Deposition of silicon-like hybrid films by PECVD on carbon-fiber-reinforced polymers for high-precision engineering applications

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Abstract. Hybrid silicon-like films have been deposited by PECVD on the surface of carbon-fiber-reinforced polymer (CFRP) laminates, used for micro-mechanical engineering applications where high strength-to-weight and high stiffness-to-weight ratios 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. Three films, made up of the same barrier layer and of three different hydrophobic layers have been grown to choose the one which best fulfils impermeability, hydrophobicity, wear and scratch resistance.

1. Introduction
Carbon-fiber-reinforced polymer (CFRP) laminates are composite materials made up of a polymer matrix (an epoxy resin) which surrounds and supports reinforcement carbon fibers of 10 μm diameter and the complexive structure is a laminate, originating from a superposition of a set of unidirectional plies (Figure 1). These materials are used for micro-mechanical applications where structural design is driven by high strength-to-weight and high stiffness-to-weight ratio requirements. However, water absorption due to the matrix causes an expansion (hygroscopic behaviour) which may result in unpredictable and unacceptable structural distortions over time. To improve long-term geometrical stability, hybrid silicon-like films have been deposited by PECVD on the surface of CFRP specimens. The films are made up of two layers (Figure 2), deposited from the same monomer (hexamethyldisiloxane) and feed gases (O₂, Ar), but with different plasma parameters, in order to
realize a film which joins barrier properties against moisture absorption and hydrophobic properties against the absorption of water during machining operations. The inner layer was deposited in high monomer fragmentation conditions [1] to obtain a film with a chemical composition approaching the SiO$_2$ one and with a dense morphological structure, i.e. with a low number of voids and micro-porosities, to prevent the diffusion of water vapour molecules in the film and consequently in the CFRP bulk. The most superficial layer was deposited in low monomer fragmentation conditions to obtain a film with a deal of apolar CH$_3$ functional groups enough to confer the material hydrophobic properties. Three films, made up of the same barrier layer and of three different hydrophobic layers (labelled #1, #2, #3), have been grown to choose the one which best fulfils impermeability, hydrophobicity, wear and scratch resistance. The film thicknesses are of the order of some hundreds nanometers.

2. Experimental apparatus
The PECVD apparatus consists of a parallel-plate, capacitive-coupled PECVD system, made up of a cylindrical stainless steel vacuum chamber 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. The monomer was heated to a temperature of about 80ºC and injected into the vessel in vapor 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, is in the range of 3-5 Pa.

3. Infrared analysis
The films chemical composition has been investigated by FT-IR spectrometry. 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 three hydrophobic layer (the curves have been offset vertically for clarity). Table 1 presents the analysis of the spectra with the relative band assignment [2,3,4]. The broadened shape of the bands, especially of the Si-O-Si asymmetric stretching band in the 1270-970 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 [5] relative to the hydrophobic layer #2. The layer #3 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 and silanol groups, 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 three hydrophobic layers. In the insert: deconvolution of the Si-O-Si asymmetric stretching band into four bands, originating from different Si-O-Si local bond angles that coexist in the film microstructure.

| Peak/band position (cm\(^{-1}\)) | Band assignment |
|----------------------------------|-----------------|
| 3600-3400                        | \(\nu\) (O-H) in SiOH bonds |
| 2960                             | \(\nu_s\) (C-H) in CH\(_x\) \((x = 1,2,3)\) bonds |
| 2900                             | \(\nu_s\) (C-H) in CH\(_x\) \((x = 1,2,3)\) bonds |
| 1270-970                         | \(\nu_s\) (Si-O) in Si-O-Si bonds [1040 cm\(^{-1}\) in network structures with Si-O-Si bond angles < 144º; 1078 cm\(^{-1}\) in structures with Si-O-Si bond angles 144º (stoichiometric SiO\(_2\)); 1120 cm\(^{-1}\) in cage structures with Si-O-Si bond angles \(\geq\)150º] and \((\text{CH}_3)_2\text{Si}=\text{O}\) vibration modes (1198 cm\(^{-1}\)) |
| 1260                             | \(\delta\) (CH\(_2\)) in Si-(CH\(_3\))\(_x\) \((x = 1,2,3)\) |
| 926                              | \(\delta\) (O-H) in SiOH bonds |
| 800                              | \(\delta\) (Si-O) in Si-O-Si bonds and Si-(CH\(_3\))\(_x\) vibration modes |
| 450                              | \(\rho\) (Si-O) in Si-O-Si bonds |

\(\nu\) stretching; \(\delta\) bending; \(\rho\) rocking; \(a\) asymmetric; \(s\) symmetric
4. Contact angle measurements
Contact angle measurements have been carried out to evaluate the film hydrophobicity. The film with the top layer #3 is the most hydrophobic (water contact angle 105º) because of the higher content of apolar CH$_3$ functional groups, as infrared analysis reveals, while the films #1 and #2 exhibit a water contact angle of 91º and 74º respectively.

5. Tribological measurements
Tribological tests were carried out by a ball-on-flat reciprocating micro-tribometer [6] to evaluate wear resistance and scratch resistance of the three 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 #1 is the one which exhibits the greater wear resistance (450 cycles under an applied normal force of 1 N), while specimen #3 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 this film presents a more organic chemical composition than the others 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.

6. Conclusions
The hybrid film with the top layer #3 is the most hydrophobic (water contact angle 105º) but it is the one which presents the lower wear resistance due to its higher carbon content. The film with the top layer #1 presents good hydrophobic properties (water contact angle 91º) and it is the one which exhibits the higher wear resistance. The adhesion of the film to the CFRP substrate is good for all the three films. So the film with the top layer #1 is the one which best fulfils barrier properties against moisture absorption, hydrophobicity, wear and scratch resistance, and therefore it is the most suitable for high-precision mechanical engineering applications.

References
[1] Creatore M A, Palumbo F and d’Agostino R 2002 Plasmas and Polymers 7 291
[2] Lucovsky G, Richard P D, Tsu D V, Lin S Y and Markunas R J 1986 J. Vac. Sci. Technol. A 4 681
[3] Pai P G, Chao S S, Takagi Y and Lucovsky G 1986 J. Vac. Sci. Technol. A 4 689
[4] Lucovsky G, Maritini M J, Srivastava J K and Irene E A 1987 J. Vac. Sci. Technol. B 5 530
[5] Grill A and Neumayer D A 2003 J. Appl. Phys. 94 6697
[6] Le H R, Sutcliffe M P F and Williams J A 2005 Tribology Letters 18 99