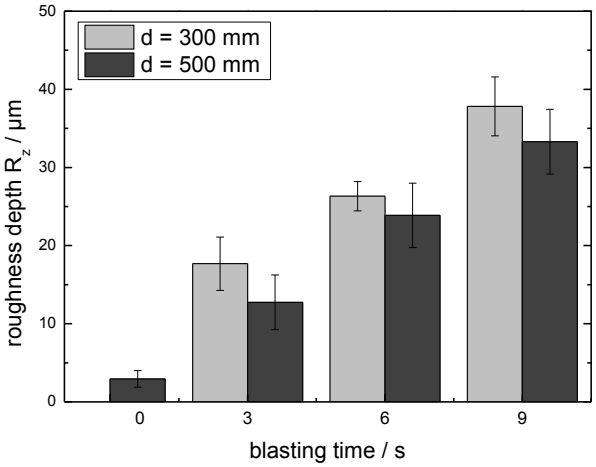

Fig. 4: Roughness depth as a function of blasting time and distance d

The increase in surface roughness can be explained with the higher wastage rate when exposing the sample at higher blasting times. A lower surface roughness at a greater distance can be attributed to the increase in the blasting radius and thus to a wider distribution of the particles across the blasted area.

Furthermore, the impact is smaller due to a lower kinetic energy of the particles. Sandblasting of the CFRP samples generates a non-uniform surface structure characterized by dimples and furrows. The difference of an untreated and pretreated sample surface is clearly visible in figures 5 to figures 9. At longer blasting times more epoxy resin of the outer layer is removed so that the carbon fibers are also damaged (fig. 8 and fig. 9). Moreover, the depth of the abrasion and the wastage rate seems to be lower at a distance of 500 mm compared to a distance of 300 mm (fig. 6 and fig. 7). The influence of the blasting time and distance shown in the SEM images is reflected in the surface roughness measurements.

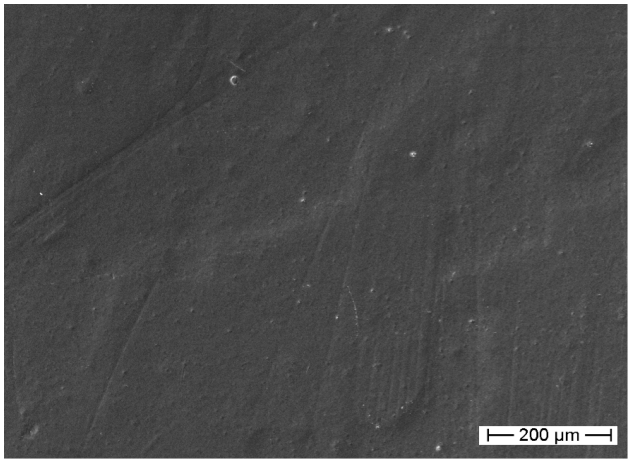

Fig. 5: SEM image of an untreated CFRP sample

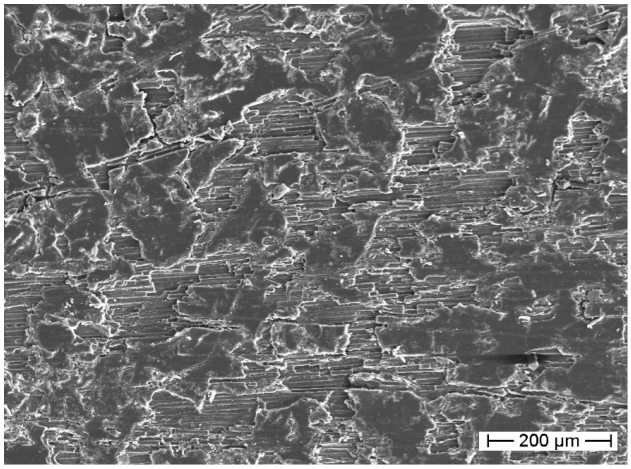

Fig. 6: SEM image of an Al_2O_3 blasted CFRP susbstrate (time 3 s, distance 500 mm).

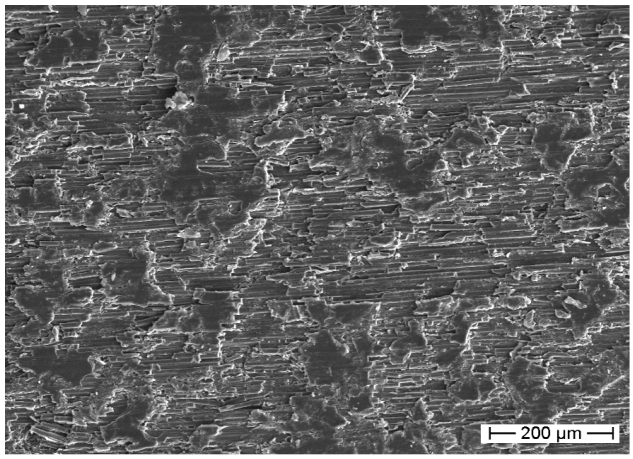

Fig. 7: SEM image of an Al_2O_3 blasted CFRP susbstrate (time 3 s, distance 300 mm).

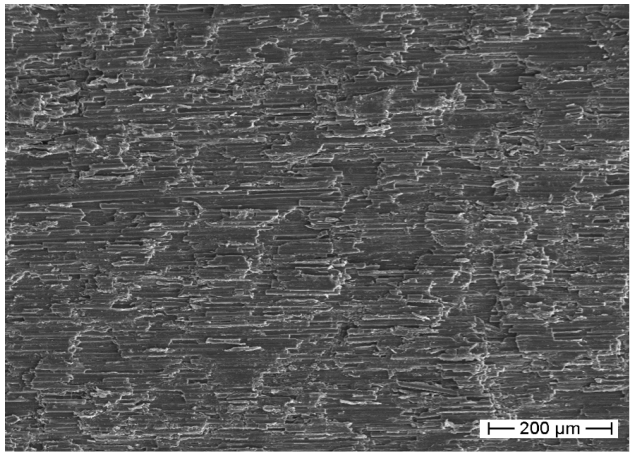

Fig. 8: SEM image of an Al_2O_3 blasted CFRP susbstrate (time 9 s, distance 500 mm).

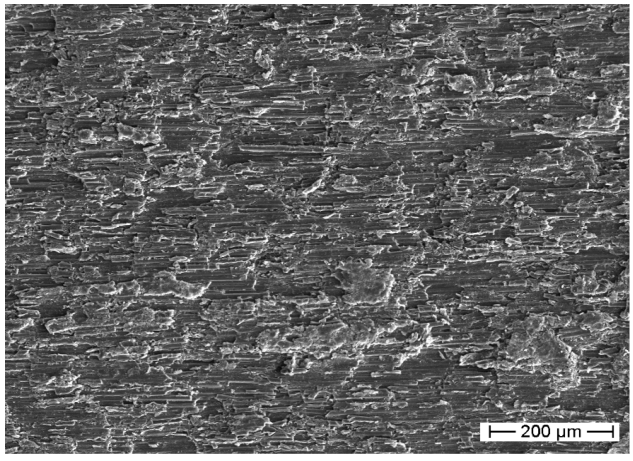

Fig. 9: SEM image of an Al_2O_3 blasted CFRP susbstrate (time 9 s, distance 300 mm).

The effect of mechanical pretreatment on the surface structure of CFRP substrates is visible after measuring the contact angle of untreated and blasted samples. Fig. 10 shows the influence of the blasting time and distance on the contact angle. The untreated samples indicate a low wettability referring to the contact angle of approximately 102°. After blasting with Al_2O_3 the contact angle increases and is not significantly changing at longer blasting times in case for a blasting distance of 300 mm. A significant change is merely noticeable between 3 s and 6 s at a distance of 500 mm. The increase in the contact angle can be attributed to the capillary depression effect [8]. With increased surface roughness the adhesion properties decrease because the fluid is not pulled into the cavities but remains on top of the embossment of the surface.

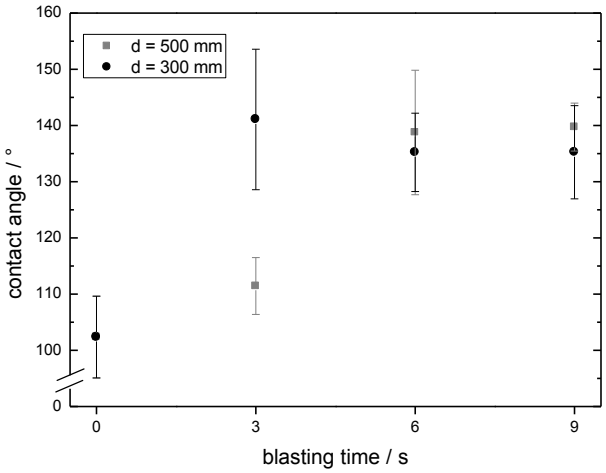

Fig. 10: Contact angle as a function of blasting time and distance d

3.2 Mechanical Testing

Fig. 11 shows the influence of the blasting time and distance on the peel strength of copper coated CFRP substrates. Although there is no significant change in variation of the blasting time the peel strength of blasted samples is approximately 10 times higher compared to untreated samples. However, an upward trend of increased peel strength at higher blasting times and shorter distances can be identified.

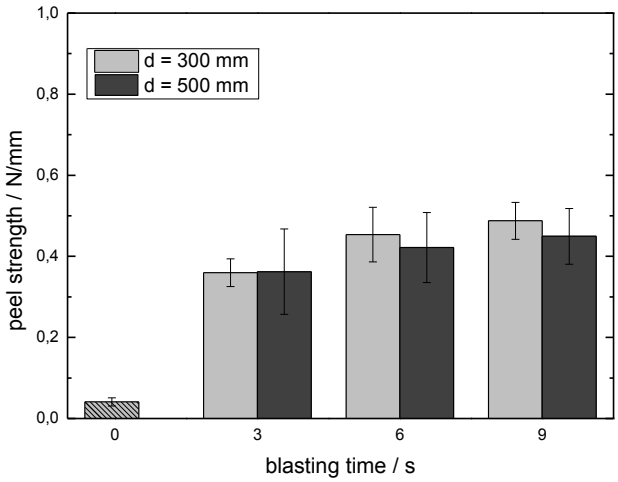

Fig. 11: Peel strength as a function of blasting time and distance d

4 Conclusions

Sandblasting with Al_2O_3 can significantly increase the peel strength of electroplated copper coated carbon fiber reinforced composites. Due to the increased surface roughness mechanical adhesion effects are responsible for adhesion of the Pd-Sn catalyst, which is necessary for the electroless depositing of 1 µm copper coating. A variation in blasting time and distance has an impact on the surface roughness and consequently on the topography of the substrates. While the surface roughness generally increases at higher blasting times it is constantly lower at an increased distance, which can be attributed to lower impact energy of the blasting particles. However, a constant increase in surface roughness is not necessarily resulting in a constant rise of the peel strength. A significant change can be identified between untreated and blasted samples whereas different blasting times and the variation in distance result in a minor change of the peel strength. It has been shown that the peel strength is dependent on the surface structure and can be influenced by sandblasting as a mechanical pretreatment method. Improvements of the peel strength by varying blasting time and distance is implied.

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