Effectiveness of Surface Treatment Techniques for Composite Bonding with Different Contamination Levels

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ABSTRACT

Various surface treatment techniques have been developed to promote adhesive bond performance for composite structural components in aerospace applications. The condition of the pre-bond surface is critical to achieving desirable bond quality. Contamination on bonding surfaces is well recognized as a major threat to ultimate bond performance. Variation in contamination level has brought additional challenges into manufacturing process control. High fidelity surface treatment techniques are required for effective removal of contaminants over a wide range of contamination levels. In this study, a common contaminant, i.e. silicone mold release, was introduced to pre-bond composite surfaces with different concentrations. Plasma and laser surface treatment techniques were performed and their effectiveness in restoring and enhancing desirable bond quality was investigated. Surface characterization techniques, including water contact angle goniometry, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy, were conducted to assess the condition of contaminated surfaces and the improvement induced by plasma and laser surface treatments. Failure modes from a customized double cantilever beam test were investigated before and after surface treatments. Fundamental mechanisms of plasma and laser surface treatments on the composite bonding surfaces were also investigated.

INTRODUCTION

Structural adhesive joints have been widely applied in multiple cold section aircraft engine components and airframe structures. Adhesive bond performance is greatly influenced by mechanical interlocking and chemical interactions between adhesive and adherend.[1-3] It is well-known that such adhesively bonded composite joints are particularly sensitive to pre-bond surface conditions, as well as the nature of adhesive materials and associated curing processes. Quality control of pre-bond surfaces has become critical to adhesive bond performance in composite bonding manufacturing processes. Contamination on pre-bond surfaces stands as a major threat to adhesive bonded structural components.[4-7] Surface treatment techniques to remove contaminants have attracted increased attention in recent years to promote bond performance and provide robust process control of adhesive bonding. Abrasion, plasma etching/activation and laser ablation have been reported for contaminant removal and bonding enhancement.[7-14]

The levels of contamination observed in manufacturing processes can span a wide range due to the inherent lack of predictability that results from multiple contamination sources, human errors and various non-conformances from the manufacturing processes. Effectiveness of surface treatments on different contamination levels, heavy and light, needs to be determined to ensure the high fidelity of adhesive bond quality.

In this work, both laser and plasma surface treatments were investigated. Pre-bond composite surfaces were contaminated with a mold release in different concentrations. Surface characterization techniques including water contact angle, Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectrometer (XPS) were applied to reveal surface wetting, functionalities and morphology as a result of different surface treatments. Double cantilever beam (DCB) tests at room temperature were performed to assess bond performance. Crack propensity in DCB testing was selected because of its sensitivity to bondline defects in comparison to other static bond stress testing.

EXPERIMENTAL

Materials:

Composite materials: Hexply® carbon fiber (IM7 and AS4) reinforced 8552 prepregs were supplied by Hexcel corp. The composite substrates were prepared from 9-10 plies of prepreg. The laminate was cured at 177°C (350°F) for 3 hrs under 0.7 MPa (100 psi).

Adhesives: Epoxy adhesives, Scotch-Weld™ EC3448 from 3M and EA9658 from Loctite, were used. The paste adhesive was applied with an adhesive dispensing gun and spread on both pre-bond surfaces with plastic trowel spreader. The film adhesive was sandwiched between composite laminates with a caul sheet on top. Shims with a total thickness of 0.127- 0.254 cm (0.005 - 0.010 in) were used to control the bondline thickness.

Contaminant: A mold release, Loctite® Frekote 44NC™ was applied in different concentrations.

Low contamination level: the diluted mold release (1:1 by acetone) was sprayed on the pre-bond surfaces with an airbrush, as shown in Figure 1, and dried at room temperature inside a hood over 4 hours. The resulting contaminant deposit was around 0.06 g/m².

High contamination level: the mold release was aggressively wiped against the pre-bond surfaces using a release paper without dilution, and dried at room temperature over 4 hours. The resulting contaminant deposit was around 0.9 g/m².

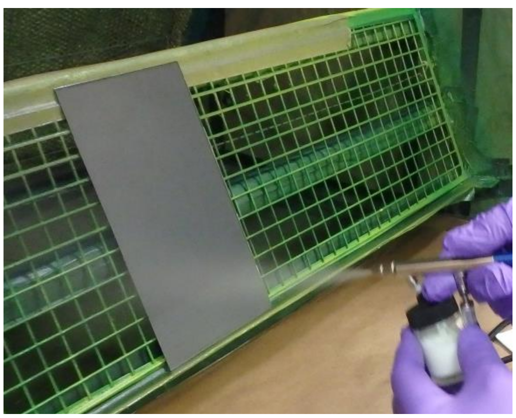


Figure 1. Contaminant sprayed with an airbrush

Surface treatments on composite pre-bond surfaces

Plasma surface treatment: Low pressure plasma treatment was applied to the contaminated pre-bond surfaces. The samples were placed inside a low pressure RF plasma chamber. A vacuum level of around 100 mTorr was established before the specific specified gas was bled in to reach a vacuum level of around 300 mTorr. The plasma source (30W) was turned on for several minutes with alternated gases of argon and air. Then the power supply of the plasma source was turned off and the plasma chamber was released brought back to atmospheric pressure.

Laser surface treatment: Laser surface treatment was applied on composite substrates using a frequency tripled Nd:YAG laser with 6 W nominal pulsed output at 355 nm and 400 kHz with 8 ps pulse duration (Ekspla, Atlantic 20 from PhotoMachining, Inc.). A thermopile sensor (model 3A) and Nova II power meter from Ophir Spirocon LLC were used to monitor the average laser power. Laser ablation produced parallel lines in the fiber direction at an average power of 80 mW, pulse frequency of 400 kHz, and a line pitch of 12.3 μm (0.0005 in), giving a small overlap between two adjacent laser passes. The scan speed was 25.4 cm/s (10 in/s) with a single-pulse fluence of 0.6 mJ/mm^2 and a total fluence of 24.8 mJ/mm^2.

Panel fabrication

Composite double cantilever beam panels, 15.2-30.5 cm by 30.5 cm (6-12 inch by 12 inch), were produced with adhesive bonded substrates in an autoclave. The adhesives were applied on the testing bondline with a 6.35 to 7.6 cm (2.5 to 3 in) long fluorinated ethylene propylene (FEP) film insert, as illustrated in Figure 2. The panels were heated at 1.7 °C/min (3° F/min) to an ultimate cure temperature under 0.275 MPa (40 psi), held for 2 hrs, and then cooled down at 1.7 °C/min (3° F/min) 3°F/min under pressure. Full vacuum was applied at the beginning and released when pressure reached 0.137 MPa (20 psi).

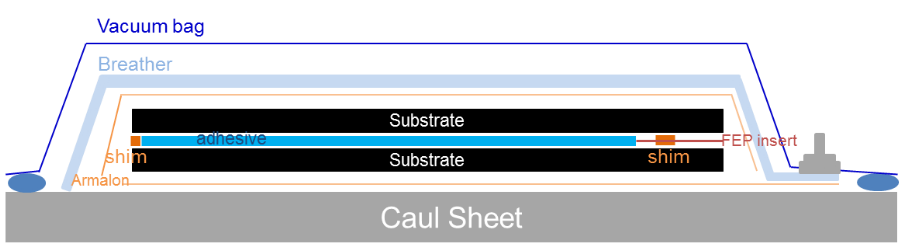


Figure2. Schematic of DCB panel fabrication

Test methods

Surface characterization: Water contact angle was measured to assess the surface tension using a goniometer (ASTM D7334). Surface chemical bond structures were investigated using an X-ray Photoelectron Spectrometer, and germanium attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FT-IR) using a germanium crystal specimen holder.

Mechanical testing: DCB panels were water jet cut into 1” wide coupons. Each coupon was pre-cracked by a 1” wide wedge. The coupon edges were painted white for the observation of crack propagation. The DCB tests were performed similar to ASTM D5528, as shown in Figure 3. Three to five coupons were measured for each panel. Fracture toughness of adhesive bond ($G_{Ic\ avg}$) was determined by equation (1) as follows.

$$G_{Ic\ avg} = \frac{E}{A * B} \quad (1)$$

where E refers to the area under the load-displacement curve, A stands for the length of crack growth, and B denotes the width of test coupon.

Figure 3. Double cantilever beam testing

RESULTS and DISCUSSION

Mold release is a major source of contamination encountered on the composite manufacturing floor. Contamination levels can span a wide range due to the differences in manufacturing conditions and process deviations. In this study, contamination determination and effectiveness of surface treatments were assessed at high and low contamination levels.

Water contact angle:

According to adsorption theory, adherend wetting is critical to adhesive bond performance. Higher surface tension exhibits lower water contact angles providing stronger adhesive bonding. In a goniometry test, water contact angles were assessed after each water drop was stabilized on a pre-bond surface. The results on different contamination levels and the effect of surface treatments are summarized in Figure 4.

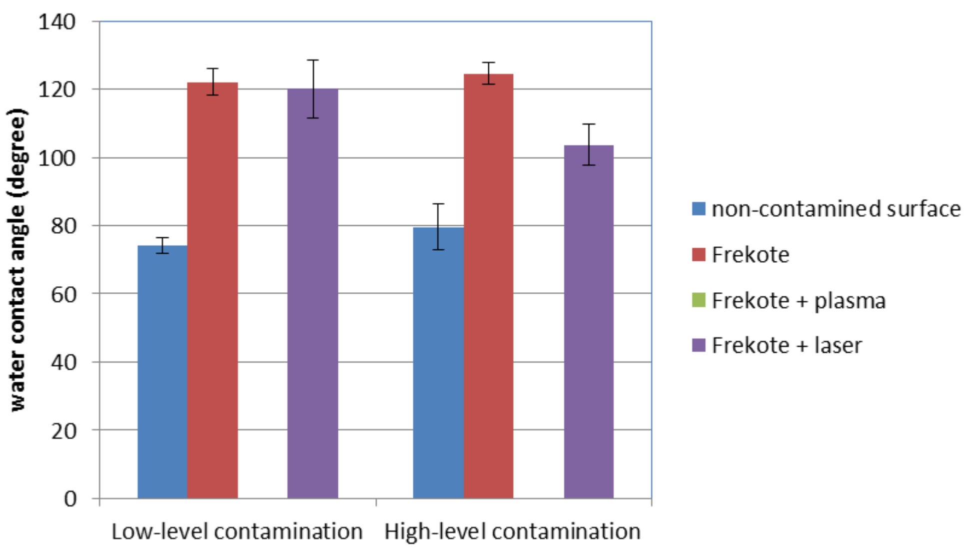


Figure 4. Water contact angle results

Surfaces contaminated with Frekote® showed much higher water contact angles than pristine surfaces due to poor wettability of low surface tension chemicals on the contaminated surfaces. Similar water contact angles were observed on the contaminated surfaces with high and low concentrations of Frekote® mold release. Plasma surface treatment displayed more significant changes in water contact angles than laser surface treatment reducing the surface tension so sharply that water contact angles became almost zero, i.e. water drops spread out quickly with no measurable water contact angles. On the contrary, laser surface treatment did not induce any dramatic changes in water contact angles. The laser ablation process creates surface topography which influenced the water contact angle whereas the plasma treatment does not.

Fourier transform infrared spectroscopy (FT-IR):

FTIR ATR analysis was performed on non-contaminated carbon fiber reinforced 8552 composite surfaces (pristine composite), low-level and high-level Frekote® 44NC contaminated composite surfaces, and contaminated composite surfaces with plasma and laser surface treatments. Three locations per each composite surface were tested to identify variations in contamination. The surfaces with low contamination levels appeared to be similar to non-contaminated surfaces. However, high-level Frekote® surfaces presented a visible oily sheen on the contaminated surfaces.

FTIR analysis was not sensitive to low contamination levels. As displayed in Figure 5, non-contaminated and low-level contaminated composite surfaces gave very similar FTIR spectra. No obvious difference in FTIR spectra was observed after plasma and laser surface treatments.

FTIR spectra detected high concentrations of silicone compounds on high-level contaminated surfaces. As shown in Figure 6, significant amount of the functional groups Si-CH_3 (absorbance peaks at 1275 cm^{-1} and 780 cm^{-1}) and Si-O (absorbance peak at 1045 cm^{-1})[13] were observed. The data showed that the silicone level was significantly decreased with either plasma or laser surface treatment, but silicon-related functionalities still existed.

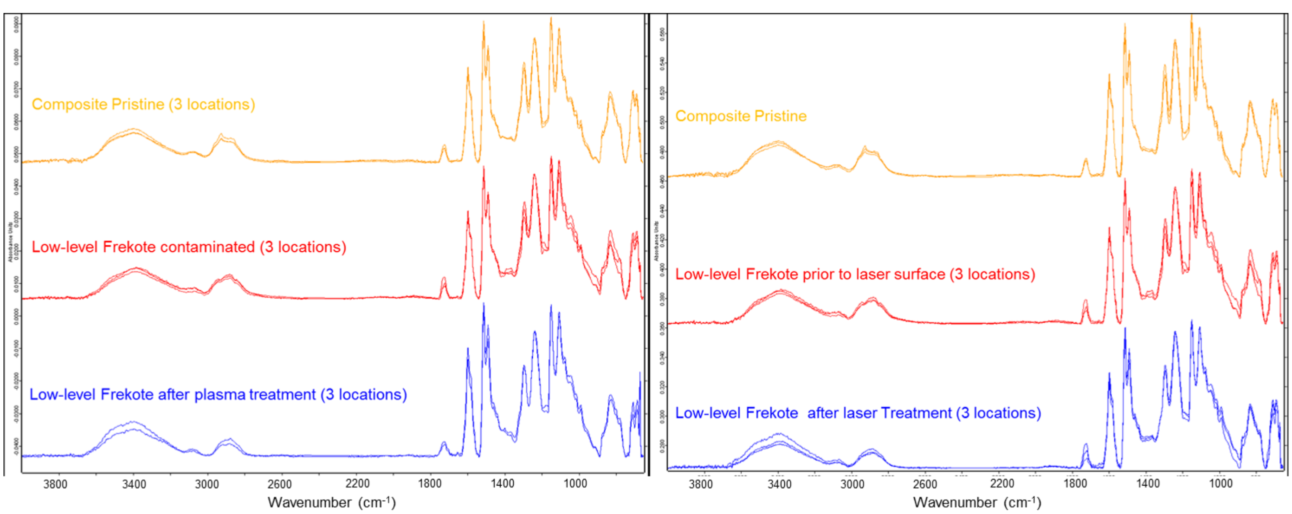


Figure 5. FTIR Spectra Comparison of composite baseline, low contamination level and surface treatments

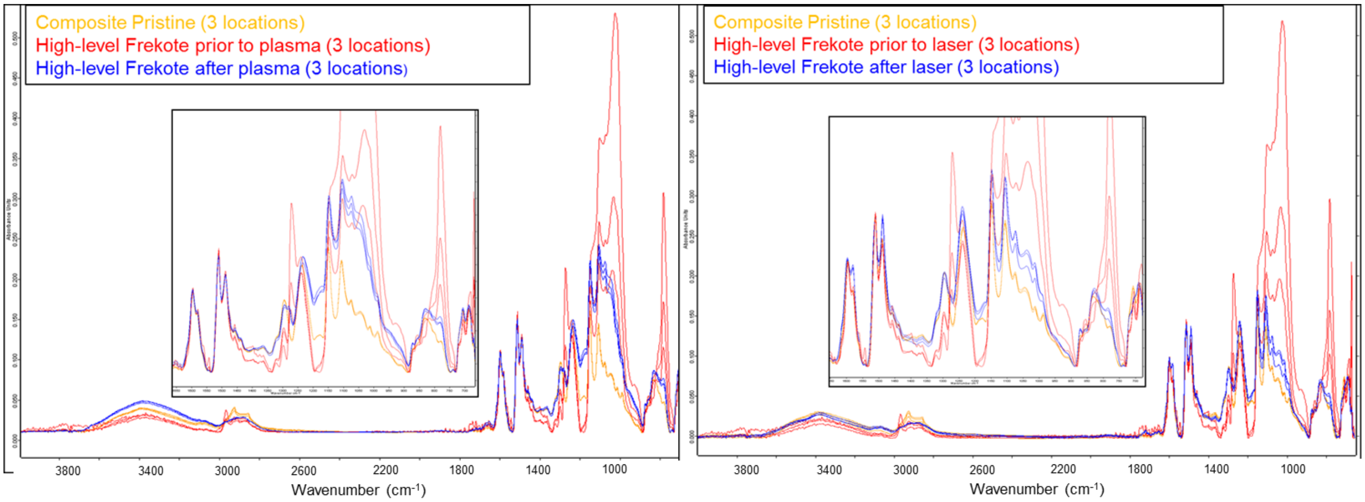


Figure 6. FTIR Spectra Comparison of composite baseline, high contamination level and surface treatments

X-ray photoelectron spectrometer (XPS):

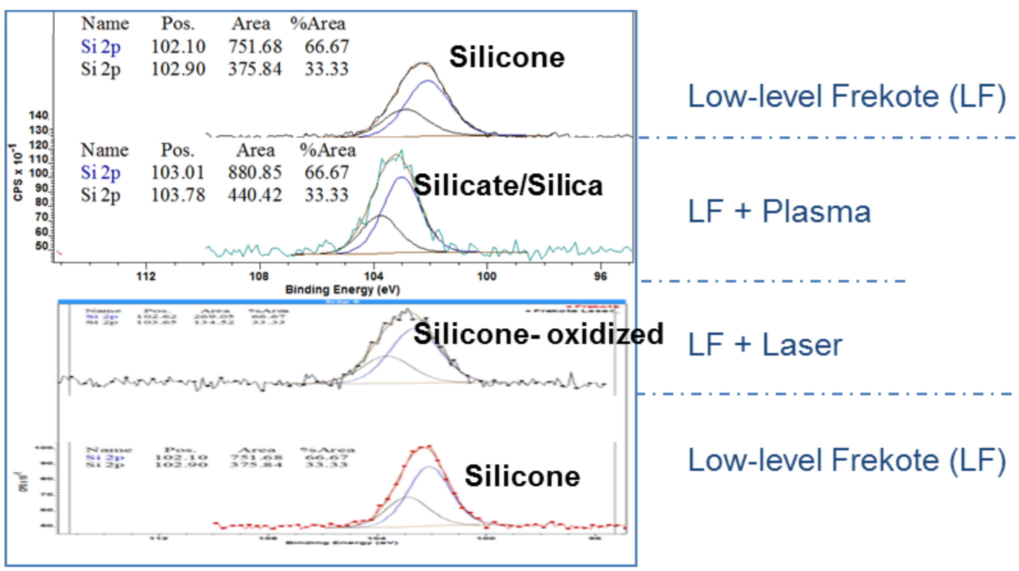
XPS is unique in its ability to provide information on the chemical state of the elements in this near surface region and is more sensitive to low concentration of surface contaminants than FTIR. This anaylitcal tool was used to reveal both the elemental concentrations and the chemical states of the elements associated with functional groups on pre-bond surfaces within a sampling depth of only 2-10 atomic layers.

Elemental results on plasma and laser surface treatments of low-level and high-level Frekote® contaminated pre-bond surfaces are summarized in Table 1. Clearly, plasma treatment promoted surface activation, and generated oxygen rich surfaces. The observation of lower water contact angles (i.e. higher surface tension) with plasma treatments was at least partially a result of the increase in such oxidized functionalities on the pre-bond surfaces. On the other hand, laser treatment acted as surface ablation, producing epoxy resin rich surfaces with more carbon and nitrogen related functionalities. The plasma treatment produced higher oxygen and silicon contents than the laser treatment independent of contamination levels. In addition, plasma treated surfaces displayed higher oxygen and silicon contents with high-level contaminated surfaces relative to low-level contaminated surfaces.

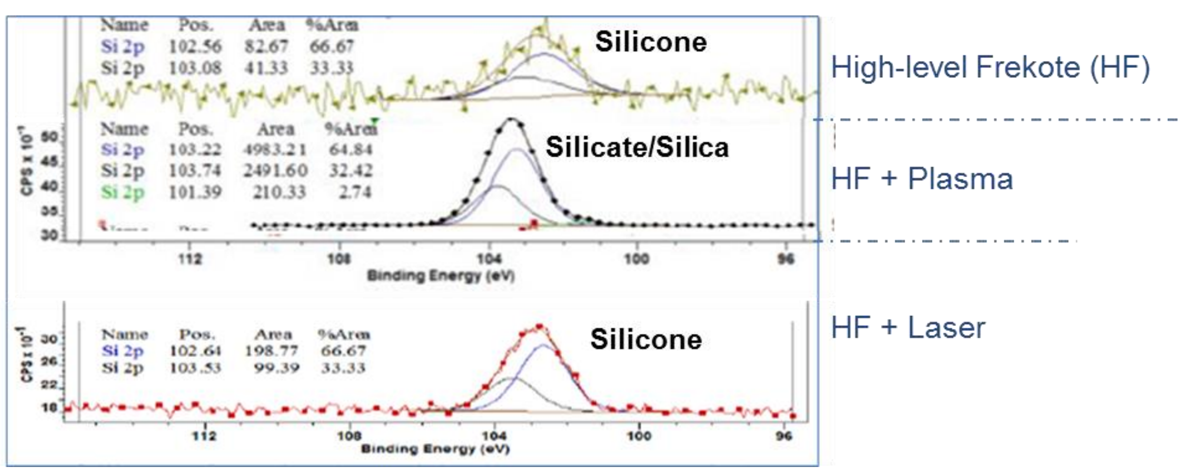
Table 1. Elemental analysis on contaminated and surface treated surfaces by XPS (atomic percentage)

	Carbon	Oxygen	Nitrogen	Silicon
Low-level Frekote (LF)				
LF + Plasma	47.7	41.6	2.6	7.4
LF + Laser	73.4	15.8	7.1	2.1
High-level Frekote (HF)				
HF + Plasma	12.9	60.9	1.6	24.3
HF + Laser	75.6	14.0	6.8	1.7

The effect of plasma and laser surface treatments on silicon functionalities are displayed in Figure 7. For both high and low Frekote® contamination levels, plasma treatment rendered a complete transformation of silicon-based contaminated surfaces from silicone functionalities to silicate & silica functionalities. The existence of silicone on pre-bond surfaces generates weak bonds due to poor bond strength between epoxy adhesive and silicone. The chemical transformation from silicone to silicate or silica would eliminate weak bond sources and recover bond performance. The effect of laser surface treatment on the Frekote® contaminated surface varied with contamination levels. For the low contamination levels, laser treatment resulted in certain reduction and oxidation of silicone functional groups. However, for the high contamination levels, significant silicone content remained after the laser surface treatment (Figure 7b). This strongly indicated that the ablation from this specific laser treatment process may not be sufficient to remove high concentrations of the contaminant. Higher laser power, multiple laser ablation processes or extended treatment time should be implemented for high contamination level pre-bond surfaces.



a. Low Frekote® contamination level



b. High Frekote® contamination level

Figure 7. Silicon functional groups associated with plasma and laser surface treatments

Double cantilever beam (DCB):
Increased fracture toughness indicates higher resistance to disbond or disbond propagation. The effect of plasma and laser surface treatments on Mode I fracture toughness is summarized in Figure 8. Plasma surface treatment was particularly effective in enhancing bond performance for both high and low contamination levels with Frekote®. Laser surface treatment also exhibited the capability to restore bond performance at low contamination levels. However, low fracture toughness values were measured with laser surface treatment on high-level contaminated surfaces, suggesting that some residual Frekote® contaminant remained on the pre-bond surfaces. In addition, plasma treatment produced even higher fracture toughness than laser treatment with both high and low contamination levels. DCB results were well aligned with the surface characterization results from XPS. Plasma surface treatment activated the contaminated surfaces by completely transforming silicone contaminants to silicate/silica. Whereas laser surface treatment mainly removed surface contaminants by ablation, and induced some oxidation on silicone at the low contamination level. Prior work has shown that higher concentrations of silicone contaminants are removed using higher laser power than that used in this study[14].

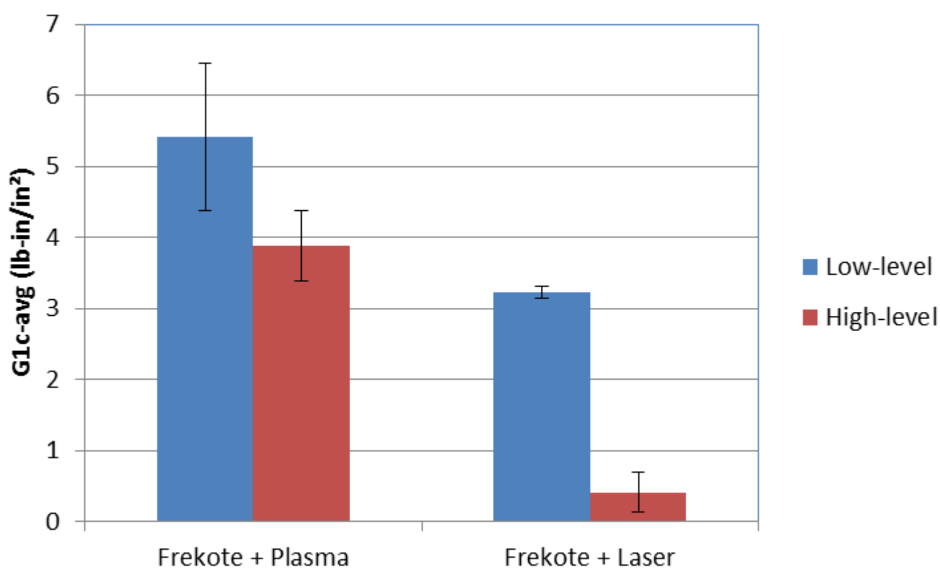


Figure 8. Effect of plasma and laser surface treatments on Mode I fracture toughness

Weak bonds from the insufficient removal of contaminant displayed predominantly adhesive failure between the contaminated composite surface and the adhesive material. Strong bonds from the plasma at high & low contamination levels, and laser surface treatment on low contamination levels, showed mixed mode failures including cohesive failure within adhesive material plus ply delamination of composite laminates, with no disbonds on the contaminated surfaces. The roughness induced by laser ablation can cause fiber tear failure modes to occur leading to a lower G_{1c}, since it is a mixture of the fracture toughness of both the matrix resin and the adhesive.

CONCLUSIONS

Plasma and laser surface treatments demonstrated capabilities to remove silicone-containing mold release residues and enhance adhesive bond performance. Plasma surface treatment was presented as an effective method of promoting bond performance in the presence of both high and low contamination levels. This approach offered significant improvement in Mode I fracture toughness while shifting the failure modes from adhesive failure to cohesive failure. Laser surface treatment promoted strong bond performance in the presence of low contamination levels, but did not provide sufficient ablation at high contamination levels to rebuild bond performance. Higher laser ablation power has been shown to address this issue. Surface characterization methods utilized in this study exhibited different capabilities in contaminant detection as a function of contamination levels. High water contact angles were observed on the surfaces with both high and low contamination levels. Water contact angles were dramatically reduced with plasma surface treatment but showed no significant change with laser surface treatment. The FTIR technique detected the contaminants at high contamination levels only, and showed less success at low contamination levels. XPS was able to detect surface contaminants at both high and low contamination levels. The plasma surface treatment chemically converted contaminant functionalities from organic silicones to inorganic silicates or silica forms at high and low contamination levels. The laser surface treatment conditions used in this study produced oxidation of silicone at low contamination level, but did not completely eliminate silicone at high contamination levels.

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