VARIATIONS IN THE FRACTURE TOUGHNESS ENERGY OF ADHESIVELY BONDED JOINTS WITH AERONAUTICAL APPLICATIONS AFTER ATMOSPHERIC PRESSURE PLASMA SURFACE PRE-TREATMENT EXPOSURE

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Abstract

Following the results of a previous study, further investigations to assess the feasibility of Atmospheric Pressure Plasma (APP) as surface pre-treatment for aeronautical epoxy/carbon fiber composite adherends prior structural assembly by adhesive bonding were performed. In this paper, evaluation of the fracture toughness energy of bonded joints (Mode I, G_{IC}) exposed to two different APP conditions was undertaken. Besides, the effects of the APP pre-treatment on the adhesive joint strength were measured by Single Lap Shear (SLS) tests. Additionally, APP-induced topographical modifications were demonstrated by Atomic Force Microscope (AFM). As a result, enhancements in the bonding behavior of APP-treated composites were observed and correlated with the formation of a nanometric peaked structure.

1 Introduction

1.1 Contamination on composite surfaces

In the last 40 years, the aeronautical industry has shown an increasing tendency to incorporate Carbon Fiber Reinforced Plastic (CFRP) materials in primary structures for cost and weight savings advantages, associated with fuel consumption decreases [1]. In this industry, the implementation of reliable manufacturing processes is of paramount importance for obvious safety reasons. As a result of these production processes, the surface of composite materials may be contaminated with release agents (i.e., to prevent adhesion of the composites to the moulds in which they are cured), exhibiting detrimental characteristics for subsequent bonding operations [2-5]. Surface preparation not only serves to remove contamination (i.e., fluorocarbon and silicon release agents), but may also increase the surface area for bonding, promote micromechanical interlocking and/or chemically modify a surface.

1.2 Surface preparation: current trends in aerospace

The main methods of surface preparation prior to adhesive bonding of aeronautical components manufactured with CFRP has traditionally been carried out by means of solvent degreasing, mechanical abrasion and use of peel-ply technique. These methods are often used in combination [4-6]. A major drawback of the surface preparation in aerospace is that it is usually carried out by hand, which causes its limited repetitiveness and its great dependence of the operator [5, 6]. Furthermore, care must be taken to ensure that only the chemistry and morphology of a thin surface layer is modified, avoiding breaking reinforcing fibers, affecting the bulk properties of the composite and, in short, weakening the adhesive bond [4]. It should be also noted that the use of these solvents in cleaning and surface preparation processes present risks of inflammability as well as safety and hygiene problems for operators [2, 3, 5]. The alternative of stripping off a peel-ply fabric with subsequent cleaning through organic solvents involves a huge amount of parameters intervening in the process and that may affect the efficiency of the adhesive bond, requiring constant quality controls [4, 5]. Therefore, it is of paramount importance to determine a reliable, cheap, continuous and reproducible method that may replace the above-mentioned techniques [5].

1.3 Future options in surface pre-treatment: Atmospheric Pressure Plasma (APP)

Alternatives like grit blasting, laser, ultraviolet radiation and plasma have shown some potential in various screenings [1, 2, 5-9], but none has found entry into series production yet, mainly due to a lack of methods for adequate assessment of surface quality. APP technique under controlled process conditions has been demonstrated to be effective at improving adhesive bonding strength and paint adhesion on polymers, particularly as a tool for activation, cleaning (i.e., contaminants removal), increasing surface energy (i.e., by changing the surface structure) [5, 6, 10-18], showing treatments with not appreciable lost of properties for reasonable storage times [5, 11]. In addition, this technology does not require auxiliary operations, and is susceptible of being automated and set up in mass production systems [11].

2 Materials and testing methods

2.1 Materials

APP technique for surface preparation on CFRP has been studied using a Hexcel (Stamford, Connecticut, USA) high performance aerospace prepreg contaminated with an Ethylene-TetraFluoroEthylene (ETFE) release film, namely Richmond (Norwalk, California, USA) Vac–Pak A-6200.001. Henkel (Rocky Hill, Connecticut, USA) Loctite Hysol EA9695 K.05 (referred to as EA9695) has been selected as the epoxy film adhesive for composite bonding. Hand prepreg lay-up and subsequent autoclave curing has been selected as manufacturing technique of the different coupons specifically fabricated for each test method or surface characterization technique. The corresponding stacking sequences are shown in Table 1.

Tests	Dimensions [mm]	Total nº of plies	Nº of semi-panels	Orientations
AFM	10 x 10	8	1	[0]
SLS	200 x 25 [19]	16	2	[0]
G_{IC}	250 x 25 [20]	16	2	$[0/0/+45/-45]_s$

Table 1. Specific features of the different coupons manufactured according to each surface characterization technique or test method.

2.2 APP-System

The surfaces of the CFRP used in this project have been pre-treated by means of an APP jet device supplied by PlasmaTreat (Steinhagen, Germany). The APP novel process was integrated in a pilot scale test work machine manufactured by Accudyne (Newark, DE, USA). This APP system can be described as a pulsed gliding arc discharge [6] and consists of three main components: a FG3002 power generator, a high voltage transformer box and three non-rotating PFW10 plasma jets. On the one hand, the generator converts the incoming electrical signal into a stepped high-frequency pulsed current, which passes through the transformer which steps up the voltage. On the other, a constant flow of clean compressed air at a pressure of 5.0 bar is blown from the industrial network to the system through a different circuit. Then, both the gas and the voltage are combined into the plasma jet chamber generating highly reactive APP species [11]. Different combinations between both, the distance substrate/plasma stream and the treatment speed, have led to the High and Low APP conditions studied in this work.

2.3 Atomic Force Microscope (AFM)

The AFM is a very high-resolution type of Scanning Probe Microscopy (SPM) for analyzing the surface topography of nonconductive samples such as polymers, consisting of a sharp tip mounted on a soft cantilever spring which scans line by line across the surface, whereby the topography is derived from the bending or deflection of the cantilever with a resolution of fractions of a nanometer [21, 22]. In this study, non-contact mode, measuring sample topography with minimum contact between the tip and the sample (i.e., between 2 and 30 nm) has been selected [23-24] to obtain AFM images which have been displayed by using a specialized color palette. The surfaces of the carbon/epoxy composites have been scanned with Explorer SPM, Tip Scanning AFM (TopoMetrix Corporation, Santa Clara, CA, USA) using a half-moon shaped silicon nitride tip in air at ambient temperature. The following characteristics have been selected: resonant frequency, 250-350 kHz; scan size was 10x10-50x50 µm. All images had 300 data points with a scan rate of 105 µm/s. From the AFM roughness analysis, area surface parameters have been determined as shown in Table 2.

Parameter [nm]	Description
R_a 1)	Arithmetic mean of the deviations in height from the image mean value.
RMS 2)	Square root of the mean value of the squares of the distance of the points from the image mean value.
R_z 3)	Arithmetic mean defined as the sum of all height values divided by the number of data points.
R_t 4)	Maximum peak-to-valley range in the area.

1) Average roughness; 2) Root-mean-square roughness; 3) Average height; 4) Maximum range

Table 2. Summary of the area surface parameters available in SPMLab software [25].

2.4 Single Lap Shear (SLS)

Bonded joints in aeronautic are designed to work under lap shear stresses [6]. The effects of the APP pre-treatment of epoxy/carbon composites on the adhesive joint strength prior bonding have been measured by SLS tests according to the related AIRBUS Specification [19] with a MTS 810 universal testing system under the test speed of 1 mm/min. The average shear strength “SLS” of the single lap epoxy/carbon composite adhesive joint expressed in MPa has been defined as the quotient between the load capability of the joint by the overlap area as shown in Equation 1[19].

$$SLS = \frac{F}{L\ W} \tag{1}$$

where F is the maximum load during the test expressed in Newton (N), L is the overlap length expressed in millimeters (mm) and W is the overlap width expressed in millimeters (mm).

2.5 Fracture toughness energy of bonded joints (Mode I, G_{IC})

Bonding line fracture toughness is a method widely shown to be sensitive to surface preparation and it demonstrates the weaker interphase in a bonded joint. Hence, in case the surface preparation is not appropriate, specimens will show a failure mode by adhesion (as shown in Figure 1) [6, 20, 26].

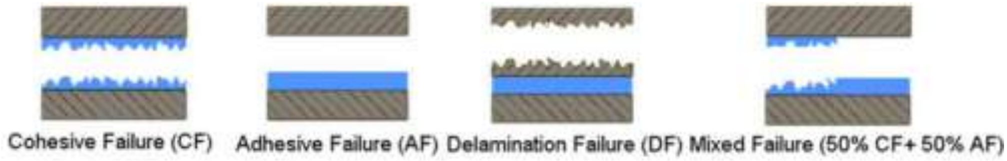

Figure 1. Failure modes of the bonded joint according to [20, 26].

The effects of the APP surface pre-treatment on the resistance to crack propagation in the epoxy/carbon composites bonded joint, formed by an intermediate adhesive layer and two carbon fiber laminates (i.e., Double Cantilever Beam specimen, DCB), has been measured by performing fracture toughness energy of bonded joints (Mode I, G_{IC}) tests according to the related AIRBUS Specification [20] using an INSTRON 1185 universal testing machine under constant crosshead speed of (10 ± 0.2) mm/min. Specimens with "piano hinges" have been used. The mode I fracture toughness energy G_{IC} of carbon fiber composites bonded joints expressed in J/m^2 has been defined as the quotient between the energy to achieve the total propagated crack length by the crack area as shown in Equation 2 [20].

$$G_{IC}=\frac{A}{a\ w}\cdot 10^6 \tag{2}$$

where *A* is the energy to achieve the total propagated crack length expressed in mm, *a* is the propagated crack length in mm ($a = a_{i+n}-a_i$) and, *w* is the width of the specimen (mm).

3 Results

3.1 Atomic Force Microscope (AFM)

Surface roughness modifications on 8552/AS4-ETFE laminates with respect to different APP treatment conditions have been investigated by means of AFM, as displayed in Table 3.

Surface		Statistical Surface Parameters [nm]			
Treatment	F.O.V[1)] [µm]	R_a	RMS	R_z	R_t
No APP	50 x 50	191 ± 23	246 ± 28	1649 ± 1146	1842 ± 872
Low APP		150 ± 26	179 ± 25	735 ± 607	1140 ± 174
High APP		119 ± 25	145 ± 30	372 ± 49	893 ± 149
No APP		31 ± 6	39 ± 7	138 ± 30	317 ± 58
Low APP	10 x 10	29 ± 2	36 ± 2	210 ± 93	350 ± 154
High APP		29 ± 5	37 ± 7	145 ± 30	304 ± 115

Note[1)] → F.O.V = Field Of View in microns

Table 3. Statistical surface parameters of 8552/AS4-ETFE laminates before and after different APP treatments (i.e., high and low) determined by AFM analysis.

It is clear from this study that the selected roughness descriptors have not detected any differences between the untreated and APP treated surfaces when selecting 10x10 µm as field of view. However, as discussed in a previous study [27] and, after examining the APP treated 8552/AS4-ETFE results at lower magnification (i.e., 50x50 µm), there are strong reasons to believe that APP has simultaneously smoothened the surface topography and created deeper valleys. Besides, there is a correlation between High, and Low APP treatments and the variation of average height and maximum range, since a lower and more homogenous distribution of the average height of the peaks and peak-to-valley distances within the 8552/AS4-ETFE 50x50 samples has been provided after High APP treatment. It should be noted that Low APP show usually big scatter of results as a result of the heterogeneity of the surface treatment [27]. In order to investigate the generation of particular APP topographical characteristics, AFM 3D pictures have been generated as shown in Figure 2.

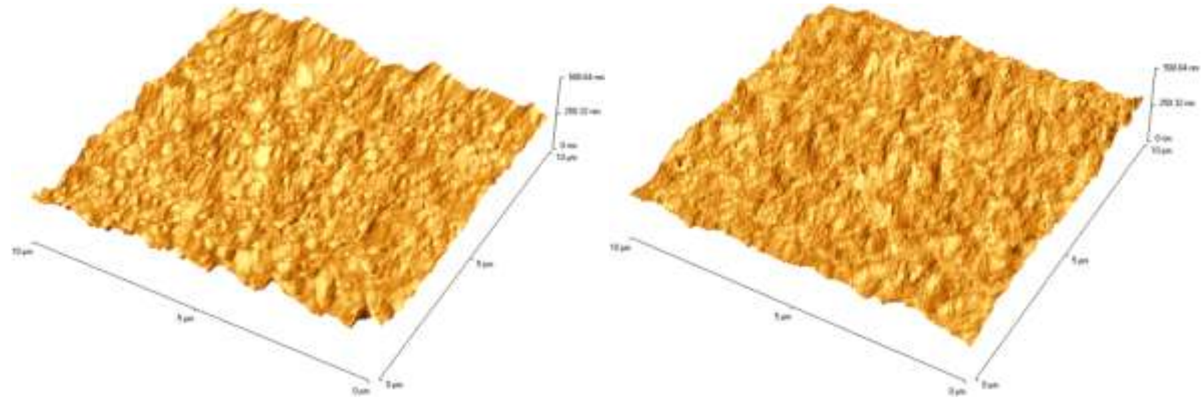

Figure 2. 8552/AS4-ETFE surface roughness by AFM (10 x 10 μm) with respect to: (a) samples without surface preparation (b) High APP treatment.

Worth noting features about the effect of High APP treatment have been found (10x10 μm), whereas 50x50 μm images have revealed no changes in the details of morphological features at lower magnifications. The 8552/AS4-ETFE samples without surface preparation (Figure 2a) have shown significant micro-roughness. However, a distinctive feature dealing with the formation of a closely spaced regular peaked structure with nanometric characteristics has been found on High APP-treated substrates at 10x10 μm (Figure 2b). These features are believed to additionally contribute to adhesion improvements. Conversely, its presence has appeared to be more subtle when Low APP treatments have been selected. Focused attempts to characterize this new nanotopography (i.e., 1x1 μm) have resulted unsuccessful since the detection limit of the AFM device has not been able to evaluate higher magnifications.

3.2 Single Lap Shear (SLS) and Fracture toughness energy of bonded joints (Mode I, G_{IC})

In order to evaluate the influence of the APP power (i.e., Low and High) on 8552/AS4-ETFE laminates bonded using EA9695 K.05 epoxy adhesive, mechanical tests such as Single lap shear (SLS) and bond line toughness (G_{IC}) have been performed (Table 4).

Surface treatment	**Mechanical Tests**	
	G_{IC} (J/m^2)	**SLS (MPa)**
Requirements	450 & No AF [28]	20 [29]
Grinding	722 ± 82 & 100% CF	30 ± 2
Low APP	633 ± 222 & 10% CF & 90% AF	23 ± 2
High APP	762 ± 36 & 100% CF	34 ± 2

Table 4. Assessment of adhesion properties by means of SLS and G_{IC} tests.

The results displayed in Table 4 together with the XPS analyses performed in a previous study [27] show G_{IC} dependence on the concentration of carbon functional groups with respect to High and Low APP treatments. According to the levels of adhesion provided by the mechanical tests, only High APP has led to good bonding characteristics on 8552/AS4-ETFE-

EA9695 laminates, exhibiting both cohesive G_{IC} failure mode and values clearly over the requirements or the mechanical abrasion reference. Previous studies [27] have shown that High APP treatment has removed adsorbed monolayers of release contaminants (e.g., fluorine values have been decreased from 25 to 10 at.%) and, has successfully activated the surface by providing oxygen-containing groups (e.g., 4% carbonyl (C=O) and 7% carboxyl (O=C- O), which favour both, hydrogen and van der Waals bonds (i.e., critical for adhesive-bonding assembly of composites). Conversely, Low APP treatment has promoted undesirable adhesive failure as shown in Table 4 and Figure 3b. Consequently, APP modification has been demonstrated to be effective in improving adhesion properties only if the selected set of parameters is able to reach the above-mentioned combination of effects (i.e., cleaning, chemical activation and nano-roughness). Interestingly, High APP has led to good adhesion properties even on surfaces containing levels of fluorine above 5 at.% [30] and, therefore, the importance of the morphological changes observed by AFM together with the chemical activation induced after High APP exposure has been highlighted. Interestingly, SLS results have always exhibited values over the requirements [29]. Thus, Low APP treatment has displayed relatively high SLS of 23 ± 2 MPa. However, these data alone have been demonstrated not to be sufficient in order to assess the effectiveness of the studied surface treatments, since Low APP G_{IC} values exhibiting high dispersion (i.e., 633 ± 222 J/m^2) and 90% of adhesive failure, AF, has been found. Therefore, attending to AIRBUS G_{IC} requirements (i.e., adhesive failure is not allowed) this set of parameters is not valid for bonding operations using EA9695 K.05 epoxy adhesive. It should be noted that the high scatter found in the G_{IC} results reflects partly the non-uniformity of the fluorine removal [27].

Figure 3 details macroscopic analyses of the mode of failure indicating that cohesive failure (CF) has predominantly occurred for the case of High APP, while adhesive failure (AF) has been found on Low APP-treated specimens. Moreover, typical test records load-displacement conducted at room temperature for each type of specimen are also shown.

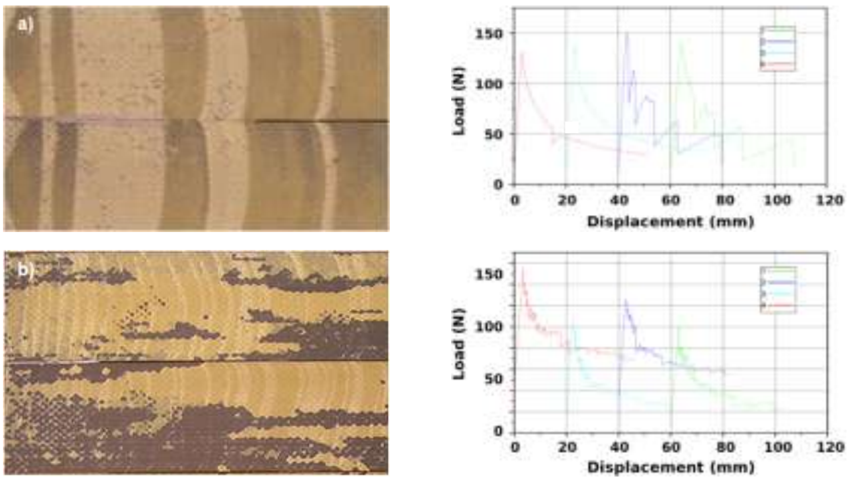

Figure 3. Failure surfaces and loading histories of G_{IC} fracture tests of the system 8552/AS4-EA9695 K.05 contaminated with ETFE: (a) High APP (i.e., 100% CF) and (b) Low APP (i.e., AF).

It is worth mentioning for the case of High APP that crack growth has been observed not to be continuous, evolving as a sequence of rapid growth and arrest phases, commonly referred to as “stick-slip” growth pattern [31]. Interestingly, each analysis has shown that G_{IC} is higher at the start of the test. This is because a 0.02 mm thickness film of ETFE placed at the loading end of the bondline to act as a starter crack is relatively blunt and, therefore more difficult to propagate [31].

4 Conclusions

APP under controlled process conditions has been demonstrated to be an adequate surface treatment for 8552/AS4 composite laminates contaminated with ETFE release film, when using EA9695 K.05 epoxy adhesive. APP effects on the adherents to be bonded can be summarized as follows: *Matrix ablation:* it has been confirmed that APP-cleaned substrates have shown a higher degree of roughness in the form of a closely spaced regular peaked structure with nanometric characteristics and, therefore, mechanical interlocking has been promoted. *Bonding behavior*: a combination of the physico-chemical effects induced by APP treatment (i.e., surface cleaning, creation of new polar functional groups and subsequent chemical linkages at the interface, and increased roughness) has been demonstrated to lead to excellent shear strengths and fracture toughness energy of bonded joints (i.e., cohesive failure). *Effects of the operating parameters:* it has been demonstrated that the cleaning efficiency, surface activation an induced nano-roughness are strongly dependent on both the APP focus/substrate gap distance, and treatment speed. Thus, the effective combination of release compounds removal, chemical activation and new topographical features have been correlated with excellent adhesion properties for the selected adhesive/substrate system only when exposed to High APP conditions. However, Low APP activations have led to poor bond interactions between treated substrates and the adhesive, since the high amount of surface contamination (i.e., Fluorine) has prevailed over the potential benefits of surface topography (i.e., limited amount of nano-patterned topography). Therefore, mechanical interlock for bonding the APP chemically modified substrates has been demonstrated to play the major role in enhancing adhesion performances. *Further studies:* first, it should be noted that to go beyond the limited roughness measurements provided by the available AFM equipment, a different approach such as SEM image analysis and determination of statistical surface parameters by Scanning Probe Image Processor (SPIP) will be required. Secondly, it should be highlighted that the aging effect of plasma-modified surfaces and its associated hydrophobic recovery is a well-known phenomenon when exposed to air, and therefore, it should be studied carefully. Finally, to assess the overall trends of APP surface pre-treatment influence on adhesive bonding strength and durability, additional coupons will be accelerated aged by conditioning hot/wet and water immersion before testing at different temperatures.

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