

IMPROVEMENT OF MOISTURE BARRIER PROPERTIES OF CFRP FOR HIGH-PRECISION ENGINEERING APPLICATIONS THROUGH SILICON-LIKE HYBRID FILMS PREPARED BY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

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ABSTRACT

Hybrid silicon-like films have been deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) on the surface of carbon-fiber-reinforced polymer (CFRP) laminates, used for high precision engineering applications (e.g. mobile parts of micro-milling machines, grinding machines, measuring machines, etc.) where high strength-to-weight, high stiffness-to-weight ratios and extremely high geometrical stability are required, to prevent structural distortions induced by the absorption of water vapour and water in liquid phase (hygroscopic behaviour). The films are made up of two layers: the inner layer was deposited from a mixture of hexamethyldisiloxane (HMDSO) as monomer, O₂ and Ar in conditions of high monomer fragmentation to confer the material barrier properties against moisture absorption while the most superficial layer was deposited from the same monomer and feed gases in conditions of low monomer fragmentation to confer the material hydrophobic properties against the absorption of water during machining operations.

Several films have been grown with different plasma process parameters. Chemical composition, water contact angle, surface energy, morphology, tribological and permeance properties have been evaluated to choose the one which best fulfils impermeability, hydrophobicity, wear and scratch resistance.

The film here proposed for CFRP materials used in ultra-high precision mechanical applications can be extended to other classes of FRP, including natural fibres composites, to prevent the degradation of their Young's module due to moisture absorption effects.

1. INTRODUCTION

The use of carbon-fibre-reinforced polymers (CFRP) laminates in structural applications where high strength-to-weight and high stiffness-to-weight ratios are required is well-established. However, because of structural distortions induced by moisture absorption effects, polymer matrix composites are not yet definitely considered suitable candidate for ultra-high precision engineering applications. Typical examples are ultra-high precision machine structures (e.g. mobile parts of micro-milling machines, grinding machines, coordinates measuring machines, ...) for which high values of mechanical properties (stiffness, damping) and, at the same time, extremely good long-term geometrical stability are required. The introduction of composite materials in this new industrial market will surely bring a great advances in term of dynamic performances and will represent a new challenge for design engineers and huge opportunities for composite manufacturers. However, moisture absorption of CFRP materials is an important problem. Absorbed moisture causes unpredictable and unacceptable structural distortions over time (even a geometrical drift of a few microns is not tolerated!) and this is still an open issue. In order to solve this problem, barrier coatings including metallic sheet coatings, elastomer polymer-based coatings, vinylester coatings and other specialty gel coats are used.

An alternative can be represented by amorphous silicon-like (Si:O_x:C_x:H_y) thin films produced by Plasma Enhanced Chemical Vapour Deposition (PECVD). This method

uses a low-pressure glow discharge to create active species, such as radicals and ions, from an original monomer (hexamethyldisiloxane in this specific case) so that polymer-like films are deposited through heterogeneous reactions between these active species present in plasma phase and the surface of the sample. In PECVD process the monomer gains energy from the plasma through inelastic collisions, especially with electrons, so that the plasma is about at room temperature, and is activated and fragmented into small molecules (or atoms) which can recombine to form larger molecules in plasma phase and/or directly react with the substrate surface. Moreover oxygen incorporation due to residual air in the reaction chamber can occur. So the chemical structure of plasma polymers is never predicted from the structure of the monomer because fragmentation and rearrangements of chemical moieties occur in plasma phase. How the starting molecules are fragmented into activated small molecular fragments in plasma phase depends from plasma parameters such as monomer and gas flow rates, radio frequency (RF) power, pressure in the reaction chamber, deposition time and geometry of the experimental system, even if the same starting molecules are used for the plasma polymerization process. Therefore PECVD technology, compared with other traditional deposition techniques, presents the possibility of gradually changing chemical composition and physical properties of the deposited films simply by the modification of the process operative conditions. If the plasma parameters are changed during the deposition process, hybrid films which join different chemical-physical properties can be realized from the same starting monomer (during the same process).

In the present work a SiO_x barrier film was deposited on CFRP substrate (unidirectional UHM carbon fibres in epoxy matrix) by PECVD from a mixture of hexamethyldisiloxane (HMDSO), O_2 and Ar in conditions of high monomer (HMDSO) fragmentation [1]. To prevent the absorption of water during machining operations in engineering applications, a more superficial thin layer was grown from the same monomer in conditions of low monomer fragmentation so that the film acquires also hydrophobic properties [2]. The result is an hybrid film which joins two properties, resistance to the permeation of water vapour and hydrophobicity, without presenting the adhesion problems that could occur in multilayer films where each layer has a totally different chemical composition. A further advantage of this film is represented by its thin thickness (submicron domain) which does not affect the final roughness of the surface (this is very important for applications where high quality smooth surfaces are required) and then no supplementary surface finishing process operations will be necessary. Moreover PECVD process does not requires high temperatures and is considered a sustainable environmental friendly process as it is performed in a closed vacuum apparatus with no emissions of VOCs (Volatile Organic Compounds).

The film chemical composition and its morphology were analyzed by Fourier Transform Infrared spectrometry (FT-IR) and Atomic Force Microscopy (AFM) respectively. The hydrophobicity of the outer film layer was investigated by water contact angle measurements while the barrier properties of the inner film layer were estimated through permeance tests. Micro-mechanical tests (using a micro-tribometer developed at Cambridge University) were carried out on CFRP samples to characterize the wear-scratch behaviour of the film. Finally the adhesion of the film to the composite substrate was investigated by Scanning Electron Microscopy (SEM).

The film here proposed for CFRP materials used in ultra-high precision mechanical applications can be extended to other classes of FRP, including natural fibres composites, to prevent the degradation of their Young's module due to moisture absorption effects.

2. EXPERIMENTAL APPARATUS

The deposition apparatus consists of a parallel-plate, capacitive-coupled PECVD system (see Figure 1), made up of a cylindrical stainless steel vacuum chamber with an internal diameter of 35 cm diameter and a height of 32 cm and with an asymmetric electrode configuration. The powered electrode is connected to a 13.56 MHz power supply coupled with an automatic impedance matching unit, while the other electrode is grounded and works as support for the samples. High purity Ar and O₂ (99.9997%) and liquid hexamethyldisiloxane (HMDSO) of chemical formula O[Si(CH₃)₃]₂ with 98% purity grade have been used. The monomer was heated to a temperature of about 80°C and injected into the vessel in vapour phase. The deposition was performed at a constant plasma pressure kept constant by a turbomolecular pump backed with a rotary mechanical pump. The process pressure, measured by a capacitive vacuum gauge, was in the range of 3-5 Pa.



Figure 1: PECVD apparatus.

3. SAMPLES AND EXPERIMENTAL DETAILS

The films have been deposited on CFRP (unidirectional UHM carbon fibres in epoxy matrix) specimens of 100 mm × 75 mm × 1 mm size and on Si (100) wafers for FT-IR measurements and for a detailed AFM analysis. All the substrates have been subjected to a cleaning pre-treatment with an Ar plasma.

The experimental conditions to grow silicon-like film with gas/vapour barrier properties or with hydrophobic properties belong to a well-established know-how about plasma processes for industrial applications involving the fields of mechanics, optics, microelectronics and food packaging. Glow discharges fed with organosilicon compounds mixed with oxidants lead to the deposition of amorphous films with chemical composition ranging from silicon (a-Si:O_x:C_y:H_z) to SiO₂, depending on the gas mixture composition, the process power and the pressure in the vessel. A film with barrier properties against moisture absorption must have a SiO₂-like chemical composition [1]. In order to grow a film with a negligible content of carbon and silanol groups (SiOH), which abate the barrier properties, a process with high levels of monomer (HMDSO) fragmentation, i.e. high power and high O₂ dilution of the monomer, has to be employed. In facts, as the O₂/HMDSO ratio increases, the higher

oxidation efficiency in plasma phase produces more SiO radicals and CO₂ volatile molecules than Si and CH radicals and leads to a marked inorganic character of the film: Si-O-Si functional groups prevail over Si(CH₃)_x groups and the film chemistry approaches the SiO₂ one. Moreover, because SiOH-rich films have a porous structure, silica-like coatings with a low content of silanol moieties have to be deposited. SiOH functionalities can be visualized as breaks in the dense network of a SiO₂ film which promote the diffusion of permeant molecules (e.g. water vapour molecules) through the film. High process powers imply a high fragmentation of the monomer in plasma phase and a high ion bombardment of the growing film which leads to a breaking of OH bonds in SiOH functional groups and to the formation of Si-O-Si linkages with a consequent densification of the film. Vice versa, a film with hydrophobic properties has to be grown in conditions of low fragmentation, i.e. with a low O₂ dilution of the monomer and a low process power. In these conditions the low fragmentation of the monomer in plasma phase implies the presence in the deposited film of a great number of apolar CH₃ groups which are responsible for the film hydrophobicity. To join barrier properties against moisture absorption and hydrophobic properties against the absorption of water during machining operations, films made up of two layers (see Figure 2), deposited from the same monomer (hexamethyldisiloxane) and feed gases (O₂, Ar) in the two different plasma regimes, have been realized.

Several films, made up of the same barrier layer, the best obtained for its impermeability to water vapour, and of different hydrophobic layers have been grown to choose the one which best fulfils the required surface properties, i. e. hydrophobicity, wear and scratch resistance. Here only the most significant results are presented. Plasma process parameters and film thicknesses, measured by a P15 KLA-Tencor surface profiler, are reported in Table 1.

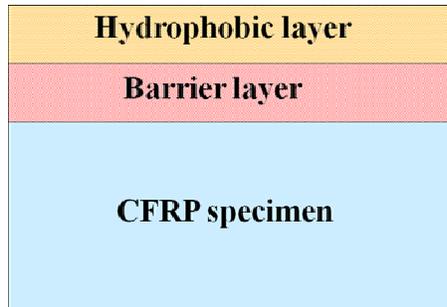


Figure 2: A schematic view of the hybrid film deposited on a CFRP specimen.

Table 1: Plasma process parameters and film thicknesses.

| | Ar flux (sccm) | O ₂ flux (sccm) | HMDSO flux (sccm) | Pressure (Pa) | Power (W) | Film thickness (nm) |
|----------------------|----------------|----------------------------|-------------------|---------------|-----------|---------------------|
| Hydrophobic layer #1 | 15 | 20 | 4 | 3 | 100 | 150 |
| Hydrophobic layer #2 | 20 | 0 | 7 | 3 | 100 | 720 |
| Barrier layer | 0 | 54 | 3 | 3 | 300 | 700 |

4. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

4.1. Infrared analysis

The films chemical composition has been investigated by Fourier Transform Infrared spectrometry (FT-IR). The analysis was carried out in transmission mode in the range of 4000-400 cm^{-1} . Figure 3 shows the absorption spectra of the barrier layer and of the two most significant hydrophobic layers which have been obtained (the curves have been offset vertically for clarity). Table 2 presents the analysis of the spectra with the relative band assignment [3-5]. The broadened shape of the bands, especially of the Si-O-Si asymmetric stretching band in the 1250-975 cm^{-1} region, suggests a wide dispersal of vibrational states which is characteristic of a film with an amorphous molecular structure. The insert in Figure 3 shows the deconvolution of this band relatively to the hydrophobic layer #1. The layer #2 exhibits a more organic chemical composition than the others. The barrier layer does not exhibit the Si-OH band in the 3100-3700 cm^{-1} region and presents a low content of carbon, so it has a chemical composition which approaches the SiO_2 one and therefore it has good barrier properties.

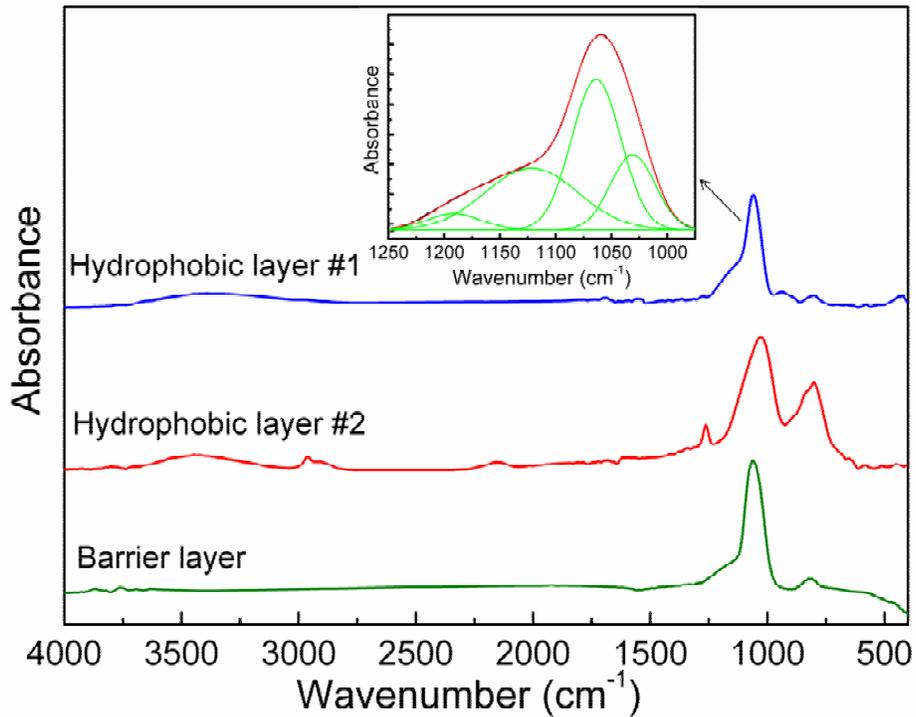


Figure 3: Infrared spectra of the barrier layer and of the two most significant hydrophobic layers that have been obtained. In the insert: deconvolution of the Si-O-Si asymmetric stretching band with regards to the hydrophobic layer #1 into four bands, originating from different Si-O-Si local bond angles that coexist in the film microstructure.

Table 2: Infrared band assignment.

| Peak/band position (cm ⁻¹) | Band assignment |
|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 3700-3100 | ν (O-H) in SiOH bonds |
| 2960 | ν_a (C-H) in CH _x (x = 1,2,3) bonds |
| 2900 | ν_s (C-H) in CH _x (x = 1,2,3) bonds |
| 1270-970 | ν_a (Si-O) in Si-O-Si bonds [1031 cm ⁻¹ in network structures with Si-O-Si bond angles < 144°; 1064 cm ⁻¹ in structures with Si-O-Si bond angles 144° (stoichiometric SiO ₂); 1122 cm ⁻¹ in cage structures with Si-O-Si bond angles \cong 150°] and (CH ₃) ₂ Si=O vibration modes (1191 cm ⁻¹) |
| 1260 | δ (CH ₃) in Si-(CH ₃) _x (x = 1,2,3) |
| 926 | δ (O-H) in SiOH bonds |
| 800 | δ (Si-O) in Si-O-Si bonds and Si-(CH ₃) _x vibration modes |
| 450 | ρ (Si-O) in Si-O-Si bonds |
| ν stretching; δ bending; ρ rocking; a asymmetric; s symmetric | |

4.2. Contact angle measurements

Contact angle and surface energy measurements have been carried out by an FKV dataphysics OCA20 goniometer to evaluate the film hydrophobicity. Contact angle (see Figure 4(a)), which is the tangent angle between a surface and a liquid droplet at their contact point, is a measure of the relative amounts of adhesive (liquid-to-solids) and cohesive (liquid-to-liquid) forces acting on a liquid. The higher the contact angle, the higher the film hydrophobicity. Surface energy has been calculated by Owens-Wendt method [6] using water and diiodomethane as test liquids. The results are reported in Table 3. This table shows also polar and dispersive contributions to the films surface energy. Polar contribution is due to Coulomb interaction between permanent dipoles and between permanent and induced dipoles, while disperse contribution is due to London forces between instantaneous dipole moments induced by time fluctuations of the charge distribution within the functional groups. The lower the polar contribution, the higher the film hydrophobicity. All the deposited films exhibit a very small polar component, which vanishes in sample #2. The film surface energy comes predominantly from the considerable presence of apolar CH_x groups. The great number of CH_x groups in sample #2 in comparison with sample #1, as infrared analysis reveals, gives the reason for the vanishing of the polar contribution and for the just dispersive nature of the surface energy. So the film with the top layer #2 is more hydrophobic (water contact angle 105°) than the film with the top layer #1 (water contact angle 91°) because of the higher content of apolar CH₃ functional groups. Figure 4(b) represents a picture of a CFRP laminate which has become hydrophobic after plasma treatment.

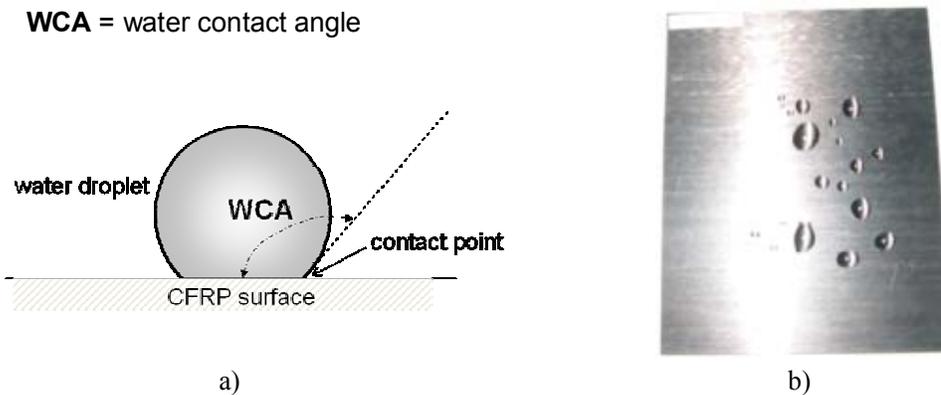


Figure 4: (a) Water contact angle (b) Picture of a CFRP laminate that has become hydrophobic after plasma treatment.

Table 3: Contact angle and surface energy results.

| | Water contact angle (degree) | Diiodomethane contact angle (degree) | Surface energy (mN/m) | Dispersive component (mN/m) | Polar component (mN/m) |
|-------------|------------------------------------|--------------------------------------------|--------------------------|-----------------------------------|------------------------------|
| Specimen #1 | 91 | 65 | 24.7 | 23.4 | 1.3 |
| Specimen #2 | 105 | 64 | 21.4 | 21.4 | 0 |

4.3. Permeance tests

The Water Vapour Transmission Rate (WVTR) coefficient of the film was measured through permeance tests, using a LYSSY GPM 200 permeability reader [7]: a value of $WVTR = 0.5 \text{ g/m}^2/\text{day}$ (ASTM E398-83 standard) was obtained, and that represents a very good results in term of barrier properties against moisture absorption, considering also that conventional polymer barrier films show a WVTR value of about $2\div 10 \text{ g/m}^2/\text{day}$. The gas permeation can also be correlated to the film thickness. In facts, with the increasing of the film thickness the coating quality enhances because an increased number of pinhole like defects, microvoids and defects in the film are sealed. On the other hand, when the film exceeds a certain thickness, which it has been estimated of about 700 nm, the coating becomes stressed and brittle.

4.4. Morphological analysis

The morphological properties of the deposited films have been investigated by Atomic Force Microscopy (AFM). AFM measurements were made in air by a Nano-R™ AFM System (Pacific Nanotechnology, Santa Clara, CA, USA) operating in close-contact mode. Silicon conical tips of 10 nm radius mounted on silicon cantilevers of 125 μm length, 42 N/m force constant and 320 KHz resonance frequency were used. Images were processed and analyzed by means of the NanoRule+™ software provided by Pacific Nanotechnology. Physical topography, roughness and dimensions of the surface

features were evaluated. To have a better comprehension of the films morphology, the films have been deposited also on Si (100) wafers. AFM pictures show that all the films present the typical island morphological structure of silicon-like films with rms roughness (root mean square roughness) evaluated on a $2 \times 2 \mu\text{m}^2$ area of the order of 1 nm for the layers deposited on Si wafers and of 10 nm for the same layers deposited on CFRP substrate. Moreover, it is clear from the images (not shown) of the layers deposited on Si wafers, which are very flat and so allow to pick out the intrinsic morphological peculiarities of the deposits, that the barrier layer is denser than the hydrophobic layers because of the small features growing during the process, as a consequence of the high monomer fragmentation in plasma phase. The high density prevents the permeation of gases and vapours through the film and so through the CFRP. Figure 5 shows a typical AFM image (3D and 2D views) of a silicon-like film deposited via plasma on a CFRP substrate.

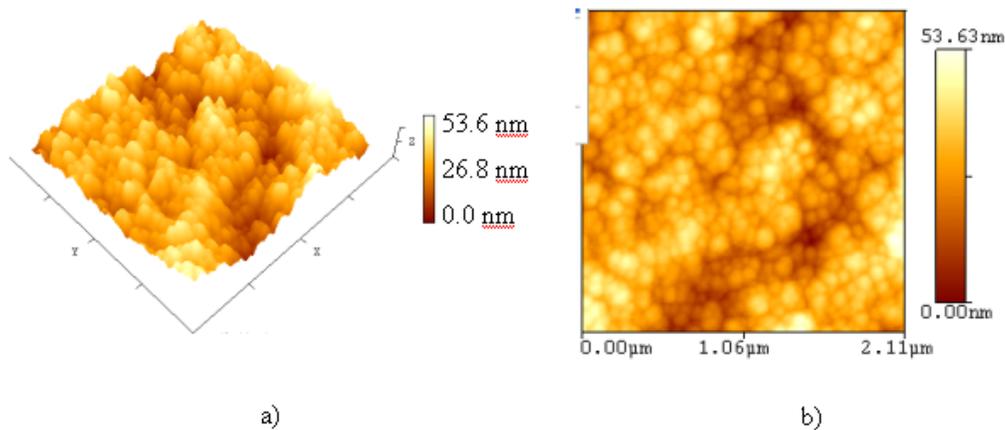


Figure 5: AFM $2 \times 2 \mu\text{m}^2$ (a) 3D and (b) 2D-views of a silicon-like film deposited via plasma on a CFRP laminate substrate.

4.5. Tribological measurements

Tribological tests were carried out by a ball-on-flat reciprocating micro-tribometer [8] to evaluate wear resistance and scratch resistance of the hybrid films. The wear resistance of the deposited films has been quantified in terms of number of reciprocating cycles taken to observe a marked change in the friction force under a constant normal force applied on the surface of the specimen. Specimen with the top layer #1 is the one which exhibits the best wear resistance (450 cycles under an applied normal force of 1 N), while specimen with the top layer #2 is least wear resistant (20 cycles under an applied normal force of 0.5 N), as we expected from the analysis of its infrared spectrum, which reveals that this film presents a top layer with a more organic chemical composition than the other and so a lower hardness. The scratch tests, employed under a normal force of 1N, show that the specimens fail in a brittle way with micro-cracks emanating from the damaged region and SEM images show a good adhesion of all the films to the composite substrate because the failure of the film and of the substrate (such as fiber failure) takes place simultaneously. Therefore, because of its higher wear resistance, the film with the top layer #1 represents a better compromise between hydrophobicity and fair mechanical properties and so it is the most suitable for high-

precision mechanical engineering applications. Figure 6 shows the failure induced by the scratch of the surface of the CFRP specimen coated with this film.

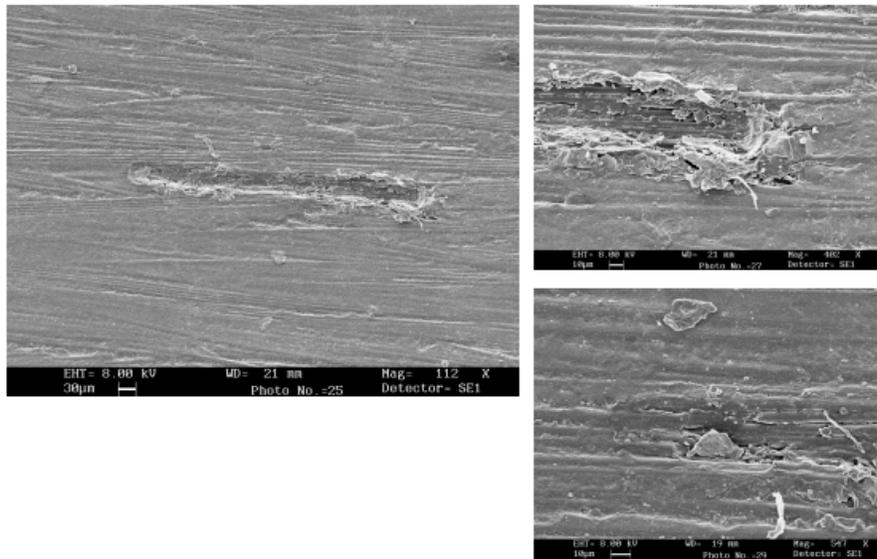


Figure 6: Failure induced by the scratch of the surface of the CFRP specimen coated with the hybrid film with the top layer #1. The overall damage left by the scratch with a diamond tip conical indenter is shown on the right hand side. Note the film failure (bottom right) and micro-cracks (top right).

5. CONCLUSION

Amorphous silicon-like ($a\text{-Si:O}_x\text{:C}_y\text{:H}_z$) thin films produced by PECVD represent an alternative to traditional coatings to protect FRP materials from the absorption of moisture and water. PECVD process does not requires high temperatures and is considered a sustainable environmental friendly process as it is performed in a closed vacuum apparatus with no emissions of VOCs (Volatile Organic Compounds). Moreover it allows to modulate chemical-physical properties of the deposited films simply by the modification of plasma parameters such as monomer and gas flow rates, radio frequency (RF) power, pressure in the reaction chamber, deposition time and geometry of the experimental system. Thus, if some plasma parameters are changed during the deposition process, hybrid films which join different chemical-physical properties can be realized from the same starting monomer. In this case, films made up of an inner layer with barrier properties and a more superficial layer with hydrophobic properties have been grown through the variation of the RF deposition power and the oxygen dilution of the monomer. Several films have been grown to choose the one which best fulfils impermeability, hydrophobicity, wear and scratch resistance. The best film we have obtained is made up of a very dense barrier layer (as AFM analysis reveals) with a thickness of about 700 nm and with a WVTR of $0.5 \text{ g/m}^2/\text{day}$ (ASTM E398-83 standard) and of a top layer with a thickness of a few hundreds of nanometers and a WCA of 91° . Higher values of WCA can be obtained but with lower values of wear resistance, due to the more organic chemical composition. Scratch tests followed by the acquisition of SEM images show that all the films realized have a good adhesion to the CFRP substrate.

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