Quality Control
Methodologies for Surface Preparation Processes for Composite Bonding

2011 Technical Review
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University of Washington
Quality Control Methodologies for Surface Preparation Processes for Composite Bonding

• Motivation and Key Issues
  – Most important step for bonding is SURFACE PREPARATION!!
  – Inspect the surface prior to bonding to ensure proper surface preparation

• Objective
  – Develop QA technique for surface preparation

• Approach
  – Investigate different surface preparations and process variables using laboratory and handheld devices
Quality Control Methodologies for Surface Preparation Processes for Composite Bonding

• Principal Investigators & Researchers
  – Brian D. Flinn (PI)
  – Ashley Tracey (PhD student, UW-MSE)
  – Jake Plummer (undergraduate, UW-MSE)
• FAA Technical Monitor
  – David Westlund
• Other FAA Personnel Involved
  – Larry Ilciewicz
• Industry Participation
  – Toray Composites
  – Precision Fabrics & Richmond Aerospace & Airtech International
  – The Boeing Company (Kay Blohowiak, Peter Van Voast, William Grace and Paul Shelley)
2010-2011 Statement of Work

• Literature review to understand state of composite bonding and surface analysis techniques
  – Map and characterize bonding processing steps to locate highest risk factors in process
  – Determine locations to incorporate in-line Quality Assurance (QA) methods
    ▪ Contact angle (CA) – Surface energy
    ▪ Fourier transform infrared spectroscopy (FTIR) – Surface chemistry
• Assess potential QA methods ability to identify less-than-desirable process conditions
• Correlate surface conditions to bond strength and durability
• Use QA methods at identified critical processing steps to evaluate process conditions and reliability of bonded joint
• Support of other AMTAS bonding research
  – FIU (bond durability)
  – U of Utah (metal bond wedge test)
Surface Energy to Probe Surfaces

• Why use surface energy to probe the surface preparation method applied to the composite for bonding?
  – One requirement of adhesion is the adhesive must wet the substrate
    ▪ This is controlled by surface energy
  – Contact angle is influenced by surface prep
Contact Angle Methodology

Brighton Surface Analyst
- Handheld device
- Water

VCA Optima Goniometer
- Bench top device
- Multiple fluids

http://www.btgnow.com

http://www.astp.com/contact-angle/optima
Goniometer Methodology

• Using a goniometer, the contact angle of a 1μL drop of fluid is measured – side view
  – Peel ply removed and contact angles measured within 1 hour
  – Four fluids, 10 drops per fluid were evaluated on each surface
  – Average contact angle and standard deviation were calculated to determine surface energies and generate wettability envelopes

• Complete wetting when θ approaches zero
• Contaminants usually lower the solid’s surface energy (increase θ)
• Surface preparations try to increase the solid’s surface energy and remove contaminants
Brighton Methodology

- Using the Brighton Surface Analyst, the contact angle of a 1.38μL drop (20 69nL drops) of water is measured – top view
  - Contact angle is calculated by fitting the circumference to the volume of the drop
  - Average contact angle and standard deviation were calculated for comparison to water contact angles measured with the goniometer

Note: rectangle in image is a reflection of light from camera

http://www.btgnow.com/SEP.html
Surface Chemistry to Probe Surfaces

• Why use surface chemistry to probe the surface preparation method applied to the composite for bonding?
  – Strong chemical bonds must form to ensure bonding
    ▪ This is controlled by surface chemistry
  – Surface preparation influences surface chemistry
  – FTIR is a well-established laboratory technique to determine surface chemistry
FTIR Methodology

A2 Technologies/Agilent Technologies FTIR

- Handheld device

Bruker Vertex 70 FTIR

- Bench top device

http://www.a2technologies.com/

http://www.aoc.kit.edu/english/612.php
FTIR Methodology

- Mid-IR FTIR set up with attenuated total reflectance (ATR)
  - Single bounce crystal
  - Absorbance peaks represent chemical bonds present in material

![An IR beam path for single bounce ATR](image)
Experimental Overview

Assess potential QA methods ability to identify less than desirable process conditions

• Surface Preparations:
  – Polyester peel ply, nylon peel ply, SRB release ply

• Peel Ply Contamination:
  – Various levels of siloxane contamination

• Process Variables:
  – Cure cycle: different dwell times (2, 8, 16 & 24 hours)
Materials

- Toray 3900/T800 unidirectional laminates
- Peel ply surface prep
  - Precision Fabric Group 60001 polyester peel ply
  - Precision Fabric Group 52006 nylon peel ply
  - Precision Fabric Group SRB release ply
- Autoclave cure (177°C, 0.6MPa)
- Fluids used for contact angle analysis:
  - De-ionized water (DI water)
  - Ethylene Glycol (EG)
  - Glycerol (Gly)
  - Diiodomethane (DIM)
Characterization of Surface Preparation

• Can contact angle and/or FTIR be used to identify differences between surface preparations on the same substrate?
  – Polyester peel ply
  – Nylon peel ply
  – SRB release ply
Contact Angle Results

Both methods detect differences in surface preparation

![Bar chart showing average H₂O contact angle for Polyester, Nylon, and SRB with Surface Analyst and Goniometer methods.](chart.png)

- Polyester: Surface Analyst 29.7°, Goniometer 78.5°
- Nylon: Surface Analyst 25.6°, Goniometer 68.6°
- SRB: Surface Analyst 41.5°, Goniometer 102°
Surface Chemistry Results

FTIR Spectra of Nylon, Polyester and SRB Plies

- Differences in surface chemistry are evident

✓ Differences in surface chemistry are evident
Surface Chemistry Results

Further Analysis: FTIR Spectra of Polyester and SRB Plies
Surface Chemistry Results

Further Analysis: FTIR Spectra of Polyester and SRB

<table>
<thead>
<tr>
<th>Compound Information</th>
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<tbody>
<tr>
<td>Compound Name</td>
<td>POLY(DIMETHYSILOXANE)</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>SiC₂H₅O₁</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td></td>
</tr>
<tr>
<td>CAS Registry Number</td>
<td>61-14-9</td>
</tr>
<tr>
<td>Sample Preparation</td>
<td>CAST FROM THF ON KBr</td>
</tr>
<tr>
<td>Comment</td>
<td>molecular formula means constitutional repeating unit</td>
</tr>
</tbody>
</table>

Si peak identifiable without subtraction
Surface Chemistry Results

FTIR Spectra of Substrate Surfaces

- Polyester
- SRB prepared
- Nylon prepared

Siloxane peak

Polyester peaks

✓ Differences in surface chemistry are evident
Characterization of Surface Preparation

Effect of Peel Ply Contamination

• Can contact angle be used to identify surface contamination?
  – Contaminants are detrimental to bonding
    ▪ Example: siloxane contamination

<table>
<thead>
<tr>
<th>Mix Solids Target Level</th>
</tr>
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<tbody>
<tr>
<td>0% (control)</td>
</tr>
<tr>
<td>0.0001%</td>
</tr>
<tr>
<td>0.001%</td>
</tr>
<tr>
<td>0.01%</td>
</tr>
<tr>
<td>0.05%</td>
</tr>
<tr>
<td>0.1%</td>
</tr>
<tr>
<td>0.2%</td>
</tr>
<tr>
<td>0.3%</td>
</tr>
<tr>
<td>0.5%</td>
</tr>
<tr>
<td>1%</td>
</tr>
<tr>
<td>2%</td>
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</table>
Goniometer Results: Wettability Envelopes

Dispersive surface energy (mN/m)

Polar surface energy (mN/m)

Increasing Si

0% CFRP (control)
0.0001% CFRP
0.001% CFRP
0.01% CFRP
0.05% CFRP
0.1% CFRP
0.2% CFRP
0.3% CFRP
0.4% CFRP
0.5% CFRP
1% CFRP
2% CFRP
Goniometer Results: Wettability Envelopes

- Contact angle sensitive to < 0.1% Si contamination
- Need to characterize with Surface Analyst
Characterization of Cure Cycle Effects

• Potential for long dwell times to affect peel ply prepared surfaces
• Does dwell time affect contact angle measurement and/or bondability?
  – 177 °C cure CFRPs with different autoclave dwell times: 2hr (control), 8hr, 16hr, 24hr

✓ Surface energy
➢ Surface chemistry
➢ Bond quality
Substrate Surfaces After Peel Ply Removal

Previous research has shown bond quality can decrease with peel ply transfer to substrate surface.
Results: Surface Analyst and Goniometer

Subtle differences in surface properties detected by both
Goniometer Results: Wettability Envelopes

1 Pocius, Alphonsus
V. Adhesion and Adhesives Technology: An Introduction. 2nd.

- Research in progress to better understand effect of cure cycle
Conclusions

• Variations in surface preparation can be detected
  – Peel ply type (Goniometer, Surface Analyst, FTIR)
  – Si contamination > 0.1% (Goniometer)

• Variations in cure cycle can be detected by CA
  – Goniometer and Surface Analyst
  – Additional research required to understand effects

• Surface energy and surface chemistry characterization methods have potential for QA
  – Manufacturing and repair
Looking Forward

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

• Future needs
  – FTIR surface characterization of process variables
  – Surface characterization vs. bond quality model
  – QA methods to ensure proper surface for bonding
  – Applicability to other composite and adhesive systems
  – Model to guide bonding based on characterization, surface prep. and material properties
Acknowledgements

• FAA, JAMS, AMTAS
• Boeing Company
• Precision Fabric Group
• Richmond Aircraft Products
• Airtech International
• Prof. Mark Tuttle (UW)
• Paul Shelley (Boeing)
Thank you

Questions and comments welcome
Appendix: FTIR Spectra of SRB and Polyester Prepared Surfaces

Polyester prepared
SRB prepared
SRB prep – Polyester prep

Peak
No peak
Peak
Appendix: Effect of Cure Cycle on Contact Angle Measurement

<table>
<thead>
<tr>
<th>Fluid</th>
<th>177C, 2hr dwell</th>
<th>177C, 8hr dwell</th>
<th>177C, 16hr dwell</th>
<th>177C, 24hr dwell</th>
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</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>78</td>
<td>69</td>
<td>69</td>
<td>72</td>
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<tr>
<td>E.G.</td>
<td>37</td>
<td>33</td>
<td>34</td>
<td>35</td>
</tr>
<tr>
<td>DIM</td>
<td>21</td>
<td>25</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>Gly.</td>
<td>65</td>
<td>64</td>
<td>61</td>
<td>72</td>
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