Surface Monitoring of CFRP Structures for Adhesive Bonding

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Introduction

In the aerospace industry, the use of carbon fiber reinforced polymers (CFRP) has enabled significant weight and fuel savings, leading to more economical and environmentally friendly large transport aircraft. To further advance aircraft performance and/or reduce manufacturing costs, there is a desire to replace mechanical fasteners with adhesive bonds [1]. Presently, for primary structures on commercial transport aircraft to meet certification criteria designated by the Federal Aviation Administration (FAA), adhesively bonded assemblies often rely on arrest features to prevent catastrophic failures. Adhesive bonding is used in secondary aircraft structures (e.g. flight control surfaces, leading and trailing edges, and engine cowls) and has demonstrated excellent reliability [1]. In cases where failures have occurred, the cause is often traced back to improper materials and process controls. Such process controls involve surface treatment and verification to ensure that the surface has been chemically activated and is free of contaminants, which may cause inadequate bonding.

Silicone based mold release agents are used during the fabrication of CFRP parts, and can cause surface contamination. Silicone can penetrate hundreds of nm into the CFRP matrix [2,3], and depending on the composite, surface treatment, adhesive and bonding process, silicone contamination can interfere with bonding even at low concentrations ($0.8 \ \mu g/cm^2$) [4].

Laser treatment can be used to remove contaminants from CFRP surfaces, and roughness can be created by the adequate adjustment of laser parameters, such as the laser pulse power, scan speed, and pulse frequency. By judiciously choosing the laser ablation parameters, it is possible to control the laser-CFRP interactions. In this way, superficial contaminants can be selectively removed without damaging the carbon fibers and the bulk CFRP material [4-7].

In this paper, two techniques for monitoring the presence of contamination on CFRP materials are investigated: laser induced breakdown spectroscopy (LIBS), and optically stimulated electron emission (OSEE). Performing LIBS with laser pulse energies below 100 μJ (μLIBS) [8,9] can minimize any surface ablation and increase surface sensitivity. OSEE is a photoemission based technique designed for inspection of deposited surface contaminants. In this study, CFRP surfaces were contaminated with polydimethylsiloxane (PDMS), a major constituent in silicone based mold release agents, in a controlled fashion to produce thin contamination layers. The coated panels were analyzed by LIBS and OSEE, laser surface treated and analyzed again to determine the ability of the laser treatment process to remove silicone as well as the ability of the measurement techniques to detect very low levels of silicone.

Experimental

Unidirectional CFRP panels (30.5 cm x 30.5 cm) were fabricated from eight plies of unidirectional Torayca P2302-19 (T800H/3900-2) prepreg. The curing process was performed in an autoclave at 177 °C and 690 kPa. Release from the caul plate was achieved using Airtech A4000V release film, a fluorinated ethylene propylene (FEP) film. Contaminated CFRP samples were produced by spraying PDMS diluted with hexanes to various concentrations, leading to different layer thicknesses. The PDMS films were dried at 100 °C for 1 hour. Using witness p-type Si[100] wafers, PDMS thicknesses were measured using ellipsometry in the wavelength range from 370 nm to 900 nm with a 10 nm step size at different incident angles: 65°, 70°, and 75°.
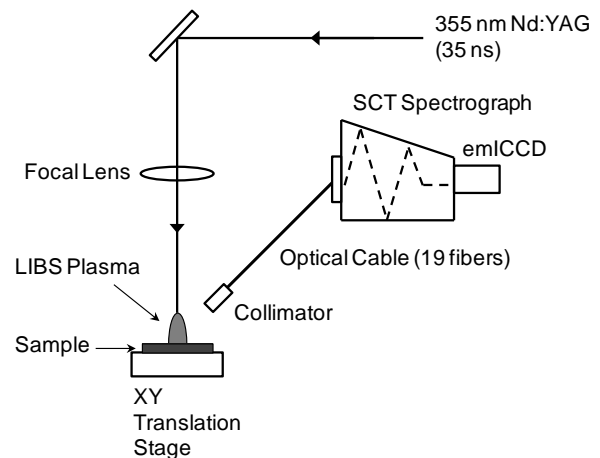

Figure 1. Schematic diagram of the LIBS system for the detection of contaminants on CFRP.

The schematic diagram of the LIBS system is shown in Fig. 1. The Nd:YAG (AVIA, Coherent) laser operates at 355 nm and ~35 ns (FWHM) pulse duration. For this work, the pulse frequency was 40 kHz. The LIBS emission is measured using a 328 mm, f/4.6 Schmidt-Czerny-Turner (SCT) spectrograph (IsoPlane SCT 320, Princeton Instruments).

The spectral response is recorded using an electron-multiplier intensified charge-coupled device (emICCD) camera (PI-MAX4: 1024 EMB, Princeton Instruments). The plasma emission is collected with a collimator and guided to the spectrograph via an optical cable with 19 200 um fibers. A grating with 1200 grooves/mm blazed at 300 nm and a slit width of 10 um are used. The emICCD camera is externally triggered by the laser synchronous output.

The LIBS spectra were generated using multiple laser pulses at the same location on the target material, and plasma emissions were accumulated on the CCD sensor.

The signal-to-noise ratio (SNR) is a quantitative measure that defines the relative intensity between the LIBS signal and the noise. The SNR is calculated as,

$$SNR = \frac{I_p}{3\sigma_b}$$

where I_p is the background-corrected height of the peak of interest, and σ_b is the standard deviation of a background-corrected spectrally quiet region away from the peak.

The OSEE probe head [10] for CFRP surface inspection has a low-pressure mercury vapor (LPMV) lamp that illuminates the surface under inspection. The photoelectrons emitted from the CFRP surface are drawn by the collector plate, which is positively biased with 200 V. The test area has a diameter of 2.54 cm, and the distance from the collector to the target surface is 5.72 mm. The LPMV chamber is maintained in an argon environment. For each measurement, the test environment is purged with argon. The 185 nm mercury emission line is typically responsible for 95% of the OSEE signal [11].

XPS analysis was performed with a Surface Science Instruments SSX-100, and a monochromatic Al K-alpha X-ray source.

Results and Discussion

An initial survey was performed on untreated CFRP in order to obtain the SNR for the C emission line at 247.9 nm, corresponding to the transition $2s^2 2p3s\ ^1P^o \rightarrow 2s^2 2p^2\ ^1S$, for different pulse energies at 40 kHz pulse frequency. For these measurements, 50 pulses hit the same location, and the induced plasma emissions were accumulated on the CCD sensor to generate one spectral frame. Figure 2 shows the SNR as a function of the pulse energy and the limit of detection (LOD), when SNR = 1.

The PDMS film was detected by the identification of the Si spectral line at 288.2 nm, which corresponds to the transition $3s^2 3p4s\ ^1P^o \rightarrow 3s^2 3p^2\ ^1D$. The CFRP samples contaminated with PDMS were characterized using 45 μJ laser pulses at 40 kHz pulse frequency. The gate delay and gate width were adjusted judiciously to obtain the best SNR for the Si spectral line at 288.2 nm.

For the detection of the Si I emission at 288.2 nm, the SNR was improved by averaging the collected frames. For Fig. 3, the CFRP surface was coated with a PDMS thickness of 5.3 ± 1.7 nm. The LIBS signal was collected using 10 frames of 50 pulses each, a total of 500 laser pulses. Each frame was acquired on a fresh surface, and the 10 frames were averaged to generate the final LIBS spectrum.
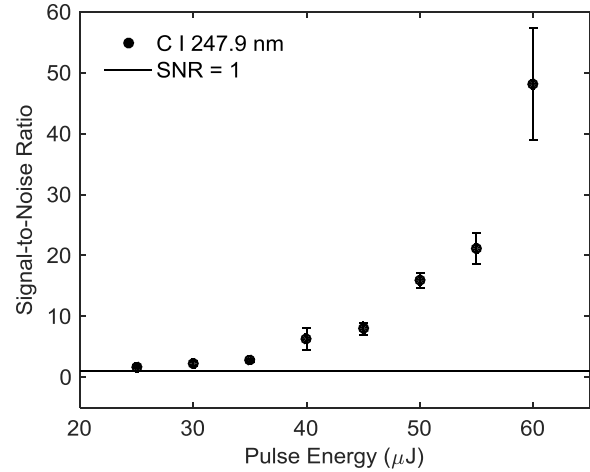
Figure 2. Measured SNR for the C line at 247.9 nm using 50 pulses on the same location. For the data at 25 μJ, the SNR is close to the $3\sigma_b$ noise level.
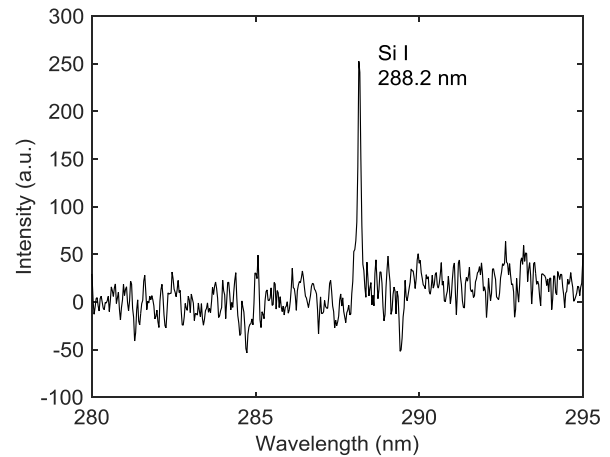
Figure 3. Background corrected Si I emission at 288.2 nm using 45 μJ pulses from a CFRP contaminated with PDMS thickness of 5.3 ± 1.7 nm. The spectrum was generated by averaging 10 frames of 50 pulses each. Each frame was taken on a fresh surface. The SNR is 4.71.

Table 1. Atomic percentages (at.%) of elements in untreated CFRP surface.

Element	Atomic percentage (at.%)
C 1s	53 ± 2
F 1s	23 ± 3.2
O 1s	16.5 ± 1.2
Si 2p	4.1 ± 0.2
N 1s	2.7 ± 0.3
S 2p	0.8 ± 0.1

The results for untreated, unintentionally contaminated CFRP have shown a Si I emission intensity at 288.2 nm similar to contaminated CFRP surfaces. The presence of Si

was also verified with XPS. Table I shows the average atomic composition for untreated CFRP.

For the OSEE experiments, the CFRP samples were laser ablated using 800 mW average laser power at 80 kHz pulse frequency, 22.86 μm line pitch, and 25.4 cm/s scan speed. With these parameters for laser treatment, both resin and contamination layers can be laser ablated simultaneously.

Dissimilar surface conditions can be differentiated by the OSEE photoemission, as shown in Fig. 5. It is evident that the untreated control sample yielded higher photoemission than that of the untreated samples contaminated with PDMS. The presence of PDMS led to a low OSEE signal response. In addition, laser ablated samples showed a significant increase in photoemission, compared to the untreated surfaces. For laser treated CFRP composites, the photoemission was favored by the exposure of undamaged carbon fibers, which are more electrically conductive than the top layer resin.
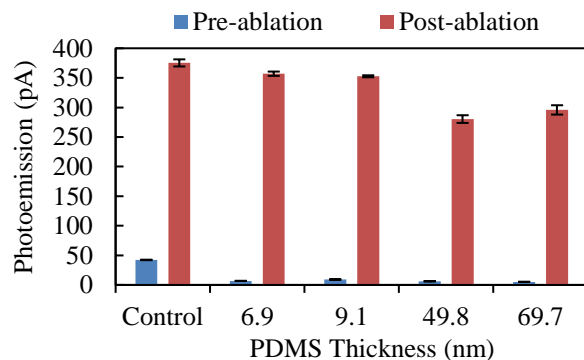

Figure 5. OSEE photocurrent for different PDMS thicknesses on CFRP surfaces.

Conclusions

LIBS detected silicon compounds by inspecting the Si I line at 288.2 nm measured from CFRP surfaces. The SNR of the Si I emission line for untreated, unintentionally contaminated CFRP samples is similar to that of purposefully contaminated ones. The ~5-nm PDMS layer did not contribute significantly to the increase in the intensity of the Si I emission line at 288.2 nm. This is because the silicon concentration is lower in comparison to the ablated volume. Therefore, LIBS is demonstrably useful for the detection of silicon compounds in CFRP composites in a rapid and nearly non-destructive manner.

OSEE detected the presence of PDMS and could differentiate laser treated surfaces from untreated and contaminated surfaces. OSEE photoemission was also favored by the electrically conductive undamaged fibers exposed from laser ablation.

LIBS and OSEE have produced promising results that indicate their applicability as techniques for in-line monitoring CFRP surface conditions prior to adhesive bonding.

Currently, research endeavors are focused on single-shot LIBS to increase surface sensitivity (depth profile) for the detection of surface contaminants on composite materials.

Acknowledgements

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