Effect of Processing Parameter Changes on the Adhesion of Plasma-treated Carbon Fiber Reinforced Epoxy Composites

R. J. ZALDIVAR,* H. I. KIM, G. L. STECKEL AND J. P. NOKES
The Aerospace Corporation, Physical Sciences Laboratory, Materials Science Department, 2350 E. El Segundo Blvd, El Segundo, CA, 90245

B. A. MORGAN
The Aerospace Corporation, MILSATCOM, System Effectiveness, 2350 E. El Segundo Blvd, El Segundo, CA, 90245

ABSTRACT: Atmospheric plasma treatment for the surface preparation of adhesively bonded composite joints appears promising as a replacement to current surface preparation techniques. However, questions remain regarding the sensitivity and optimization of various plasma processing parameters on final composite bond properties. In this study, we continue to investigate how plasma surface treatment processing variables ultimately affect the surface chemistry and bonding behavior of a graphite–epoxy composite. The plasma power level, the working distance of the plasma head, the carrier gas (helium) flow rate, the duration of plasma exposure, and the active gas (oxygen) concentration within the plasma were varied and correlated to surface chemistry variations using X-ray photoelectron spectroscopy (XPS). The carboxyl concentration on the surface was then measured as a function of these changes and correlated to lap shear strengths. In addition, samples were monitored using XPS to evaluate the decay behavior of the surface treatment as a function of time. Treated specimens in both inert and air environments exhibited similar decay profiles. Large changes were not observed until after 24 days of out-time. The effects of plasma treatment, duration of plasma exposure, and out-time on the crack delamination resistance ($G_{IC}$) of bonded parts were assessed. $G_{IC}$ measurement indicated that solvent wiped bonded specimens exhibited a purely adhesive failure with unstable crack growth. Specimens with abrasion treatment exhibited reduced performance with cracks initiated in the adhesive traveling through both the adhesive–composite interface as well as the outer surface plies of the composite substrate. We believe damage to the composite substrate due to surface preparation caused this failure mode. On the other hand, plasma-treated specimens exhibited consistent failure modes for all treatments above 12 passes. The failures were entirely cohesive with the very high bond strength promoting crack propagation only within the adhesive. The $G_{IC}$ values indicated that the plasma-treated composites were two times as resistant to fracture as conventionally prepared specimens.

*Author to whom correspondence should be addressed. E-mail: rafael.j.zaldivar@aero.org
Figures 1, 13 and 14 appear in color online: http://jcm.sagepub.com


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INTRODUCTION

PLASMA TREATMENT AS a means of surface preparation for the bonding of composite hardware is being studied to address many of the consistency and reliability concerns related to current widely used processes [1,2]. Plasma treatment has proven to be an effective approach for the treatment of polymers; however, there are a number of drawbacks. The primary drawback is the need to operate at reduced pressures, thus requiring vacuum chambers that limit the size and shape of the objects to be treated [3]. The recent availability of a plasma source that operates at atmospheric pressure and relatively low temperatures has made it an ideal alternative to vacuum plasmas [4]. The atmospheric plasma treatment process is noncontacting, requires minimal operator intervention, and can be applied to complex shapes, while significantly reducing the risk of physical damage to the composite [5]. This atmospheric plasma process utilizes a capacitive discharge at atmospheric pressure to produce a uniform high-density mix of ions, electrons, and free radicals. These reactive species are then directed onto a surface where the desired chemistry occurs. Figure 1 shows a schematic of the atmospheric plasma unit, a linear translation stage, and a sample, as typically configured in our laboratory. The translation stage is programmable and used to make highly reproducible plasma exposures.

In our previous paper [6], we investigated the plasma surface treatment of graphite/epoxy composites bonded with an epoxy adhesive. In that paper, all of the plasma conditions were maintained constant except the treatment duration. X-ray photoelectron spectroscopy (XPS) data showed that as the duration of the plasma treatment was increased the carboxyl content on the composite surface also increased. The resultant adhesive shear strength of the bonded composite also exhibited a similar increase with increased exposure time, as shown in Figure 2. Changes in surface morphology or surface wetting alone could not account for the observed improvements in mechanical behavior. Others [7] have shown similar increases and have also attributed the improvement to the specific chemical species formed on the surface of the resin prior to bonding.

Figure 1. Schematic showing the test set-up for the surface preparation of composites using the SurFx atmospheric plasma treatment unit.
However, many questions remain unanswered with regards to this relatively new process. In this article, we investigate the role of various plasma processing parameters on the formation of carboxyl groups on the surface, a chemical species identified in our previous paper as an adhesion promoter. Parameters such as the duration of plasma treatment, the plasma probe distance to the substrate, the power, the helium flow rate, and oxygen content are correlated with the chemistry changes on the composite surface and with adhesive strength to assess how these processing variables relate to mechanical performance. Additionally, the aging characteristics of the plasma-treated samples were investigated. Crack delamination resistance tests of bonded plasma-treated composites are reported, which continues the assessment of composite bond durability begun in our previous paper. The comparison is made in all cases to current, widely used, surface preparation techniques: solvent wipe and abrasion.

**EXPERIMENTAL**

**Materials**

The composite materials investigated in this study were manufactured using Nelcote E765 epoxy with AS4 PAN-based carbon fibers. The laminates were laid up using 0.0127 cm. thick unidirectional prepreg tape and were stacked in a unidirectional orientation. Eight prepreg plies were used for each cured composite. The laminates were processed using an autoclave and were cured to 121°C under a pressure of 0.69 MPa (100 psi) and then subsequently post-cured in an oven at 177°C for 2 h.
Plasma Treatment

All of the composites investigated in this study were treated using a Surfx Technologies AtomFlo-250 atmospheric plasma unit. The plasma is composed of a mixture of helium and oxygen gases with 99.99% purity. The plasma conditions for the control samples were fixed at 96 W of radio frequency (13.56 MHz) power, 0.450 L/min of oxygen as the active gas, 1.0 mm working distance, and 15 L/min of helium as the carrier gas. The control conditions were chosen to allow flexibility in adjusting the processing variable conditions while always maintaining a plasma afterglow. The plasma head (Surfx PS02129) has a 25 mm linear beam. The bond area of each sample was wiped with acetone and rinsed with isopropanol prior to plasma treatment. During plasma treatment, the samples were placed on a stationary stage and a robotic arm holding the plasma head was scanned at a constant rate across the specimen face. LABVIEW was used to control the robotic arm and a scan rate of 25.4 mm/s was used for all specimen treatments. Samples were typically evaluated within 2 h of treatment unless otherwise stated. The plasma exposure is defined in terms of the number of passes by the plasma head over the test surface. According to Gonzalez et al. [8] the effective beam width of the plasma head used in this investigation is 21.0 mm. Using the analysis described in their paper, the exposure time of the sample in the plasma equals the beam width divided by the scan rate (25.4 mm/s) times the number of scans: 

\[ t = 0.84 \text{s(number of scans)} \]

One scan is defined as one complete travel across the pre-bonded composite surface in one direction. Sixteen passes were chosen because our previous worked showed that there was a large increase in mechanical performance after this range of treatment without any significant microstructural changes of the surface. The variations on the control parameters designed to assess process sensitivity and robustness are shown in Table 1.

X-ray Photoelectron Spectroscopy

An XPS system manufactured by SSI using Al K\(_\alpha\) source was used for surface chemical analysis as a function of plasma treatment of the composite samples. Analyzer pass energies of 150 and 50 eV were used for wide scans and high-resolution spectra respectively. The XPS analysis chamber was pumped by an ion pump and had a base pressure of \(1 \times 10^{-10}\) Torr.

Table 1. Plasma treatment variables that were modified during processing of composites (16 passes = 13.4 s).

<table>
<thead>
<tr>
<th>Distance (mm)</th>
<th>He flow (Lpm)</th>
<th>Oxygen flow (Lpm)</th>
<th>Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.4</td>
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<tr>
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<td>15.0</td>
<td>0.4</td>
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<td>15.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Distance 3</td>
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<td>15.0</td>
<td>0.4</td>
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<td>0.4</td>
</tr>
<tr>
<td>Helium 2</td>
<td>1.0</td>
<td>25.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Oxygen 1</td>
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<td>0.3</td>
</tr>
<tr>
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<td>15.0</td>
<td>0.65</td>
</tr>
<tr>
<td>Power 1</td>
<td>1.0</td>
<td>15.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Power 2</td>
<td>1.0</td>
<td>15.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Mechanical testing

LAP SHEAR STRENGTH TESTING

All composites tested in this investigation were 177°C cured specimens. Glass-epoxy doublers were bonded to one side of the 15 cm × 15 cm laminates. The bond area was wiped with isopropanol prior to plasma treatment and bonding. The preparation of multiple single lap joint assemblies was followed according to ASTM D-3165 [9]. Henkel EA9394 epoxy paste resin was used for all bonding. A bond line gap of 0.13 mm was maintained for all specimens using bond line wire. A standard overlap length of 15.2 mm was used. The adhesive was allowed to cure at room for a minimum of 24 hours and then post-cured at 80°C for 2 h. The 15 cm × 15 cm laminates were then cut into 2.54 cm wide specimens and subsequently tested. An Instron with a 44 kN load cell was used for all lap shear tests. A crosshead speed of 2.5 mm/min was used for all testing.

FRACTURE TOUGHNESS TESTING

Mode I, crack opening, interlaminar fracture toughness was measured by the double cantilever beam technique following test procedures specified in ASTM D 5528 [10]. With this technique, a unidirectional composite having a built-in delamination is loaded across the delamination in tension, as shown in Figure 3. The interlaminar fracture toughness is given by the strain energy release rate, $G$, which is defined as follows:

$$G = [-1/b]dU/da,$$

where $U$ is the total elastic strain energy in the sample, $b$ is the sample width, and $a$ is the delamination length.

For this investigation, samples were prepared by bonding two 8-ply laminates together using Hysol EA9394 adhesive with a bond line gap of 0.13 mm. A PTFE insert 63 mm long was placed at one end of the 127 mm long assembly to form the built-in delamination. The 25 mm wide samples were pin-loaded through the loading tubes, as shown in Figure 3.

![Figure 3. Schematic drawing of double cantilever beam for determination of mode 1 fracture.](image)
using an Instron Universal Testing Machine having a 220 N load cell. The samples were loaded at an initial crosshead speed of 0.51 mm/min. The edge of the samples was polished and painted with liquid paper to enable measurement of delamination growth during testing with the aid of stereo microscope instrumented with a digital camera. As the test proceeded, the crosshead speed was increased to 1.3 mm/min for \( \Delta a > 10 \text{mm} \). The modified beam theory, as described in ASTM D 5528, was used to calculate the strain energy release rate. The modified beam theory expression for the strain energy release rate of a double cantilever beam is:

\[
G_{IC} = \frac{3P\delta}{2b(a + |\Delta|)},
\]

where \( P \) is the load, \( \delta \) is the load point displacement, \( b \) is the sample width, \( a \) is the delamination length, and \( \Delta \) is a correction factor, which is defined in ASTM D 5528.

## RESULTS AND DISCUSSION

### Effect of Processing Variables on Carboxyl Species Formation and Adhesive Strength

Table 1 shows the plasma treatment variables modified in this investigation. The first line shows the control settings for our baseline tests. The following lines show changes in working distance, helium flow rate, oxygen flow rate, and power. Observable plasma afterglow was maintained during sample treatment for each of the 10 sets of process parameters. As shown in Figure 2, our previous investigation indicated that after approximately 16 passes a maximum degree of change would be observed. Additional treatment did show an increase with passes; however, the rate of improvement was diminished with continued treatment. In addition, our investigations show that treatment limited to this extent of duration shows no evidence of microstructural changes on the composite surface [6].

Figure 4 shows typical high resolution C 1s XPS spectra of our composite surface after treatment. A detailed analysis of the XPS spectra of the C 1s region allows a determination of the functional groups present on the surface after plasma treatment. The singular peak at 285.0 eV has been identified as characteristic of the hydrocarbon peak \((-\text{C}_x\text{H}_y\text{z})\) [11]. Subsequent plasma treatments of the surface create new peaks at the shoulder of the original hydrocarbon peak related to binding energies for each new functional group created. In the spectrum shown there are additional peaks at 286.2, 288.2, and 289.2 eV. The peak at 286.2 eV has been attributed to alkoxy groups \((-\text{C}=\text{O})\); the peak at 288.2 eV to carbonyl groups \((-\text{C}=\text{O})\); and the peak at 289.2 eV is representative of carboxyl groups \((-\text{C}=\text{O})\). The carboxyl peak shows best correlation to increases in bonding strength as shown and modeled in our previous paper, and in Figure 2. The formation of the other species using both O 1s and C 1s XPS spectra with treatment resulted in no trends or additional pertinent information with regards to adhesive bond strength. Therefore, the plasma test parameters investigated in this study were correlated against carboxyl concentration as well as adhesive bond strength.

Figure 5 shows the effect of distance from the plasma source on carboxyl concentration. We evaluated working distances from 0.5 to 5.0 mm and found a direct correlation between distance and the carboxyl concentration formed on the surface of the treated part. As distance increases, the concentration of carboxyl species is reduced, corresponding
Figure 4. High resolution XPS analysis of functional groups on composite surface after plasma treatment.

Figure 5. The effect of the plasma probe-to-specimen distance on the carboxyl concentration and adhesive strength of the treated composite.
with a decrease in the plasma intensity on the surface of the composite. Jeong and coworkers have characterized the ionic state and constituent concentrations in the afterglow of this type of atmospheric plasma [12]. The reactive species identified consisted of oxygen atoms, metastable oxygen molecules, and ozone. They have shown that the concentration of oxygen atoms remains constant out to 1 mm from the probe, and then drops by a factor of 3 from 1 and 10 mm. As the distance increases beyond 1 mm, the oxygen atoms react with oxygen molecules to form ozone whose concentration increases up to 80 mm from the probe. In a separate investigation, Jeong et al. [13] confirmed that the etching rate observed for polyimide films declined rapidly from the leading edge adjacent the plasma to essentially zero at 20 mm distance. It was shown that the decay profile for oxygen atoms generated from the plasma corresponded well with this etching rate. Their results showed that the oxygen atoms are the active species and therefore in order to maximize treatment of organic materials the distance from the probe must be minimized to prevent the oxygen atoms from recombining with other molecules. The carboxyl concentration at the composite surface follows a similar trend with distance, as shown in Figure 5; therefore, one would prefer to plasma treat specimens as close as practical to the plasma head to maximize the activation of surface sites. Figure 5 shows the effect of this treatment on the composite lap shear strength. As expected, a direct correlation can be observed with regards to the carboxyl concentration formed on the surface of the material and the increase in strength for the given condition. However, ultimately for the duration of plasma treatment time, the volume or concentration of oxygen atoms would be expected to dictate the maximum carboxyl concentration for a given distance.

The effect of plasma power on carboxyl content and bond strength was also investigated. As shown in Figure 6, there does not appear to be a strong correlation between

![Figure 6](image)

**Figure 6.** The effect of the power on the carboxyl concentration and adhesive strength of the treated composite.
these variables. In order to form the plasma, a critical breakdown voltage must be overcome for the specific gas being used. The breakdown voltage for helium at atmospheric pressure has been described by Moravej et al. [14]. All of our test conditions utilized enough power to generate a plasma. Therefore, increasing the power did not appear to generate any additional benefits with regards to an increase in the surface carboxyl concentration of our substrate. There was also no significant trend in lap shear strength over the range of power tested, as shown in Figure 6. Jeong et al. [12] have studied the effect of RF power on the concentration of atoms generated from this type of plasma. Their results suggest that the concentration of all of the oxygen species, except ozone, increase in concentration with power. The temperature of the plasma also increases with power. However, over the range of power conditions tested in our laboratory any increase in oxygen concentration may not have been sufficient to translate into chemical changes on the surface of our composite samples.

The effect of oxygen flow rate on the carboxyl content concentration is shown in Figure 7. As the oxygen flow rate is increased, the carboxyl concentration on the surface of the composite was shown to increase. This increase in carboxyl content corresponds with an increase in shear strength as also shown in Figure 7. However, the change from 0.3 to 0.4 L/min. only accounts for a change of approximately 2–2.5 vol.% oxygen, a seemingly small change for the strong trend that we have measured. Recently, Gonzalez et al. [8] have assessed the importance of the reactive oxygen species in a helium–oxygen atmospheric plasma. They showed that the oxygen species generated in the plasma greatly accelerated the surface reaction rate. The addition of 0.5 L/min of oxygen to a helium plasma that normally relied on the oxygen present in the atmosphere increased the rate

![Figure 7. The effect of the oxygen flow rate on the carboxyl concentration and adhesive strength of the treated composites.](image-url)
constants for surface activation by thirteen times. Since oxygen atoms are the chemically active species for the plasma treatment process it would tend to follow that an increase in the oxygen flow rate would increase the degree of oxidized groups on the surface of the composite as was observed. However, power and oxygen flow rates are not entirely independent from one another when generating an oxygen–helium plasma. Higher input powers are required to sustain the oxygen and helium discharge [15] at higher oxygen levels. It appears that the addition of oxygen reduces the electron density which is most likely due to the fact that oxygen is an electronegative species so it consumes electrons and lowers their concentration. Therefore, even though the oxygen concentration increases resulting in improvements in strength, the efficiency of the plasma may be somewhat reduced since we are maintaining the power constant. By adjusting both variables with respect to each other the efficiency could be increased and further improvements may be achieved.

Figure 8 shows the effect of helium flow rate on the surface carboxyl concentration of the treated composite. Oxygen flow rate is held constant during this process. In Figure 8, the carboxyl concentration increases from 11.5% to 17% as the helium flow rate decreases from 25 to 6 L/min. The adhesive strength again shows good correlation with the changes in the surface carboxyl concentration. We believe the increase in surface carboxyl content with reduced helium flow rate is a result of the greater relative oxygen concentration within the plasma. The helium flow rate range tested translates into a change in concentration from 1.5 to over 6.0 vol.% oxygen. Reducing the helium flow rate therefore increases the concentration of oxygen reaching the surface of the composite and results in a more activated surface. Both, reducing the helium flow rate and increasing the oxygen
flow have similar effects. Figure 9 shows a plot of oxygen volume in the plasma using both sets of data from Figures 7 and 8. As observed, as the volume of oxygen within the plasma increases, the carboxyl concentration and adhesive strength also increase. However, non-linearity can be observed at higher oxygen volumes, most likely due to decreases in plasma efficiency which can be attributed to the power variable.

### Aging Characteristics of Plasma-treated Composites

A number of studies have focused on the aging characteristics of plasma-treated surfaces prior to bonding [16,17]. Understanding the stability of a plasma-treated polymer composite is one aspect critical for the implementation of this surface preparation technique. Depending on the polymer, a surface can revert from a ‘wettable’ state to a more hydrophobic condition with time. Numerous researchers have observed that modified surfaces are susceptible to aging effects when exposed to air [18]. This process of aging has been postulated to be due to a combination of effects: (a) a reaction of the surface with atmospheric constituents such as water vapor and oxygen, (b) a reorientation of polar moieties away from the surface into the bulk of the material, or (c) an increase in organic contamination above the treated substrate with exposure time. However, in general, these arguments in the literature are speculative, thus it is difficult to assess their relative impacts and to develop practical mitigations. From our studies, we would like to better understand how specific changes in the surface chemistry occur as a function of extended out-time, initial dosage, and aging environment and what effect, if any, aging has on interfacial bonding and subsequent mechanical performance.
Table 2 shows the elemental composition spectra for our composite system as a function of out-time using our standard process parameters. The specimen was aged either in ultra-high vacuum (1 × 10⁻¹⁰ Torr) or in an ambient laboratory environment after plasma treatment. Figure 10 shows a plot of the O/C ratio for both samples. As shown, initial changes are relatively rapid over the first 5 days but then appear to stabilize with time.

Table 2. Elemental composition from XPS survey spectra.

<table>
<thead>
<tr>
<th>Aging environment</th>
<th>Out-time exposure period (days)</th>
<th>1</th>
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<th>3</th>
<th>10</th>
<th>18</th>
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Figure 10. Relative oxygen-to-carbon ratio on surface of composite specimens as a function of aging in vacuum and air environment.

Table 2 shows the elemental composition spectra for our composite system as a function of out-time using our standard process parameters. The specimen was aged either in ultra-high vacuum (1 × 10⁻¹⁰ Torr) or in an ambient laboratory environment after plasma treatment. Figure 10 shows a plot of the O/C ratio for both samples. As shown, initial changes are relatively rapid over the first 5 days but then appear to stabilize with time. The specimen that
is aging in vacuum decays at an initially slower rate than the specimen aging in air. However, after 24 days the rate of decrease has stabilized and the O/C ratio is approximately at the same level for both samples. Since the adhesive strength has been shown to best correlate with the amount of carboxyl groups on the surface, the carboxyl group concentration for both specimens was plotted as a function of out-time. As shown in Figure 11, the largest changes also occur within the first 5 days and then appear to stabilize with time. The overall decay profiles are similar for both conditions, with a slightly higher concentration for the vacuum aged specimen. After 24 days, the carboxyl concentration for both samples has decreased by approximately 50% from that of the initial values.

If the aging or the decrease of the carboxyl concentration is due to a reaction with atmospheric constituents such as water vapor or oxygen, one would expect to see a corresponding increase in the oxygen concentration on the surface. However, our data suggest the opposite trend. Furthermore, thin films containing carboxyl groups have been reported to be stable in air [19,20] and, therefore, we believe the carboxyl groups on our plasma-treated polymer composites should also be relatively stable. Some discussions in the literature speculate that changes due to aging are caused by reorientation of polar moieties away from the surface and into the bulk of the material. If surface reorganization is responsible for the apparent loss of surface carboxyl concentration, we would expect it to be sensitive to the environment. For example, polar moieties such as carboxyl groups would point outward to form hydrogen bonds with water or oxygen molecules in air. However, in ultra-high vacuum, there should be significantly less driving force for such changes.

![Figure 11](https://via.placeholder.com/150)

**Figure 11.** Decay of carboxyl concentration on composite surface as a function of time in different storage environments.
reorientation due to lower partial pressure of these polar molecules. Yet the relative change of the carboxyl concentration between the two environments was not significantly disparate over the time frame of the experiments.

Surface contamination due to the accumulation of adventitious hydrocarbon is a well-known phenomenon. A recent study by Strein and Allred [21] described the growth of an organic contamination layer on a silicon surface. The growth increased for up to a week after which the growth stabilized. An increase in organic contaminants on the surface would appear as a relative decrease in oxygen concentration as a function of time, consistent with our data shown in Figure 10. Our data also suggests that the rate of growth for the contamination layer is significantly slower in vacuum due to the lower amount of low molecular weight organic compounds in an ultrahigh vacuum. The formation of the contaminant layer appears self-limiting; once a complete monolayer is formed, the surface energy stabilizes and therefore no longer promotes the growth of the layer regardless of the environment. This mechanism is again in line with the observed behavior. The thickness of the typical organic contaminant layer on surfaces is estimated to be about 0.6–0.7 nm [19,21].

A critical issue pertaining to this study is determining whether this contamination layer has any adverse effect on bonding. It has been reported that physisorbed organic contaminants can be readily displaced in the presence of molecules or films that have greater chemical interaction with the surface. This fact has been used to form self-assembled monolayers on surfaces prepared in out-of-vacuum conditions [22,23]. In our test, the adhesive strengths after 24 days of out-time exhibited a negligible drop as shown in Table 3, and this is consistent with our belief that the plasma-generated carboxyl groups are actually masked by a layer of contaminants on the surface when exposed to air. During bonding the loose layer of organic material is displaced or dissolved by the adhesive and the true carboxyl concentration is left to contribute to the adhesive strength of the bond.

**Fracture Toughness of Plasma-treated Composites**

In addition to evaluating the ultimate adhesive bond strength for a given surface treatment, the durability of the bonded interface must also be assessed. Understanding how a surface treatment improves the resistance of a treated interface to crack growth is integral in improving reliability of bonded joints. Figure 12 shows examples of load–displacement curves for an abrasion surface treated composite and a plasma-treated composite both

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**Table 3. Fracture toughness and lap shear strength for various surface treatments.**

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Surface treatment</th>
<th>Strain energy release rate (J/m²)</th>
<th>Lap shear strength (MPa)</th>
<th>Failure mode</th>
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<tr>
<td>0A</td>
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bonded with EA9394 epoxy. The fracture toughness values measured for each surface treatment are shown. The amount of load necessary to initiate and maintain crack growth in the plasma-treated specimen is considerably higher for an equivalent degree of crack growth in the abrasion-treated specimen. Table 3 summarizes the effect of various treatment conditions on the delaminations resistance of the bonded composite.

As shown in Table 3, the abrasion treatment resulted in a fracture toughness value of 263 J/m² in comparison to 280 J/m² for the untreated solvent-wiped condition. However, since the coefficient of variation for these test results is approximately 12% they may not be statistically different. Plasma treatment on the other hand shows nearly a two-fold increase, at higher extremes of plasma treatment. These data make the case that plasma treatment not only provides an improvement in static strength but also provides a mechanism by which the durability of the bonded surface is greatly enhanced. In order to better understand this delamination resistance behavior, the fracture surfaces of the failed test specimens were analyzed. Figure 13 shows the fracture surfaces of a solvent wiped, abrasion-treated, and plasma-treated composite laminate. The composite that was only solvent-wiped shows the gray bonding adhesive on one side of the laminate while the opposing face shows only the laminate. This failure mode is a purely adhesive failure. In other words, once the crack is loaded sufficiently, it travels to the weakest interface, which in this case is the composite to adhesive interface. This explains the fairly low fracture toughness value for the control condition. The fracture surface of the abrasion-treated sample provides some insight into the reduction in strength and toughness relative to the untreated, solvent-wiped condition. For the abrasion condition, the crack propagates along the adhesive–composite interface, but also travels within the first ply of the composite laminate. Normally, the composite laminate has higher strength and toughness than the adhesive–composite interface; otherwise the untreated, solvent-wiped sample would fail within the laminate. Our results imply that the abrasion treatment damaged the first ply of the composite laminate. Mechanical abrasion is a widely used treatment for the removal of unwanted contamination and is thought to promote mechanical interlocking. However, some composites may be more prone to damage than others. Generally, all composites are treated equally when performing abrasion type treatments so the possibility of damage to sensitive laminates is highly likely. Factors such as the fiber volume, the type and modulus of the fiber used on the outer laminate, as well as primary lay-up of the part may all affect laminate damage susceptibility.
The third fracture surface in Figure 13 shows an example of a plasma-treated composite. In this case, one can observe the bonding adhesive on both sides of the fracture, which is indicative of a purely cohesive failure. Furthermore, there is no evidence of failure within the laminate indicating that plasma treatment did not induce sub-surface damage. The improved bonding at the interface due to plasma treatment forces the crack to remain within the adhesive rather than traveling through the adhesive-to-laminate interface. Figure 14 shows a schematic representing the failure mechanism for each of the surface treatments.
preparations applied to the laminates prior to bonding. All of the plasma treatment specimens failed cohesively within the bonding adhesive. As shown in Table 3, increased duration or number of plasma treatment passes provides an improvement in the fracture toughness behavior of the bonded composite. Table 3 also shows the \( G_{IC} \) value for a specimen that was treated, and then aged for 25 days in atmosphere prior to bonding. As previously shown in Figure 11, the carboxyl concentration drops as a function of out-time and stabilizes after 24 days as did our adhesive strength specimens. The delamination resistance of the aged composite appears to drop by less than 10% and retains most of the cohesive type failure mode of the unaged plasma-treated specimen. This behavior demonstrates the excellent out-time stability of the surface.

CONCLUSIONS

(1) The plasma process variables investigated in this study resulted in changes to the surface chemistry of the treated composites. These changes, notably carboxyl content, correlated well with adhesive bond strength.

(2) The working distance from the probe to the treated substrate should be minimized to optimize the availability of oxygen atoms reaching the surface prior to recombination. A reduction in distance increased the carboxyl content concentration and resulted in increases in bond strength.

(3) An increase in oxygen concentration in the plasma occurring through either a reduction in helium flow rate or an increase in oxygen concentration resulted in an increase in carboxyl content and resulting adhesive strength. However, the result appears to saturate at higher concentration of oxygen and is believed to be a result of decreases in plasma efficiency.

(4) The range of power investigated in this study did not appear to affect surface chemistry of the substrate. No corresponding changes were observed in mechanical performance.

(5) Aging of plasma-treated samples showed a corresponding decrease in oxygen content as a function of time. The specimens in vacuum decayed initially at a slower rate than those in air. The decrease in oxygen content is a result of an increase in organic contaminants during storage. The C/O ratio appeared to stabilize after 24 days.

(6) The adhesive strengths after 24 days of out-time exhibited a negligible drop over freshly treated specimens exhibiting excellent stability. This is in line with the belief that the concentration of carboxyl groups does not significantly decrease but is actually masked by a layer of contaminants on the surface. During bonding the loose layer of organic material is displaced by the adhesive and the true carboxyl concentration is left to contribute to the adhesive strength.

(7) The crack delamination resistance of plasma-treated composites was significantly improved compared to that of composites bonded using conventional surface preparation techniques. An increase in \( G_{IC} \) values from 280 to 525 J/m\(^2\) was achieved. The plasma-treated specimens exhibited a cohesive failure while the other treatments were adhesive in nature. Abrasion techniques also exhibited first ply damage for the composite investigated in this study.

(8) Aging of the treated specimen also exhibited a minimal loss in fracture toughness after 24 days of out-time, consistent with static adhesive bond strength tests. This behavior exhibits the excellent out-time stability of the surface even after close to 1 month of exposure at room temperature conditions.
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REFERENCES


