CHEMICAL SURFACE TREATMENT OF PES MODIFIED EPOXY RESIN AND THE INFLUENCE OF ITS MORPHOLOGY ON THE ADHESION OF METAL COATING

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Abstract
This study has shown that the chemical treatment of PES modified epoxy resin leads to increased adhesion strengths after metallization. PES separated from the epoxy matrix via a chemical reaction and spinodal decomposition. The content of the PES varied from 1 wt.%, 2 wt.% to 5 wt.%. The phase separation was observed by TEM. As an etching medium acetic acid was applied to selectively dissolve the PES. The etching time varied from ½ h, 1h to 2 h. SEM and profilometry showed an influence of etching time and PES content. Whereby the roughness could be controlled directly. Peel-test was performed to investigate the adhesion force to separate the metal coating from the epoxy substrate. The correlation between roughness and adhesion force was mostly affirmed.

1 Introduction

The growing importance of carbon fiber reinforced polymers (CFRP) within the automotive and aerospace industries implicates steadily growing requirements to the materials performance. In the aerospace industry carbon fiber reinforced epoxy can be used as material for cryogenic storage systems for instance to store liquid hydrogen. 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 and even compared to conventional fuel systems. Standard material for cryogenic storage systems is stainless steel. The use of CFRP leads to a weight reduction of approximately 60 % and therefore demonstrates a high lightweight potential [18].

However, standard epoxy composites are not sufficiently tight for the storage of liquid hydrogen, so that it requires the application of a metal coating as a permeation barrier. Suitable coating processes are vacuum-metallization (e.g PVD or CVD), indirect metallization (e.g. hot foil stamping) and plating processes (e.g. electroless / electrolytic plating) [2, 18, 19]. Hot foil stamping is a suitable and economical viable method for relatively simple 2D geometries [2, 9]. 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 suitable coating process mainly because of fast deposition rates, high ductile coatings and low process temperatures compared to PVD or CVD processes.

Regardless which coating process is selected to generate a coating or coating system on CFRP for permeation barrier purposes, it is generally very difficult to create consistently high

adhesive strength levels between the composite and the coating materials [1].
This is due to the much lower polarity of the polymer surface in comparison to the coating material [11]. To increase the adhesion of the polymer substrate with this secondary coating layer, surfaces are often treated in a way a) to increase the surface roughness for mechanical adhesion, or b) modify the surface energy to increase the wettability and adsorption [2].
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 [10].
For thermoplastics the knowledge about achieving a high adhesion of metal coatings is known in case for electroless deposited copper on polybutylene terephthalate where butylene is dissolved to increase the surface roughness. In case of polyetherimide etching with permanganate, the imide ring of the molecule is open and allows the copper ions to be incorporated into the system, which results in a high adhesion of the copper coating. Etching of epoxy resin using such pre-treatment is very difficult due to the narrow processing window. This leads to difficulties achieving a structured surface, as either too long times or too aggressive media will lead to its destruction. [12].
There is therefore a lack of knowledge in the field of copper plated carbon fiber reinforced epoxy composites in combination with a sufficient chemical pre-treatment in order to achieve high adhesion strengths. This study focuses on the effect of chemical treatment of PES modified epoxy resin and the influence of its morphology on the adhesion of a metal coating. This study presents a correlation between the surface properties of the substrates and the peel strength of the metalized material as well as the parameters of the pretreatment process.

2 Materials and testing methods

2.1 Substrate Material

In this study a bisphenol-A type epoxy resin (Epikote L20 / Epikure 960 from Momentive) was modified with polyethersulfone with a particle size diameter < 250 µm (PES E1010 from BASF) and cured with a diamine curing agent. The epoxy composite material was manufactured with casting molds in a 1-part setup. The neat resin plate thickness was 2 mm and a curing cycle of 4 h at 60 °C was performed according to the resin manufacturer's datasheet.

2.2 Surface pretreatment

The PES modified epoxy surface must be pretreated prior to metallization of the material. The method investigated in this study is chemical etching with acetic acid. The parameters investigated are etching time (0.5 h, 1 h and 2 h) and PES concentration (1 wt.%, 2 wt.%, 5 wt.%). 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 experiments. Constant parameters are blasting pressure of 2 bars and a blasting angle of 90°. After the sandblasting treatment the samples were cleaned in an ultrasonic bath with equal parts of ethanol an water for 30 min at 25 °C**.**

2.3 Coating Process

The epoxy substrates were coated by a combination of electroless and electrolytical plating process. Direct electrolytical plating of epoxy is impossible due to the electrical insulation of the polymer matrix. On account of this, a thin adherent conductive layer was chemically deposited on the epoxy 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 50 to 100 µm.

2.4 Surface Structure

The roughness measurements were carried out with a Universal Surface Tester (UST) 100 from Innowep GmbH. A 60° steel cone with a radius of curvature of 30 µm was used as 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 and ASTM D 7127 – 05. In order to obtain representative information about the roughness the surface of the samples were measured by 10 lines with a parallel distance of 2 mm and a measuring length according to DIN EN ISO 4287 which is dependent on the surface topology and the wavelength filter. The mean roughness index and the roughness depth are measured to characterize the surface roughness:

$$R_z = \frac{1}{n}(R_{z1} + R_{z2} + \cdots + R_{zn}) \quad (1)$$

where R_z is the roughness depth and n the amount of measured sections.

$$R_a = \frac{1}{l}\int_0^l |Z(x)|dx \quad (2)$$

where R_a is the mean roughness index and l the measuring length.

The microscopical surface and cross section investigations of the epoxy samples were carried out by light and electron microscopy. An optical microscope was used, to show the deposits on the interfacial side on the substrates after the mechanical testing of the adhesion strength and to visualize the adhesion mechanism after the coating process with the cross section samples. A scanning electron microscope (SEM), Jeol JSM-IC 848, was used to inspect the topography of the untreated and pretreated epoxy surfaces. The samples were gold sputtered prior to the SEM investigation.

2.6 Peel strength

The Peel-Test was carried out according to ASTM B 533-85 by using a universal testing machine, Zwick Z2.5. 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.

$$\sigma_V = \frac{F_a}{b} \quad (3)$$

where σ_V is the adhesion strength in N / mm, *b* the width of the peeled stripe and F_a the measured force

3 Results and Discussion

3.1 Surface structure after pre-treatment

The pretreatment process will influence the surface structure of the epoxy surface 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 variation of the pre-treatment parameters etching time and PES concentration results in a significant increase in surface roughness. Table 1 shows the mean roughness index and the roughness depth of etched PES modified epoxy resin as a function of the etching time and PES concentration. As expected, it is clearly visible that with no thermoplastic modification the etching media has no effect on the surface structure because epoxy resin is chemically resistant to acetic acid. Moreover, the increase in PES concentration in the epoxy resin leads to higher surface roughness after pre-treatment. This is due to the higher amount of PES, which can be attacked by the etching medium at the surface with respect to a homogeneous distributed modifier. The increase in etching time also leads to an increase in surface roughness but the change in PES concentration has a more significant effect on the surface roughness than the change in time. So a high amount of thermoplastic modifier exposed at the surface is more convenient for the attack of the etching medium than a low amount with longer etching times.

PES concentration (wt.%)	Etching time (h)	R_a (µm)	R_z (µm)
0	0	0.14 ± 0.01	0.90 ± 0.09
	0.5	0.13 ± 0.01	0.88 ± 0.08
	1	0.12 ± 0.02	0.78 ± 0.12
	2	0.12 ± 0.01	0.75 ± 0.04
1	0	0.14 ± 0.01	0.98 ± 0.09
	0.5	0.47 ± 0.11	2.76 ± 0.54
	1	0.54 ± 0.17	3.53 ± 0.87
	2	0.49 ± 0.14	3.22 ± 0.79
2	0	0.20 ± 0.01	1.24 ± 0.10
	0.5	1.35 ± 0.37	10.72 ± 2.07
	1	2.60 ± 0.54	27.50 ± 5.36
	2	3.41 ± 0.85	35.63 ± 7.00
5	0	0.18 ± 0.01	1.16 ± 0.11
	0.5	2.47 ± 0.02	16.91 ± 2.42
	1	20.18 ± 1.06	90.42 ± 4.52
	2	29.45 ± 2.82	153.86 ± 9.17

Table 1. Surface roughness of PES modified epoxy resin as a function of concentration and etching time

Figure 1 displays the effect of the chemical pre-treatment with acetic acid of unmodified and PES modified epoxy resin. The figure represents an etching time of 2 h at different PES concentrations. It is clearly visible that with a higher amount of PES modifier more PES particles can be attacked by the etching medium and therefore a higher surface roughness can be achieved.

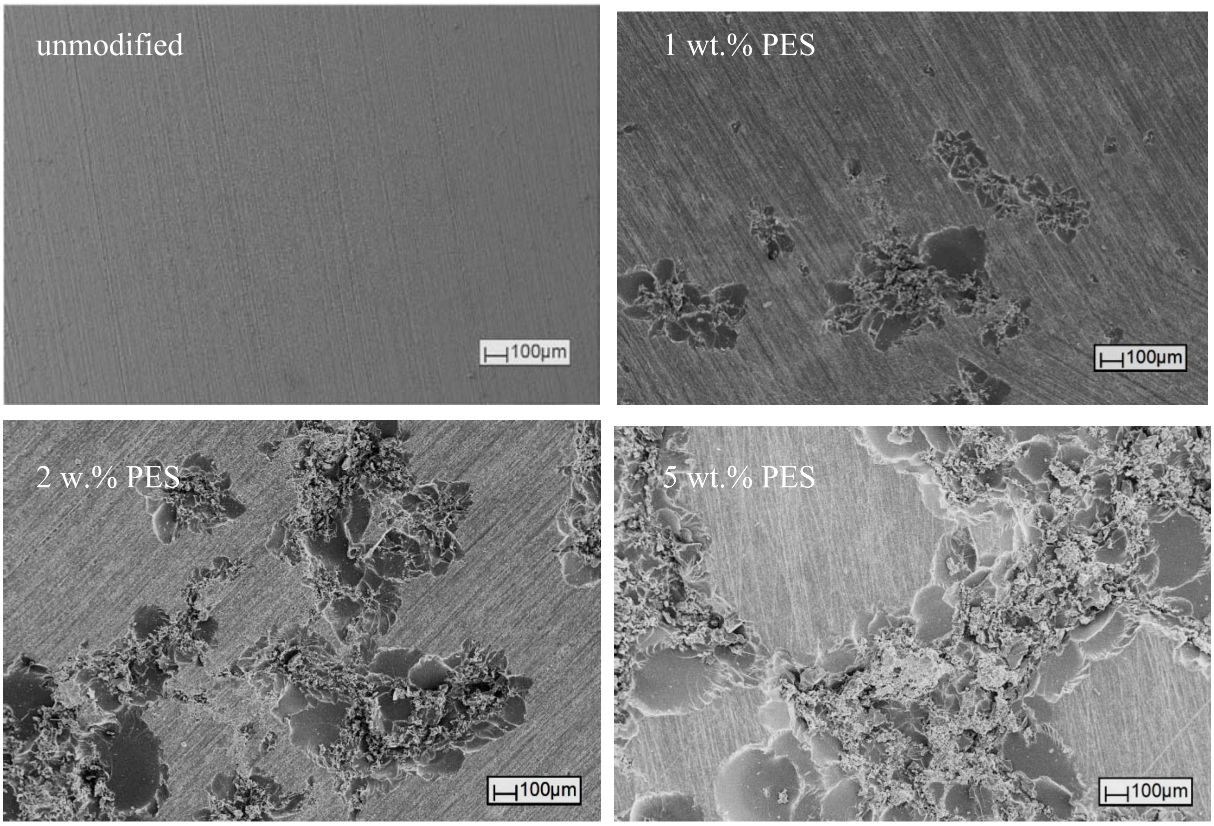

Figure 1. SEM images of chemical pre-treated epoxy resin with acetic acid after 2 h and different concentrations

The acetic acid can solve the thermoplastic PES particles out of the epoxy resin and therefore leave the desired rough and non-uniform surface.

3.2 Epoxy resin / Metal layer adhesion

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. Figure 2 shows the influence of the etching time and PES concentration on the peel strength of copper coated PES modified epoxy substrates. Compared to the reference sample (0 h treatment) the peel strength could be significantly increased after a modification of 5 wt.% PES in the epoxy resin and slightly increased after a modification of 2 wt.% PES. There is no increase in peel strength visible after a modification of 1 wt.% PES. Moreover the adhesion strength in this case drops after an etching time of 2 h. This could be due to possible contamination on the surface of the substrate in case of this series, which would interfere with the plating process and lead to lower adhesion strength values. Although there has been an increase in surface roughness in all cases after thermoplastic modification and chemical pre-treatment the peel strength is not increased in the same matter. This indicates that the surface roughness is not the only parameter, which will contribute to the adhesion strength. In other words, high surface roughness does not automatically result in high peel strength. In general the surface structure is responsible for the mechanical adhesion mechanism. It is also important to create certain undercuts at the surface in order to promote mechanical interlocking effects, which will result in high adhesion strengths. An increased surface roughness is necessary for the appearance of such undercuts but they do not contribute to the effective surface roughness because the measuring tip is not able to detect them.

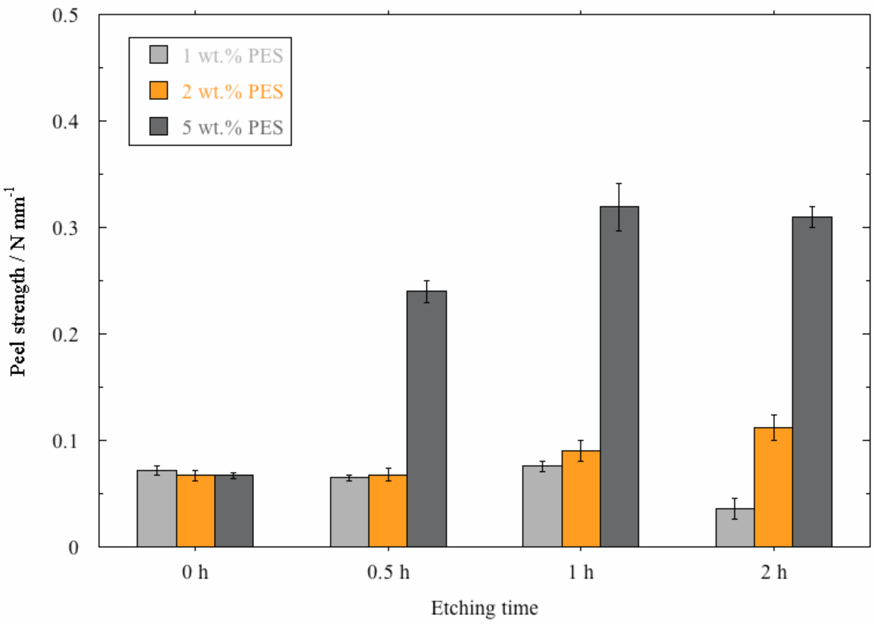

Figure 2. Influence of different PES concentrations and etching time on the peel strength of copper plated

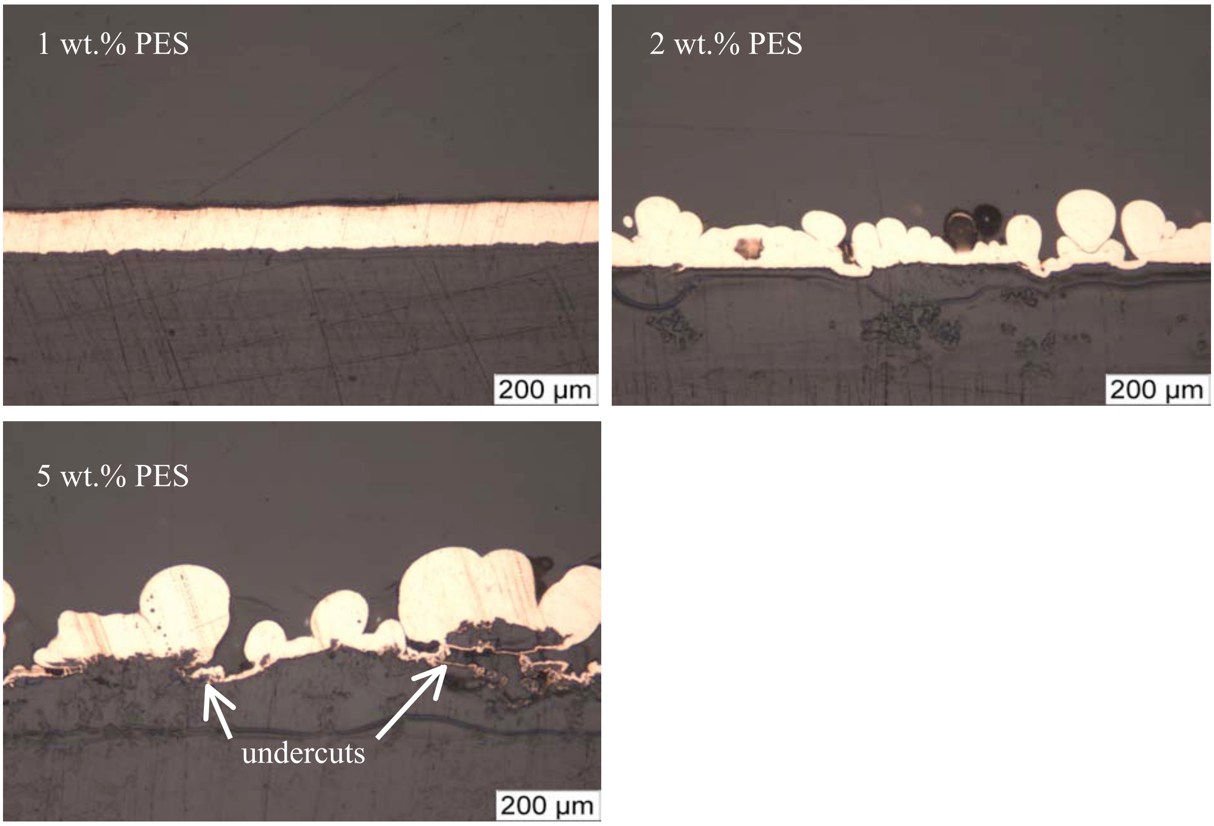

Figure 3. Copper plated PES modified epoxy resin after etching of 2 h

In figure 3 the interaction between surface roughness and the appearance of undercuts is visible. The figure shows cross section images of copper plated epoxy resin modified with different PES concentrations after an etching time of 2 h. With higher PES concentration or higher roughness respectively the appearance of undercuts increase. Therefore mechanical interlocking is possible and adhesion strength is increased. It is also visible that with significantly increased surface roughness the coating thickness becomes more inhomogeneous which could deteriorate the peel strength as the quality of the coating is influencing the adhesion as well. Within the electroplating process the coating thickness is not controlled by the change of the surface roughness but set as a constant parameter. Therefore if the absolute roughness depth is higher than the set coating thickness it will lead to an inhomogeneous coating. This is also indicating the fact that the peel strength is not only dependent on the surface roughness.

4 Conclusions

In this paper, the effect of chemical pre-treatment on the surface structure of PES modified epoxy resin and on its peel strength of plated copper is studied. The pre-treatment method investigated was chemical etching with acetic acid. It has been shown that the peel strength can be significantly increased. Due to the increased surface roughness and the appearance of undercuts, generated by selectively dissolving PES particles, mechanical adhesion effects are responsible for high adhesion of the copper coating. It has also been shown that not only surface roughness is the main factor which leads to an increased peel strength. A variation in etching time and PES concentration has an impact on the surface roughness and consequently on the topography of the substrates. It has been shown that the peel strength is dependent on the surface structure and can be influenced by etching with acetic acid as a chemical pre-treatment method.

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