Improving Adhesive Bonding of Composites Through Surface Characterization

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FAA Sponsored Project Information

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• FAA Technical Monitor: Ahmet Oztekin
• Collaborators: The Boeing Co., Henkel, Epic Aircraft, Textron
Detection & effect of amine blush

- **Motivation and Key Issues**
  - Bond failures have been attributed to amine blush

- **Objective**
  - What are the conditions for amine blush and how to measure blush?
  - What are the effects on bond quality?
  - Prevention & Mitigation

- **Approach**
  - Previous work:
  - Cured “traveler” coupons
  - T-peel testing
  - Current work:
  - Wet adhesive FTIR
  - Bondline microscopy
  - T-peel testing
  - Nano indentation
Introduction

- Amine blush is a surface phenomenon in amine cured epoxy systems
- “Whitish, hazy, waxy, oily, soft, sweaty” surface coating
- Problematic in RT cure systems processed in high humidity environments
- Weak layer in bond

Source: AMT composites, amtcomposites.co.za

Environmental Bonding Requirements per Cirrus SR22T SRM
Primary amine in mixed paste adhesive can:

- Diffuse to surface (ΔSE)
  - React with CO₂, H₂O and form blush

- React with epoxide (reactivity)
Introduction

\[ \lambda = \frac{\pi k_1 (\Gamma a)^2}{4D} \]

\( k_1 = \text{epoxy} - \text{amine reaction rate constant} \)
\( \Gamma = \text{Langmuir capacity} \quad a = \text{Langmuir affinity} \)
\( D = \text{diffusivity} \)

- Observed surface concentration of amines in a curing epoxy mixture
- Damköhler number \( \lambda \): ratio of reactivity to diffusivity of primary amine. Low: amines stay at surface. High: amines cure with epoxy
Introduction

• Gaps in knowledge & understanding of amine blush:
• 1) How fast does amine blush form on adhesive surface?
  – Effect of temperature, humidity, adhesive formulation
• 2) Relationship between surface blush and blush layer thickness in adhesive bondlines
• 3) Relationship between blush layer thickness and bond strength
Outline

• Methods
  – FTIR
  – Traditional and Fluorescence Microscopy
  – T-peel bond strength test

• Model compound studies
  – Effect of stoichiometry
  – Effect of thickener concentration

• Commercial system studies
  – T-peel bondline analysis

• Preliminary results
  – Blush Mitigation
  – Nano-indentation
Methods

• Bonding using paste adhesives
• We study the time period between spreading and close-out
• All samples made in lab conditions: 68 °F, 40% RH
Methods - FTIR

- Attenuated Total Reflectance (ATR) FTIR is ideal for analyzing surface effects
- IR beam penetrates ~0.5 - 3 μm of sample depth
Methods – FTIR – Wet adhesive study

- Apply .18 mm (7 mil) adhesive layer to microscope slide
- Collect IR spectra from surface using ATR, after varying exposure time
Methods – FTIR – Wet adhesive study

Carbamate peaks (1564 & 1478 cm\(^{-1}\)) increase as exposure time increases

- Use epoxide as reference peak

\[ \text{blush ratio} = \frac{A_{1564}}{A_{1508}} \]
Methods – Visual analysis techniques

- Blush is hazy white layer, can be visually distinguished from epoxy
- Epoxy emits blue fluorescence under UV light - is fluorescent signature of blush different?
- Need observations from bondline itself rather than representative samples
Methods - Microscopy

- Manufacturing process for microscopy samples
- Dual .18 mm layers squeezed to single .18mm layer
- Sectioned with wafering saw and polished
Methods – Fluorescence Microscopy

- Thermo EVOS FI Microscope
- Blue, green, red wavelengths & filters, designed for biological dyes
- Overlay single-color images to highlight subtle features
- Is blush more obvious with other wavelengths of light?

<table>
<thead>
<tr>
<th>Dye</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAPI</td>
<td>357</td>
<td>447</td>
</tr>
<tr>
<td>GFP</td>
<td>470</td>
<td>510</td>
</tr>
<tr>
<td>Texas Red</td>
<td>585</td>
<td>624</td>
</tr>
</tbody>
</table>
Methods – FTIR Microscopy

- Nicolet Continuum IR microscope
- Collect FTIR spectra from different sample locations
- 50 μm² areal resolution
Methods – T-peel bond strength testing

• T-peel measures bond strength (ASTM D 1876)
• Schematic of T-peel specimens
• Photo: Specimen during testing
Methods – T peel bond strength testing

- T-peel sample manufacturing
- Dual .25 mm (10 mil) layers squeezed to single .25 mm (10 mil) layer
- Cut into 300 mm long T-peel specimens with 75 mm unbonded length
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## Model Formulations

<table>
<thead>
<tr>
<th>Epoxy monomers</th>
<th>S.E.(dynes/cm)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGDDM MY720</td>
<td>~48 (high viscosity)</td>
<td>Tetrafunctional epoxy</td>
</tr>
<tr>
<td>DGEBA Epon 828</td>
<td>43.0</td>
<td>Bifunctional epoxy</td>
</tr>
<tr>
<td><strong>Amine monomers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DETA</td>
<td>41.8-47.0</td>
<td>Pentafunctional short chain aliphatic</td>
</tr>
<tr>
<td>MMCA Laromin C260</td>
<td>35.2</td>
<td>Tetrafunctional, cyclic</td>
</tr>
<tr>
<td>POPDA Epikure 3274</td>
<td>~20-25</td>
<td>Tetrafunctional, long-chain aliphatic “blush resistant”</td>
</tr>
</tbody>
</table>

- 2 standard epoxies and 3 standard curing agents
Model formulations

- Fastest-forming, most extensive blush in TGDDM-DETA
- Little blush in other TGDDM-containing formulations
- No blush in DGEBA-containing formulations
• Downselect to TGDDM-DETA for extended study
• Blush formation visible on same timescale as FTIR
Model formulations – TGDDM-DETA FTIR

- Add fumed silica (Cab-o-sil) for closer approximation of paste adhesive
- Increasing wt% Cab-o-sil causes slower, less extensive blush
- Viscosity-based change to Damköhler number?

\[ \text{blush ratio} = \frac{A_{1564}}{A_{1508}} \]
Model formulations – TGDDM-DETA microscopy

- Inclusions of amine blush visible at 7.5 min
- Full bondline presence at 10 min
- 20 min and 40 min extensive presence
Model formulations – TGDDM-DETA Fluorescence

- Overlay of DAPI and GFP images
- Blush inclusions visible at 7.5 minute exposure (increased intensity)
- Blush presence indicated at 10, 20, 40 min
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• 5 commercial paste adhesives studied
• Can be grouped by rate of blush formation:
  • Fast: Magnolia 56, Hysol EA 9360
  • Slow: PTM&W ES 6292, Hysol EA 9394
  • None: Hexion MGS 418
Commercial systems – EA 9360 microscopy

- Blush formation is visible in bondline after 20 minutes post-spread exposure
- Ratio of blush to bondline thickness increases, plateaus over time
Images using DAPI (blue) and GFP (green) filters
Blush layer clearly visible
Commercial systems – EA 9360 FTIR microscopy

- FTIR microscopy samples 50 μm area
- Compare blush layer to epoxy layer
- Interior layer is carbamate formation
Commercial systems – microscopy of T-peel bonds

- Amine blush visible in 30 minute sample with fluorescence imaging
Commercial systems – EA 9360 T-peel strength

- 90% reduction in T-peel strength as exposure time increases
- Failure modes change from cohesive to adhesive (interface)
- Caveat: working life 50 minutes
Commercial systems - Comparison of metrics

- As a predictor of T-peel strength loss, FTIR is conservative
- Bondline thickness ratio is more accurate
- Visible blush in bondline: indicator of bond strength problems
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• Mylar and mesh placed on adhesive & removed before FTIR scan
• Plastic adhesive spreader used to rake over surface before FTIR scan
• All effective at reducing amine blush
• Highly dependent on operator use
• Thickness of bond line reduced due to adhesive removal
New UW capabilities for bonding research

- Hysitron TI 180 Nanoindenter with nanoDMA and heated stage
- Capable of mapping $E$, $T_g$, hardness across a bondline at 3nm resolution
- Potential for quantifying blush via mechanical property change
- Other bonding research and micron scale mechanical measurements
Nanoindentation

- Depth of penetration measured and area of contact is determined by indenter geometry (Berkovich tip)
- Hardness is found by dividing force by area of contact
- Reduced modulus is calculated based on slope of unloading curve
Load Control Mode

- Nanoindenter applies specified load and holds for several seconds, then releases load.
- Force vs. Displacement curve generated.
  - Viscoelastic behavior can be seen at the peak, as the material continues to deform while the 1000µN force is held for 5s.

Acrylic adherend: 1000µN force applied at 100µN/s and held for 5s then removed.
Displacement Control

- Nanoindenter indents samples to a specified depth, holds for several seconds, then withdraws from sample
- Force vs Displacement curve generated
  - Stress Relaxation
  - Load drops while displacement held constant

Acrylic adherend: 1000 nm deep indent applied at 100 nm/s, held for 5s, then removed at 100 nm/s
AFM Imaging Mode

- Surface topography is measured and image generated
- AFM image to the right shows surface topography around an indent
- Scan Line Profile image shows surface roughness as the probe travels forward and reverse horizontally across sample
- 3D image of surface can be created using surface topography data
XPM (Accelerated Property Mapping)

• XPM modes allows for high speed nanoindentation of area up to 94µm x 94µm
• Fast, shallow indents are performed and Force vs Displacement curves generated
• Arrays of individual measurements can be plotted to generate maps of mechanical property gradients
  – Reduced modulus and hardness

\[
E_r = \frac{S\sqrt{\pi}}{2\sqrt{A}} \quad H = \frac{P_{\text{max}}}{A}
\]
XPM on Bond Interface

- Epoxy-Acrylic interface probed via 4x4 XPM array
- Each pixel correlates to a single indent
- Hardness and reduced modulus of epoxy about 1.3x higher than acrylic
Conclusions

• Blush formation rates can be observed with FTIR analysis
  – Model systems slowed by increasing filler concentration
  – Commercial paste adhesives can be categorized by formation rate

• Microscopy can identify blush layers in bondlines
  – Layer thickness grows over time
  – Fluorescence microscopy a valuable technique

• Blush layers reduce T-peel bond strength
  – How much? Unclear as yet

• As metric for T-peel strength loss:
  – FTIR peak blush ratio is conservative
  – Visible bondline blush layer is accurate within current data
Future work on amine blush

• Explore mitigation strategies
  – Protective disposable film layer
  – Disruptive disposable mesh layer
  – “Combing” to break up blush
  – Thick adhesive layers for aggressive, turbulent squeeze-out

• Explore humidity dependence
  – 10-60% RH environmental chamber

• Correlate blush layer thickness with bond strength
  – Decouple working life from blush formation rate
  – Study T-peel strengths in other adhesives
Looking forward

• **Benefit to Aviation**
  • Better assurance that paste adhesives and use conditions will result in good bonds
  • Establish a correlation between blush detection methods and bond strength for industry use

• **Future needs**
  • Further study on several adhesive systems
  • Standardized optical microscopy techniques
  • Correlation with Nano-indenter mechanical property measurements
Thank you! Questions? Suggestions?
Other work slides
Introduction

- Amine blush in paste adhesives leads to lowered bond strength – danger of kiss bonds & delaminations
- 2010 – Wing disbond/fuel leak attributed to amine blush in bonded structure – FAA Airworthiness Directive issued
Introduction

- Proposed reactions for amine blush
- Primary amine reacts with CO\(_2\) to form carbamate (salt, network)
- Carbonates and bicarbonates also proposed
Methods - FTIR

<table>
<thead>
<tr>
<th>Species, bond type</th>
<th>IR peak (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxide, aromatic</td>
<td>1508</td>
</tr>
<tr>
<td>Carbamate, asymmetric</td>
<td>1550-1610</td>
</tr>
<tr>
<td>Carbamate, symmetric</td>
<td>1450-1350</td>
</tr>
<tr>
<td>Carbamate, stretch</td>
<td>1300-1260</td>
</tr>
<tr>
<td>Protonated amine</td>
<td>1479-1474</td>
</tr>
</tbody>
</table>

- FTIR studies of amine blush indicate carbamates form \(\text{blush ratio} = \frac{A_{1564}}{A_{1508}}\)
- Epoxide aromatic 1508 cm\(^{-1}\) as a reference; asymmetric carbamate \(~1560\) cm\(^{-1}\) as blush indicator
Commercial systems – EA 9360

- EA 9360 paste adhesive hardener forms white crystals in air
- FTIR indicates carbamate formation
- Does using open-air exposed hardener affect blush formation rate?
Commercial systems – EA 9360 hardener open-air

- Samples of hardener exposed to ambient for 0-40 days
- Mixed with epoxy, spread for blush formation rate study
Commercial systems – EA 9360 hardener open-air

- As part B exposure increases, blush ratio formation appears to slow
- After 40 days, some induction period before blush formation onset
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