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Surface characterization of carbon fiber reinforced polymers by picosecond laser induced breakdown spectroscopy

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ABSTRACT

Adhesive bonding of composite materials requires reliable monitoring and detection of surface contaminants as part of a vigorous quality control process to assure robust and durable bonded structures. Surface treatment and effective monitoring prior to bonding are essential in order to obtain a surface which is free from contaminants that may lead to inferior bond quality. In this study, the focus is to advance the laser induced breakdown spectroscopy (LIBS) technique by using pulse energies below 100 μJ (μLIBS) for the detection of low levels of silicone contaminants in carbon fiber reinforced polymer (CFRP) composites. Various CFRP surface conditions were investigated by LIBS using ~10 ps, 355 nm laser pulses with pulse energies below 30 μJ. Time-resolved analysis was conducted to optimize the gate delay and gate width for the detection of the C I emission line at 247.9 nm to monitor the epoxy resin matrix of CFRP composites and the Si I emission line at 288.2 nm for detection of silicone contaminants in CFRP. To study the surface sensitivity to silicone contamination, CFRP surfaces were coated with polydimethylsiloxane (PDMS), the active ingredient in many mold release agents. The presence of PDMS was studied by inspecting the Si I emission lines at 251.6 nm and 288.2 nm. The measured PDMS areal densities ranged from 0.15 to 2 μg/cm^2. LIBS measurements were performed before and after laser surface ablation. The results demonstrate the successful detection of PDMS thin layers on CFRP using picosecond μLIBS.

1. 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 (fewer emissions) 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. 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 improperly treated materials and process controls. Such process controls involve surface treatment and characterization to ensure that the surface has been chemically activated and is free of contaminants.

Silicone based mold release agents are used during the fabrication of CFRP parts and can cause surface contamination. Silicone can penetrate hundreds of nanometers 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 μg/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 near the surface and without thermally decomposition of the CFRP matrix resin [4–7].

Effective techniques for monitoring the pre-bonding surface conditions are crucial to obtain adherent surfaces free from bond-degrading contaminants. Pre-bonding surface treatment and surface contamination detection are necessary to enhance surface conditions of aerospace composites prior to adhesive bonding and to improve

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the reliability of the bonded structures, so they can thus meet FAA-designed certification criteria for aircraft structures. From a practical viewpoint, the ability to detect contaminants must be sensitive, rapid, amenable to automation, and must require minimal or no sample preparation in order for it to be adopted by industry.

In this paper, laser induced breakdown spectroscopy (LIBS) is investigated for monitoring the presence of silicone contamination on CFRP materials. Microjoule picosecond laser pulses can produce high peak power levels that can surpass the optical breakdown thresholds of many materials. Picosecond pulses are shorter than the thermal relaxation times of polymers, leading to minimum heat transfer to the material outside the laser-excited volume. Most of the ultrashort pulse energy induces photochemical ablation, and consequently, there is minimal thermal stress. Low-energy pulses are required to minimize the ablation damage to the composite surface during LIBS analyses. The aim of this paper is to demonstrate that single UV picosecond pulses can be used for LIBS analysis of silicone contaminants on CFRP. The LIBS measurements were conducted with single laser shots on previously untested, i.e. "fresh", surfaces at low pulse energies. Performing LIBS with laser pulse energies below 100 μJ (μLIBS) [8,9] can minimize surface ablation and increase surface sensitivity. 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 panels contaminated with PDMS were analyzed by LIBS prior to and after laser ablation to determine the ability of the laser treatment process to remove silicone as well as the ability of LIBS to detect very low levels of silicone.

2. LIBS

LIBS [10,11] is an elemental characterization technique that detects the photonic emissions from the laser induced plasma plume to obtain the chemical information of a target material. The hot induced plasma plume generated by the laser pulse expands into the ambient gas. As the plasma plume cools down, it emits photons at different wavelengths that are characteristic to the target material. Some advantages of LIBS are that measurements can be performed rapidly and without sample preparation. LIBS can provide chemical analysis of elements in different forms (solid, liquid, or gaseous).

2.1. Laser-material interactions

For picosecond and ultrashort pulses, the primary interaction is laser-matter, which affects the electrons in the solid. The electrons are heated by the laser pulse, and the transfer of energy to the lattice by collisions takes more time than the incident laser pulse duration. Picosecond and ultrashort pulses excite the target surface rapidly. For polymers, if the laser energy irradiated on the material is sufficient, bond dissociation occurs by multiphoton transition. Such a photochemical mechanism produces mechanical stress to break bonds, and the material is removed from the target surface by fragmentation [12,13]. There is minimal energy transferred to the regions outside the irradiated material volume, producing less thermal-stress in the material.

2.2. μLIBS

The extension of LIBS toward lower pulse energies, typically < 100 μJ, is known as μLIBS [14–18]. The benefits of μLIBS include the use of the lower energy pulses and higher pulse frequencies that most modern laser systems yield. In μLIBS, the decay time of the emission line couples with an even faster decay of the continuum emission, making possible the detection of the LIBS signal using ungated detectors [16–18]. The improved ratio of line-to-continuum emission and small pulse energy in μLIBS can be optimized to achieve the limit of detection (LOD) using conventional LIBS, which is in the mJ regime [15]. In addition, the ablation crater size decreases with lower pulse energies, and thus, the technique may be considered nondestructive. Also, since the ablation crater dimensions are reduced, the spatial (lateral) and depth resolutions are enhanced [8,19]. Moreover, given the lower laser pulse energies, compact and economic laser sources can be employed in LIBS systems.

3. Experimental

3.1. Materials

Unidirectional CFRP panels (30.5 cm × 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 of the composite panel from the caul plate was achieved using Airtech A4000V release film, a fluorinated ethylene propylene (FEP) film. Tool and caul surfaces were pre-treated with Zyvax WaterShield, a silicone-based mold release agent dispersed in water. For LIBS measurements, the laminates were cut with a water jet into square samples of 1.27 cm × 1.27 cm. X-ray photoelectron spectroscopy (XPS) was performed on a Surface Science Instruments SSX-100 spectrometer with a monochromatic Al K-alpha X-ray (1.486 keV photon energy) source. The spot size was 800 μm × 800 μm.

3.2. Sample contamination

Contamination on CFRP samples was produced by spraying PDMS diluted with hexanes to various concentrations, leading to different layer thicknesses. The PDMS coated samples were dried at 100 °C for 1 h. Using witness p-type Si[100] wafers, PDMS thicknesses were measured by variable angle spectroscopic ellipsometry (VASE) using a J.A. Woollam VB-400 control module and HS-190 scanning monochromator. Data were collected in the wavelength range from 370 nm to 900 nm with a 10 nm step size at three incident angles: 65°, 70°, and 75°. From these measurements, the thickness of PDMS on the CFRP surfaces was inferred.

3.3. Laser ablation

Laser ablation was performed with a Nd:YVO_4 laser system (Atlantic 20-355, EKSPLA) operated at 355 nm with a nominal pulse duration of ~10 ps, 80 mW average power, and 400 kHz pulse frequency. The calculated average photon flux of the focused laser beam was 7.17×10^{22} photons/s/cm^2. The average laser power was measured with a thermopile sensor (30A-BB-18, Ophir-Spiricon) and a laser power meter (Nova II, Ophir-Spiricon). During ablation, the CFRP sample was held stationary while the galvanometer unit scanned the composite surface. CFRP specimens were laser ablated with parallel lines, which were produced in the fiber orientation at 12.7 μm line pitch and 25.4 cm/s scan speed.

3.4. Surface morphology

Depth measurements of LIBS craters produced with single shots were performed with an optical surface profiler (NewView 6000, Zygo) equipped with a 20X Mirau objective and a 1X zoom lens. CFRP surfaces were coated with Pd-Au for surface morphology analysis using a JEOL JSM-5600 scanning electron microscope (SEM) operated at an accelerating voltage of 15 kV.