INFLUENCE OF PEEL PLY TYPE ON ADHESIVE BONDING OF COMPOSITES

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Materials Science Department, University of Washington Seattle, WA 98195-2120
*The Boeing Company, Seattle WA

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ABSTRACT

The adhesive bond quality of two commercially available, aerospace grade carbon fiber epoxy prepregs (176 °C cure) was investigated using peel ply surface preparation. A variety of peel plies (nylon, polyester, epoxy preimpregnated polyester, epoxy preimpregnated fiberglass, and epoxy preimpregnated nylon) were used to create different surfaces for bonding. The surfaces to be bonded were characterized using several techniques after peel ply removal. Scanning electron and optical microscopy were used to evaluate the fracture surface produced by removal of the peel ply. The surface chemistry was studied using X-Ray PhotoSpectroscopy (XPS). Surface energies were measured using contact angles with several different fluids. Samples were bonded with aerospace grade film adhesives with a FEP release film strip to create a pre-crack for Mode I fracture evaluation. After fracture testing, the surfaces were examined to determine mode of fracture: adhesion, cohesive within adhesive or cohesive within matrix. The results of the fracture testing are used as a measure of bond quality. Adhesion failures were classified as a weak bond, cohesive failures as a strong bond. Bond quality is discussed with respect to the results of surfaces created by removal of the peel plies.

KEY WORDS: Adhesive Bonding, Surface Analysis, Surface Preparation Processes

1.0 INTRODUCTION

Peel ply surface preparation for co-bonding and secondary bonding of primary composite structures is becoming more common as the usage of composites is increasing in commercial aircraft. Peel ply surface preparation is attractive from a manufacturing and quality assurance standpoint because it reduces costs and minimizes the human factors present in other surface preparation techniques, such as grinding and grit blasting. However, there is not a fundamental understanding of the process variables that ensure a high quality, durable bond.

Pocius [1] summarized these mechanisms of adhesion as seven fundamental criteria for the creation of strong bonds:

1) The adhesive and adherend have the same solubility parameter to allow diffusion.
2) The adherend has micromorphology and the adhesive has low enough viscosity to completely fill these features to maximize mechanical interlocking.
3) The adhesive and adherend must come into intimate contact, minimizing interfacial flaws.
4) The adhesive should have surface energy less than the critical wetting tension of the adherend so that wetting can occur (and intimate contact will exist).
5) The adhesive and adherend have opposite character in order for acid/base interactions to take place.
6) In adverse environmental conditions provide for interfacial covalent bonding, as secondary bonds will not be sufficient.
7) Weak boundary layers are removed or modified to be cohesively strong.

In practice, peel ply treatment has been found to be an effective and efficient for the manufacturing of some primary bonded composite structures. Peel ply is a woven synthetic fabric added as the last layer in the lay-up and cured to the composite part to be bonded. Two general forms of peel ply are available: “Dry” peel ply which is a woven cloth and “wet” peel ply which is a dry peel ply that has been impregnated with a polymer resin, basically a peel ply prepreg. With a dry peel ply, during cure, the viscosity of the epoxy in the prepreg drops and impregnates the peel ply between the fibers and in gaps where warp and weft meet. What happens during cure with a wet peel ply has not been found in the literature, but one can postulate that some degree of mixing between the substrate resin and peel ply resin occurs and some excess resin may bleed out.

After cure, the peel ply is then removed from the surface immediately before bonding. The characteristics of a surface created by peel ply removal are directly influenced by how the peel ply separates from the laminate and any mixing or interactions that take place between wet peel ply resin and substrate resin systems. Additionally, peel plies that may work for one resin or adhesive system may be ineffective with others. The advantages claimed for wet peel plies include better bond strength and durability, better control of the fracture/release path between peel ply and laminate surface, tailoring of the resin for subsequent bonding and decreased likelihood of leaving peel ply filaments on the laminate surface.[2] The disadvantages of the wet peel plies include higher cost and prepreg type quality control procedures (out time, moisture, etc). There are other areas of concern including the effect of adding an additional resin system to bonded structures. Resin incompatibilities are to be avoided.

The possible modes of peel ply removal can be seen in Figure 1, and are either 1) the fracture of the epoxy resin between the peel ply and the underlying carbon fibers, due to strong bonding of the peel ply to the composite matrix during cure (dark blue) or 2) interfacial fracture between the peel ply fabric fibers and the epoxy matrix, if the strength of the chemical bond formed between the peel ply and the matrix is insufficient (pink). 3) the peel ply fibers may fracture and leave material on the composite surface (green) or 4) there may be interlaminar failure in the composite (turquoise). In the first mode, a fresh epoxy surface is created that should be chemically active and easily bonded. Though ideal, this is rarely the only mode of fracture present. In the second mode, the chemistry of the surface created may be affected by the nature of the peel ply material surface. Peel ply coatings or fiber surface treatments may be transferred to the surface to be bonded and affect the future bond.[3] The third mode may occur if the bond between the peel ply and epoxy is stronger than the peel ply fibers, and the fourth if the interlaminar strength of the laminate is low or the peel ply is removed incorrectly.
Benard et al [4-6] have been investigating surface roughening as a method to increase bond quality. By examining polyester and polyamide peel plies in 176°C cure systems they have corroborated the results of Bardis and Kedward [7] that roughening a surface that has been prepared by peel ply removal is only an asset when bonds were poor without doing so, and can actually be detrimental when bonds are already strong. They also took contact angle measurements of the prepared surfaces, and found that the surfaces that bonded the best had the lowest angles.

Bossi et al [8] have studied the effectiveness of peel ply, hand sanding, grit blasting, plasma etching, and laser ablation as surface preparation in paste adhesive systems. Pretreatments that cleaned the surface and provided sufficient roughness were found to be critical for bond quality, and grit blasting was the most successful. In addition to mechanical testing to determine the resulting bond quality, the group is trying to determine surface measurements that could be used for quality assurance. Roughness measurements with a portable hand stylus profilometer were recommended. While X-ray photoelectron spectrometry was found to accurately show contamination of the surface or exposed carbon fibers (both creating unacceptable surfaces), it is not practical as a factory technique. They found that contact angle measurements used to determine surface energies and wettability envelopes could predict adhesive wetting of the surface and expose if contamination was present.

Recent research on a unidirectional composite laminate with a different resin system prepared using polyester peel plies resulted in good bonds with film adhesives.[9] Surfaces prepared with nylon peel plies resulted in poor bonds with Metal Bond 1515-3, but acceptable bonds with the AF555 adhesive. These results raise several new questions regarding the effects of peel ply surface preparation on bond quality and the effectiveness of peel ply surface preparation on different composite laminates. Our current research has focused on bond quality of surfaces prepared using a variety of peel plies cured on two different carbon fiber epoxy prepregs and then bonded with two epoxy based film adhesives (Metal Bond 1515-3 and AF555).
Currently bond quality is assessed by destructive testing, usually through measurement of strain energy release rate, $G_{IC}$ in Mode I or shear strength tests and fractography of test specimens. In Mode I loading a strong correlation exists between $G_{IC}$ and the dominant failure mechanism of the bonded sample. Fracture can occur in three possible ways: 1) failure at the bondline, termed adhesion failure 2) cohesive failure in the adhesive or 3) cohesive failure in the composite substrate. Fracture along the bond line is associated with low values of $G_{IC}$ and a poorly prepared or contaminated surface and is generally considered unacceptable. Cohesive failure in the adhesive or substrate is associated with high values of $G_{IC}$, and acceptable surface preparation assuming the adhesive and matrix were properly processed. The production of lap shear or Mode I DCB specimens according to ASTM standards such as ASTM 5528-01, ASTM3528-96 and/or ASTM 5568-01 is very costly and time consuming.[10-12] A modified peel test has been developed to quickly evaluate bond quality by only examining the fracture of the bonded specimen torn apart in Mode I loading.[13] This test, coined the Rapid Adhesion Test (RAT) is not proposed as a substitute or replacement for ASTM type testing, but rather as a quick, inexpensive screening test that can be used to evaluate multiple variations of surface preparation, substrate, adhesive and/or processing combinations. It is estimated that the RAT method takes 90% less time and materials than ASTM Mode I tests. The RAT method is further described in the materials and methods section and will be used to evaluate bond quality in this investigation.

2.0 MATERIALS AND METHODS

2.1 Materials
Two commercially available aerospace grade carbon fiber-176 °C (350°F) curing epoxy prepregs from different manufacturers were used in this investigation. One was a unidirectional tape with T-800 fibers preimpregnated with a toughened, hot melt epoxy system, Toray 3631. The second was a 3K-70 plain weave impregnated with a solvent thinned toughened epoxy resin, Cytec-Cycom 970. Panels for surface characterization and bonding were produced with five different peel plies described in Table I using a typical vacuum bag lay-up with peel plies against the tool surface. A single ply of prepreg covered with peel ply was cured to a 0.51mm (0.020 inch) thick 2024-T3 PAA treated adherend without adhesive to create the modified peeling adherend, as shown in figure 2, for use in the mode I Rapid Adhesion Test (RAT) method developed at the Boeing company.[14] Two different 176 °C (350°F) curing epoxy based film adhesives (AF555 from 3M and MB1515-3 from Cytec) were used to bond the samples to a 1.60mm (0.063 inch) 2024-T3 PAA treated substrate with a 50.8 mm (2 inch) wide strip of FEP placed between the adhesive and the composite as shown in figure 2.

Table I: peel plies used in this study

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Matrix</th>
<th>Comments/source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>None</td>
<td>Precision Fabrics 60001</td>
</tr>
<tr>
<td>Nylon</td>
<td>None</td>
<td>Precision Fabrics 52006/51789</td>
</tr>
<tr>
<td>Polyester</td>
<td>Epoxy</td>
<td>Henkel EA 9895, 176 C curing epoxy</td>
</tr>
<tr>
<td>Nylon</td>
<td>Epoxy</td>
<td>Cytec MXM 7934/ PF51789</td>
</tr>
<tr>
<td>E-glass</td>
<td>Epoxy</td>
<td>Hexcel Style 7781- F161-108</td>
</tr>
</tbody>
</table>
**2.2 Processing**

All panels underwent a standard cure cycle of 176° C (350°F) for 2 hours under 0.58 MPa (85psi) in an autoclave with full vacuum maintained throughout the cure cycle. Representative samples were taken for surface characterization with peel plies intact. The remaining panels had the peel plies removed and epoxy based film adhesives were applied. No sanding, grit blasting, solvent wipe or other surface preparation was used. A strip of non-porous fluorinated ethylene propylene (FEP) release film was placed at the edge of the panel to create a 50.8 mm (2.0 inch) starter crack for fracture toughness testing as shown in figure 2. Bonded samples were cured using the same parameters as the initial panels. Bonded specimens were machined for RAT testing according to the cutting diagram in figure 3.

![Stage 1 sample preparation](image)

**Stage 1 sample preparation**
- Al 0.51 mm
- Prepreg
- Peel ply

- remove peel ply immediately before stage 2 cure

**Stage 2 sample preparation – bonded to cured stage 1 adherend**
- Adhesive
- FEP crack starter
- Al 1.60mm

Figure 2. Lay-up diagram for RAT specimens. The modified peeling adherend is cured in stage 1.

![Figure 2](image)

Figure 3. Cutting diagram for RAT specimens.

The samples were tested using the RAT method, a modified peel test with one of the adherends previously cured with a composite skin, to introduce a Mode I loading as shown in figure 4. Previous work has shown excellent agreement between the RAT method and the more commonly used DCB test with mode of failure correlating with $G_{IC}$ values.[13]
Figure 4: Rapid Adhesion Test (RAT) method after peeling using a 50.8 mm (2 inch) radius cylinder. Note: Failure mode is primarily cohesive in this example.

After fracture testing, the surfaces were examined to determine type of failure: adhesion, cohesive within adhesive or cohesive within substrate matrix. The type of failure was used as a measure of bond quality: adhesion failures were classified as a weak bond, cohesive failures as a strong bond. In some instances, both cohesive and adhesion failure were found—this is termed a mixed failure and was not considered an acceptable bond. Fracture path was determined using visual examination followed by stereoscopic and scanning electron microscopy (SEM).

2.3 Surface Analysis Techniques

In this study, fractography on all samples was performed using a JOEL JSM-7000F SEM, after sputter coating with a platinum target. Images were taken after peel ply removal as well as after mechanical testing. Post-fracture images show whether specific features acted as crack initiation sites, and they can distinguish between interfacial failure and thin-layer cohesive failure. SEM can also expose if there are small patches of interfacial failure in a primarily cohesive failure (or vice versa).

The transfer of material from the peel plies was investigated through XPS analysis of 176°C cure prepreg samples immediately after the removal of peel plies. All XPS results were gathered using a Surface Science Instruments M-Probe spectrometer in which environment pressure does not exceed 0.14 mPa (1x10^-8 torr). Survey scans and high-resolution XPS spectra over the C (1s) peak are recorded to find chemical composition using nominal pass energies of 150 and 50 eV, respectively. Analyses are over elliptical spots with major axes of approximately 1.7 mm and minor axes of approximately 0.4 mm, to depths of between ten and twenty atom
layers of the sample surface. The samples in this study are non-conducting, therefore a low energy electron load-gun set at ~4.0 eV is used for charge neutralization of the samples. All spectra measurements are corrected for the charging by setting the hydrocarbon C (1s) peak to 285.0 eV.

Contact angles were measured with a Ramé-Hart Tilting Contact Angle Goniometer model 100-00 115 with overall magnification 23X and working distance of 57mm. These measurements were used to determine the surface energy of all composite systems tested, and ten measurements were taken with each fluid on each surface immediately after removal of peel ply or adhesive backing. The fluids used were ethylene glycol, deionized water, glycerol, formamide, tetrabromoethane, dimethyl sulfoxide (DMSO) and diiodomethane. The polar, dispersive and total surface energies of the substrates were determined using a Klaeble plot constructed from the contact angle measurements and literature values of polar and dispersive components of the fluids. [15-17]. The wettability envelopes for the peel ply prepared surfaces were calculated using a program developed by Tuttle [18] and modified by one of the authors (Clark).

3.0 RESULTS

3.1 Surfaces created by Peel Ply Removal

3.1.1 Surface Topography
For a peel ply to be successfully used as a surface treatment for bonding, the first criterion is that the peel ply can be removed from the composite substrate without damaging the panel. If reinforcing fibers are damaged during peel ply removal (mode 4, figure 1) then surface preparation was not acceptable. This occurred in one combination of substrate and peel ply: the fiberglass-epoxy peel ply could not be removed from the Toray 3631 tape without pulling carbon fibers from the substrate as shown in figure 5. No further characterization or testing was conducted on this peel ply/substrate combination.

Figure 5: Unsuccessful attempt at removing fiberglass-epoxy prepreg peel ply from Toray 3631
It was also very difficult to remove the fiberglass-epoxy peel ply from the Cytec Cycom 970 substrate—often the peel ply would fracture and peeling would need to be reinitiated with a razor. The four remaining peel plies were removed without much effort from both substrates. Representative SEM micrographs of the composite surfaces after peel ply removal are shown in Figures 6 to 10. The surface topography was not significantly influenced by the substrate except for the fiberglass-epoxy peel ply as discussed above. Since the peel ply controlled the surface morphology, SEM micrographs are shown for only the Cytec 970 substrate to avoid duplication with the Toray 3631 substrate. Figure 6 is the surface created by the removal of PF60001 polyester from Cytec 970. The imprint of the polyester peel ply weave is clearly visible on the surface. Also visible are ductile tendrils curling up from the epoxy surface as noted by the arrows. These are typical of a ductile polymer fracture and likely are remnants from the PF60001 polyester peel ply fibers. The tendrils were too small to characterize by energy dispersive spectrometry (EDS) in SEM and require further analysis by XPS to confirm the source.
Figure 6. SEM micrograph of Cytec 970 after removal of PF60001 peel ply before bonding. Note tendrils (highlighted by arrows) present on surface, likely remnants of polyester peel ply fibers.

Figure 7 is the surface created by the removal of PF51789 polyester from Cytec 970. The imprint of the nylon peel ply weave is clearly visible on the surface. Also visible are ductile wisps on the epoxy surface as noted by the arrows. These are typical of a ductile polymer fracture and are likely remnants from the PF51789 nylon peel ply fibers. The tendrils were too small to characterize by energy dispersive spectrometry (EDS) and require further analysis to confirm the source.
Figure 7. SEM micrograph of Cytec 970 after removal of PF51789 peel ply before bonding. Note tendrils (highlighted by arrows) present on surface, likely remnants of polyester peel ply fibers.

Figure 8 is the surface created by the removal of EA 9895 from Cytec 970. The imprint of the polyester peel ply weave is clearly visible on the surface. No ductile remnants were found on this surface after careful examination of several areas at high magnification. Also note the rectangular regions of fracture epoxy that occurred between the warp and weft tows due to the loose nature of the peel ply fabric weave.
Figure 8. SEM micrograph of Cytec 970 after removal of EA9895 peel ply before bonding. Note area of epoxy fracture between warp and weft tows as noted by arrows.

Figure 9 is the surface created by the removal of PF51789 polyester peel ply that had been preimpregnated with Cytec MXM 7934 epoxy resin. The imprint of the nylon peel ply weave is clearly visible on the surface. Also visible are ductile wisps on the epoxy surface as noted by the arrows. These are typical of a ductile polymer fracture and are likely remnants from the PF51789 nylon peel ply fibers. The tendrils were too small to characterize by energy dispersive spectrometry (EDS) and require further analysis to confirm the source.
Figure 9. SEM micrograph of cytec 970 after removal of nylon-epoxy prepreg peel ply before bonding. Note ductile wisps left on surface as noted by arrows.

Figure 10 is the surface created by the removal of fiberglass-epoxy prepreg peel ply from Cytec 970. This surface is much different than any of the previous surfaces. There is no imprint of the glass peel ply fibers visible on the surface. The mode of fracture was almost completely in the epoxy matrix (mode 1 in figure 1). Occasionally a glass fiber was found imbedded in the surface. Theoretically this should produce the best surface for bonding. There is a fracture texture visible on the substrate surface that most likely resulted from fracture near the glass fibers, but not at the glass fiber-epoxy interface. The coupling agent used on the E-glass fibers prior to epoxy impregnation created a strong bond between the glass fiber and the epoxy matrix, whereas the bond between the nylon or polyester is not nearly as strong. The difference in
elastic modulus between the glass (~68 GPa) and thermoplastic peel ply fibers (~2GPa) would also create a different stress condition during the peel ply removal which may affect the crack propagation path. [19]

3.1.2 Surface Chemistry
XPS was used to further characterize the composition of the composite surface after peel ply removal. XPS survey scans results for the nine remaining substrate-peel ply combinations are given in Table III. Several observations consistent with the SEM results were noted.

1) Substrates cured with polyester peel ply have the highest oxygen concentrations, likely from the C=O bond in polyester. The highest oxygen concentrations (>25 At. %) were measured in

Figure 10. SEM micrograph of Cytec 970 after removal of fiberglass-epoxy prepreg peel ply before bonding. Arrow guides readers eye to an E-glass fiber left on the substrate.
samples cured with PF60001 polyester peel ply consistent with the ductile tendrils visible in SEM (Figure 6)

2) Substrates cured with nylon peel plies have the highest nitrogen concentrations likely from the C=N amide bond in nylon, consistent with the ductile wisps visible in SEM (figure 7).

3) The Cytec 970/fiberglass-epoxy prepreg system showed significant Si and Br. The Si is most likely from the E-glass fiber and the Br from a fiberglass prepreg resin additive

4) Bromine was also detected when the EA9895 peel ply was used, again likely from an additive in the Henkel resin.

5) Sulfur was detected in most of the samples from Toray 3631 prepreg, likely from an elastomeric toughening agent in the resin. The sample cured with EA9895 did not show any detectable sulfur. This could be due to a resin layer deposited by the EA9895, that obscures the toughened substrate.

Table III. Surface composition (atomic percentage) of substrates after removal of peel ply as determined by XPS.

<table>
<thead>
<tr>
<th>Substrate Peel ply</th>
<th>Carbon (At.%)</th>
<th>Oxygen (At.%)</th>
<th>Nitrogen (At.%)</th>
<th>Silicon (At.%)</th>
<th>Bromine (At.%)</th>
<th>Sulfur (At.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytec 970 PF60001</td>
<td>73.8</td>
<td>25.2</td>
<td>1.0</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Cytec 970 PF51789</td>
<td>76.1</td>
<td>12.4</td>
<td>11.5</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Cytec 970 Hexcel 7781/E-glass</td>
<td>74.5</td>
<td>17.1</td>
<td>5.0</td>
<td>2.3</td>
<td>1.1</td>
<td>**</td>
</tr>
<tr>
<td>Cytec 970 MXM 7934/PF51789</td>
<td>77.5</td>
<td>12.9</td>
<td>9.6</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Cytec 970 EA9895</td>
<td>76.8</td>
<td>19.6</td>
<td>3.1</td>
<td>**</td>
<td>0.5</td>
<td>**</td>
</tr>
<tr>
<td>Toray 3631 PF60001</td>
<td>70.5</td>
<td>25.9</td>
<td>1.6</td>
<td>1.3</td>
<td>**</td>
<td>0.6</td>
</tr>
<tr>
<td>Toray 3631 PF51789</td>
<td>77.1</td>
<td>13.3</td>
<td>9.0</td>
<td>**</td>
<td>**</td>
<td>0.7</td>
</tr>
<tr>
<td>Toray 3631 Epoxy/nylon</td>
<td>76.2</td>
<td>12.1</td>
<td>10.7</td>
<td>**</td>
<td>**</td>
<td>1.0</td>
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<tr>
<td>Toray 3631 EA9895</td>
<td>79.0</td>
<td>18.3</td>
<td>1.2</td>
<td>**</td>
<td>1.5</td>
<td>**</td>
</tr>
</tbody>
</table>

3.1.3 Surface Energies and Wettability
The surface energies and wettability envelopes determined from contact angle measurements are presented below. The contact angles and surface energies calculated using klaeble plots are given in Table IV. The wettability envelopes computed using the “wet” program from Tuttle are shown in Figures 19 and 20 for the Toray 3631 and Cytec-Cycom 970 substrates with the various peel plies. The surface energies of the uncured adhesives are also shown in those figures. The
results are similar to previous results with polyester and nylon peel plies, except for that for the fiberglass prepreg peel ply. Surfaces prepared with polyester fibers tend to have a greater dispersive component, whereas surfaces prepared with nylon peel ply fibers tend to have a greater polar component. This is consistent with the XPS results and lead to the hypothesis that the surface created by removing a thermoplastic fiber from an epoxy resin has some amount of the fiber left on the surface. This may range from an atomic layer to relatively large wisps or tendrils that can be observed in the SEM (figures 6, 7 & 9). However, the data from the Cytec 970 substrate cured with the fiberglass prepreg peel ply has very different characteristics. The surface energy is much high and the wettability envelope is much larger. This is consistent with the different fracture observed in the SEM- Figure 10 where fracture occurred through the epoxy matrix and not at the peel ply fiber interface, or perhaps interphase as XPS and contact angle measurements infer.

Table IV. Contact angle and surface energies for substrate-peel ply combinations and uncured adhesive films

<table>
<thead>
<tr>
<th>Substrate-Peel ply</th>
<th>contact angle, degrees</th>
<th>$\gamma_d$ (mN/m)</th>
<th>$\gamma_p$ (mN/m)</th>
<th>$\gamma_{tot}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytec970-PF60001</td>
<td>76.9</td>
<td>56.2</td>
<td>15.6</td>
<td>38.7</td>
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<tr>
<td>Cytec970-PF51789</td>
<td>47.8</td>
<td>51.6</td>
<td>20.2</td>
<td>32.8</td>
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<tr>
<td>Cytec970-EA9895</td>
<td>64</td>
<td>53.1</td>
<td>21.0</td>
<td>32.0</td>
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<tr>
<td>Cytec970-MXM9734/51789</td>
<td>54.2</td>
<td>54.5</td>
<td>29.1</td>
<td>42.2</td>
</tr>
<tr>
<td>Cytec970-Hexcel7781/E-glass</td>
<td>103</td>
<td>66.9</td>
<td>14.1</td>
<td>na</td>
</tr>
<tr>
<td>Toray 3631-PF60001</td>
<td>78.3</td>
<td>63.9</td>
<td>25.7</td>
<td>41.4</td>
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<tr>
<td>Toray 3631-PF51789</td>
<td>59.9</td>
<td>na</td>
<td>32.0</td>
<td>44.3</td>
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<tr>
<td>Toray 3631-EA9895</td>
<td>80.3</td>
<td>64.6</td>
<td>29.8</td>
<td>38.5</td>
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<tr>
<td>Toray 3631- MXM9734/51789</td>
<td>55.7</td>
<td>30.3</td>
<td>na</td>
<td>na</td>
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<tr>
<td>3M- AF555 uncured</td>
<td>75.3</td>
<td>na</td>
<td>68.1</td>
<td>74.1</td>
</tr>
<tr>
<td>Cytec MB1515-3 uncured</td>
<td>70.5</td>
<td>na</td>
<td>49.5</td>
<td>53.9</td>
</tr>
</tbody>
</table>
Figure 11. Wettability envelopes for Toray 3631 substrate after removal of various peel plies. Surface energies of the fluids and uncured adhesives are also shown.

Figure 12. Wettability envelopes for Cytec Cycom 970 after removal of various peel plies. Surface energies of the fluids and uncured adhesives are also shown.
3.2 Mode I fracture results from the RAT method

Strong, durable bonds in composite materials require that chemical bonds form during the curing of the adhesive. Mechanical interlocking can give some degree of bond strength, especially in shear loading, however in aggressive environments and/or mode I loading strong chemical bonds are necessary. Mode I fracture tests have been shown to be a good predictor of long term bond quality. Both the fracture energy GIC and mode of failure: cohesive vs. adhesion have been shown to be important. The results from the RAT method for the nine substrate-peel ply-adhesive combinations are presented below, using mode of failure as a measure of bond quality. Only 100% cohesive failures, either in the adhesive or the substrate are defined as good bonds by the authors. Samples that fail with a mixed failure mode part cohesive and part adhesion are questionable and greater than 50% adhesion failure is defined as a poor bond. The results of the bonds tested using the RAT method are presented in Table V.

Table V. Results from Mode I RAT method for substrate-peel ply-adhesive combinations

<table>
<thead>
<tr>
<th>Substrate Adhesive</th>
<th>PEEL PLY USED FOR SURFACE TREATMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB1515-3</td>
<td>PF60001</td>
</tr>
<tr>
<td>Cytec 970</td>
<td>MIXED</td>
</tr>
<tr>
<td>Cytec 970</td>
<td>MIXED</td>
</tr>
<tr>
<td>AF555</td>
<td></td>
</tr>
<tr>
<td>Toray 3631</td>
<td>ADHESION</td>
</tr>
<tr>
<td>MB1515-3</td>
<td></td>
</tr>
<tr>
<td>Toray 3631</td>
<td>ADHESION</td>
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Representative SEM micrographs of the fracture surface on the substrate side of the bond are shown in figures 13-18 to show cohesive, mixed and adhesion failure. Henkle EA9895 peel ply produced surfaces that produced strong bonds with both substrates and both adhesives as can be seen in figures 13 and 14. The fiberglass prepreg peel ply produced surfaces that bonded well, when it could be removed from the substrate as shown in Figure 15. The results from the two “dry” peel plies (nylon and polyester) were more variable: At best the failures were classified as mixed, figure 16 and at times almost complete adhesion failure was observed figure 18. These conflicts with previous results with a different 176 °C cure carbon fiber-epoxy substrate where strong bonds were formed on substrates cured with PF60001 polyester and with certain adhesives on PF51789 nylon.[9]. The epoxy impregnated nylon peel ply bond as well with the AF555 on the Cytec 970 substrate, however bonded poorly on the Toray 3631 as seen in figure 18.
Figure 13. SEM micrograph of RAT sample Cytec 970 prepared with EA9895 peel ply bonded with MB1515-3 showing 100% cohesive failure in the composite. The carbon fibers and epoxy matrix are visible. No evidence of peel ply texture indicating adhesion failure was found.
Figure 14. SEM micrograph of RAT sample Toray3631 prepared with EA9895 peel ply bonded with MB1515-3 showing 100% cohesive failure in the composite. The carbon fibers and epoxy matrix are visible.
Figure 15. SEM micrograph of RAT sample Cytec 970 prepared with Hexcel7781-Eglass prepreg peel ply bonded with MB1515-3 showing 100% cohesive failure in the composite. The carbon fibers and epoxy matrix are visible. No evidence of peel ply texture indicating adhesion failure was found.
Figure 16  SEM micrograph of RAT sample Cytec 970 prepared with PF60001 peel ply bonded with MB1515-3 showing mixed adhesion and cohesive failure. The adhesion failure is noted by arrow pointing to area where imprint of peel ply is still visible.
Figure 17. SEM micrograph of RAT sample Toray3631 prepared with PF60001 peel ply bonded with MB1515-3 showing mixed adhesion and cohesive failure. The adhesion failure is noted by arrow pointing to area where imprint of peel ply is still visible.
The important question to be answered is: Can the surface characteristics presented above predict bond quality? Theoretically wetting is a necessary but perhaps not sufficient condition for the formation of strong bonds. Wetting is controlled by the surface energies of the surface, and the adhesive in a given environment. If the surface energies of the adhesive fall within the wettability envelope of the surface the adhesive should wet the surface. However, this does not necessarily mean that strong bonds have been formed. This point has been illustrated in this work by the fact that poor bonds were formed even though the adhesives fell within the wettability envelopes of the prepared surfaces. DMSO has been suggested as a suitable fluid to replace water in a “water break” test to check for contamination, since its polar and dispersive surface energies are close to most epoxies. [8]. DMSO wet out on all of the substrate surfaces in
this study, even when poor bonds were formed. Caution is advised in using this approach to
determine the suitability of surfaces for bonding. Poor wetting of DMSO would certainly be a
red flag and likely indicated a surface is not suitable for bonding, however the converse is not
true. More detailed surface characterization using SEM and XPS provided more information
regarding the condition of the substrate surface to be bonded. Remnants of polyester and nylon
peel ply fibers on the surface were revealed by high magnification inspection and XPS spectra
with high levels of oxygen or nitrogen respectively. Adhesion or mixed adhesion/cohesive
failure were seen in all but one system in these cases.

4.0 CONCLUSIONS

1) Peel ply surface preparation that works with one peel ply-prepreg-adhesive system will
not necessarily work if any one of the three is changed.
2) Peel ply fiber and resin interactions during cure, and the resulting matrix properties near
the peel ply fibers play an important role in the surface created when the peel ply is
removed.
3) The fracture path during removal of peel ply has a strong effect on the quality of the
bond. Peel ply remnants on the substrate surface were shown to be detrimental to bond
quality.
4) Henkel EA9895 wet peel ply produced substrate surfaces that bonded well to the
adhesives used in this study.
5) Contact angle measurements and wettability envelopes are useful in understanding the
nature of the surface, but have not be shown to predict the quality of bonds
6) Detailed surface analysis using SEM and XPS provide information need to determine the
nature of surfaces created by peel ply removal.

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