NEW APPROACH TO SURFACE PREPARATION FOR ADHESIVE BONDING OF AERONAUTICAL COMPOSITES: ATMOSPHERIC PRESSURE PLASMA. STUDIES ON THE PRE-TREATMENT LIFETIME AND DURABILITY OF THE BONDLINE

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Keywords: adhesive joint, surface treatment, atmospheric pressure plasma, epoxy/carbon fiber composite.

Abstract
In two previous studies, promising results regarding the feasibility of Atmospheric Pressure Plasma (APP) as surface preparation for aeronautical composites prior to structural assembly by adhesive bonding were presented. In this paper, further investigations to assess the viability of this pre-treatment technique were performed. Thus, APP treatment effects on both the lifetime of the pre-treatment and the long-term durability of composite adhesive bonds were demonstrated by Contact Angle (CA) measurements, Surface Free Energy (SFE) by using both Owens-Wendt-Rabel-Kaeble (OWRK) and Test Inks (TI) analyses and Single Lap Shear (SLS) tests. As a result, the effective combination of release compounds removal, chemical activation and new topographical features were correlated with excellent long-term adhesion properties.

1. Introduction

1.1. Manufacturing processes for advanced composites: surface contamination

Advanced composite materials have transformed civil aircraft development due to cost savings advantages associated to fuel consumption decreases since the 1970s. Thus, their use has been extended from small non load-bearing components to a variety of secondary and primary structures [1-3]. The surface of composites may be contaminated with fluorocarbon or silicon release agents that prevent parts to bond permanently to the mold during curing operations. Therefore, detrimental characteristics for subsequent adhesive bonding processes are expected. In this regard, surface preparation is of utmost importance to guarantee the long-term quality of composite adhesive bonds since it removes release agent residues, increase the surface area for bonding and promote mechanical keying and/or chemical activation [4-7].

1.2. Surface preparation before structural adhesive bonding: current trends

Surface pre-treatment of thermosetting aeronautical components prior to adhesive bonding has traditionally been carried out by means of solvent degreasing, mechanical abrasion and peel-ply removal, either separately or in combination [6-8]. However, this crucial step to develop strong and durable adhesive bonds has several disadvantages. First of all, although the manufacturing procedure is performed by trained and competent personnel, manual processes such as the aforementioned techniques are highly dependent on the operator. This is particularly important when only the chemistry and morphology of a thin surface layer shall be modified without weakening both reinforcing fibers and bulk matrix [6-8]. Secondly, the alternative of stripping off a peel-ply fabric with subsequent cleaning through organic solvents requires continuous and close monitoring for quality assurance due to the large amount of parameters that may affect the efficiency of the bond [6, 7]. Finally, the use of solvents may present risks of inflammability as well as safety and health problems for operators [4, 5, 7]. Therefore, it is crucial to determine a reliable, cheap, continuous and reproducible method that may replace the current state of the art technologies [7].

1.3. Future options for surface pre-treatment

The required levels of surface roughness, contaminants removal or activation of composite adherends have shown promising results in various screenings involving alternatives like grit blasting, laser, ultraviolet radiation and plasma techniques [3, 4, 7-18].

1.3.1. Atmospheric Pressure Plasma (APP)

The techniques for producing stable plasmas at atmospheric pressure have been known since the late XVIII century [19]. In the past decade, however, there has been a burst of research activity due to the unique effects and utility of the plasmas in the processing of industrial materials. The list of potential benefits for adopting APP technology is broad. APP is an interesting alternative to other pretreatment methods because of high throughput in-line manufacturing process capabilities (i.e., no dimensional drawbacks), potential for automation including multiple nozzles, relatively low costs and power consumption (e.g., systems can operate using electricity and compressed air; no vacuum or special gases are required) and low requirements on personal and environmental safety [13, 14, 20]. APP technique under controlled process conditions has been proved to be effective at enhancing adhesive bonding strength on polymers [7, 11, 13-17].

1.3.2. Lifetime of APP treatment

The aging effect of plasma-modified surfaces and its associated hydrophobic recovery is a well-known phenomenon when exposed to a nonpolar medium such as air [21], and therefore, it should be studied carefully. This process might result from a combination of several effects: (i) surface restructuring, a term which describes a thermodynamically driven reorientation of polar groups away from the surface into the subsurface; (ii) reactions of the surface with the atmospheric constituents such as oxygen, water vapor and CO_2 [21]; (iii) diffusion of mobile low molecular weight (i.e., LMW) species from the bulk polymer to the surface; (iv) and the reaction of residual free radicals [22].

1.3.3. Long-term durability of composite adhesive bonds

It is crucial to guarantee a long-lasting cohesive bond failure within the adhesive, both initially and throughout the joint's service lifetime [5]. As known, structural adhesive joints must be capable of both developing good strength properties shortly after cure and maintaining these characteristics over their expected lifetime. It is well established that heat and moisture contribute to the deterioration of adhesive properties [5]. Specimens exposed to elevated temperatures and high humidity are known to absorb water and therefore tend to significant degradation in the mechanical performance. The extent of this loss depends on the material systems employed as well as the hygrothermal loading history [5, 23, 24].

2. Materials and testing methods

2.1. APP-System

The surfaces of the advanced composites used in this project were 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 generates a pulsed gliding arc discharge [7] and consists of three main components: a FG3002 power generator, a high voltage transformer box and three nonrotating 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 [25]. Different combinations between both, the distance substrate/plasma stream and the treatment speed, led to the APP conditions studied in this work [26, 27].

2.2. Materials

APP technique was studied using a Hexcel (Stamford, USA) 8552/AS4 epoxy/carbon high performance aerospace prepreg. During the manufacturing process, the prepreg was in contact with an Ethylene-TetraFluoroEthylene (ETFE) release film, namely Richmond (Norwalk, USA) Vac–Pak A-6200.001. Henkel (Rocky Hill, USA) Loctite Hysol EA9695 K.05 (referred to as EA9695) was selected as the epoxy film adhesive for composite bonding. Hand prepreg lay-up and subsequent autoclave curing were 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.

Test	Dimensions [mm]	Total nº of plies	Nº of semi-panels	lay-up
CA	150 x 75	8	1	[0]
TI	150 x 75	8	1	[0]
SLS	200 x 25 [19]	16	2	[0]

Table 1. Specific features of the different coupons manufactured according to each test method.

2.3. Contact Angle (CA) measurements

CA measurements were carried out according to the related Airbus Specification [28] using a KSV CAM 101 (KSV Instruments, Inc., Helsinki, Finland) goniometer and employing distilled water, di-iodomethane, ethylene glycol, o-tricresyl phosphate and α-bromonaphtalene as test liquids.

2.4. Surface Free Energy (SFE) analysis

2.4.1 SFE according to Owens-Wendt-Rabel-Kaeble (OWRK)

This method considers the SFE of a solid as being a compromised of two components: dispersive and polar [29, 30]. To apply this method, the polar and disperse component surface tensions for the probe liquids of known surface tension [31] shall be combined with CA measurements. In a linear regression of the plot of y against x, the polar component is obtained from the square of the slope of the curve m and the dispersive from the square of the ordinate intercept b (Figure 1).

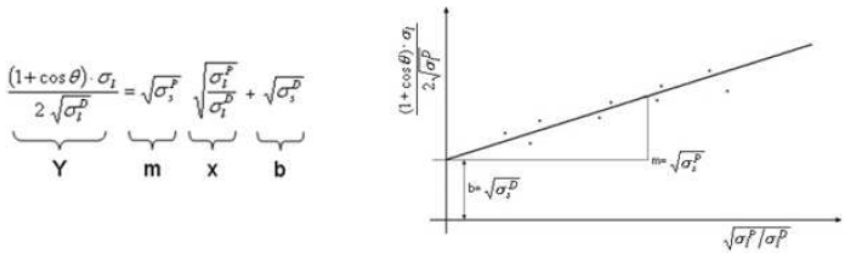

Figure 1. Disperse and polar fractions of SFE of a solid according to the OWRK method.

2.4.2 SFE according to Test Inks (TI)

Wetting tension test solutions from PlasmaTreat (Steinhagen, Germany) were used during this study. These test inks are solvent-based, colored fluids [32] stored in glass bottles available in the following mJ/m^2 levels: 28, 34, 46, 54, 60, 64 and 72. The values of these test fluids were determined according to the Wilhelmy plate method [33]. This technique presents an alternative to the OWRK analysis and it is especially interesting for industrial environments.

2.5 Single Lap Shear (SLS)

Bonded joints in aeronautic are designed to work under lap shear stresses [7]. The effects of the APP pre-treatment of epoxy/carbon composites on the adhesive joint strength prior bonding were measured by SLS tests according to the related Airbus Specification [34] 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:

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

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

3. Results

3.1. Effects on the lifetime of APP

Evaluation of the APP treatment lifetime on treated 8552/AS4 epoxy/carbon adherends contaminated with ETFE release film was performed by means of CA and SFE including both

OWRK and ethanol/water-based TI analyses. The samples were wrapped in aluminum foil after APP treatment and stored at normal RT conditions up to a maximum of 504 hours.

Surface Treatment	Time (h)	Average Contact Angle (°)					Surface Free Energy [mJ/m^2]			
		H_2O	$C_2H_6O_2$	CH_2I_2	$C_{21}H_{21}O_4P$	$C_{10}H_7Br$	σ^P_S	σ^D_S	Total	TI
No	-	84±3	76±3	59±5	55±3	43±2	3	26	29	34-46
APP	0	31±3	15±1	45±3	23±2	41±3	33	25	58	>72
	3	30±2	21±2	44±3	29±3	41±3	34	25	59	>72
	120	32±2	16±2	43±2	25±3	40±3	32	26	58	>72
	504	31±3	13±2	42±3	21±3	33±4	31	27	58	>72

Table 2. Durability of the APP treatment on epoxy/carbon 8552/AS4-ETFE surfaces by CA measurements and SFE analysis (i.e., OWRK and TI) before and after APP treatment.

It is noteworthy that the chemical modifications introduced by APP treatment were stabilized in the first few hours, leading to similar level of CA measurements with time (Table 2). Besides, the ageing of 8552/AS4-ETFE APP treated surfaces is found to be negligible since variations in CA measurements were not observed after 21 days. In addition, it should be highlighted that that the CA data obtained using non-polar liquids (i.e., $C_{21}H_{21}O_4P$, $C_{10}H_7Br$ and CH_2I_2) confirmed the effect of electrostatic repulsion between fluorine (i.e., EFTE) and highly electronegative elements suggested in a previous study [26]. Figure 2 shows increases in wettability using water and diiodomethane droplets 504 hours after APP treatment.

Figure 2. Increase of wettability on epoxy/carbon 8552/AS4-ETFE composites before (a-c) and 21 days after APP treatment (b-d), corresponding to water (left) and diiodomethane (right) droplets, respectively.

Interestingly, SFE-OWRK values for the samples exposed to APP reported in Table 2 are almost double the SFE values without surface treatment. It is also important to note that this increment is mainly due to the production of polar groups derived from the APP treatment, favoring chemical bond formation [26].

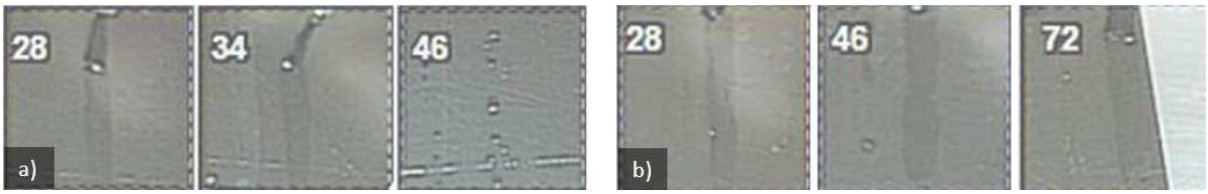

Figure 3. SFE of 8552/AS4-ETFE composites by means of TI before (a) and 21 days after APP treatment (b). Note that before APP, only the test fluids of 28 and 34 mJ/m^2 remained as homogenous films. The effects of APP after 21 days were demonstrated since any of the increasing TI pulled back into droplets.

Alternatively, the effects on the lifetime of APP preadhesion treatment of composites were studied by determining SFE by TI analysis. It is noteworthy that only the test fluids of 28 and 34 mJ/m^2 remained as homogenous films after their application on the raw surface. When higher test solutions were applied, the liquid pulled back into small droplets and thus, the SFE of the substrate was found to range between 34-46 mJ/m^2. The benefits of durable surface wettability through APP exposure were demonstrated when the complete set of TI (up to 72 mJ/m^2) formed a continuous film and none of the liquids reticulated. Based on these results,

the long-term stability of 8552/AS4-ETFE APP-treated surfaces is demonstrated and therefore, it could be inferred that optimum adhesion properties are expected up to 504 hours. For complete assessment, the durability of the APP treatment may also be corroborated by mechanical means on 8552/AS4-ETFE samples. However, a previous study already underlined a correlation between the above mentioned CA and SFE values after APP with excellent mechanical behavior (i.e., SLS and G_{IC} tests) so that the specific requirements were fulfilled [26, 27].

3.2. Durability of the bond-line

This section includes a discussion to assess the overall trends of APP surface pre-treatment influence on adhesive bonding strength and durability by SLS test method. Thus, 8552/AS4 epoxy/carbon specimens bonded with EA9695 K.05 epoxy adhesive were accelerated aged by conditioning hot/wet (i.e., 70ºC and 85% relative humidity level) and water immersion (i.e., 70ºC) during 2000 hours before being tested at RT and 80°C. An estimation of the durability of the adhesion of the cured bond line on the APP pre-treated adherends was assessed by comparison of "fresh" and aged specimens.

Surface Treatment	**As Received**		**2000h 70°C and 85 RH**		**2000h 70°C Water**	
	RT	**80°C**	**RT**	**80°C**	**RT**	**80°C**
Requirements [35]	20	20	17	15	17	15
ETFE ref. (grinding)	30±2	32±2	23±1	24±1	25±1	20±1
ETFE APP	34±2	31±1	29±2	24±1	28±2	18±1

Table 3. Durability of the bond-line by SLS adhesive joints tests of APP-treated 8552/AS4-ETFE composites.

As indicated in Table 3, APP-treated samples after hot/wet and water immersion exposure were proven both to excel the bonding SLS strength requirements for high performance applications [35] and to match the mechanical results obtained when using the state of the art technique (i.e., grinding). It should be noted that the fluorinated surfaces under study shown low SLS results dispersion after conditioning. Thus, it was also demonstrated that APP-induced changes onto the surface (i.e., mainly due to synergetic effects of fluorine removal, surface nano-roughness formation and long-lasting chemical activation [26, 27]) were homogeneously distributed and result in excellent and reliable mechanical performances even when affected by moisture-induced degradation.

4. Conclusions

Following the promising results obtained in two previous studies, further investigations to assess the feasibility of APP as surface pre-treatment technique prior to structural adhesive bonding for aerospace applications were performed. The APP effects on both the lifetime of the pre-treatment and the long-term durability of 8552/AS4-ETFE epoxy/carbon composite adhesively bonded by using EA9695 K.05 epoxy adhesive can be summarized as follows:

Effects on the lifetime of APP: the challenge of long-term modifying the low wetting behavior of ETFE-contaminated composite surfaces was successfully accomplished after APP treatment. The storage of APP activated samples (wrapped in aluminum foil at room temperature) for at least 21 days with no noticeable degradation was confirmed to be feasible according to the different tests performed. Therefore, the effective combination of release compounds removal (i.e., fluorine), chemical activation by formation of new oxygen-containing functional groups such as carbonyl (C=O) and carboxyl (O=C-O) and new topographical nano-patterned topographical features induced by APP are expected to be

correlated with excellent long-term adhesion properties up to at least a maximum of 504 hours.

Durability of the bond-line: regardless of the different conditioning (i.e., hot-wet and water immersion environments) and selected test temperatures (i.e, RT and 80°C), no decline of adhesion properties have been observed by comparison of "fresh" and aged specimens. Therefore, it could be concluded that the results obtained for SLS strength of bonded joints subjected to long-term isothermal exposure under hot/wet conditions and water immersion have presented compelling evidence for the bonding stability effect of APP treatment on the mechanical properties.

In summary, it can be concluded from the foregoing studies that Atmospheric Pressure Plasma (APP) technique is a promising method for the industrial surface preparation of epoxy matrix composites prior structural bonding, leading to an automatic and repetitive process suitable for mass production, assuring both quality and reliability.

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