PLASMA TREATMENT OF COMPOSITE SURFACES FOR AERONAUTICS APPLICATIONS

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Objectives

This study has checked the ability of surface analytical techniques and plasma treatment to be applied to manufactured composite materials in order to develop wettability regulation for future industrial composite surface treatments. These treatments include gluing, moulding, coating or painting processes.

To predict adhesive properties of the solid material, required analytical tools and plasma treatments have to be studied and adapted to the characteristics of composite samples issued from manufacturing plant. Actually, these surfaces may be rough and are attempted to present a microscopically contaminated surface. These surfaces could be chemically unhomogeneous, contaminated by process environmental materials and subjected to high desorption under high vacuum. All these points could be critical.

Materials and Techniques

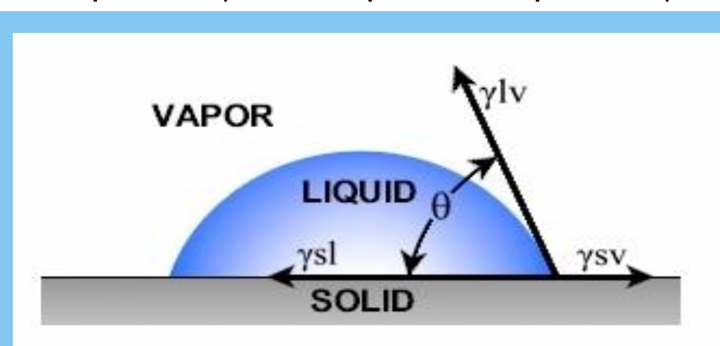
Surfaces of laboratory polymerized **epoxy resin** and industrial manufactured carbon/epoxy **composite** samples have been studied.
Epoxy resins were made of epoxy thermoset resin Epolam from Axson. Carbon/epoxy **composites** were manufactured by an aeronautics company using an infusion process.
Both surfaces have been investigated in terms of roughness by **PROFILOMETRY, SEM and AFM observations**. Surface chemical composition has been achieved by **XPS** spectroscopy. **Wettability measurements** have given access to the surface energy, calculated by Owens method.

CF4 cold plasma has been chosen in order to functionalize the surface and interact onto the wettability.

The equilibrium contact angle for a liquid drop on a smooth surface is related to the various interfacial tensions by the Young equation : $\gamma_{LV} \cos\theta + \gamma_{SL} = \gamma_{SV}$
where γ_{LV} is the surface tension of the liquid, γ_{SV} is the surface tension of the solid in equilibrium vapor from the liquid drop and γ_{SL} is the interfacial tension between the solid and the liquid [1].

The chosen method to evaluate the surface energy was proposed by Owens and Wendt in 1969, based on the simplified Fowkes equation : $\gamma = \gamma^D + \gamma^P$
The surface free energy is the sum of a dispersive component γ^D and a polar component γ^P.

Two reference liquids are necessary; a polar and an apolar . We used water and diiodomethane.



The surfaces are usually supposed to be ideal, which means smooth, homogeneous and chemically inert with the liquid to be used : so our model **epoxy resin**.

For rough surfaces, studies have been developed based on Wenzel model (1936) and on Cassie model (1944) for heterogeneous surfaces [2].
So, on a rough surface, the wetting gets better in hydrophilic situations and a hydrophobic behaviour becomes more hydrophobic because of the roughness [3] [4].

Fig. 1 : Wenzel (a) and Cassie (b) models.

Results

Laboratory polymerized **epoxy resin**

Manufactured carbon/epoxy **Composite**

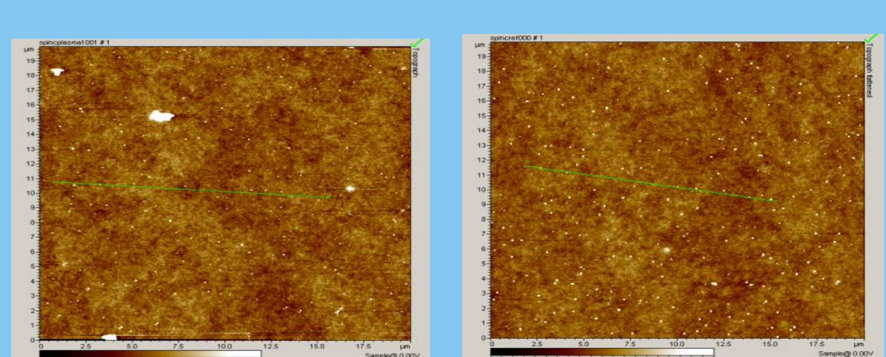


Fig.2 : AFM images of untreated (left) and after plasma treatment (right) epoxy surface .
Ra value of 5,3 nm.

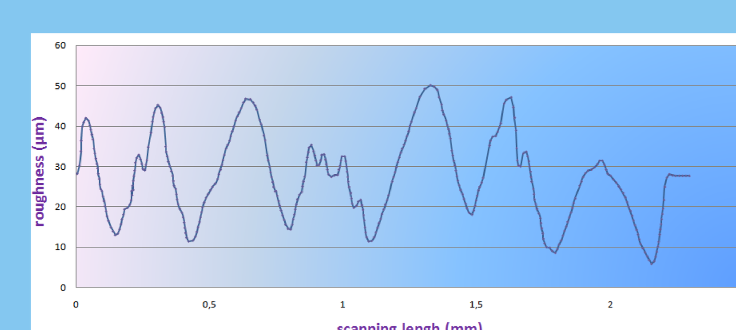


Fig.3 : Profilometry of composite surface.
Ra value of 8 microns.

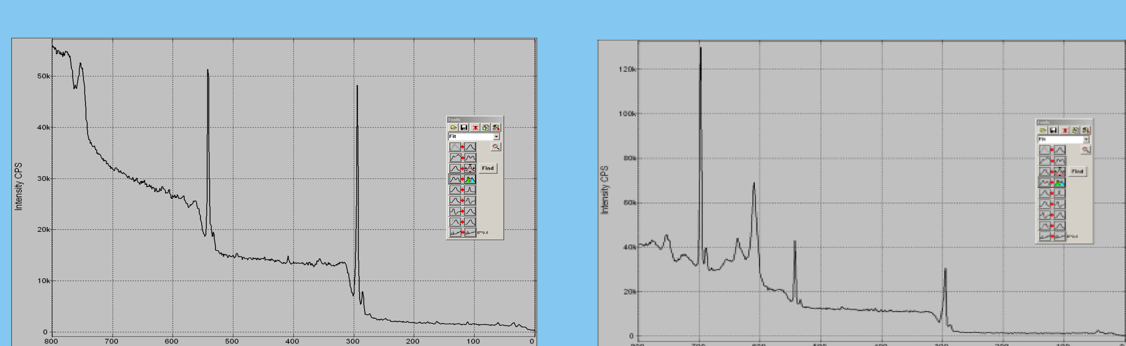


Fig.4 : Broad XPS spectrum of untreated (left) and plasma treated (right) epoxy surface

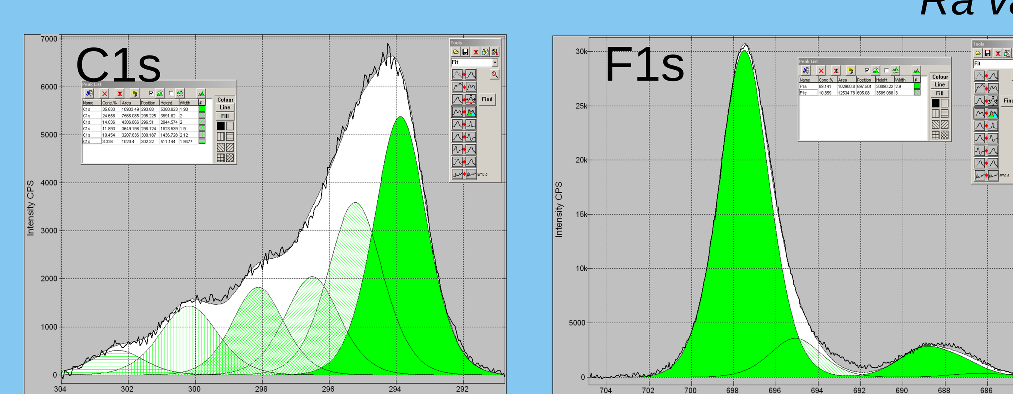


Fig.5 : Plasma fluorination occurs also on the composite samples as shown by CFx bondings on C1s and F1s XPS spectra.

Composite surface	*Chemical bond*	*Peak position (eV)*	*Atomic percentage (%)*
After plasma	C-H/C-C	285 eV	36 %
	C-O	286,4 eV	25 %
	CF	288 eV	14 %
	CO-O	289,2 eV	12 %
	CF_2	291,3 eV	10 %
	CF_3	293,4 eV	3 %

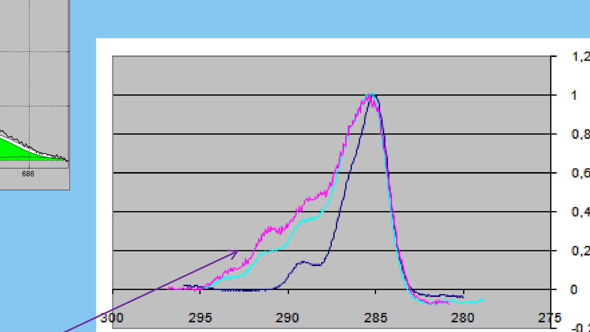


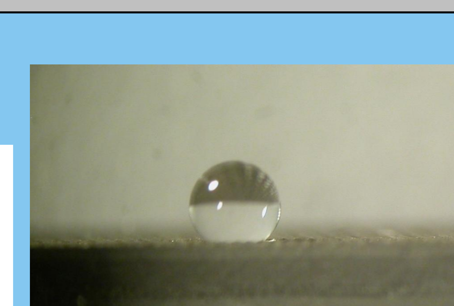
Fig 6 : Angular XPS emphasizes bondings which are contained in the very first layers of the analysed depth [6]. Results at 55° increase CFx groups detection. Calculation gives an estimation of 2,5 nm of average fluorination in our plasma conditions.

Epoxy resin	*Contact angles*	*Components of surface energy*	*Total surface energy*
Untreated	Water : 74 (±3)° Diiodo : 41 (±3)°	$\gamma_S^p = 7$ mJ/m^2 $\gamma_S^d = 34$ mJ/m^2	$\gamma_S = 41$ mJ/m^2
After plasma treatment	Water : 96 (±3)° Diiodo : 67 (±3)°	$\gamma_S^p \approx 2$ mJ/m^2 $\gamma_S^d = 23$ mJ/m^2	$\gamma_S = 25$ mJ/m^2

This fluorination is causing non wetting behaviour [5].
After CF_4 plasma treatment, the surface energy of both model epoxy and composite falls down of about 50%.

Composite surface	*Contact angles*	*Components of surface energy*	*Total surface energy*
Untreated	Water : 67 (±3)° Diiodo : 53 (±3)°	$\gamma_S^p = 25{,}1$ mJ/m^2 $\gamma_S^d = 14{,}5$ mJ/m^2	$\gamma_S = 39{,}6$ mJ/m^2
After plasma treatment	Water : 128 (±3)° Diiodo : 91(±3)°	$\gamma_S^p = 0{,}2$ mJ/m^2 $\gamma_S^d = 13{,}5$ mJ/m^2	$\gamma_S = 13{,}7$ mJ/m^2

Water drop deposited on composite surface before (left, θ=67°) and after plasma treatment (right, θ=128°) showing that plasma fluorination leads to non wetting surface



Conclusions and perspectives

This study shows reproducible analytical tools on both resin and composite. Techniques as particular as XPS- especially in terms of ultra high vaccum - has been shown to be accessible on production samples of composite. The composite surface is non flat with a roughness of about 8 microns. Its surface energy is about 40 mJ/m^2. After CF_4 plasma treatment, the composite surface gets 30% of fluorine which is mainly bounded to carbon skeleton : 27% of carbon atoms are linked to CF_X groups. After plasma, the surface energy has fallen down to 13,7 mJ/m^2. This result is promising for industrial composite wettability regulation.

References

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