Improving Adhesive Bonding of Composites Through Surface Characterization (of Peel Ply Prepared Surfaces)

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The Joint Advanced Materials and Structures Center of Excellence
Improving Adhesive Bonding of Composites Through Surface Characterization

• Motivation and Key Issues
  – Peel ply surface preparation is being used for bonding primary structure on Boeing 777 and 787 and other commercial transport aircraft
  – Good bonds are produced but questions remain:
    • What are appropriate techniques to inspect surfaces?
    • What are key factors for making a good/poor bond?
    • How to predict material and surface preparation compatibility?

• Objective
  – Further understand the effect of peel ply surface preparation on the durability of primary structural composite bonds through surface analysis coupled with mechanical testing and fractography
Improving Adhesive Bonding of Composites Through Surface Characterization

• Approach: Use Advanced Characterization Techniques To Understand The Role Of:
  – Prepreg (resin system, toughening agents, etc)
  – Adhesive (film adhesives)
  – Surface Preparation (peel ply material)
On The Surface Structure And Bond Quality
FAA Sponsored Project Information

- Principal Investigators & Researchers
  - Brian D. Flinn (PI)
  - Fumio Ohuchi (Co-PI)
  - Molly Phariss (Ph.D. Candidate, U. of Wa.)
  - Brian Clark (Masters student, U of Wa.)
- FAA Technical Monitor
  - Peter Shyprykevich (retired) and Curtis Davies
- Other FAA Personnel Involved
  - Larry Ilcewicz
- Industry Participation
  - Boeing: Peter Van Voast, William Grace, Paul Shelly
  - Precision Fabrics Group, Cytec, Toray, 3M
- JAMS Participation
  - Mark Tuttle (U. of Wa.): Wettability envelopes
  - Lloyd Smith (WaSU): Parallel study on durability
Background

Bond quality is dependent on

- Chemical Bonding
  - Surface Preparation
    - Remove/Prevent Contamination
  - Material Compatibility
    - Create Chemically Active Surfaces
- Mechanical Factors
Peel Ply Surface Preparation

Fracture Possibilities Upon Peel Ply Removal

- Fracture of the epoxy between peel ply and carbon fibers
  - Fresh, chemically active, epoxy surface is created
- Interfacial fracture between the peel ply fabric fibers and the epoxy matrix
- Peel ply fiber fracture
- Interlaminar failure
Characterization and Testing

ESCA/XPS: X-Ray Photoelectron Spectroscopy

- X-Ray probes energy distribution of valence and nonbonding core electrons
- Gives chemical composition of surface (first few atomic layers)
- Peel ply removed just prior
- Survey scans and high-res scans over C (1s) peak
Contact Angle Measurement

- 4 Fluids
- On laminates after peel ply removal
- On uncured film adhesives
- Kaelble plots to determine polar and dispersive surface energies
  \[ \gamma_s = \gamma_s^d + \gamma_s^p \]
- Wettability envelopes calculated
  - Using WET program (M. Tuttle).
Samples were produced with standard composite processes and characterized. Peel ply was removed before bonding. The samples were bonded with film adhesive. Characterization was performed via XPS, SEM, and Contact Angle measurements. The $G_{IC}$ testing was conducted according to ASTM D-5528.
Materials and Methods

• Test Samples produced with different:
  – Peel Plies (Nylon & Polyester)
  – Prepregs (250F & 350F cure systems)
  – Variety of Film Adhesives

• Surfaces and Bonds characterized by
  – SEM, XPS, Contact Angle (wettability)

• Laminates bonded and machined in to DCB specimens (ASTM 5573 & BSS-7273)
Peel Ply Surface Prep. - SEM Results

- All samples show acceptable surface on macro scale
  - Interfacial fracture between the peel ply fabric fibers and the epoxy matrix
  - Limited epoxy fracture between peel ply fibers

Composite surface after removal of:

Nylon
Polyester
SRB
### 350 Cure System Results

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Polyester Prepared</th>
<th>Nylon Prepared</th>
<th>SRB Prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Failure Mode</strong></td>
<td>Cohesive</td>
<td>Cohesive &amp; Interlaminar</td>
<td>Adhesion</td>
</tr>
<tr>
<td><strong>$G_{IC}$ (J/m$^2$)</strong></td>
<td>909.6</td>
<td>910.7</td>
<td>93.9</td>
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<tr>
<td><strong>Adhesive B</strong></td>
<td>Cohesive</td>
<td>Adhesion</td>
<td>Adhesion</td>
</tr>
<tr>
<td><strong>$G_{IC}$ (J/m$^2$)</strong></td>
<td>812.3</td>
<td>122.1</td>
<td>86.0</td>
</tr>
</tbody>
</table>

$G_{IC}$ and $H_2O$ Contact Angle do not always correlate

- $G_{IC}$: Polyester $>>$ Nylon $>$ SRB
- Contact Angle: Nylon $<$ Polyester $<<$ SRB
Klaeble plots determined polar and dispersive surface energy components.

- Measured contact angles, known energies of fluids used to plot points
- Linear fit yields
  - Slope: $\sqrt{\gamma_s^d}$
  - Intercept: $\sqrt{\gamma_s^p}$

$$\gamma_s^{\text{tot}} = \gamma_s^p + \gamma_s^d$$

<table>
<thead>
<tr>
<th>Peel Ply</th>
<th>$\gamma_s^d$</th>
<th>$\gamma_s^p$</th>
<th>$\gamma_s^{\text{total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon</td>
<td>25.0</td>
<td>20.3</td>
<td>45.3</td>
</tr>
<tr>
<td>Polyester</td>
<td>30.3</td>
<td>13.7</td>
<td>44.0</td>
</tr>
</tbody>
</table>

Differences in energy components
- Polyester $\rightarrow$ greater dispersive
- Nylon $\rightarrow$ greater polar
Wettability envelopes showed the difference in the prepared surfaces.

- Fluids inside the envelope will wet spontaneously
  - Critical condition for bonding?
- Wettability envelopes a potential method to determine suitability of a surface for bonding
- Epoxy adhesives* on boundary for nylon prepared surfaces

* Literature values for aerospace epoxies
- Curves generated using WET program (M. Tuttle)
XPS Survey Scan Results

Laminate surfaces before bonding, after peel ply removal

- Si explains SRB low bond quality….Siloxane coating transfers
- Amount of N on nylon peel ply prepared sample surprising

<table>
<thead>
<tr>
<th>Peel Ply</th>
<th>%C</th>
<th>%O</th>
<th>%N</th>
<th>%Si</th>
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<tr>
<td>Nylon</td>
<td>77.5</td>
<td>12.6</td>
<td>9.8</td>
<td>Tr.</td>
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<tr>
<td>Polyester</td>
<td>75.5</td>
<td>21.6</td>
<td>1.9</td>
<td>Tr.</td>
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<tr>
<td>SRB</td>
<td>68</td>
<td>24.2</td>
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<tr>
<td>Peel Ply</td>
<td>Species</td>
<td>BE (eV)</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>--------------</td>
<td>---------</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>Nylon</td>
<td>CC/CH</td>
<td>285</td>
<td>71</td>
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<tr>
<td></td>
<td>CN</td>
<td>286.2</td>
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<td></td>
<td>Amide (NC=0)</td>
<td>288</td>
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<tr>
<td>Polyester</td>
<td>CC/CH</td>
<td>285</td>
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<tr>
<td></td>
<td>CO/(CN)</td>
<td>286.5</td>
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<td></td>
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<tr>
<td></td>
<td>COO</td>
<td>289.2</td>
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<tr>
<td></td>
<td>Shakeup?</td>
<td>291.8</td>
<td>2.4 (broad)</td>
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<tr>
<td>SRB</td>
<td>CC/CH</td>
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<td>CO</td>
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<td></td>
<td>COO</td>
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<td></td>
<td>Shakeup?</td>
<td>291.8</td>
<td>1.1 (broad)</td>
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</tr>
</tbody>
</table>

Amide detected on nylon prepared surface - nylon transfer to surface?

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A Closer Look at the Laminate Surface

Laminate surface after removal of nylon peel ply

Nylon from peel ply on surface before bonding?
Bond Quality Depends on:
• Peel Ply Material and Adhesive
  – Polyester peel ply: high toughness bonds, cohesive failure both adhesives
  – Nylon: low toughness, adhesion failure
  – One adhesive bonded well to all surfaces
• $H_2O$ Contact angle did not correlate well with $G_{IC}$
• Wettabillity envelopes more accurate
• XPS can provide important chemical information
250F Cure Systems

• 2 Peel Plies: Polyester 60001 and Nylon 52006
• 3 prepregs-260 ºF cure
  – HexPly® F155
  – Yokohama G7781
  – Cytec MXB7701
• 6 adhesives-260 ºF cure
  – 3M AF500; 3M AF163-2;
  – Henkel EA 9696; Henkel EA 9628
  – Cytec FM94; Cytec FMx 209
• Bond quality assessed by failure mode
  – Adhesion (poor) vs. Cohesive (good)
# Peel Ply Material-250F Cure

## SUMMARY

**Nylon - Strong**

**Polyester - Weak**

<table>
<thead>
<tr>
<th>RAT results</th>
<th>key:</th>
<th>strong bond</th>
<th>mixed strong / very strong bonds</th>
<th>mixed results</th>
<th>weak bond</th>
<th>other</th>
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<td>adhesive:</td>
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<tr>
<th>600C1 (polyester)</th>
<th>3M AF500</th>
<th>3M AF163-2</th>
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</tbody>
</table>

| Prepreg:          |      |             |                                  |               |           |       |
| adhesive:         |      |             |                                  |               |           |       |

| peel ply:         |      |             |                                  |               |           |       |
| adhesive:         |      |             |                                  |               |           |       |

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<td></td>
<td></td>
</tr>
</tbody>
</table>

| Prepreg:          |      |             |                                  |               |           |       |
| adhesive:         |      |             |                                  |               |           |       |

| peel ply:         |      |             |                                  |               |           |       |
| adhesive:         |      |             |                                  |               |           |       |

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Bond Quality Depends on:

- Peel Ply Material and Adhesive
  - Nylon: high toughness bonds, cohesive failure all adhesives
  - Polyester peel ply: low toughness, adhesion failure
  - One adhesive bonded well to all surfaces

- Opposite Trend than 350 F system
  - Nylon bad, Polyester good
Effect of Peel Ply Texture

- 350F Laminates produced with 9 different peel plies
  - 4 polyester and 5 nylon peel plies
  - Surface characterization: SEM, profilometry, contact angle
  - Bond quality: Measure with $G_{IC}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Precision Code</th>
<th>Warp (ends/in.)</th>
<th>Fill (picks/in.)</th>
<th>Thickness (mil)</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Polyester</td>
<td>60001</td>
<td>70</td>
<td>50</td>
<td>5-6</td>
<td>BMS 8-308</td>
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<tr>
<td>Polyester</td>
<td>60001 VLP</td>
<td>70</td>
<td>50</td>
<td>5-6</td>
<td>Calendered</td>
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<td>Polyester</td>
<td>60004</td>
<td>120</td>
<td>59</td>
<td>4.5-5.5</td>
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<tr>
<td>Polyester</td>
<td>60005</td>
<td>90</td>
<td>58</td>
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<td>Nylon 6,6</td>
<td>52006</td>
<td>160</td>
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<td>Nylon 6,6</td>
<td>50000</td>
<td>60</td>
<td>50</td>
<td>6.5-7.5</td>
<td>Twill weave</td>
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<td>Nylon 6,6</td>
<td>40000</td>
<td>76</td>
<td>51</td>
<td>7.5-8.5</td>
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<td>Nylon 6,6</td>
<td>41661</td>
<td>60</td>
<td>50</td>
<td>6.5-7.5</td>
<td></td>
</tr>
</tbody>
</table>
SEM’s of As-Received Peel Plies

- Fine 160 x103 (PF 52006)
- Medium 101 x 82 (PF 52008)
- Coarse 60 x 50 (PF 52000)

- Different weaves, deniers, filament diameters will produce different surfaces
Peel Ply Removal (?)

Acceptable

Not Acceptable

Not Acceptable

Not Acceptable
Effect Peel Ply Texture

- All polyester peel plies successfully removed
- Nylon peel plies were more difficult to remove
  - Fine weaves were removed without damage
  - Coarse weaves have not been removed without damage to laminate (3 attempts, different technicians)

<table>
<thead>
<tr>
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<th>Code</th>
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Effect of Peel Ply Texture

- Peel ply texture does not seem to affect bond quality

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Effect Peel Ply Texture

- Wettability Envelopes

Curves generated using WET program (M. Tuttle)
Peel Ply Texture Summary

Material and 350F system

– Polyester peel plies easier to remove, bond better
– Nylon peel plies more difficult to remove
  • Coarser peel plies could not be removed without damaging laminate
– Similar trends in wettability envelopes
  • Nylon greater polar component
  • Polyester greater dispersive
– Texture does not have significant effect on $G_{IC}$
Effect of Peel Ply Source

- Many Polyester and Nylon Peel Plies Available
- Why Might There Be a Difference?
  - Different fiber source—impurities, MW, properties
  - Different weaves
  - Different processing—scouring and heat setting
  - Different quality control
- Measure $G_{IC}$ and Characterize Surfaces
Peel Ply Material Source

- Adhesion failure on some surfaces with polyester peel plies!
Peel Ply Material Source

• XPS on Laminates Cured with Different Airtech peel plies

- Peel ply “F” has highest oxygen content
- Peel Ply “F” closest match to Precision 60001

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Peel Ply Material Source

XPS on:
As received Airtech and PFG polyester peel plies
Laminates Cured with Airtech and PFG polyester peel plies

Typical compositional scan

Peel Ply “F” close match to Precision 60001

Summary of composition scans
Peel Ply Material Source

- Wetting Envelopes on Laminates Cured with Different Peel Plies

- Peel ply “F” and “60001” have similar wettability envelopes

Curves generated using WET program (M. Tuttle)
Peel Ply Material Source

- Slight differences in peel ply can be important
- For Polyester 60001 and Ply F
  - Different failure modes and energies
    - 900 J/m² vs. 700 J/m²
  - Similar Surface Chemistry
- More research needed to understand fundamentals of peel ply surface preparation
Conclusions

• Bonding Depends on
  – Prepreg system
  – Peel Ply Material
  – Adhesive

• Characterization Techniques (XPS, SEM and Wettability) provide useful information to help understand bonding requirements
A Look Forward

• Benefit to Aviation
  – Better understanding of peel ply surface prep.
  – Greater confidence in adhesive bonds

• Future needs
  – Contact angle (wetting) vs. bond quality
  – Peel ply-resin interactions
  – Applicability to other composite and adhesive systems
  – Model to guide bonding based on characterization, surface prep. and material properties
The Rapid Adhesion Test (RAT) Method

- A quick, low cost test which assesses the adhesion between metal-composite bonds.
- A modification of metal-to-metal peel test developed by Boeing.
- The backing adherend clamped to while the peeling adherend is removed.
- Failure mode representative of bond
  - Adhesion Failure-Poor Bond
  - Cohesive Failure-Strong Bond
- Failure modes correlate with DCB test with ~90% less cost and flow time.

Peeling adherend (0.020” Al PAA+ single ply of composite-peel ply surface)
Adhesive film
FEP crack starter
Backing adherend (0.063” Al-PAA)
RAT Method Assessment

Cohesive failure (left) vs. Adhesion failure (right)

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