

# SURFACE MODIFICATION OF AERONAUTIC COMPOSITE MATERIALS BY ATMOSPHERIC PRESSURE PLASMA (APP) FOR COMPOSITE BONDING

M.A. Torrijos<sup>a\*</sup>, Z. Martín<sup>b</sup>, R. Ávila<sup>c</sup>

<sup>a</sup> *Fundación para la investigación, desarrollo y aplicación de materiales compuestos (FIDAMC)*

<sup>b</sup> *Airbus Group Innovations*

<sup>c</sup> *Airbus Operations, S.L.*

\* *miguel.torrijos@fidamc.es*

**Keywords:** surface treatment, atmospheric pressure plasma, composite bonding.

## Abstract

The surface preparation prior to bonding constitutes one of the biggest industrial challenges for the implementation of structural bonding in large composite structures in aerospace applications. Besides, these methods are difficult to automate and labour intensive, which results in a strong impact on quality and costs. APP surface modification offers significant potential to increase quality and reliability, providing a very attractive alternative to the conventional surface preparations for bonding Carbon Fiber Reinforced epoxy-matrix composites. It cleans and activates the treated surfaces, enhancing the quality of the bonded joints. Moreover, it is easily automatable and industrially scalable, which results in time/costs savings of processing.

APP treatment parameters have been investigated to identify the optimal processing window in terms of surface preparation prior to bonding operations.

Surface characterization tests (contact angle measurements, X-Ray photoelectron spectroscopy and scanning electronic microscopy) and mechanical tests (G1c) of a state-of-the-art structural intermediate-modulus (IM) fiber reinforced toughened epoxy prepreg material have been carried out in order to study the surface modification induced by APP and the quality of the bonding. The results show a proper surface activation, removal of contaminants and enhanced mechanical properties of the bonded joints.

## 1. Introduction

There is a long tradition of adhesive bonding in the aircraft industry. Aircraft manufacturers identified a long time ago that the joining of aircraft structural elements with adhesive bonding is a key technology for designing low weight and high fatigue resistant structures with attractive costs. However, the adhesive bonding of structural elements is still an industrial challenge. Thus, further technical progress in this area is crucial for increasing the functional and the economic benefit. One of the fields to be explored is the automated pretreatment of the surfaces before the bonding operation. The surface preparation methods currently used (structural peel-ply, sanding operations) are difficult to automate and labour intensive [1,2] which results in a strong impact on quality and costs.

APP surface modification ensures quality and reliability, and provides a very good alternative to the conventional surface preparations of carbon fiber (CF) reinforced epoxy-matrix composites (CFRP). It cleans and activates the treated surfaces being able to replace sanding operations and even the use of peel ply with similar or improved surface finishing.

The benefits of the APP treatment would cover not only the technical improvement of the final product, but also, since it is easy automatable, its implementation to an industrial level process would result in savings in processing time / costs. The main objective of this project has been the identification of the APP treatment parameters that define the optimal processing window, with the final aim of demonstrating the efficiency of this technique in terms of surface preparation prior to composite bonding operations. The technical parameters examined in this project have been APP treatment speed and Plasma jets-surface distance.

In this work it was studied two different APP treatments that arise from the combination of different treatment speeds with different jets-surface distances. Thus, the treatments used were: APP0 (high Specific Plasma Intensity [SPI]), APP1 (medium SPI) and APP2 (low SPI).

The effect of different combinations of speed / jet-surface distance was evaluated for the CFRP material studied in this project.

For this purpose, several techniques have been used. The criterion taken for the selection of parameters was based on the observed changes in surface energy, topography, surface chemistry and bond-line performance (G1c) on the surfaces after the treatment.

## **2. Experimental section**

### *2.1 Materials*

The materials used in this study are listed below:

#### **Prepregs**

Structural intermediate-modulus (IM) fiber reinforced toughened epoxy prepreg material.

#### **Release Agents**

AIRTECH - Release film WL-5200 (ETFE)

Henkel LOCTITE-FREKOTE F700NC (release agent)

#### **Adhesive**

Adhesive film Henkel LOCTITE EA9695

### *2.2 Manufacturing*

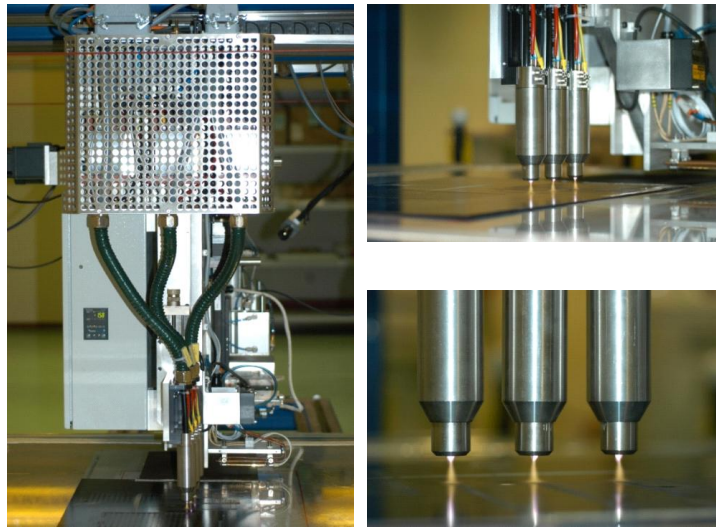
#### *2.2.1 Laminates manufacturing*

Panels of 300 x 300 mm (subsequently machined to get coupons with different sizes depending on the test to be performed), were fabricated and later modified with plasma. The panels were manufactured by hand and also by automatic prepreg lay-up followed by autoclave curing at FIDAMC.

#### *2.2.2 APP surface pre-treatment*

The main components of the plasma equipment used for this work are a high voltage transformer box and three non-rotating PWW10 plasma jets. Figure 1 shows the APP equipment provided by Plasmatreat GmbH used in this project and located at Airbus-Getafe facilities. The generation of highly reactive APP species (polar groups, free radicals, ions, electrons...) occurs within the jets. By means of a high-voltage a pulsed electric arc is

generated. A gas, in our case compressed air, flowing past the discharge section, is excited, ionized at a pressure of 5.0 bar, becoming plasma state.



**Figure 1. APP equipment (AOSL-Getafe)**

### 2.3 Surface characterization

The surface analysis techniques employed are briefly described below:

#### 2.3.1 Contact Angle (CA) measurements. Surface Free Energy (SFE) calculation.

Contact Angle measurements on polymer surfaces are sensitive to the chemical composition of the top molecular layer. It is the simplest and most straightforward approach to obtain surface free energies (i.e., polar and dispersion bonding forces).

CA measurements have been carried out using a KSV CAM 101 goniometer at Airbus Operations-Getafe.

The Surface Free Energy (SFE) was calculated by the Owens-Wendt-Rabel and Kaelble (OWRK) method.

#### 2.3.2 Scanning Electron Microscopy (SEM).

SEM is essentially a technique for the observation of surfaces and is especially applicable to the examination of the microstructure of adherents and failure surfaces. The specimens for SEM observations were prepared through Chrome deposition by sputtering technique.

#### 2.3.3 X-ray Photoelectron Spectroscopy (XPS).

XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material by irradiating it with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material. XPS requires high or ultra high vacuum.

All XPS measurements were performed with a Kratos Axis Ultra photoelectron spectrometer. Experiments were conducted at room temperature with a base pressure in the  $1.3 \times 10^{-6}$  Pa range.

#### 2.4 Mechanical tests: Fracture toughness energy characterization G1c

Several carbon fibre laminates have been manufactured using atmospheric pressure plasma (APP) surface treatment prior bonding. The aim of this study is to perform G1c mechanical tests obtained in bonded parts, using different sets of plasma parameters and then, to evaluate the mechanical behaviour of the secondary bonded joints when the surfaces to bond are surface treated with APP. These mechanical tests were carried out in a MTS universal testing machine with a 100kN load cell. The fracture toughness energy test, G1c, have been performed in accordance with the AIRBUS specifications AITM 1-0053 issue 3. All tests were carried out at room temperature. The specimen failure mode has been studied according to the AIRBUS specifications as well.

### 3. Results and discussion

The goal of this project was to evaluate the reproducibility of the APP surface preparation and its efficiency in terms of bonding performance as well as determining the set of the APP parameters identified as optimum. Thus, the results achieved enable the APP pre-treatment as a good alternative to conventional current pre-treatments before bonding. Here, the most relevant results are presented and discussed.

#### 3.1 Contact Angle (CA) and Surface Free Energy (SFE) Calculations.

Table 1 displays the SFE values ( in percentage) calculated from CA measurements.

Specimen	% in SFE values respect to the untreated sample
Untreated	0
APP0( High specific plasma intensity)	+ 80.74
APP1( Medium specific plasma intensity)	+ 67.49
APP2( Low specific plasma intensity)	+ 66.8

**Table 1. SFE changes (in %) after APP respect to the untreated sample.**

As expected, after exposing the CFRP surfaces to the APP, the surface free energy increases. This phenomena is due to the changes in the topology of the surface (normally, creation of some kind of micro-roughness) induced by the thermal component of the plasma, and specially, due to the increase of the oxygen concentration by the incorporation of new polar functionalities (carbonyl (C=O) and carboxyl (O=C-O) groups).

Comparing with the pristine (untreated) sample, the SFE values after APP exposure are increased by 72% (81% in the case of the sample after APP0 treatment and ~67% in the case

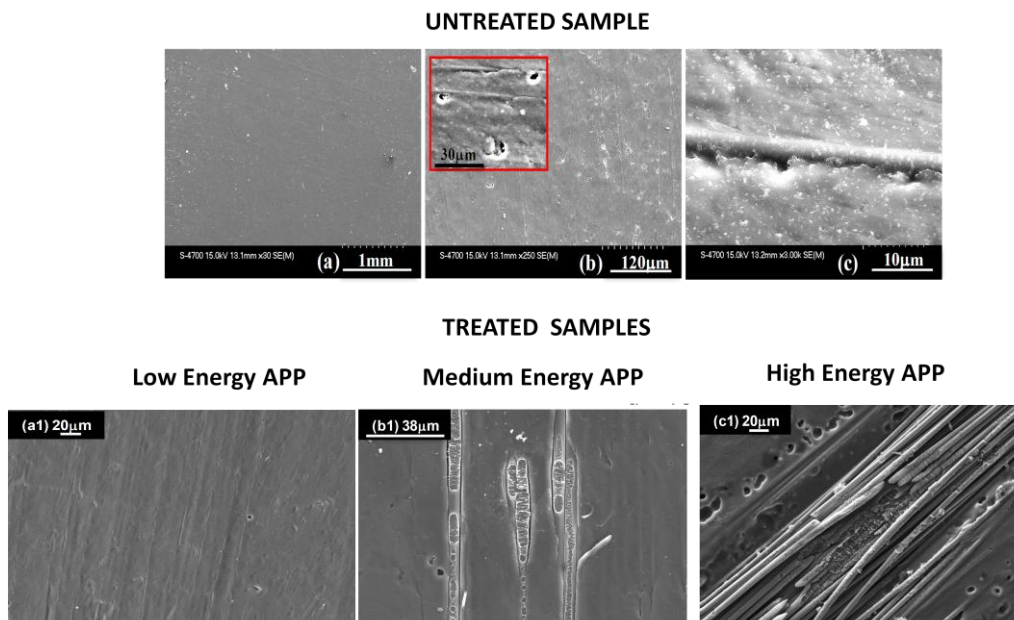
of APP1 and APP2 treatments). Therefore, a higher SFE will favour chemical bond formation when selected adhesives are applied.

### 3.2 SEM Observations.

The changes in the surface-morphology of the samples after their treatment with APP are discussed below. Figure 2 shows a selection of SEM micrographs representing the surfaces corresponding to the tool side of CFRP samples: untreated (upper row), and samples treated with APP0, APP1 and APP2 (lower row).

The surface of the untreated samples present the typical slight roughness present on the tool side of the CFRP panels right after the manufacturing. Also, some superficial fibers can be observed as well as resin moieties, probably, together with some residues from the manufacturing processes.

If we look at the same surfaces after modifying them, the surfaces appear a bit smoother and totally clean of small particles, so do the samples modified with APP2.



**Figure 2. SEM images at 18 kV acceleration voltage of the surface of CFRP (tool side) treated with APP. Upper row shows images of pristine samples as reference. Lower row shows images of samples treated with APP2 (Low specific plasma intensity), APP1 (Medium specific plasma intensity) and APP0 (High specific plasma intensity).**

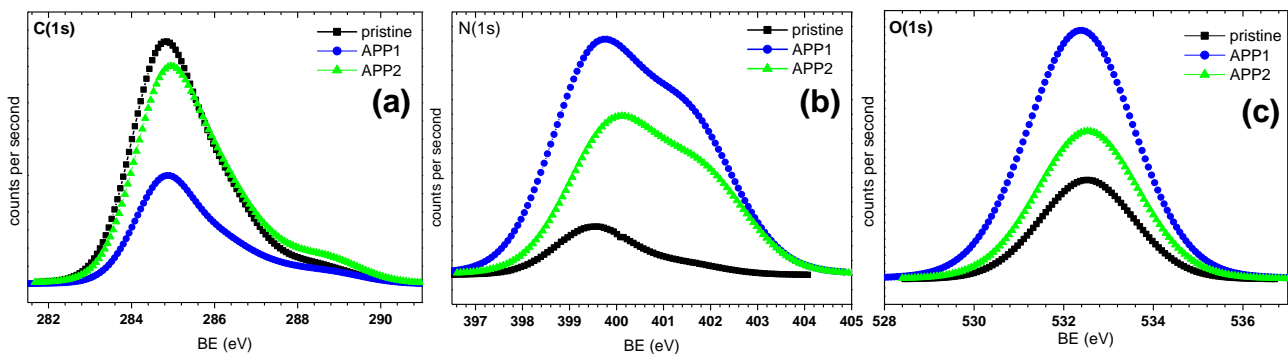
Apart from this, no dramatic changes in the surface morphology are seen except for the presence of nano/micro-pores homogenously distributed on the resin matrix. These features are believed to play a positive role enhancing mechanical interlocking effects with an adhesive. About the carbon fibers, no gaps between fiber and matrix are visible what indicates that the plasma treatment has not affected the fiber-matrix adhesion, which could be detrimental for the mechanical behavior of the composite and for the bond line strength. The most superficial fibers (those less buried within the resin matrix) appear neither damaged nor affected by the plasma treatment. Anyhow, apparently these pores affect just the first layer of the resin coating the fiber, not affecting the integrity or structure of de fiber.

These observations hold for the treatments APP1 and APP2, being the morphology of the surface very similar after their plasma-modification. The only difference between them could be that pores on surfaces treated with APP1 look a little bit deeper (the difference is very small though). However, the samples exposed to APP0 shows much more amount of exposed fibers and therefore damaged.

### 3.3 XPS measurements.

The spectral curve represents, in a first approximation, the density of unoccupied electronic states, which is an intrinsic characteristic of each compound and can be used as a clear mark, a fingerprint, to recognize a particular type of binding structure. The spectra are dominated by three photoelectron peaks, corresponding to electrons originated in the 1s orbitals of carbon, nitrogen and oxygen atoms of the samples surfaces.

Figure 3(a) corresponds to the absorption edge C1s of the surfaces. Looking at the binding energies of the C1s region in the pristine surface, the three characteristic peaks of the epoxy chemistry are identified: the main signal, at 284.8 eV, corresponds to the hydrocarbon bond C-C, the one at 286.2 eV correspond to C-O, C-N bonds. The signal at 288.2 eV corresponds to the C-O, COOH bonds. Comparing with the surfaces after the plasma treatment, the width of the C1s peak was expanded after surface treatment, which indicates that the cohesive structure was changed by responding to other atoms through plasma surface treatment. New functional groups of C=O and O-C=O (or N-C=O) were created, as indicated by the evolution of the original peak at 288.2 eV, to two peaks at 287.4 eV and 288.8 eV (corresponding to C=O and O-C=O respectively).



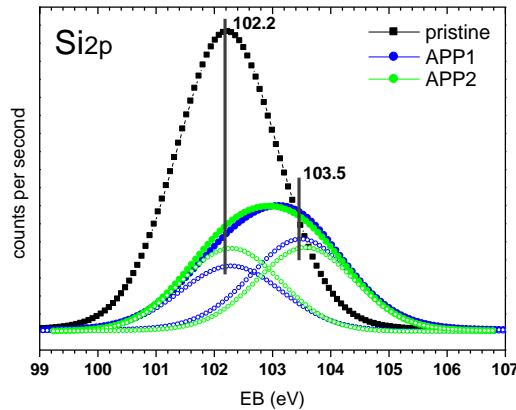
**Figure 3 . XPS spectra of CFRP tool surface (pristine, after treatment with APP1 and APP2) at the edges (a) C1s, (b) N1s and (c) O1s**

Figure 3(b) corresponds to the absorption edge N1s. It can be observed a broadening of the peaks showing pronounced shoulders in the region of higher energy, this indicates an increase in the degree of activation due to the relatively high activation of the amide type group [3,4,5]. These signals are due not only to the cross-linking agent residue, but specially to the incorporation of new polar functionalities (Nitrogen atoms) through the plasma treatment, hence, the high intensity of these peaks and the high N atomic percentage.

Figure 3(c) corresponds to the absorption edge O1s. The untreated surface presents the O1s signal at 532.5eV, corresponding to C-O and C=O bonds. After the plasma treatment this O1s peak moves slightly to 532.4 eV indicating the presence of carbonyl bond (C=O) and further oxidation to carbonate ester, O=C-O bond.

At this point, the incorporation of new polar functionalities is clear.

Comparing APP1 with APP2, both N/C and O/C atomic ratios increase after APP treatment, being this increase much bigger when APP1 is applied to the surface than when APP2 conditions are used, as expected given the higher intensity treatment of APP1.



**Figure 4. XPS spectra of CFRP tool surface (pristine, after treatment with APP1 and APP2) at the edge Si(2p)**

Figure 4 shows the XPS deconvoluted spectra since small changes in the peak fit will be very significant. Remember that the surface preparation by means of APP aims not only to activate the surface by incorporation of polar functionalities, but also, to throw off possible contaminants, such as the silicone left by the release agent F700NC (which contains silicon on its formulation) on the surface laminate during its manufacturing.

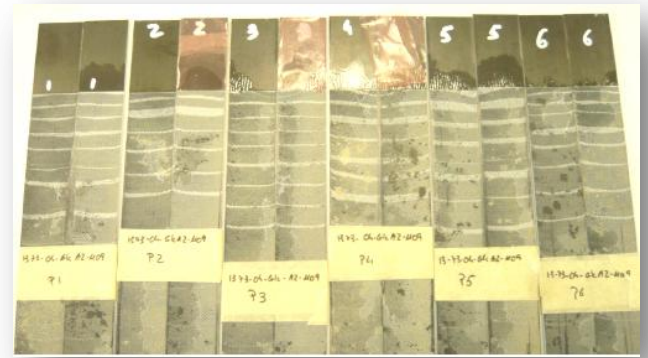
Note that in the case of the untreated surface, the spectrum could not be resolved as a two peak curve since no obvious line features were found within the Si2p environment (there was no evidence of secondary peaks), contrary to what happens in the surfaces after APP treatment.

Even though Si2p remains in the surface its concentration is reduced to the half after APP treatment. Moreover, there is a change in the absorption peaks from 102.2 eV to 103.5 eV, pointing that more than the half of the remaining Silicone molecules (102.2 eV, hydrophobic), transferred to the surface by the release agent, have become silicates (hydrophilic) due to the oxidation of the surface by APP treatment.

### 3.4 *G<sub>IC</sub>* tests

To evaluate the mechanical properties and the quality of the adhesive bond in CFRP panels whose surfaces were prepared (modified) by APP, fracture toughness energy and bond line failure mode were characterized by means of  $G_{IC}$  tests. As above mentioned, the CFRP panels were joined through secondary bonding (tool side– adhesive film –tool side).

Specimen	% of G1c results variation respect to the reference	Failure mode
Reference (grinding)	0	Non cohesive
APP0( High specific plasma intensity)	+ 7.1	Delamination
APP1( Medium specific plasma intensity)	+ 9.9	Cohesive
APP2( Low specific plasma intensity)	+ 10.5	Cohesive



a)

b)

**Figure 5. a) G1c results (in %) for specimens treated with APP0, APP1 and APP2 respect to the reference (surfaces prepared by means of grinding). b) Image showing the specimen surfaces of APP2 samples after G1c tests.**

Focusing on the coupons-surface prepared by APP, the predominant failure modes are cohesive ((APP1 and APP2) or delamination (APP0)) with the fracture energies values exceeding the obtained when grinding is used to prepare the surfaces (Figure 5). In addition, when APP is applied at high SPI, the samples show a clear tendency to produce delamination failure mode in the bonded joints. The apparent damage (surface alterations) caused on the substrates surfaces at this distance appear to favor the pullout of the fibers in G<sub>IC</sub> tests. At medium SPI, the cohesive failure mode was observed. At low SPI, the predominant failure mode was also cohesive.

#### 4. Conclusions

APP is a very promising surface treatment technique prior to bonding in CF epoxy resin composite bonded joints. It produces the cleaning of the surface, increases the surface energy by creating a micro-roughness and by chemical activation by incorporation of new polar groups. Moreover it is a very clean technique, specially comparing it to sanding, it has low requirements on personnel qualification due to the high potential for automation, it is environmentally friendly and it is easy to industrialize.

In addition, APP optimum parameters (jet/panel distance and treatment speed) have been identified in order to produce the best results regarding adhesion performance and failure mode. Low energy APP treatments (high jet/panel distances and high treatment speeds) results in good mechanical behaviour and cohesive failure mode.

#### References

- [1] Gheorghiu M., Popa G., Pascu. M.C 126 (1997) 295. *Macromol. Symp.*
- [2] Carrino L., Morno G., Polini W. 121 (2002) 273. *J. Mat. Proces. Tech.*
- [3] R.W. Paynter. 26, (1998) 674. *Surf. Interface Anal.*
- [4] T. R. Gengenback, R. C. Cbatelier, H.J. Griesser. 24 (1996) 271. *Surf. Interface Anal.*
- [5] C. A. Dai, Y. H. Lee, A. C. Chiu, T. A. Tsui, K. J. Lin, K. L. Chen, M. W. Liu. 47 (2006) 8583. *Polymer*