Improving Adhesive Bonding of Composites Through Surface Characterization

Effect of amine blush on bond quality

Brian Flinn, Greg Iglesias, Alex Stark, Russell Kilgannon

Materials Science and Engineering
University of Washington
Improving Adhesive Bonding Through Surface Characterization

• Motivation and Key Issues
  – Weak bonds in paste adhesives from amine blush
  – Can amine blush be detected?
  – Effect on bond quality?

• Objective
  – Develop quality assurance techniques for amine blush

• Approach
  – Investigate adhesives, humidity, temperature and time
  – Characterize adhesive surface and bond strength
Improving Adhesive Bonding Through Surface Characterization

• Principal Investigators & Researchers
  – Brian D. Flinn (PI)
  – Greg Iglesias, UW-MSE, now at Epic Aircraft
  – Alex Stark(UW-MSE)
  – Russell Kilgannon UW MSE, now at Boeing

• FAA Technical Monitor
  – Curtis Davies

• Other FAA Personnel Involved
  – Larry Ilcewicz, Cindy Ashforth

• Industry Participation
  – Epic Aircraft
  – Textron Aircraft
  – The Boeing Company
Amine Blush AKA Blooming

- Well known phenomena in epoxy resin systems
  - “Greasy surface”
  - Cosmetic issue - white powdery surface
  - Poor paint adhesion
- Not well documented in adhesives
- Occurs on exposed surfaces before gel
  - Atmosphere containing CO₂
  - Moisture
  - Time
  - Temperature
- Formation of carbamates and carbonates
- Cesena wing skin delamination incident (Dec. 2010)
Amine Blush

What is supposed to happen to an adhesive?

- **Linear Mw build-up....**

\[
\begin{align*}
\text{NH}_2 & \text{--} \text{NH}_2 \\
\text{+} & \text{+} \\
\text{NH}_2 & \text{--} \text{NH}_2
\end{align*}
\]
**Amine Blush**

What happens instead?

\[ \text{CO}_2 + \text{H}_2\text{O} \quad \Rightarrow \quad \text{H}_2\text{CO}_3 \]
From the atmosphere

\[ \text{H}_2\text{CO}_3 + \text{RNH}_2 \quad \Rightarrow \quad \text{RNHCOOH} + \text{H}_2\text{O} \]
Amine curing agent carbamic acid

\[ \text{RNHCOOH} + \text{RNH}_2 \quad \Rightarrow \quad \text{RNH}_3^{+}\text{OCONHR} \]
carbamate

**Primary and Secondary Amines**

\[ \downarrow \]

Ammonium Carbamate

**Tertiary Amines**

\[ \downarrow \]

Ammonium Bicarbonate

Problems:
- surface tackiness
- incomplete cure
- poor adhesion
Detecting Amine Blush - FTIR Peaks

☆ Carbamate
~1100 cm$^{-1}$ (C=O symmetric stretching)
~1400 cm$^{-1}$ (C-N stretching)
~1550 cm$^{-1}$ (C=O asymmetric stretching)

Carbamate

Analysis of the CO2 and NH3 Reaction in an Aqueous Solution by 2D IR COS. Formation of Bicarbonate and Carbamate, 2008.
Detecting Amine Blush - FTIR Peaks

◆ Bicarbonate
~1350 cm\(^{-1}\) (C-O symmetric stretching)
~1450 cm\(^{-1}\) (C-O asymmetric stretching)

Analysis of the CO2 and NH3 Reaction in an Aqueous Solution by 2D IR COS. Formation of Bicarbonate and Carbamate, 2008.
Experimental Overview

Investigate the effect of amine blush on bond quality and correlate with surface characterization measurements

• Expose paste adhesives to various times and humidity's
  – Visual inspection
  – pH
  – FTIR

• Measure bond quality of down selected adhesive
  – Rapid Adhesion test
  – Fracture Energy, GIC by double cantilever beam (DCB) test
  – Lap Shear Strength
  – Fractography
Blush Production

Intrinsic Factors
• Amine content
• Diluents
• Gel time
• Stoichiometry
• Compatibility

Testable Factors
✓ Temperature
✓ Humidity
• Induction
✓ Time after application
• Primer thickness
• Bond gap

Epoxy adhesive
amine blush
Weak layer in bond
Materials and Methods

- Toray T800/3900 laminates
  - DCB Unidirectional panels
  - Lap Shear [0/+45/-45/0]\textsubscript{2} panels
- Surface Preparation
  - Abrasion
- 5 different paste adhesives
- Controlled humidity chamber (25% or 80% RH)
  - Control specimen assembled immediately after spreading/combing
  - 30 min exposure after spreading/combing (within pot life spec)
- Characterize surface of paste adhesives
  - Visual
  - pH (litmus paper- really designed for aqueous soln’s)
  - FTIR (ATR)
- Bond Quality
  - $G_{IC}$ Fracture Energy (DCB) ASTM D5528
  - Lap Shear Strength (ASTM D3165)
  - Fractography
## Materials

### Adhesives

<table>
<thead>
<tr>
<th>Material</th>
<th>Mix Ratio (A:B)</th>
<th>Pot-Life</th>
<th>Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGS L285/H-285</td>
<td>2:1 by volume</td>
<td>45 min</td>
<td>24 hrs @ 74F + 15 hrs @ 140F</td>
</tr>
<tr>
<td>MGS L285/H287</td>
<td>2:1 by volume</td>
<td>4 hr</td>
<td>24 hrs @ 74F + 15 hrs @ 140F</td>
</tr>
<tr>
<td>ProGlas 1300</td>
<td>4:1 by volume</td>
<td>20-25 mins</td>
<td>4 hours @ 150F</td>
</tr>
<tr>
<td>Hysol EA956</td>
<td>100:58 by weight</td>
<td>30 min</td>
<td>5-7 Day RT Cure.</td>
</tr>
<tr>
<td>Hysol EA9360</td>
<td>100:43 by weight</td>
<td>60 min</td>
<td>5-7 Day RT Cure</td>
</tr>
</tbody>
</table>
Blush Production and Detection

Equipment

- Hum/Temperature Sensors
- Heratherm OGS100
- Litmus paper
- Bruker Vertex 70 FTIR
  - ATR
Bond Quality

- DCB Mode I strain energy release rate \( G_{IC} \) and failure mode
  - 3 samples per condition
  - Area method for \( G_{IC} \) calculations
    - E: area of curve
    - A: crack length
    - B: specimen width

\[
G_{IC} = \frac{E}{A \times B}
\]

- Double Lap Shear
  - 5 samples per conditions
Visual Test Results

Henkel EA 9360

LH
HH

Henkel EA 956

LH
HH
Visual Test Results

ProGlas 1300  High Humidity (~80%)  and Room Temperatures...

30 mins  1 hour  2 hours
# pH Test Results - ProGlass 1300

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>Humidity (%)</th>
<th>Temperature (F)</th>
<th>Proglas 1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>83</td>
<td>72</td>
<td>7</td>
</tr>
<tr>
<td>15</td>
<td>83</td>
<td>72</td>
<td>7</td>
</tr>
<tr>
<td>30</td>
<td>83</td>
<td>72</td>
<td>9</td>
</tr>
<tr>
<td>45</td>
<td>83</td>
<td>73</td>
<td>11</td>
</tr>
<tr>
<td>60</td>
<td>84</td>
<td>75</td>
<td>11</td>
</tr>
<tr>
<td>75</td>
<td>84</td>
<td>75</td>
<td>8.5</td>
</tr>
<tr>
<td>90</td>
<td>85</td>
<td>77</td>
<td>8.5</td>
</tr>
<tr>
<td>105</td>
<td>85</td>
<td>77</td>
<td>8</td>
</tr>
<tr>
<td>120</td>
<td>85</td>
<td>77</td>
<td>8</td>
</tr>
</tbody>
</table>

Amines are alkaline – high pH
Carbamates and carbonate are salts - more neutral
Carbamate and carbonate peaks develop with exposure.
# Summary of Surface Characterization

## Blush Detection in Adhesives

<table>
<thead>
<tr>
<th>Material</th>
<th>Visual</th>
<th>pH</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGS L285/H-285</td>
<td>YES*</td>
<td>NA</td>
<td>YES</td>
</tr>
<tr>
<td>MGS L285/H287</td>
<td>retest</td>
<td>retest</td>
<td>retest</td>
</tr>
<tr>
<td>ProGlas 1300</td>
<td>YES*</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Hysol 956</td>
<td>YES*</td>
<td>NA</td>
<td>YES</td>
</tr>
<tr>
<td>Hysol 9360</td>
<td>YES*</td>
<td>NA</td>
<td>YES</td>
</tr>
</tbody>
</table>

*Blush visible in later stages, hard to detect in early stage

➢ FTIR was most consistent in detecting all stages
# RAT Results-Humidity Exposure

<table>
<thead>
<tr>
<th>Panel Specimens (1-9)</th>
<th>Failure Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Controlled</td>
<td>Interlaminar/Cohesive</td>
</tr>
<tr>
<td>Low Humidity</td>
<td>Cohesive in Adhesive</td>
</tr>
<tr>
<td>High Humidity</td>
<td>Cohesive in Adhesive</td>
</tr>
</tbody>
</table>
• $G_{IC}$ values decreased significantly after 30 minute exposure to 25% and 80% RH
• Differences correspond with amine blush by surface characterization
DCB Results-Humidity Exposure

- Fracture mode: Cohesive in adhesive but different appearance
- Differences correspond with amine blush by surface characterization
DLS strength Results-Humidity Exposure

- $G_{IC}$ values decreased significantly after 30 minute exposure to 25% and 80%
- Differences correspond with amine blush by surface characterization
Summary of Key Results - Amine Blush

• Visual inspection
  – Hard to detect beginning stages
  – Late stages visible

• pH measurements
  – PH increases, then decreases
  – Hard to wet out in many adhesives

• FTIR measurements
  – Detected changes in surface chemistry

• Mechanical properties significantly decrease
Conclusions

• Amine blush can lead to weak bonds
  • time
  • moisture
  • temp
• FTIR can detect amine blush
• pH might be used for quick detection in early stages

Need to account for amine blush when paste bonding
Ongoing and Future Work 2015-16

• Amine Blush in Paste Adhesives
  - Map blushing conditions for various adhesives
  - Quick detection methods- more work on pH-Litmus paper
  - Other detection methods
  - Refinement of FTIR technique
  - Can it occur in film adhesives
  - Can it be mitigated- Combing?
  - Effect of higher temperature cures
Ongoing and Future Work 2015-16

• QA Techniques for Surface Preparation
  – Inverse Gas Chromatography (iGC) for surface energy
  ➢ Compare iGC results with prior research using contact angle (CA) measurements and bond quality

• Study of Aged Bonded Structure-TBD
  • Do adhesive properties change over time?

• Accelerated Aging of Bonds-TBD
  • methods

• Bonded Repair of Aged Aircraft  TBD
  • Surface Prep. QA
Acknowledgements

• FAA, JAMS, AMTAS
• Boeing Company
  – Paul Vahey, Paul Shelley, John Osborn, Kay Blohowiak
• Epic Aircraft
  – David Pate
• Textron Aircraft
  – Shannon Jones
• Precision Fabrics Group
• Airtech International
• UW MSE
Questions and comments are strongly encouraged.

Thank you.
• Amine Blush in Paste Adhesives
  – Amine rich surface can form under certain conditions
  – Can lead to weak/poor bonds with paste adhesive
  ➢ Can amine blush be detected?
  ➢ How much amine blush is acceptable?
  ➢ Working with GA partners (Epic, Textron)

• Bonded Repair of Aged Aircraft (TBD)
  • Surface characteristics of scarfed surface
  • Surface chemistry
  • Surface energy
  • Bond strength