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Adaptation of a *dry* metalorganic chemical vapor deposition metallization process to a *wet* chemical pretreatment of polymers

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A wet chemical pretreatment is applied on a carbon fiber reinforced polymer composite in order to provide a metalorganic chemical vapor deposition metallization layer with satisfactory adhesion. The pretreatment modifies the surface composition and the surface energy by forming a high concentration of surface polar groups. It also creates a multiscale roughness which results in a nonuniform topography; the etching efficiency being dependent on the considered surface area. Hence, previously underlying C fibers become exposed at the free surface and this modifies the reactivity toward metallization in these surface regions. The adhesion and resistivity of the Cu films are then impacted by such heterogeneity. This is exemplified by the visual inspection of adhesive tapes used for testing adhesion where Cu is exclusively removed at the location of bare C fibers. Addition of water vapor during the first step of the chemical vapor deposition process results in the formation of a copper oxide buffer layer. The latter perfectly wets the entire substrate surface, making the copper layer uniform while preserving adhesion and improving the electrical resistivity.

I. INTRODUCTION

Using polymer-based composites instead of metals offers similar mechanical properties while providing weight gain, leading to energy savings and reduced environmental impact. One of the major challenges in the use of polymer composites in the aerospace, or information and communication technology sectors is the recovery of the electrical conductivity or the electromagnetic shielding. This can be achieved by the deposition of a metallic film on the surface. For specific applications where this surface is not accessible by line-of-sight processes, it is relevant to proceed by metalorganic chemical vapor deposition (MOCVD).¹ One of the obstacles to be resolved in this case is the adhesion at the metal/polymer interface. It is usually weak; one of the reasons being the low surface energy of polymers. To overcome this issue, the reactivity and the topography of the polymer surface can be modified by physical and/or chemical means. This can be achieved by increasing the surface roughness of the polymer to enhance the mechanical anchoring and by increasing the surface concentration of reactive chemical groups. Usual pretreatments are for instance UV irradiation,^{2,3} plasma treatments,⁴⁻⁸ grafting of an adherent interlayer,⁹⁻¹⁶ deposition of a thin film containing oxygenated polar groups,^{2,17,18} or wet chemical treatments.¹⁹⁻²⁵ Anyway, reactivity of the surface must be high enough toward metal atoms, ions, or precursors in order to favor the conformal wetting of the surface roughness and then obtain a strong adhesion. In some case, polymer composites show a heterogeneous surface with varying reactivity that is detrimental to the final interfacial adhesion of the metal.^{2,26}

In the present study, we investigate the effect of an oxidizing wet pretreatment on the adhesion and the uniformity

of a MOCVD processed Cu film on carbon fiber reinforced polymer (CFRP) composites. The choice of the pretreatment is based on the work by Siau *et al.* on the influence of swelling and oxidizing solutions on the surface roughness and reactivity of FR4 glass/epoxy substrates.²¹⁻²⁵ The authors correlated the pretreatment duration and temperature with the peel strength of electrodeposited Cu films. They demonstrated that these solutions render the surface reactive toward metal deposition and increase the surface roughness, favoring mechanical anchoring and thus resulting in higher peel strengths. The sweller species penetrates into the interchain volume of the polymer and forces the polymer chains to bend and expose their polar groups at the surface. The surface roughness is increased when these polar groups react with the oxidizing agent. The etching rate depends on the surface concentration of polar groups:²⁵ the higher, the more oxidized the surface is likely to be, and the larger the pits are likely to form.

Even though the use of an oxidizer alone, such as potassium permanganate (KMnO_4), can increase the surface roughness of the epoxy polymer, it is significantly more efficient if an alcohol-based sweller is used beforehand. Hence, the maximum root mean square (RMS) value obtained after oxidation of the surface is increased from 400 to 600 nm when the surface is initially treated with a sweller.²² The authors also reported that the use of the sweller results in a fourfold increase of the peel strength, namely from 0.75 to 2.75 N.²⁵ These results were obtained for a specific combination of pretreatment conditions, consisting in the use of the sweller for 450 s followed by oxidation at 80 °C for 600 s. In these conditions, the resulting RMS roughness equals 275 nm.

It is important to keep in mind that this pretreatment is dedicated to deposition of metallic films by wet methods (electroless, electrodeposition, etc.). The objective of the

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present work is to assess if it is suitable for a dry MOCVD process operating at temperatures higher than 100 °C. For this reason we will use the above reported conditions as a starting point for the investigated composite materials. The applied metallization process is based on the recently reported MOCVD deposition of Cu on CFRPs from the organometallic precursor (hfac)Cu(I)(MHY) (Gigacopper[®]) where (hfac) is hexafluoroacetylacetonate and (MHY) is 2-methyl-1-hexen-3-yne.² This process yields polycrystalline and dense Cu films with uniform thickness which however present some pores at the interface and between large grains. They are poorly adherent to the CFRP surface. An *in situ* H₂O vapor flush of the sample during the first minutes of Cu deposition help growing smooth and highly conductive films without however significantly improving the adherence to the epoxy substrate relatively to the direct deposition of Cu on as received CFRP surfaces.²⁶

In that which follows, we report on the physical and chemical changes of the surface of the composite polymer induced by the commercial CircupositTM pretreatment (surface morphology, chemistry, and energy). We determine how they affect the adhesion strength and resistivity of a metallic film deposited afterward. And we finally show that a buffer layer is requested to make the entire surface reactive toward Cu MOCVD.

II. EXPERIMENT

A. Sample preparation and Circuposit pretreatment

Composites substrates are synthesized in a home-made vacuum infusion reactor from RTM6 resin and C fibers woven fabric. The preheated resin is injected in the mold under vacuum and the laminate is polymerized at 180 °C for 2 h. The obtained composite substrates are 1-mm thick with an epoxy finished surface. The surface of interest is smooth and corresponds to the face which has been pressed against the mold. Substrates are first cleaned with detergent, rinsed thoroughly, and then degreased with acetone and ethanol, before they are dried with pure Ar (99.999%). The Circuposit pretreatment consists in the following three successive aqueous baths (Rohm and Haas): a swelling solution containing 60–80 vol. % 2-(2-butoxyethoxy)ethanol (Circuposit Hole Prep 3304), an alkaline oxidizing solution containing 45–65 g/l of KMnO₄ (Circuposit Promoter 3310/4140), and a neutralizing solution containing 25–40 vol. % methanesulfonic acid (Circuposit Neutralizer 3319/4190). All baths are mechanically stirred. Clean substrates are placed in the first bath containing the swelling solution for 450 s at 80 °C. Then follows a two-stage cascade rinsing with distilled water before the samples are placed in the second bath containing the oxidizing solution for 600 s at 80 °C. After another two-stage cascade rinsing, the samples are immersed in the final neutralizing bath for 300 s at 50 °C, and rinsed. Finally, they are dried with Ar and immediately introduced into the MOCVD reactor for Cu deposition.

B. Cu deposition by DLI-MOCVD

Direct liquid injection (DLI-)MOCVD of Cu is performed in a horizontal cold wall reactor, described in Refs. 2, and 26

from Gigacopper. A 60 g/l solution of Gigacopper in anhydrous octane (Sigma-Aldrich, 99.99%) is injected into the reactor at a flow rate of 0.76 g/min. Deposition conditions are 195 °C, and 5 Torr. The corresponding deposition rate in these conditions is 37 nm/min, resulting in a 21 μm thick film for a 60 min process time.² For the buffer layer deposition, a second vaporization chamber produces water vapor that is added to the precursor gas mixture at a flow rate of 330 sccm for 12 min, then Gigacopper is injected alone during 48 min (0.76 g/min).

C. Bare and coated surfaces characterizations

Surface roughness is determined on untreated, pretreated, and coated samples by optical interferometry (S Neox Sensofar) capable of measuring surface roughness (Ra) down to 0.1 nm and peak-to-valley heights of up to several millimeter, on a surface area of 6 mm². Surface roughness is also determined at the microscale by atomic force microscopy (AFM, Agilent Technologies model 5500) operating in contact mode in ambient conditions. AFM images are processed with the GWYDDION software.²⁷

Cross section micrographs of Cu films are prepared and observed with a FEI Helios 600i-EDS apparatus equipped with a focused ion beam (FIB) and a field emission gun scanning electron microscope (SEM). A 40 × 2 × 1 μm³ Pt film is deposited before FIB cutting in order to protect the surface and limit curtain effects.

The chemical composition of the pretreated composite surface is investigated by x-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-alpha apparatus [hν(Al Ka) = 1486.6 eV]. The pass energy is fixed at 40 eV. A Shirley background is systematically subtracted.

Contact angle measurements are performed with the sessile drop method on a GBX Digidrop apparatus. Five liquids with different polarities are used to determine the surface energy of the pretreated composite: water, diiodomethane, bromonaphthalene, glycol ethylene and glycerol. The optimum droplet volume and the duration between droplet depositions and angle measurements were determined in a preliminary study (data not shown). They are chosen so as to ensure the repeatability of the contact angle measurements (eight droplets for each liquid). The surface energy c_s is calculated using the Owens and Wendt's method,²⁸ which also provides the dispersive and polar components of the solid surface (respectively, c_s^d and c_s^p , where $c_s^d + c_s^p = c_s$).

Sheet resistance R of the metallic films is determined with a Signatone four-point probe resistivity meter. The applied current is set at ca. 10 mA. The electrical resistivity q is determined using Smits' formula²⁹

$$q = R \times 4.532 \times t;$$

where t is the film thickness (cm) and 4.532 is a correction factor which is specific to the device geometry and depends on the spacing of the probe tips and on sample dimensions.

Tests involving a 3 M 810 adhesive tape are performed to visually qualify the adhesion of the metallic coating with the composite substrate. The procedure follows European

standard NF EN ISO 2409. 6×6 perpendicular incisions spaced by 2 mm form a grid on the coating on top of which the tape is applied. After 1 min, the tape is manually peeled at a constant rate and under a 60° angle to the horizontal. Depending of the surface area of the peeled Cu film, the adhesion is classified on a scale from 0 to 5, class 0 corresponding to a perfectly adherent layer.

III. RESULTS AND DISCUSSION

A. Surface topography

After a thorough cleaning as described in Sec. II A, observations on a 6 mm^2 nontreated surface [Fig. 1(a)] by optical profilometry reveals the presence of defects and scratches on the CFRP sample surface. XPS also shows the presence of siloxane groups (Sec. III B hereafter) at the surface, likely coming from release agents.^{30,31}

During the oxidizing step, a deep purple coloration appears on the samples, which instantly turns into dark blue-green when immersed into the neutralizing bath. After pretreatment, the samples keep this blue-green coloration and surfaces appear rougher to the eyes. Figure 1(b) shows that the pretreatment etches the polymer matrix to the extent of exposing bare carbon fibers to the free surface. The RMS roughness of this pretreated surface is $4.11 \mu\text{m}$ versus $1.51 \mu\text{m}$ for the untreated reference. This increase in roughness is mainly due to the creation of deep defects and the

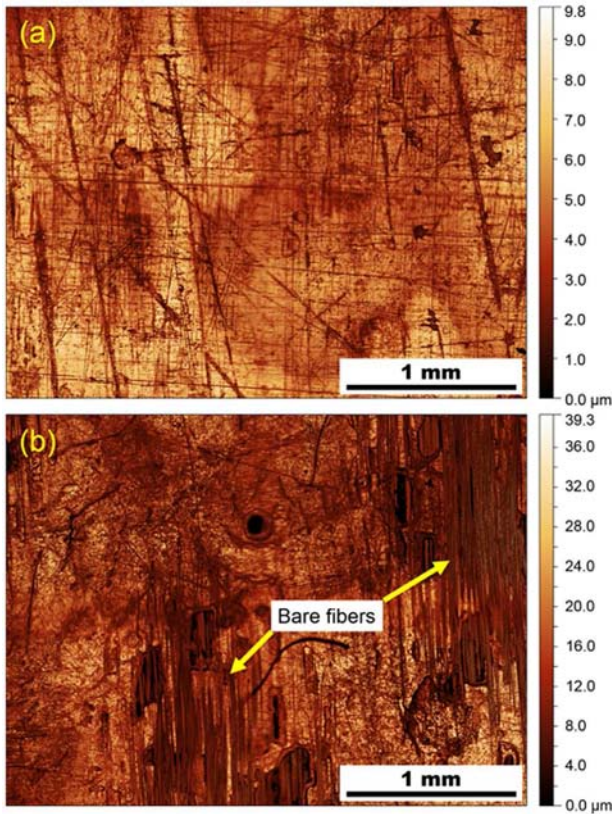


FIG. 1. (Color online) Surface profile of an untreated (a) and pretreated (b) composite. The analyzed surface area is 6 mm^2 and the sample tilt is corrected computationally.

uncovering of carbon fibers. Then, whereas the surface composition is pure polymer before pretreatment, it turns binary (C fibers/epoxy) with the pretreatment. We will observe the consequences of such a heterogeneity on the subsequent Cu film adhesion.

AFM micrographs shown in Fig. 2 confirm the heterogeneity of the sample surfaces: different morphologies and features are observed depending on the coarse location of scanning on the CFRP surface. A selection is shown in Fig. 2 where the left image is taken as representative of the untreated composite. Its surface is smooth with a RMS roughness of 75 nm . Some sparse cavities are found whose depth and diameter extend up to 300 nm and $11 \mu\text{m}$, respectively. On the pretreated composite, such cavities and pores

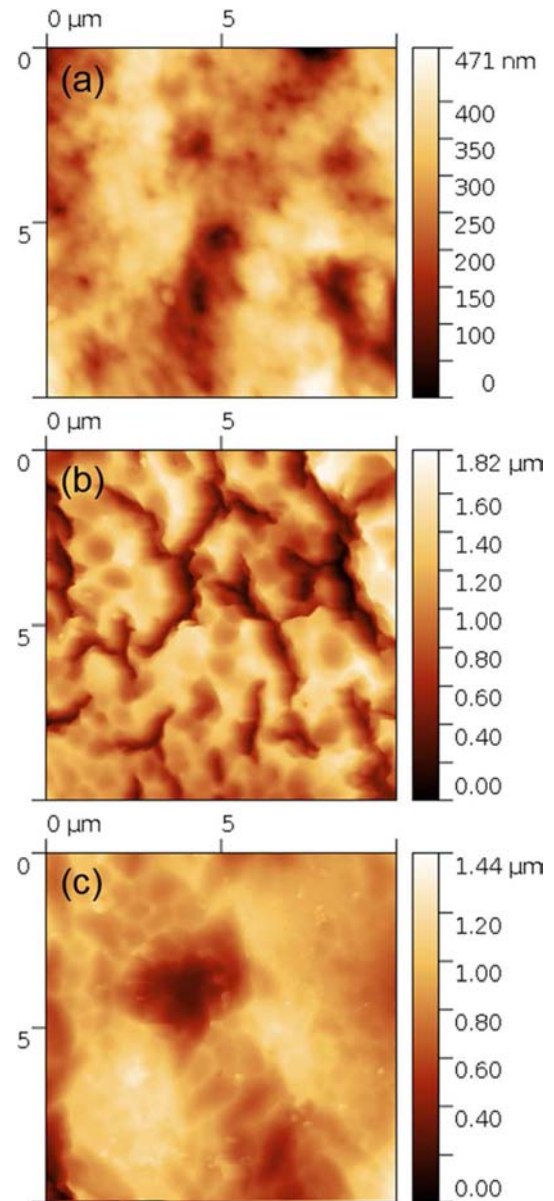


FIG. 2. (Color online) AFM images of an untreated surface (a), and two pretreated surfaces with Circuposit solutions [(b) and (c)]. Each AFM image is corrected by a polynomial of degree 2 algorithm.

are also visible but still very sparse. Their depth and diameter vary in the range 100–750 and 300–2000 nm, respectively. The local probing and consequently the limited statistical weight of the AFM measurements do not allow concluding on the creation of a larger number of pores. However, we observe that the pretreatment effectively etched existing pores, making them larger and deeper (see full scale change from untreated to pretreated). The average RMS roughness among the pores is 200 nm for a $10 \times 101 \text{ m}^2$ probed surface area. The RMS ratio between non-treated and pretreated surface is approximately 3: it is comparable to the one obtained at a microscopic scale by optical profilometry on a larger surface area. The RMS value is also consistent with the value found by Siau *et al.* (275 nm on greater surface areas), and fits in the range expected for optimum mechanical anchoring.²⁵

B. Surface composition

Figure 3 shows the C1s, N1s, and O1s core-level XPS spectra of an untreated (left column) and a pretreated sample (right column) where intensities (AU) were normalized to 1. Surface compositions are determined and summarized in Table I including minor contaminant species (siloxane, Mn oxides, chlorides, etc.). Chemical shifts for peaks

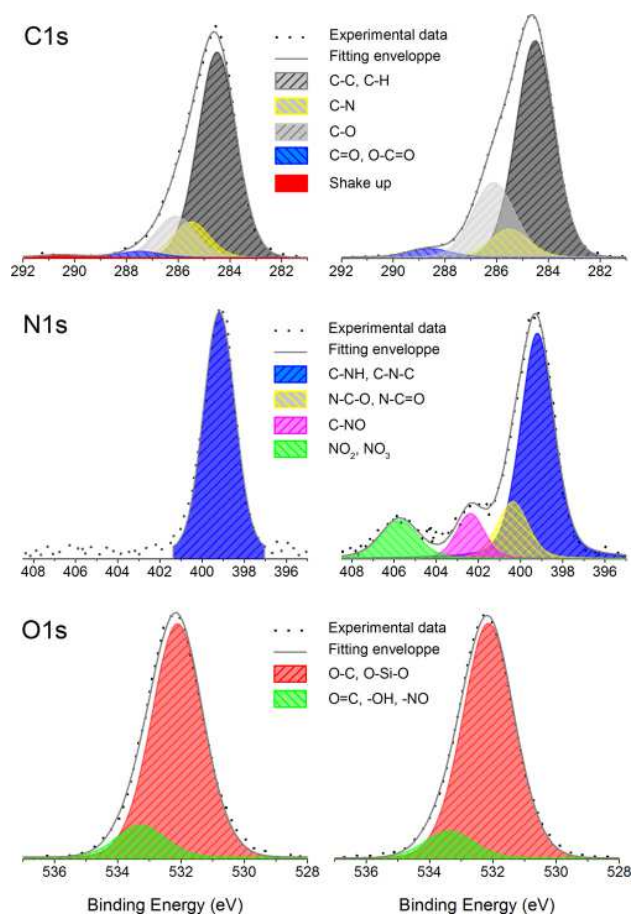


FIG. 3. (Color online) XPS C1s, N1s and O1s spectra of an untreated (left Column) and a pretreated (right Column) composite surface.

decompositions are taken from previous studies on epoxy surfaces.^{2,32,33}

The surface composition of the untreated sample is 76.2 at. % C, 13.9 at. % O, 6.5 at. % N, and 3.4 at. % Si. It contains a few oxidized species, hence a relatively low O/C ratio of 0.18, and a null O/N ratio. These ratios must be corrected because some O originates from siloxanes and Mn oxides. So more relevant values are obtained by calculating ratios on the sole oxygenated C1s or N1s peaks contributions. In that case, the O/C ratio equals 0.05 [i.e., $(\text{C-O} + \text{C=O}, \text{O-C=O})_{\text{at. \%}} / \text{C}_{\text{at. \%}}$]. Additionally, we observe a weak p-p* shake up satellite, which is typical of the energy loss of electrons coming from sp^2 carbon atoms in phenyl rings.

Analyses of the pretreated samples show an elemental composition of 64.9 at. % C, 21.8 at. % O, 4.5 at. % N, 7.8 at. % Si, and a total of 1 at. % of Cl, S, F, and Mn oxide. The O content is much higher, and then the O/C ratio almost doubled to 0.34. The *corrected* O/C and O/N ratios equal 0.27 and 0.38, respectively. This is mainly due to the creation of C-O, C=O, N-O, and N=O groups as extracted from the decompositions of the C1s and N1s spectra of Fig. 3, right. We also note the disappearance of the shake up satellite, which is a consequence of the oxidation of the phenyls C atoms whose hybridization turned sp^3 .

XPS characterizations demonstrate that the pretreatment is efficient for oxidizing the epoxy surface. It increases significantly the surface concentration of polar groups; in the form of -CO, -COO and -NO groups for the epoxy material under study. Nevertheless, we also found a total 1 at. % of contaminants at the surface (Cl, S, F, Mn). These species come from the different commercial baths involved in the preparation of the CFRP and were not removed by rinsing, cleaning, or turbopumping before XPS measurements. Hence, they are somehow in strong interaction with the epoxy. This pollution impacts the repeatability or consistency of the surface composition before each MOCVD deposition. Finally, Si is found in siloxane environment, which is quite common for the surface of demolded epoxy pieces. The fact that the Si concentration gets higher after the Circuposit pretreatment is supposedly due to the digging of underlying siloxane residues, that were trapped during polymerization.^{30,31}

C. Surface energy

Figure 4 presents the contact angles obtained with the five liquids on the untreated and the pretreated CFRP surfaces (top), along with the corresponding Owens–Wendt plots²⁸ of the two surfaces (bottom). The contact angle is lower on pretreated surfaces. In particular, the contact angle of water decreases from 88.6° to 55.6° . An exception is observed for diiodomethane, for which the contact angle increases from 51.6° to 66.6° . Whereas this latter behavior is questioning, the consequence on the determination of the surface energy is negligible (see the origin points of both Owens–Wendt plots). Correlation coefficients r^2 are 0.950 and 0.915 for the untreated and the pretreated surfaces, respectively, revealing an estimated error of 10%. Surface

TABLE I. Surface compositions of the untreated reference and a pretreated sample based on the decomposition of XPS spectra.

| Orbital | Bond | BE (eV) | FWHM (eV) | Ref. (at.%) | | Pretreated (at. %) | |
|---------|-----------------------------------|-------------|-----------|-------------|------|--------------------|------|
| C1s | C-C, C-H | 284.5 | 1.7 | 53.5 | 76.2 | 41.8 | 64.9 |
| | C-N | 285.5 | 1.6 | 8.7 | | 5.5 | |
| | C-O | 286.1 | 1.8 | 11.3 | | 15.7 | |
| | C=O, O-C=O | 287.5/288.8 | 1.9 | 1.8 | | 2 | |
| | p-p* | 290.5 | 2.3 | 0.9 | | 0 | |
| N1s | C-NH, C-N-C | 399.3 | 1.8 | 6.5 | | 2.9 | 4.5 |
| | N-C-O, N-C=O | 400.5 | 1.7 | N/A | | 0.7 | |
| | C-NO | 402.5 | 1.5 | | | 0.5 | |
| | NO ₂ , NO ₃ | 405.9 | 2 | | | 0.5 | |
| O1s | O-C, O-Si-O | 532.1 | 1.9 | 12.3 | 13.9 | 19.7 | 21.8 |
| | O=C, -OH, -NO | 533.4 | 1.8 | 1.6 | | 2.1 | |
| Si2p | Siloxane | 102.1 | 2 | 3.4 | | 7.8 | |
| Cl2p | N/A | 200.0 | 0.6 | N/A | | 0.2 | |
| S2p | | 168.2 | 2.5 | | | 0.6 | |
| F1s | | 688.4 | 2.1 | | | Trace | |
| Mn2p3/2 | Oxide | 642.3 | 3.4 | N/A | | 0.2 | |
| Mn2p1/2 | | 653.5 | 3.1 | | | | |

energies and their polar and dispersive components are presented in Table II.

The untreated composite is hydrophobic. Overall, the pretreatment increases the surface energy of the composite by 26%. It has a more significant effect on the polar component of the surface energy as it increases by 75%, making the pretreated composite more hydrophilic. This is consistent with the XPS results which show an increase of the surface concentration of polar groups.

D. Cu films deposition

Figure 5 shows surface and cross-section SEM micrographs of the Cu films deposited on untreated [Fig. 5(a)] and pretreated CFRP coupons, without [Fig. 5(b)] and with [Fig. 5(c)] addition of water vapor in the first steps of Cu deposition.

The Cu film deposited on the untreated composite presents a dense surface with a RMS roughness of 1.31 μm

determined on a surface area of 6 mm². The cross section shows that porosities are present at the interface and between Cu grains. Some of these grains are large and extend from the interface to the free surface, exhibiting crystallographic facets (an effect of the preferential channeling of ions along certain crystallographic orientations during FIB cutting).

The Cu film deposited on the pretreated surface is also porous. It is readily observed on the SEM images of the surface which exhibit open porosities and a much higher RMS roughness of 3.31 μm. It is further confirmed by the cross section image showing pores at the metal/substrate interface, at grain boundaries, and within grains. The fact that pores are still present at the interface after pretreatment demonstrates the incomplete wetting of the composite surface by Cu.

With water injection during the first step of deposition, a mixed nanocrystalline/amorphous 0.21 μm-thick layer is formed between the composite surface and the Cu coating. We showed in a previous work that this layer is composed of Cu₂O.²⁶ The intermediate Cu oxide layer presents a high density of small grains demonstrating the better wettability of the composite surface. Indeed, oxidation of Cu is a known process to enhance the adhesion of epoxy/Cu leadframe joints.^{34–36} The top surface of the Cu coating is dense and grains are finer than in the previous case. As a consequence, the RMS roughness is lower and equals 1.31 μm. On the cross section image, we observe that the contact along Cu grain boundaries is continuous, the microstructure is refined and the interface looks sharper. While Cu films on pretreated samples have an average thickness of 11 μm, Cu films on

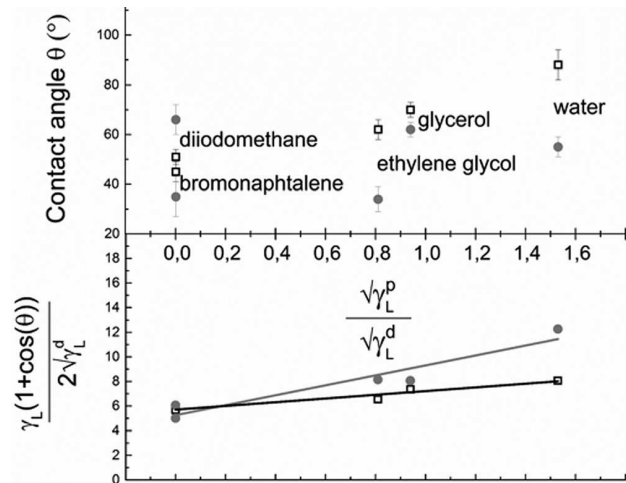


Fig. 4. Contact angles of the five liquids on untreated (empty squares □) and pretreated (filled circles ●) CFRP surfaces (top), and the Owens–Wendt plots for the two surfaces (bottom).

TABLE II. Surface energy of an untreated and pretreated composite determined by the Owens–Wendt method.

| | c_s (mJ/m ²) | c_s^d (mJ/m ²) | c_s^p (mJ/m ²) | r^2 |
|----------------------|----------------------------|------------------------------|------------------------------|-------|
| Untreated composite | 35 | 33 | 2 | 0.950 |
| Pretreated composite | 44 | 27 | 17 | 0.915 |

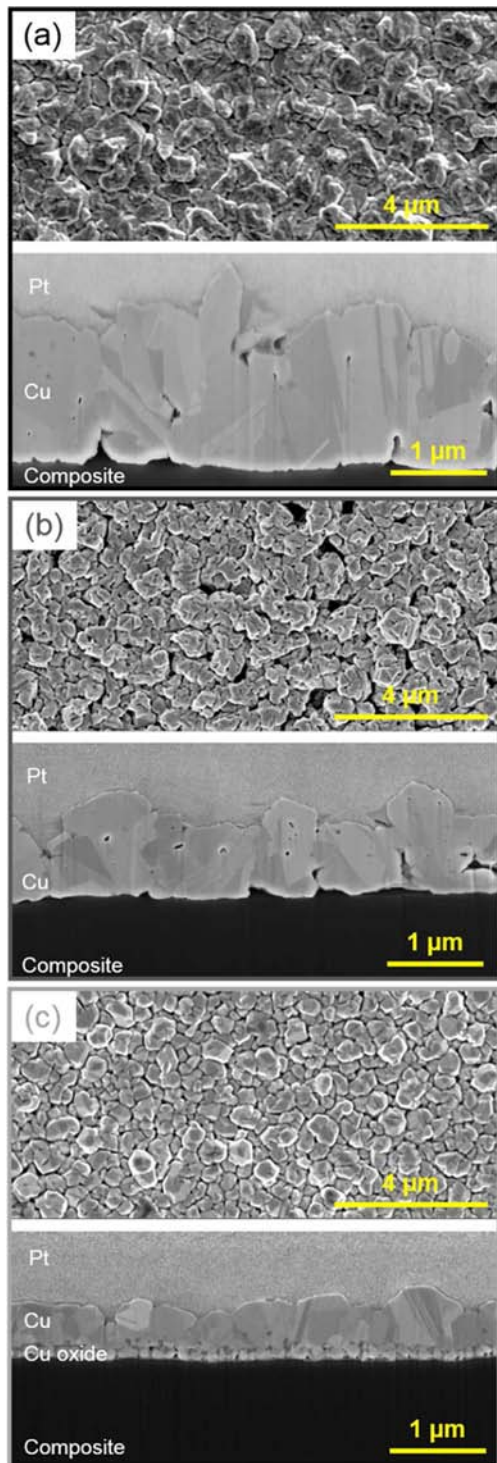


FIG. 5. (Color online) Surface and cross-section SEM images of Cu layers deposited on an untreated (a), and on pretreated surfaces, without (b) and with water injection during the first step of the MOCVD process (c).

pretreated samples and involving water during deposition are usually thinner (around 0.71 μm).

E. Adhesion

We now analyze the peeled tapes following the classification of the European standard NF EN ISO 2409 described in

Sec. II C. Figure 6 presents optical photographs of the adhesive tapes after the adhesion tests.

The copper layer without pretreatment [Fig. 6(a)] almost entirely peels off. It corresponds to a class 5, i.e., the interfacial adhesion is null.

The Cu layer with pretreatment [Fig. 6(b)] remains adherent on the major part of the substrate areas. The peeled surface area is in the range 5%–15% corresponding to class 2. We observe that the peeled fragments correspond to the denuded carbon fibers of the surface. Therefore, adhesion is strong enough on the epoxy surface but weak on C fibers. Another explanation could be a sizing degradation by the pretreatment when the fiber/matrix interface is close to the treated surface.

The Cu layer with the pretreatment and the Cu oxide buffer layer [Fig. 6(c)] entirely remains on the substrate. Peeling is less than 5%, hence this sample fits into class 1. The Cu oxide layer suppressed the heterogeneity arising from the binary composition of the surface (C fibers/epoxy).

F. Electrical resistivity measurements

The Cu film processed on the untreated CFRP sample present a resistivity of $3.21 \times \Omega \text{ cm}$, typical of MOCVD samples in these deposition conditions (resistivity values show a standard deviation of $0.31 \times \Omega \text{ cm}$ calculated on nine measurements). The film deposited on the pretreated surface has a much higher resistivity of $28.51 \times \Omega \text{ cm}$. With the interfacial Cu oxide layer, the value is intermediate and equals $20.81 \times \Omega \text{ cm}$. Therefore, though the Circuposit series is efficient to ensure adhesion of the Cu coating, it is also responsible for the degradation of the electrical resistivity. The origin of such an increase may be due to the contamination of the Cu film by S, F, MnO_x , or Cl, as found on the surface by XPS. We also assume that the MOCVD process at 195°C activates the thermal desorption of species and polymer fragments that were trapped during the pretreatment.

Another cause can be found in the degradation of the microstructure. With Circuposit alone, we observe a slight increase of pores density and a decrease of grains size. This creates interfaces which may reduce the transport of electrons. On the other hand, samples involving the Cu oxide layer show less porosities. Hence, resistivity decreases but not to the level of magnitude of the untreated sample. Again, there is an interplay between microstructure and chemical contamination. An additional step should be implemented

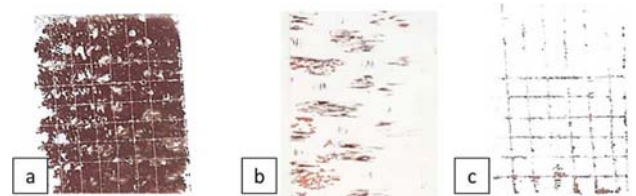


FIG. 6. (Color online) Peeled tapes used for adhesion tests on samples without pretreatment (a), pretreated with Circuposit (b) and pretreated with Circuposit and involving water during deposition (c). Grids are 1 cm^2 .

before MOCVD metallization in order to suppress these effects that are detrimental to the electrical resistivity.

IV. SUMMARY AND CONCLUSIONS

Overall, the Circuposit pretreatment does increase the surface roughness of the composites but not uniformly. Etching is found to be much more efficient in areas with already existing pores and in areas with underlying carbon fibers closer to the surface. It results in partial exposure of these fibers to the surface. The average RMS roughness determined from the AFM images processing is 200 nm, which is in the same range as similar studies.²⁵ The pretreatment increases the surface concentration of polar groups (-CO, -NO, -COO) and consecutively increases the surface free energy by 26%, and its polar component by 75%. However, this is not sufficient to ensure a strong wetting of the surface by Cu. Since we already observed this kind of behavior with a plasma pretreatment,² we assume that surface oxidation alone might not be adapted to render the now-rougher epoxy surface reactive to the MOCVD metallization from the (hfac)Cu(MHY) precursor. As a consequence, mechanical anchoring of the Cu grains onto the composite is not perfect. Nevertheless, the adhesion of the metallic layer onto the substrate is fairly good, except on bare C fibers. Adding water during deposition creates a sublayer of copper oxide which exhibits a good wetting of the whole composite surface. This sublayer also promotes the growth of a dense Cu layer, and results in an improved adhesion of the global coating. Figure 6 interestingly sums up the proposed reactivity scenario, by showing:

- (1) The poor original adhesion of a Cu layer when deposited on the untreated epoxy CFRP [Fig. 6(a)]. *The coating is entirely peeled off with the tape.*
- (2) The selective reactivity of the pretreated surface toward Cu deposition [Fig. 6(b)]. *Only the coating deposited on top of C fibers is peeled off with the tape.*
- (3) The uniform reactivity of the CFRP surface toward Cu oxide deposition from the precursor + water vapor gas mixture [Fig. 6(c)]. *The adhesive tape test leads to a class 1 result, making it acceptable at an industrial level.*

Finally, the increase of the electrical resistivity of the Cu coating is due to an interplay between contamination and microstructure modifications. The Cu oxide layer attenuates this effect, but an additional step must be introduced before MOCVD deposition in order to suppress remaining contaminants.

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