IMPROVING ADHESIVE BONDING THROUGH SURFACE CHARACTERIZATION: REVERSE THE CURSE OF THE NYLON PEEL PLY?

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ABSTRACT

The purpose of this research was to determine the effect of atmospheric pressure plasma treatment on Mode I strain energy release rate (G_{IC}) and failure mode of bonded peel ply prepared carbon fiber reinforced polymer composites. Previous research showed that Toray T800/3900-2 carbon fiber reinforced epoxy composites prepared with Precision Fabrics Group 52006 nylon peel ply and bonded with MetlBond 1515-3M structural film adhesive failed in adhesion at low fracture energies when tested in the double cantilever beam (DCB) configuration. Other research suggested that plasma treatment may be able to activate these “unbondable” surfaces and result in good adhesive bonds. Nylon peel ply prepared 177 °C cure carbon fiber reinforced epoxy laminates were treated with atmospheric pressure plasma after peel ply removal prior to bonding. Surface characterization methods, including contact angle and Fourier transform infrared (FTIR) spectroscopy, were used to determine how plasma treatment changed nylon peel ply prepared surfaces. DCB specimens were bonded with MetlBond 1515-3M and tested to determine failure mode and G_{IC}. Plasma treated samples had acceptable failure modes and fracture energies that were triple that of peel ply only samples. It was demonstrated that atmospheric pressure plasma reversed the curse of this nylon peel ply. Fracture data was correlated to surface characterization results to understand the effect of plasma treatment on the surface and resultant bond quality.

1. INTRODUCTION

Structural joints, though necessary in the design of structures, unavoidably form localized stresses due to discontinuities. One way to minimize these stresses is by using adhesively bonded joints rather than mechanically fastened joints. In comparison to mechanical fasteners, bonding reduces stress concentrations, reduces weight, and eliminates the need for sealants to protect against environmental damage. In addition, bonded joints can be designed to take advantage of the ductile response to loading of the adhesive [1]. Adhesive bonds are used extensively for large aerospace structures, such as the Boeing 787 or Airbus A350. Though there are many advantages of bonding, commercially available technology to measure adhesive bond quality without destroying the bond is lacking. Therefore, bonds are currently certified through strict process control.

Adhesive bonds are dependent on the chemistry of the interface and control of surface chemistry is critical to bond quality [1,2]. Thus, the most important step in bonding is surface preparation, which prevents or removes contaminants that can adversely affect bonding while also creating
chemically active sites to maximize bond strength. One type of surface preparation used for composites is peel ply. A peel ply is a polymer fabric (e.g. polyester, nylon) that is the last layer applied to a composite part before cure and is removed directly before bonding. Figure 1 shows the removal of peel ply and the resulting surface.

Figure 1. Removal of peel ply from CFRP.

Peel ply is an attractive surface preparation due to its consistency and repeatability, though some opposition exists to its use, especially nylon peel plies, without subsequent abrasive techniques [3]. Each combination of composite, surface preparation, and adhesive must be validated to ensure a good bond [3]. Other studies also support the materials system specificity of peel ply surface preparation [3,4,5,6]. For example, previous research showed that different peel ply types resulted in different failure modes and Mode I strain energy release rates ($G_{IC}$) for carbon fiber reinforced plastic (CFRP) bonded with MetlBond 1515-3M film adhesive [4]. Table 1 shows an example of the varying modes for different peel ply surface preparations on a given CFRP system [4]. The $G_{IC}$ and failure modes were determined using Mode I Double Cantilever Beam (DCB) testing [4].

Table 1. DCB fracture surfaces of peel ply surfaces bonded with MB1515-3 adhesive [4].

<table>
<thead>
<tr>
<th>Failure Mode</th>
<th>Polyester Prepared</th>
<th>Nylon Prepared</th>
<th>SRB Prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{IC}$</td>
<td>812±35 J/m² (4.6±0.20 in*lbf/in²)</td>
<td>122±15 J/m² (0.70±0.09 in*lbf/in²)</td>
<td>&lt; 94 J/m² (&lt; 0.54 in*lbf/in²)</td>
</tr>
</tbody>
</table>

In situations where the incorrect peel ply is used or where the peel ply yields insufficient bond performance, additional surface preparation, such as an abrasive or energetic technique, is typically required to produce an acceptable surface for bonding. One type of energetic technique that shows significant potential for improving interface quality is atmospheric pressure plasma treatment [7]. In addition to minimizing downstream wastes from subsequent surface preparation, plasma treatments can be automated, thus reducing process variability while increasing reliability and processing rates [7].
This study focused on atmospheric pressure plasma treatment of CFRP prepared with nylon peel ply for bonding with MetlBond 1515-3M film adhesive. After peel ply removal, surfaces were plasma treated at two raster speeds and subsequently bonded. Bond quality was measured using the DCB test to determine failure mode and \( G_{IC} \). Failure modes in CFRP adhesive bonds include interlaminar within the substrate, cohesive within the adhesive, and adhesion failure as defined in Figure 2. Adhesion failure is unacceptable, whereas interlaminar and cohesive failures are acceptable failure modes for verifying bond quality. Typically, cohesive failures result in higher fracture energies than interlaminar failures and adhesion failures result in the lowest fracture energies [8]. Surface characterization was also performed to understand how atmospheric pressure plasma treatment changes peel ply prepared composite surfaces. Surface characterization techniques included contact angle (CA) measurements and Fourier transform infrared (FTIR) spectroscopy. This paper will discuss how atmospheric pressure plasma treatment applied to composites prepared with an incorrect peel ply affect that surface and resulting bond quality.

![Figure 2. Adhesive bond failure modes: (a) cohesive, (b) adhesion and (c) interlaminar.](image)

**2. EXPERIMENTATION**

**2.1 Specimen Preparation**

For this study, 10-ply panels of carbon fiber reinforced epoxy prepreg composite (Toray T800/3900 unidirectional tape) prepared with a nylon peel ply (Precision Fabrics Group, Inc. 52006) were fabricated. These panels were prepared by laying up [0], CFRP laminates, vacuum bagging the panels, and curing them in an autoclave. The autoclave cure cycle for the specimens was as follows:

1. Heat to 57.2 °C (135 °F) at a rate of 1.1 °C/min (2 °F/min), increase pressure to 0.6 MPa (89 psi) at a rate of 0.1 MPa/min (20 psi/min), soak for 0 min
2. Heat to 177 °C (350 °F) at a rate of 5.6 °C/min (10 °F/min), maintain pressure of 0.6 MPa (89 psi), soak at 177 °C and 0.6 MPa for 120 min
3. Cool to 10 °C (50 °F) at a rate of 5.6 °C/min (10 °F/min), maintain pressure of 0.6 MPa (89 psi), soak for 0 min
4. Decrease pressure to 0 MPa (0 psi) at a rate of 0.1 MPa/min (20 psi/min), maintain temperature of 10 °C (50 °F), soak for 0 min

After cure, the specimens were cut to the appropriate dimensions for surface analysis measurements and DCB testing. Three scenarios were studied: (1) control (no plasma), (2) 2.54 cm/s (1 in/s) plasma treatment, and (3) 15.24 cm/s (6 in/s) plasma treatment. These conditions
will be defined as “control” for no plasma, “high” for 2.54 cm/s plasma, and “low” for 15.24 cm/s plasma. Atmospheric pressure plasma treatment was performed with a PlasmaTreat model FG1001 plasma generator equipped with a model RD1004 single flume jet. The distance between the head of the plasma device and the substrate was fixed at 1.27 cm (0.5 in). Also fixed was a 50% overlap of each raster pass using the rotating flume. In cases when plasma treatment was used, the peel ply was removed directly before treatment. After treatment, samples were wrapped in aluminum foil to protect surfaces from gross contamination while in transit to another location for bonding or surface characterization. All samples were bonded or measured with CA and FTIR within 4 hours of peel ply removal.

2.2 Contact Angle Measurements

Sessile drop CA measurements were collected using a VCA Optima Goniometer. Laminates were cut into test panels of 10.2 cm (4 in) by 12.7 cm (5 in). The stage was confirmed to be level prior to CA analysis. Drops 1 µL in volume were dispensed from the syringe and placed onto the test surface by raising the stage and “catching” the drops. The drop orientation with respect to the goniometer camera was 0 or 90 degrees with respect to the peel ply texture orientation, as defined in Figure 3. Previous research has shown CAs measured at peel ply orientations of 0 and 90 degrees are not significantly different and, in comparison to intermediate orientation angles, provide the most conservative measurements [9].

![Camera](image_url)

**Figure 3. SEM image showing 0 and 90 degree peel ply imprint orientation.**

Fluids used for CA measurement were deionized water (DI H₂O), ethylene glycol (EG), glycerol (GLY) and diiodomethane (DIM). These fluids were chosen because of their diversity in polar and dispersive components of surface energy. DI H₂O is mostly polar, DIM is mostly dispersive, and GLY and EG have polar and dispersive components between the two extremes as shown in Table 2. An image of the side-view of the drop was frozen at a predetermined time of 5 seconds and the CAs were measured using the goniometer software. Figure 4 shows the instrument and an example drop image showing measured CAs.

**Table 2. Polar and dispersive surface energies for CA fluids.**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\gamma^p$ (mJ/m²)</th>
<th>$\gamma^d$ (mJ/m²)</th>
<th>$\gamma^{tot}$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized Water [10]</td>
<td>50.2</td>
<td>22.0</td>
<td>72.2</td>
</tr>
<tr>
<td>Diiodomethane [11]</td>
<td>0</td>
<td>50.8</td>
<td>50.8</td>
</tr>
<tr>
<td>Ethylene Glycol [10]</td>
<td>19.0</td>
<td>29.3</td>
<td>48.3</td>
</tr>
<tr>
<td>Glycerol [10]</td>
<td>30</td>
<td>34</td>
<td>64</td>
</tr>
</tbody>
</table>
A total of 20 measurements (10 drops) were averaged for each CA value reported. Averages were used to calculate polar and dispersive surface energies of the composite from the Owens-Wendt surface energy model [12]. The surface energies were calculated using equation [1].

\[
\frac{\gamma_{lv}(\cos \theta + 1)}{2\gamma_{lv}^p} = \sqrt{\frac{\gamma_{sv}^d}{\gamma_{lv}^d}} + \sqrt{\gamma_{sv}^p}
\]  

In equation [1], \(\gamma_{lv}\) is the total surface energy between the liquid and the vapor (surface tension), \(\gamma_{lv}^p\) is the polar component of the surface tension, \(\gamma_{lv}^d\) is the dispersive component of the surface tension, \(\gamma_{sv}^p\) is the polar component between the solid and the vapor, and \(\gamma_{sv}^d\) is the dispersive component between the solid and vapor. From equation [1], which takes the form \(y = mx + b\), the y-coordinate and the x-coordinate were calculated and plotted from the data. A line was fit to these points, generating a Kaelble plot [13,14], which shows the relationship between the CAs obtained per probe fluid. The polar surface energy of the composite was calculated to be the y-intercept of the Kaelble plot squared (\(\gamma_{sv}^p = b^2\)). The dispersive surface energy was the slope squared (\(\gamma_{sv}^d = m^2\)).

2.3 FTIR Measurements

An Agilent Technologies Exoscan FTIR was used to collect spectra from the prepared surfaces. The Exoscan, which was configured for diffuse reflectance, used one background spectrum for a series of specimens. Figure 5 shows an infrared beam path for diffuse reflectance. The background was then ratioed to the specimen spectra. Data collection was 90 scans with 16 cm\(^{-1}\) resolution in the MIR data range (4000-650 cm\(^{-1}\)). Seven spectra were collected per sample.
Figure 5. An infrared beam path for diffuse reflectance.

The GRAMS IQ software package was used for multivariate analysis of FTIR spectra. Multivariate analysis is a powerful tool for the examination of chemical spectra because it can help identify differences in peak locations and peak intensities that are otherwise not obvious. Principal component analysis (PCA) was used to determine differences between spectra. Two principal components were used. Spectra required preprocessing before PCA for a difference to be observed. Multiplicative scatter correction and a gap first derivative with 5 smoothing points were preprocessing steps used. The multiplicative scatter correction was used to overcome unknown pathlength effects inherent to the diffuse reflectance technique. The first derivative was used to magnify differences between spectra by amplifying changes in slope of the spectral peaks while reducing effects of baseline offsets. Smoothing points were used to reduce the influence of noise.

2.4 DCB Testing

Individual DCB adherends 15.24 cm (6 in) by 38.1 cm (15 in) in size were bonded with MetlBond 1515-3M film adhesive (159 g/m² [0.0325 psf] areal weight) after peel ply removal and subsequent application of atmospheric pressure plasma. A fluorinated ethylene propylene (FEP) release film crack starter was employed as shown in Figure 6.

Figure 6. Cross sectional view of bonding lay-up.

The cure cycle for the bonded assemblies was as follows:

1. Heat to 57.2 °C (135 °F) at a rate of 1.1 °C/min (2 °F/min), increase pressure to 0.3 MPa (45 psi) at a rate of 0.1 MPa/min (20 psi/min), soak for 0 min

2. Heat to 177 °C (350 °F) at a rate of 5.6 °C/min (10 °F/min), maintain pressure of 0.3 MPa (45 psi), soak at 177 °C and 0.3 MPa for 120 min
3. Cool to 10 °C (50 °F) at a rate of 5.6 °C/min (10 °F/min), maintain pressure of 0.3 MPa (45 psi), soak for 0 min

4. Decrease pressure to 0 MPa (0 psi) at a rate of 0.1 MPa/min (20 psi/min), maintain temperature of 10 °C (50 °F), soak for 0 min

After cure, the bonded assemblies were cut into individual specimens 1.27 cm (0.5 in) by 33.0 cm (13 in) in dimension. Average, maximum, and minimum bondline thicknesses per sample are shown in Table 3. Six measurements were collected for each DCB specimen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum (µm)</th>
<th>Minimum (µm)</th>
<th>Range (µm)</th>
<th>Average (µm)</th>
<th>Standard Deviation (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>191.7</td>
<td>119.4</td>
<td>72.3</td>
<td>148.3</td>
<td>12.0</td>
</tr>
<tr>
<td>low</td>
<td>143.5</td>
<td>101.9</td>
<td>41.6</td>
<td>125.3</td>
<td>9.6</td>
</tr>
<tr>
<td>high</td>
<td>177.8</td>
<td>90.7</td>
<td>87.1</td>
<td>129.5</td>
<td>15.9</td>
</tr>
</tbody>
</table>

$G_{IC} = \frac{E}{A \times B}$

3. RESULTS AND DISCUSSION

3.1 Contact Angle Measurements

Contact angle measurements were significantly different for peel ply only (control) samples compared to those treated with atmospheric pressure plasma upon peel ply removal. Figure 7 shows this result. DI H$_2$O, EG, and GLY CAs were lower on plasma treated samples than on control specimens. DIM CAs did not change significantly with plasma treatment. This could be due to the addition of polar groups, such as –OH, –COOH, –OOH, onto the surface as a result of atmospheric pressure plasma treatment [16]. All liquids with a polar component wetted plasma treated peel ply surfaces more than peel ply only surfaces. DIM was the only probe fluid without a polar component and its CA remained unchanged after plasma treatment. Some differences in CA measurements were observed between the two plasma treatment speeds examined. For DI H$_2$O and GLY, the CAs on the high sample were lower than on the low sample. It should also be noted that GLY completely wetted the low surface 30 seconds after the drops were placed on the surface.
The significant difference in CA measurements translated to a significant difference in surface energies, as shown by Figure 8. Plasma treated samples had higher polar and therefore higher total surface energies than the peel ply only sample. Compared to the control, plasma treatment increased total surface energy 20.1 mJ/m$^2$ and 21.9 mJ/m$^2$ for low and high samples, respectively. The larger polar component may be attributed to the addition of polar groups onto the surface, as mentioned previously. It also appeared that the polar component increased 3.6 mJ/m$^2$ while the dispersive component decreased 1.8 mJ/m$^2$ from the low treatment to the high treatment. Overall, the dispersive component of the surface energy for plasma treated samples appeared lower than control samples but the difference was small (1.8 and 3.6 mJ/m$^2$ lower for low and high plasma treatments, respectively). This difference may not be significant and could be due to the use of average CA measurements to calculate surface energy. It could also be due to an underestimation of the surface energy from calculations. In cases where the fluid wetted the surface, a CA of 0° (and 1°, which showed no difference) was used for calculations. A ~0° CA can occur on a surface when the surface energy of the fluid is at or below the critical wetting surface energy of the solid.
3.2 FTIR Measurements

FTIR spectra for all samples were not visually different as shown by Figure 9. PCA was thus used to determine spectral differences. PCA showed slight differences between sample sets. As shown by Figure 10, high samples were identified to be different than control samples on the first principal component (PC1), as these are two distinct groups shown on the plot. There were two possible outliers, which are also identified in Figure 10. The low samples were not identified as significantly different from either high or control samples, as the spacing within the low sample set is on the order of the spacing between the groups. The difference detected between the samples could be due to the amount of oxygen and nitrogen on the surfaces of the substrates. It would be expected that the sample plasma treated with the slowest raster speed (high) would have the most oxygen on the surface while the control sample would have the least. The lack of difference between the low sample and the other samples could be due to the sampling depth of the instrument. Diffuse reflectance FTIR samples to a depth up to about 10 µm [17]. This results in signal from the bulk of the sample, which would be the same for all the samples. Atmospheric pressure plasma only penetrates a small depth on the order of a few nanometers [16]. Thus, the surface would need to be sufficiently altered in order for the signal from FTIR measurements to be significantly different. Other chemical analysis techniques, such as x-ray photoelectron spectroscopy (XPS) may be explored in the future to understand chemical differences at the surface due to plasma treatment.
Figure 9. Representative spectra for control, high and low samples.

Figure 10. Scores plot from PCA of control, high and low spectral data preprocessed with a gap 1st derivative and 5 smoothing points.
3.3 **DCB Testing**

CA and FTIR measurements detected differences between control and plasma treated peel ply prepared composites. To determine if this difference correlated to a change in bond quality, samples were fabricated for DCB testing. As shown in Figure 11, plasma treatment resulted in an approximately three-fold increase in $G_{IC}$ compared to control samples. This could be attributed to an increase in polar groups on the plasma treated surfaces compared to control surfaces. Polar functional groups have previously been shown to promote adhesion [18,19,20]. Fracture energies were not significantly different for plasma treated samples. This correlated well to CA measurements, which showed plasma treated samples to be significantly different from control samples.

![Figure 11. Average $G_{IC}$ measurements for control, low and high plasma samples with standard deviation error bars.](image)

The difference observed in $G_{IC}$ is supported by failure mode. Control samples showed adhesion failure, which correlated to low fracture energies. Plasma treated samples showed mixed failure modes (cohesive and interlaminar), which explained the higher fracture energies. Representative fracture surface images are shown in Figure 12.
4. CONCLUSIONS

4.1 Contact Angle Measurements
DI H$_2$O, EG, and GLY CA measurements were significantly different for control and plasma treated samples. This may be due to the addition of polar groups onto the surface, causing probe fluids with polar components to wet plasma treated samples more than control samples. DIM CAs did not change with plasma treatment. The difference in CA measurements resulted in a significant difference in surface energies for plasma treated samples compared to the control. Plasma treatment increased total surface energy 20.1 mJ/m$^2$ and 21.9 mJ/m$^2$ for low and high samples, respectively, compared to the control.

4.2 FTIR Measurements
FTIR analysis showed that differences between spectra from plasma treated and control samples was not obvious. PCA of preprocessed spectra showed high samples and control samples could be identified as different groups. Low samples were not identified as significantly different from high or control samples for this analysis. The lack of difference could be due to the sensitivity of diffuse reflectance FTIR to the small amount of surface material affected by plasma treatment. XPS or other surface sensitive techniques may be explored in the future to understand chemical changes at the surface of atmospheric pressure plasma treated versus control samples.

4.3 DCB Testing
DCB testing correlated well to CA measurements. Plasma treatment resulted in a threefold increase of $G_{IC}$ compared to control samples. This could be due to an increase in polar groups on the surface due to atmospheric pressure plasma treatment. Polar groups, such as –OH, are known to promote adhesion [18,19,20]. Fracture energies were not significantly different for plasma treated samples. Control samples showed adhesion failure modes and plasma treated samples showed cohesive and interlaminar failure modes.
5. ACKNOWLEDGMENTS

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6. REFERENCES

14 Rulison, C. So You Want to Measure Surface Energy? In *Technical Note #306* (1999), Kruss
USA.


17 Fundamentals of FTIR Spectroscopy.

