



CLEANSKY

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Denis Dowling University of Dublin		20/9/13 <i>Denis Dowling</i>
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Dassault-Aviation	Pierre Michelin	

***The Topic Manager in charge of this call for proposal must approve the deliverable and send it to the Project Officer.**

Abstract - This report provides an overview of the PlasmaClean project which investigated the use of air atmospheric plasma treatments for the removal of organic contaminants on both titanium and composite substrates. Process monitoring was evaluated using reflectance infra-red spectroscopy combined with optical emission spectroscopy (OES) and acoustic techniques. Based on this study the air plasma treatment combined with OES has been shown to exhibit considerable potential for controlled contaminant removal during the manufacture of aerospace composites. After the Introduction section this report summarises the results of the main project tasks as follows:.

- Evaluation results on the use of nebulizers for the controlled contamination of composite surfaces
- Evaluation reflectance IR and / or mass spectrometry for the chemical examination of contaminants
- Evaluation of the effectiveness of the atmospheric plasma jet system for contaminant removal based on chemical analysis and paint adhesion study
- Surface mapping and control during atmospheric plasma treatments

1. Introduction

Over the last 60 years military and commercial aircraft manufactures have steadily replaced traditional heavier metal materials for lightweight carbon composites. More recently there has been a very significant increase in their use, with a 4 to 5 fold increase between 1985 and 2012. To reduce weight further, thereby increasing fuel efficiency and decrease environmental pollution, designers are considering the use of composites in ever increasingly critical parts of the aircraft. However composites do have a number of disadvantages in their use in the aerospace, wind and marine sectors, some of which are: high raw material, fabrication and assembly costs; (b) anisotropic strength (i.e. in-plane and out-of-plane strength); (c) susceptibility to delamination due to temperature cycling, surface moisture ingress and chemical attack; (d) manufacturing defects.

Failure to provide a chemically clean surface prior to adhesive bonding can significantly reduce the failure strength of the joint due to the incorporation of interfacial defects, or incorrect curing; both of which can result in the failure of the bond under critical stress conditions. The surface contaminates may arise from the manufacturing process such as mould release agents (for example: Henkel FreKote 710-NC), or by chance finger prints. Even under strict assembly protocols an assortment of organic and inorganic surface contaminates may be present; these include, but not limited to: intentionally introduced via: semi-permanent mould release agents, lubricants and rubber and silicon based synthetic adhesives from pressure sensitive tapes; plus accidental contaminates from manual human handling, for example fingerprints and hand barrier creams. In this study the use of air plasma treatments using the PlasmaTreat system (Figure 1), was evaluated for contaminant removal.

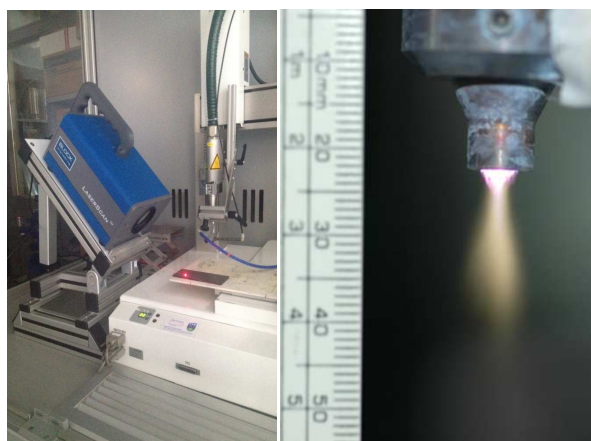


Figure 1: PlasmaTreat air plasma jet system along with the Block IR system (left), close up view of the air plasma jet (right)

2. Evaluation results on the use of nebulizers for the controlled contamination of composite surfaces

This section of the project focused on the examination of contaminants typically found within a manufacturing environment of aircraft components. These contaminants were: FreKote 710-NC, thumbprints, Boelube, hand barrier cream and the adhesives from three pressure sensitive tapes. All these contaminants were applied onto composites, however only FreKote and Bolube could be detected by reflectance FTIR, these were therefore the focus of this project. As an example of a deposited contaminant the typical thick of Frekote on silicon wafer along with the associated water contact angle is given in table 1.

Table 1. FreKote film deposition

Material	Transfer morphology	Matrix	FreKote thickness	Water contact angle (degree)
Silicon wafer	N/A	N//A	N/A	36.5
FreKote Sprayed 1 pass	Patterned	Silicon	3-5 nm	40-60
FreKote Sprayed 2 pass	Patterned	Silicon	4-8 nm	50-60
FreKote Sprayed 4 pass	Patterned	Silicon	10-22 nm	80-90
FreKote Sprayed 6 pass	Clear film	Silicon	15-22 nm	105
FreKote Dabbed	Clean film with a particles	Silicon	2-5 nm	105

3. Evaluation of reflectance IR and / or mass spectrometry for the chemical examination of contaminants

Due to the ease of equipment-up and equipment cost the use of infra-red spectroscopy (FTIR) was selected for the examination of contaminants. The FTIR examination of the treated composites was carried out using the in-situ Block Engineering reflectance spectrometer (Figure 2). A literature review indicated that the observed vibrations are should be found as follows: plane vibrations typical of an aromatic ring structure (870 cm^{-1}), in plane rings (1020 cm^{-1}), the oxirane ring stretching vibrations of an epoxy (1250

cm^{-1}), asymmetric stretching vibrations (1275 cm^{-1}), and CH_2 waggle (1370 cm^{-1}). Figure 1 shows the change in the FreKote IR spectra, associated with the air plasma treatment.

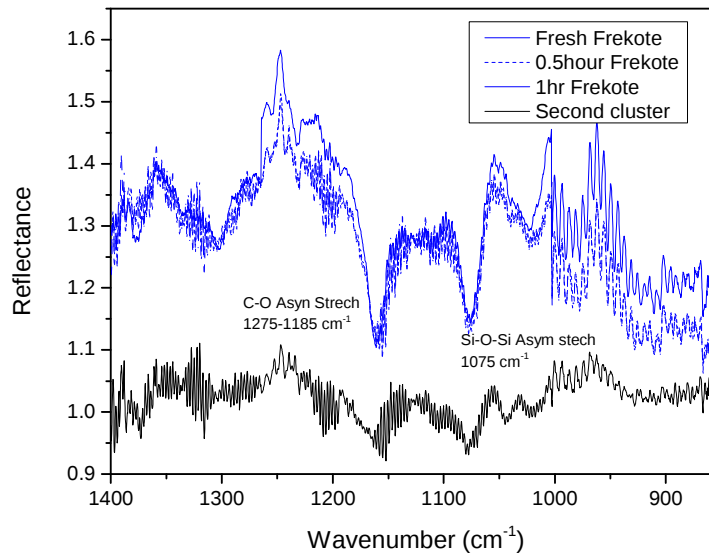


Figure 2: Reflectance FTIR of FreKote 710-NC ('fresh' as deposited, 0.5 and 1 hour after deposition and after plasma cleaning donated by 'second cluster'). Note the almost complete removal of the peaks after plasma treatment.

The performance of the Block Engineering LaserScan system was systematically evaluated as an in-situ monitoring technique; however some difficulties were identified with the use in continuous in-situ monitoring, as follows:

1. It was found that the LaserScan software as received was not user-friendly and the system cannot be used as a real-time metrology tool. Furthermore Block Engineering took a number of months to provide more reliable software
2. In use, it has been found that auto lens change in the software produced a step change in signal amplitude thus introducing mistakes in the interpretation of the spectra
3. The IR signals that demonstrate the removal of FreKote are very weak, and this can lead to errors in the interpretation of the spectra
4. To upgrade the software for remote control and data logger, Block Engineering quoted a further 20k Euro. Given the initial cost of 80k euro the LaserScan is very expensive for the information obtained
5. It has been found that there is a problem with surface registration due to heterogeneous (resin an weave) and the LaserScan A-B method of measurement. This is major problem when performing large scale manufacturing of aircraft grade composites; particularly when copper mesh on composite is used.

These issues indicate that the LaserScan is likely to be difficult to use in an industrial environment, particularly as it could lead to many false positive errors.

4. Evaluation of the effectiveness of the atmospheric plasma jet system for contaminant removal based on composite to composite bond strength and a paint adhesion study

4.1 *Composite to composite bonding* - Aircraft grade 5-harness weave carbon composite were used in this study. The composite is a Hexply® 8552/5H Prepeg, that consists of carbon fibre (AS4) pre-impregnated with a toughened epoxy resin and has a dry glass temperature of $T_g = 200^\circ\text{C}$. A total of 48 composite coupons were prepared for the plasma cleaning and subsequent for bond adhesive testing. The coupons were tested using the following protocols:

1. A 5 to 8 nm layer of FreKote 710-NC was applied onto the composite surface by wiping using lint-free cloth (approximate thickness was determined using ellipsometry). The treated composites were then air cured for 1 hour then plasma treated.
2. A 5 to 8 nm layer of Frekote 710-NC was applied and immediately after the application of this 'fresh' Frekote layer the surface was plasma treated.

Table 2. Coupon treatments

Test	No. coupons	Frekote wipe (1 hour air curing)	Plasma/Methanol treatment	Plasma speed
1	6	No	19 mm x 10 Pass	30 mm/s
2	6	No	16 mm x 10 Pass	30 mm/s
3	6	No	14 mm x 10 Pass	30 mm/s
4	6	5-8 nm Frekote	No	N/A
5	6	5-8 nm Frekote	Methanol wipe	N/A
6	6	5-8 nm Frekote	19 x 10	30 mm/s
7	6	5-8 nm Frekote	16 x 10	30 mm/s
8	6	5-8 nm Frekote	14 x10	30 mm/s

For both sets of protocol the plasma PlasmaTreat Open air atmospheric plasma parameters investigated where: treatment frequency 23 kHz, 80% voltage, 80% plasma cycle time (PCT) and 3000 mbar air pressure. A plasma scan rate of 30 mm/s with a step size of 2 mm was used to apply the cleaning treatment to the composite surface. The cleaning experiments performed over a fixed nozzle to surface gap distance of 19, 16 and 14 mm. In addition prior to adhesive bonding the WCA of the treated surface was measured and recorded. Table 2 lists the FreKote 710-NC and plasma treatment protocols. After treatment the six coupons within each test group were composite to composite bonded using a lap area of 25 x 25 mm to form three joints per test. Aerospace grade FM 300 adhesive was used for the lap joint. The joints were press-clave cured using the following temperature and pressure conditions -

2 hours ramp up to 177°C and stabilised there for 1 hour at 45 psig and then allowed to cool overnight before the lap shear test performed. Once cooled the coupon joint were cleaned, and labelled prior to destructive shear pull testing. A servo-hydraulic Instron

8502 test machine was used to investigate the lap-shear strength (LSS) of the bonded composite joints. Table 3 provides the tabulated results of these tests.

Table 3. Destructive shear pull test.

Test	# coupons	Joints made	Mean Load (N)	Mean extension (mm)	WCA prior to bonding	Surface appearance post SPT
1	6	3	7853	0.61		Cohesive failure
2	6	3	5911	0.77		Cohesive failure
3	6	3	10288	1.04	10 $\pm$ 1	Weave failure
4	6	3	1633	0.10	110 $\pm$ 1	Interfacial failure
5	6	3	9611	0.45	72 $\pm$ 1	Interfacial failure
6	6	3	2840	0.20		Interfacial failure
7	6	3	7050	0.76		Interfacial failure
8	6	3	9370	1.08	10 $\pm$ 1	Weave failure

The lap-shear strength results are presented in graphical form format, as demonstrated in Figure 3. In this figure the horizontal x-axis is the measured joint extension (mm) prior to failure and the vertical y-axis is the lap-shear strength (in MPa) prior to joint failure. The LSS was defined as the peak load before failure divided by the overlap area. Examination of Figure 3 show there are three data cluster sets emanating from the bottom left to the top right and they are aligned along the broad linear rate of increase of 0.08 mm per MPa.

The first data cluster (titled *not removed*) contains the test groups 4 (Frekote non plasma treated) and test series 6 (FreKote 710-NC plasma treated at the highest jet to substrate distance of 19 mm). These groups present the lowest fracture toughness as exemplified by their low extension before fracture, typically 0.1 mm. their visual mode of failure is interfacial which is also good indication of poor fracture toughness.

The second data cluster (titled *cleaned*) contains test groups 1, 2, 5, and 7 which represent a mixed set of treatments: FreKote 710-NC methanol clean, FreKote 710-NC plasma cleaning at 16 mm and plasma cleaning of composite at 19 and 16 mm gap distance. These groups yield a typical extension prior fracture ranging between 0.4 and 0.9 mm and exhibit partial composite mode of fracture. It is important to note here that the FreKote wipe coupons (with no solvent cleaning) treated at 16 mm gap, have higher toughness parameters than the three Frekote methanol wipe coupons.

The third cluster (titled *ablation*) contains test groups 3 and 8, which were plasma treated at a 14 mm gap distance: the two groups within the cluster contain both Frekote wipe and composite only. In these test groups the plasma has etched the 1 micron thick resin top layer to expose the weave strands producing a characteristic grey appearance and these composites exhibited a typical water contact angle of 10°. SEM image of the plasma treated surface reveal no thermal damage to the composite, but some pitting as shown in Figure 4. The latter is characteristic of an ablation process. This observation is supported by profilometer measurements that indicate the surface is pitted to a depth of 6-10 microns. Under these processing parameters the substrate composite was damaged yet yielded higher applied force values. Post shear pull test properties are similar, in that the two test groups have similar high extension prior to fracture of 1 mm and an appearance

of weave fracture mode. Samples within the first cluster exhibited interfacial failure, while those in the second exhibited a mixed failure mode. This third cluster group exhibited cohesive failure (weave) as detailed also in Table 2.

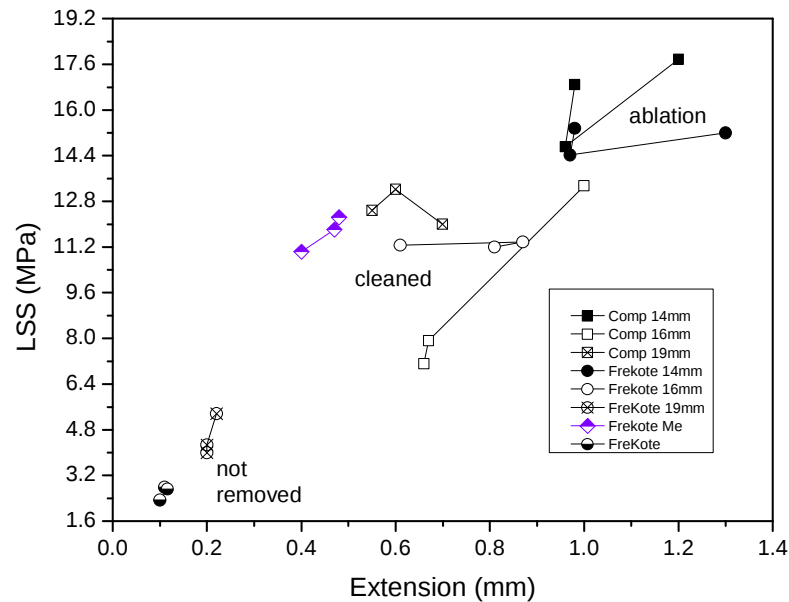


Figure 3: Results of the shear pull tests on the FM 300 adhesive bonded composites, after the pre-treatments highlighted on the graph. The graph plots joint extension (mm) and lap-shear strength (MPa) prior to joint failure.

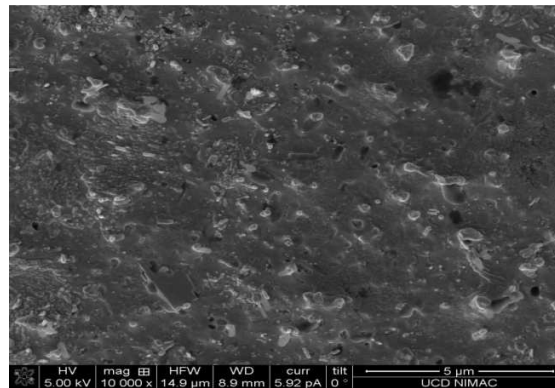


Figure 4: Pitting observed in the composite surface due to ablation by the air plasma

Paint adhesion to contaminated composite trials - A comparison study of aerospace grade primer and paint adhesion on both the carbon composite as well as titanium was performed. This study examined two contaminants (FreKote 710-NC and Boelube paste), with a range of cleaning protocols as follows:

- Atmospheric Pressure Plasma Jet (APPJ) at gap distance of 19 and 16 mm

- Commercial solvent wipes obtained from PT technology (4 different wipe types were evaluated, each containing either a solvent or as a dry wipe).
- Wipe impregnated with methanol.

In accordance with cross hatch testing of paint applied to contaminated composites (Figure 5), it was found that a 5-8 nm thick air cured FreKote 710-NC was more difficult to remove, than that of the Boelube paste. Dry wiping of these contaminants was found to be ineffective. The following were the conclusions from this comparative study.

1. The use of the air plasma, methanol and PT Technology wipes were all effective at removing 5-8 nm of air cured Frekote and Boelube paste from composite surfaces (as long as they do not have a surface copper weave).
2. The plasma cleaning treatments and methanol wipes were found to be effective for the removal of a 5-8 nm layer of Frekote, or Boelube paste from titanium surfaces. The PT Technology wipes were found not to be as effective on this surface.
3. Five passes of the air plasma removes 5-8 nm of Frekote from the surface of titanium. An additional 5 passes (total of 10 passes) of the jet, are required to remove Frekote from composite surfaces. The Boelube pastes contaminate is removed with 5 passes.

It is concluded from this study that there is a specific delineation in the cleaning protocols. The air plasma treatment was found to be effective at the removal of contaminants whose thickness in this study, is likely to be significantly higher than that experienced in normal composite or titanium aerospace handling operations.



Figure 5: Test samples used in the paint adhesion test (evaluated using the cross-hatch technique)

5. Surface mapping and control during atmospheric plasma treatments

Two real-time composite mapping strategies were examined in this study. These were electro-acoustic and optical emission spectroscopy (OES).

Electro-acoustic mapping

Electro-acoustic mapping has the ability to located composite surface and register nozzle-to composite surface. Distance registration start close to the plasma distal point (above which the acoustic signal is constant). The distal point for the PlasmaTreat source is in

the order of ~ 10 mm. Within the distal point the amplitude of the acoustic signal progressively increases with the inverse of distance. It was concluded from this study that the use of the acoustic signal can also be translated into plasma induced surface temperature, when the data is benchmarked using optical pyrometry techniques. While this technique has considerable potential, it can under certain circumstances be difficult to discriminate the plasma distal point in contact with the surface. The reason for lack of discrimination may be due to the wide bandwidth filter requirement for this parameter. The overall conclusion is that OES has greater potential as a process monitoring technique.

OES mapping

Optical emission spectroscopy mapping of composite surfaces differs from electro-acoustic mapping as the emission signal contains chemical information from the plasma cleaned surface. To access plasma-surface interaction information the optical chain needs to focus on the reaction volume using an off-axis position (~ 45 degree from plume flow axis). It is important to note that this method of interrogation is different from a Patent by Boeing (US Application 20050124074), on the use of this technology as it only describes in-line (vertical imaging) and perpendicular imaging of the plasma plume. With the off-axis method both geometric effects and chemical species evolving with the plasma-surface reaction are observed. The main chemical emission band observed emanating from the composite surface is the hydroxyl group OH ($\lambda = 306-309$ nm). The amplitude of the OH band also increases with plasma exposure time.

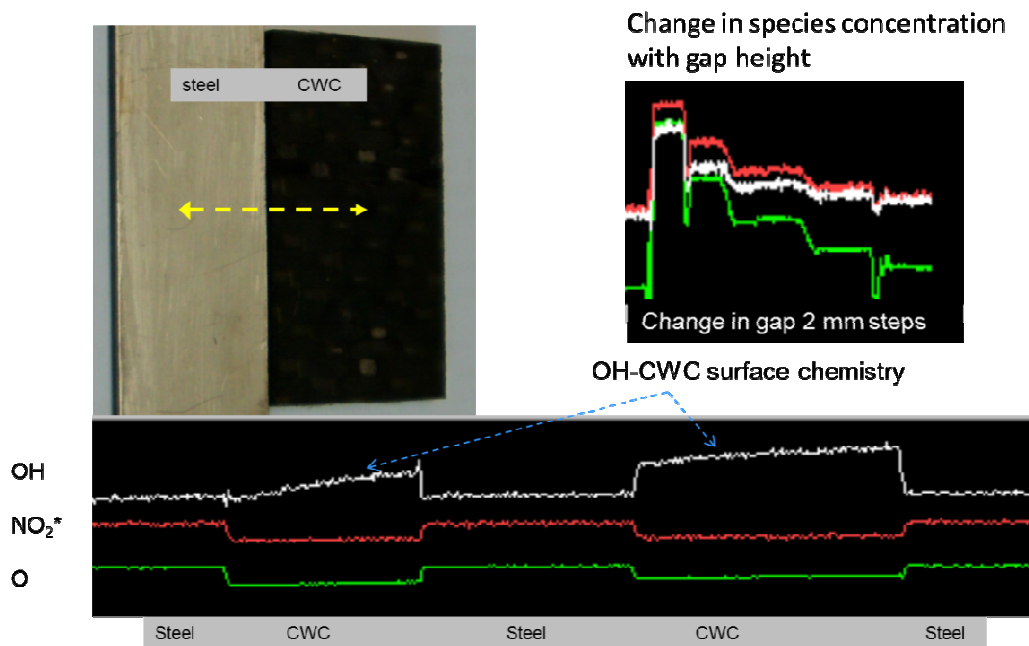


Figure 6: In-situ OES measurements of Oh, NO₂* and O lines in real-time, obtained as the PlasmaTreat jet is scanned across steel and composite (CWC) surfaces. Sampling rate 2 Hz and scan rate of 30 mm.s⁻¹. The image on the top right demonstrates the sensitivity of the OES technique to changes in step heights as the jet moves across a composite surface.

Figure 6 shows an example the OES software being used to detect differences between both steel and composite surface in a scanning run across a number of steel and composite (CWC) surfaces. Note how both NO₂* and atomic O line intensities decrease to a new steady level relative to steel surface, whereas the OH band increases at a steady rate with time over the steel surface. It is concluded from the OES study that the technique is very sensitive to any thermal damage to the composite substrate, it can detect changes associated with the jet moving between metal and composite surfaces and it is also sensitive to changes in the jet to substrate distance (1 mm step heights).

6. Conclusions

Over an 18 month period the *PlasmaClean* project has investigated plasma removal on contamination with thickness in the range 5-10 nm. The main contamination type investigated being FreKote 710-NC, either sprayed or dabbed on to the surface of silicon wafer and aircraft grade composite substrates. Atmospheric plasma jet conditions were investigated in the removal of FreKote from composite surfaces. The degree of contamination removal and damage where investigated using reflection FTIR spectroscopy, electro-acoustic emission and OES. The FTIR measurement was found not to true real-time metrology technique as an A-B measurement had to be used, whereas electro-acoustic and particularly OES metrology can be used in real-time, once synchronised to the plasma scan over the composite surface was achieved.

With respect to composite surface mapping during plasma processing:

1. Stand-off FTIR can detect down to approx. 2 nm of FreKote on a composite surface. The removal of this contaminant can also be detected. This FTIR technique cannot however be performed in real-time due to the heterogeneous nature (resin and weave), of the composite. The onset a composite thermal decomposition however can be readily detected using these measurements. Once this deterioration occurs there is a rapid deterioration in the composite-to-composite or composite to paint bond adhesion strength.
2. Conditions have been developed to successfully remove a FreKote layer (thickness 5-8 nm) from composite surfaces, using the PlasmaTreat air plasma system. After the contaminant removal the composite surface exhibited the same adhesion enhancement in pull adhesion test studies, that is achieved for composites which had been plasma activated but whose surface had not been contaminated with FreKote. In particular composite-to-composite bond tests were obtained both for the freshly deposited FreKote and for the surface that had been left to air dry for 1 hour after the application of the FreKote. The effectiveness of the plasma treatment was not found to be influenced by FreKote drying time.
3. The air plasma system was also found to be effective in the removal of contaminants prior to painting. Cross hatch tests demonstrated that the plasma was effective in the removal of contaminants both on both metallic (titanium) and composite surfaces.
4. Off-axis real-time electro-acoustic measurements provide information on the nozzle-to-surface distance within the visible plume distal point. This measurement can be

correlated directly with the composite surface temperature under a given set of plasma treatment conditions. It can therefore be used as a low cost process control technique.

5. Off-axis real-time OES of the plasma-composite reaction volume provides information on emission species (i.e. OH band) emanating from the composite surface. This can be used for in-process control to avoid thermal damage by the plasma. The technique is also sensitive to changes in the composition of the surface (metal to composite) and also height differences (to 1 mm) on a given surface.
6. For industrial applications electro-acoustic and OES both appear to be cost effective process control techniques for mapping the treated surface temperature as well as its surface chemistry. Both techniques have potential for process control for the atmospheric pressure plasma processing of composites, once they are calibrated using more expensive analytical methods such as reflectance FTIR.

In conclusion therefore this project has successfully demonstrated that air plasma treatments can be successfully used to remove organic contaminants on the surface of both aerospace composites and metals. The optical emission spectroscopy technique can be used as non contact diagnostic method for the determination of the chemical species present on the surface of metallic materials and composites during atmospheric plasma jet treatments. Any thermal damage caused by the air jet can be identified by changes in the OES spectra obtained of the plasma plume during treatment.