Identification and Validation of Analytical Chemistry Methods for Detecting Composite Surface Contamination and Moisture

Xiangyang Zhou
University of Miami

Rajiv Srivastava and Richard Burton
Florida International University
Identification and Validation of Analytical Chemistry Methods for Detecting Composite Surface Contamination and Moisture

• Motivation and Key Issues
  – Adhesive bonding has been used in the manufacture and repair as a direct competition to mechanical fastening.
  – Adherent surface preparation is a critical issue to the structural integrity and durability of bonded structures.

• Objective
  – benchmark surface preparation quality assurance methods
  – identify and validate definitive analytical chemistry methods to provide sufficient in-field quality assurance.

• Approach
  – Literature review and analysis
  – Surface chemistry analysis
  – Electrochemical sensor development
  – Experimental validation
FAA Sponsored Project Information

- Principle Investigators & Researchers
  - Xiangyang Zhou, Richard Burton
  - Rajiv Srivastava, Dwayne McDaniel, Weihua Zhang, Wongbon Choi,
  - Sam Hill, Yao Ge, Shejie Tang, Ling Wang (Graduate Students)
- FAA Technical Monitor
  Curtis Davies
- Industry Participation
  - DME Corporation
    6830 N.W. 16th Terrace
    Fort Lauderdale, Florida 33309 USA
Main Results

- Literature database
- Summary of literature review
  - Surface treatment
  - Surface chemistry analyses
- An electrochemical sensor for surface chemistry analysis
- Novel carbon nanotube sensor for humidity sensing
- AFM study of the peel plies
Research Roadmap

Information collection and analyses

Chemical analyses

Surface analysis criteria

Information collection and analyses

Candidate field analysis technologies

Technology validation

Effective field analysis technology

Strength & durability versus surface pretreatment

The Joint Advanced Materials and Structures Center of Excellence
Literature Database

The Joint Advanced Materials and Structures Center of Excellence
Effect of Various Surface Pretreatment Method

<table>
<thead>
<tr>
<th>Treatment type</th>
<th>Material</th>
<th>Nature of treatment</th>
<th>Surface tension</th>
<th>Surface roughness</th>
<th>Surface chemistry</th>
<th>Bond strength</th>
<th>Durability</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Abrasion and solvent wipe</td>
<td>Thermoset and thermoplastic</td>
<td>Remove mold release</td>
<td>Y</td>
<td>Y</td>
<td></td>
<td>Increased found for thermosets</td>
<td>Good for thermosets</td>
</tr>
<tr>
<td>(2) Grit blasting</td>
<td>Thermoset and thermoplastic</td>
<td>Remove mold release</td>
<td>Y</td>
<td>Y</td>
<td></td>
<td>Increased found for thermosets</td>
<td>Good for thermosets</td>
</tr>
<tr>
<td>(3) Acid etch</td>
<td>Thermoset and thermoplastic</td>
<td>Etch</td>
<td>Y</td>
<td>Y</td>
<td></td>
<td>Slight increase</td>
<td>Poor</td>
</tr>
<tr>
<td>(4) Peel- ply</td>
<td>Thermoset</td>
<td>Remove mold release</td>
<td>Y</td>
<td>Y</td>
<td></td>
<td>Increase</td>
<td>Good</td>
</tr>
<tr>
<td>(5) Tear- ply</td>
<td>Thermoset</td>
<td>Remove mold release</td>
<td>Y</td>
<td>Y</td>
<td></td>
<td>Increase</td>
<td>Good</td>
</tr>
<tr>
<td>(6) Corona discharge</td>
<td>Thermoplastic</td>
<td>Oidising</td>
<td>Y</td>
<td></td>
<td></td>
<td>Double</td>
<td>Good (90 days)</td>
</tr>
<tr>
<td>(7) Plasma treatment</td>
<td>Thermoplastic</td>
<td>Ablation and/or oxidation</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Increase</td>
<td>Good (90 days)</td>
</tr>
<tr>
<td>(8) Flame treatment</td>
<td>Thermoplastic</td>
<td>Oidation</td>
<td>Y</td>
<td></td>
<td></td>
<td>Increase</td>
<td>More research is necessary</td>
</tr>
<tr>
<td>(9) Laser treatment</td>
<td>Thermoset and thermoplastic</td>
<td>Ablation and oxidation</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Increase</td>
<td></td>
</tr>
</tbody>
</table>

*Depends on polymer matrix material. Y - Yes
Covalent bond formation between adherend and adhesive-Effect of Surface O- and N- Functional Groups (Anchor Groups)
## Concentration of O versus Strength

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Treatment</th>
<th>Surface composition (at%)</th>
<th>Failure load/N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>HDPE</td>
<td>No treatment</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2.1 V, Pt edge, 50 passes</td>
<td>95.5</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>2.4 V, Pt edge, 50 passes</td>
<td>96.2</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>2.9 V, Pt disc, 5 min</td>
<td>92.4</td>
<td>7.6</td>
</tr>
<tr>
<td>PP</td>
<td>No treatment</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>3.25 M nitric acid, 60 s</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2.1 V, Pt edge, 50 passes</td>
<td>92.6</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>2.4 V, Pt edge, 50 passes</td>
<td>93.1</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>2.9 V, Pt edge, 50 passes (H$_2$SO$_4^-$)</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2.9 V, Pt disc, 300 s, not touching</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2.9 V, Pt disc, 300 s, far removed</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SBS</td>
<td>No treatment</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2.5 V, Pt edge, 50 passes</td>
<td>83.6</td>
<td>14.6$^b$</td>
</tr>
<tr>
<td>PS</td>
<td>No treatment</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2.9 V, Pt disc, 300 s</td>
<td>94.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Quality Control

- Materials certification,
- Pretreatment certification
- Adhesive application certification,
- Bonding certification,
- Technician certification,
- Process flow management

\[
N_{\text{adsorbed}} < N_{\text{adsorbed (critical)}}
\]

\[
N_{O^-&N^-} > N_{O^-&N^- (critical)}
\]

The Joint Advanced Materials and Structures Center of Excellence
Electrochemical Sensor

Solid-State Electrochemical Sensor

The Joint Advanced Materials and Structures Center of Excellence
Solid-state Electrochemical Sensor
Solid-state Electrochemical Sensor
Test results

- $Z_{\text{imag}}$, Ohm
  -25 -20 -15 -10 -5 0

- $Z_{\text{real}}$, Ohm
  0 5 10 15 20 25

- $\Omega$

- $\text{Hz}$
Test Results

Potential / Volts (vs. Pt|H₂ electrode)

Current / Ampers

Potential / Volts (vs. Pt|H₂ electrode)

The Joint Advanced Materials and Structures Center of Excellence
Carbon Nanotube Based Humidity Sensor

The Joint Advanced Materials and Structures Center of Excellence
Atomic Force Microscopy Study of Peel Ply
The Joint Advanced Materials and Structures Center of Excellence
\[ \sigma = \frac{F_{\text{max}}}{4\pi R \cos \theta} \]
Atomic Force Microscope
Previous SEM and XPS Results on Peel Ply Surfaces

• Polyester (PF 60001): No transfer, strong bonds

• SRB (PF 60001): Siloxane coating transfer, weak bonds

• Nylon (PF 52006): Fiber transfer, bond strength depends on adhesive
Nylon Peel Ply Surface
Polyester Peel Ply Surface
SRB Peel Ply Surface
Force vs. distance for nylon peel ply surface
Force vs. distance for SRB peel ply Surface
Conclusions

• Certification of pre-bond surface preparation quality requires implementation of effective surface chemistry inspection technologies for each and every step of the surface preparation procedure to ensure the strength and durability of the bonded aviation structures.

• Solid-state electrochemical sensor is a promising candidate technology for in-field surface chemistry analysis.
Conclusions

• No sign of contamination was found on polyester peel ply surface
• Some small size particles were found on nylon peel ply surface
• Some contaminating particles were found on SRB peel ply surface
• The SRB surface shows a more complicated force spectrum than the nylon peel ply surface.
A Look Forward

• Benefit to Aviation
  – Better understanding of the pre-bond surface preparation methods
  – Better understanding of bond strength and durability versus surface preparation
  – Novel in-field, online certification and assurance technology for surface preparation
  – Reduced costs for surface preparation and adhesive bonding processes

• Future needs
  – In-field, online analytical detection and monitoring technologies for manufacture, chemical, environmental, and energy industries.