International Journal of Adhesion and Adhesives 84 (2018) 257–264

Contents lists available at ScienceDirect

International Journal of Adhesion and Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Correlation of optically stimulated electron emission with failure mode of adhesively bonded epoxy composites

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ARTICLE INFO

Keywords:
Photoemission
Surface characterization
PDMS
Contamination
DCB

ABSTRACT

Carbon fiber reinforced polymers (CFRP) reduce weight in aerospace and automotive applications while maintaining or improving structural performance. Additional performance gains can be realized with composites if adhesive bonding is used in place of mechanical fasteners for structural assemblies. Surface preparation for adhesive bonding plays a critical role in the assembly process. Effective techniques for monitoring the pre-bonding surface conditions are crucial to obtain surfaces free from bond-degrading contaminants, e.g. mold release agents, which are widely used in CFRP manufacturing. In this work, optically stimulated electron emission (OSEE) was used prior to and after laser ablation to measure deposited levels of polydimethylsiloxane (PDMS) on CFRP (Torayca P2302-19). OSEE was also used to model the contamination layer thickness. After the specimens were adhesively bonded with a modified epoxy film adhesive (Loctite EA 9696 Aero), they were subjected to double cantilever beam (DCB) tests to investigate the hypothesis that surface contamination species and levels affect the fracture characteristics of adhesively bonded joints. This study relates OSEE photocurrent and the classification of the bond failure modes to their PDMS surface contamination levels prior to adhesive bonding. DCB test results show that (1) the region under the traces within the load and unloading boundaries consistently correlates with the bond strength and the probability of different failure modes, and (2) bond performance at fracture depends on the surface PDMS film thickness coating prior to laser surface treatment. The decrement in bond performance in this study correlates to the OSEE readings of contaminant levels on the adherent surfaces.

1. Introduction

A successful bond between adjacent structural components must fulfill the service requirements established by the manufacturer for any given structure. Typically, these requirements include the ability to transfer loads across bonded regions under operating conditions during the useful lifetime. Operating conditions include exposure to environmental conditions (specifically large temperature and humidity changes and extreme weather conditions) as well as, for example, fuel spills or leakage of hydraulic and other fluids onto bond regions.

Success in establishing a bond between two surfaces depends on the conditions of the surfaces involved in the adhesive bonding process. Important components in the study of bonding are the cleanliness and chemical activation of the surface. The contaminant species and their respective concentrations are potential variables in determining bond quality. In this study, the following areas were examined: (1) surface cleanliness and techniques to measure surface concentrations of specific contaminants, and (2) surface ablation to remove contamination and to provide a chemically active surface to improve adhesive bonding.

Laser ablation, as a method to prepare the surface prior to adhesive bonding, is under investigation [1–3]. In previous work [2–5], it has been shown that by adjusting the laser parameters, it is possible to selectively remove the surface contamination without damaging the underlying carbon fibers or producing interlaminar damage. Under certain conditions, laser surface ablation can generate roughness, which can improve bond performance by enabling mechanical interlocking. This surface treatment provides opportunity for automation and reproducibility in the surface preparation process.

Optically stimulated electron emission (OSEE) is a photoemission based technique designed for inspection of surface cleanliness [6–10]. Consistent with an absorption process that follows the Beer-Lambert law, contamination and adherents on surfaces change the photoelectron emission from the photoemitting target surface. Reactions between a surface and contaminants cause an alteration of the surface electron

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https://doi.org/10.1016/j.ijadhadh.2018.04.003
Accepted 29 March 2018
Available online 12 April 2018

work function, which affects the efficiency of electron emission from the surface. Therefore, surface cleanliness affects photoemission based currents.

This paper presents the capabilities of OSEE as a surface quality monitoring technique for CFRP by establishing a relationship between bond failure and OSEE readings of the surface contamination level. Each specimen set was contaminated with a measured surface concentration of polydimethylsiloxane (PDMS), a major component of silicone based mold release agents, and then ablated. Silicones, even at low concentrations, are known to cause problems with adhesive bonding on CFRP surfaces [11,12]. Pre- and post-laser-ablation CFRP surfaces were examined with OSEE and other techniques. Mechanical testing, consistent with ASTM D5528-13 [12,13], was performed by applying tensile load to the adhesively bonded CFRP specimens to determine failure modes, as per ASTM D5573-99 [14].

The sensitivity and accuracy of OSEE in distinguishing unfavorable CFRP surface conditions were also investigated. A separate set of specimens, cut from eight-ply CFRP and designed to fit the OSEE instrument measurement chamber, was used to establish the sensitivity of the OSEE measurement system to PDMS levels used in the DCB specimens. The failure modes in the DCB study were correlated to the results obtained with the OSEE technique. The effects of laser parameters on the OSEE signal response were analyzed when CFRP surfaces were laser treated using different scan speeds and average laser power levels.

2. Photoemission

2.1. Optical absorption by surface contamination

In the OSEE technique, ultraviolet (UV) source radiation impinges on the target surface with a photon energy $E = h\nu$, where h is Planck's constant, and ν the incident photon frequency. When a contamination film covers the top of a target surface, the incident intensity I_0 from the UV light source travels through the contamination layer. The incident intensity undergoes photon absorption and scattering in the contamination layer. For a contamination film thickness that extends from $x = 0$ to $x = l$, the transmitted intensity I_t at $x = l$ that excites the surface is less than the incident intensity I_0 at $x = 0$. As the UV radiation passes through the contamination layer, it produces a decrease in the incident intensity I_0. The incident intensity I_0 is proportional to the photocurrent i_0 detected by OSEE. This is true when no contamination is present. However, when there is a contamination film on the target surface, the transmitted intensity I_t, after passing through the contaminant and striking the target surface, is proportional to the photocurrent i_t. If the absorption coefficient of the contaminant is $\alpha(\lambda)$, which depends on the wavelength λ, and the thickness is l, the decrease in the photocurrent owing to an absorbing medium is described by

$$i_t = i_0 e^{-\alpha(\lambda) l} \quad (1)$$

Solving for l gives

$$l = \frac{1}{\alpha(\lambda)} \ln\left(\frac{i_0}{i_t}\right) \quad (2)$$

By applying Eq. (2), contamination thickness can be determined from optically stimulated photoemission data on Si wafers used as witness surfaces to monitor contaminant exposure on CFRP.

2.2. Work function dynamics

The impingement of the UV photons on the target surface affects the photoelectron emission from that surface. If a photon is not absorbed by the contaminant layer, it will strike the target substrate surface, and cause the emission of an electron according to the Einstein equation,

$$E_{max} = h\nu - \phi \quad (3)$$

where E_{max} is the maximum kinetic energy of an electron emitted from the surface, and ϕ is the work function of the contaminated target surface. Photoelectron generation occurs when the incident energy is greater than the threshold energy of the surface. In addition, the difference between the source photon energy and the contamination-altered work function of the target surface affects the efficiency of the electron emission [15].

3. Experimental

3.1. Materials

The methods for the composite fabrication and the sample preparation have been previously described [3,12]. For the OSEE experiments, unidirectional CFRP panels (30.5 cm × 30.5 cm, 1.85 mm thick) 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 for 2 hours under 690 kPa (6.9 atm). Release from the caul plate was achieved using Airtech A4000V release film, a fluorinated ethylene propylene (FEP) film, which was placed between the caul plate and the prepreg plies. Tool and caul surfaces were pre-treated with Zyvax WaterShield, a silicone-based mold release agent dispersed in water. The vacuum bagging setup and its constituents for the fabrication of unidirectional CFRP panels are shown in Fig. 1. The laminates used for OSEE measurements were cut with a water jet into square specimens of 3.81 cm × 3.81 cm. For the fracture toughness test, 10-ply CFRP panels (30.5 cm × 30.5 cm, 2.08 mm thick) were prepared with the same procedure and machined by a water jet along the carbon fiber direction to produce samples of 2.5 cm × 24.1 cm.

3.2. Sample contamination

Composite surfaces, except for the control surface, were contaminated prior to laser ablation. Contamination on CFRP samples was produced by spraying PDMS diluted with hexanes to various concentrations, leading to different layer thicknesses. Using witness silicon wafers (Si[100], 10.2 cm diameter), low (~10 nm) and medium (~60 nm) contamination levels were measured by using variable angle spectroscopic ellipsometry (VASE) [16–18] with 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 different incident angles: 65°, 70°, and 75°. Using witness aluminum coupons, the film thickness of high contamination levels (~1 μm) was determined by weight difference using an analytical balance with a nominal resolution of 0.01 mg. Both methods, VASE and weight difference, were used to infer the thickness of PDMS on CFRP.

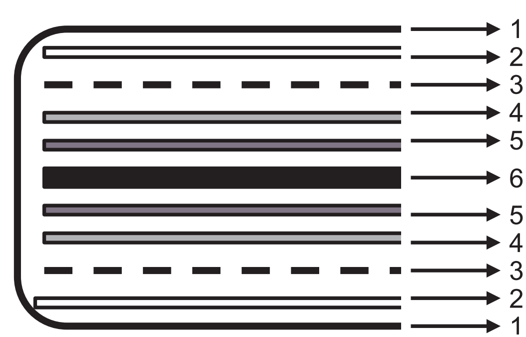

Fig. 1. Vacuum bagging setup for the fabrication of unidirectional CFRP panels (both the eight-ply, used for OSEE data, and the 10-ply, used for fracture testing): 1. Low temperature bag material, 2. Breather fabric, Airtech Airweave N10, 3. Porous release layer, Airtech Release Ease 234 TFP, 4. Stainless steel caul plate, 5. FEP release film, Airtech A4000V, and 6. Plies of prepreg, Torayca P2302-19.