Improving Adhesive Bonding of Composites Through Surface Characterization

Effect of amine blush on bond quality

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Improving Adhesive Bonding Through Surface Characterization

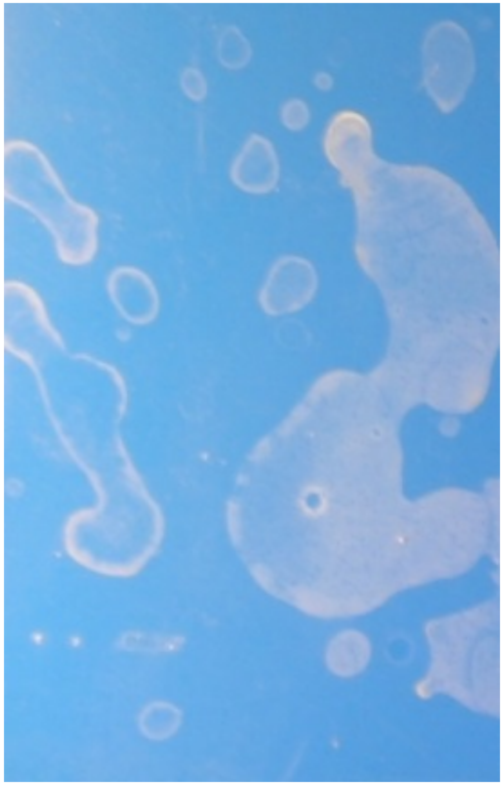
- Motivation and Key Issues
  - Weak bonds in paste adhesives from amine blush
  - Can amine blush be detected?
  - Effect on bond quality?
- Objective
  - Develop quality assurance techniques for amine blush
- Approach
  - Investigate adhesives, humidity, temperature and time
  - Characterize adhesive 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 CO_2
  - Moisture
  - Time
  - Temperature
- Formation of carbamates and carbonates
- Cesena wing skin delamination incident (Dec. 2010)



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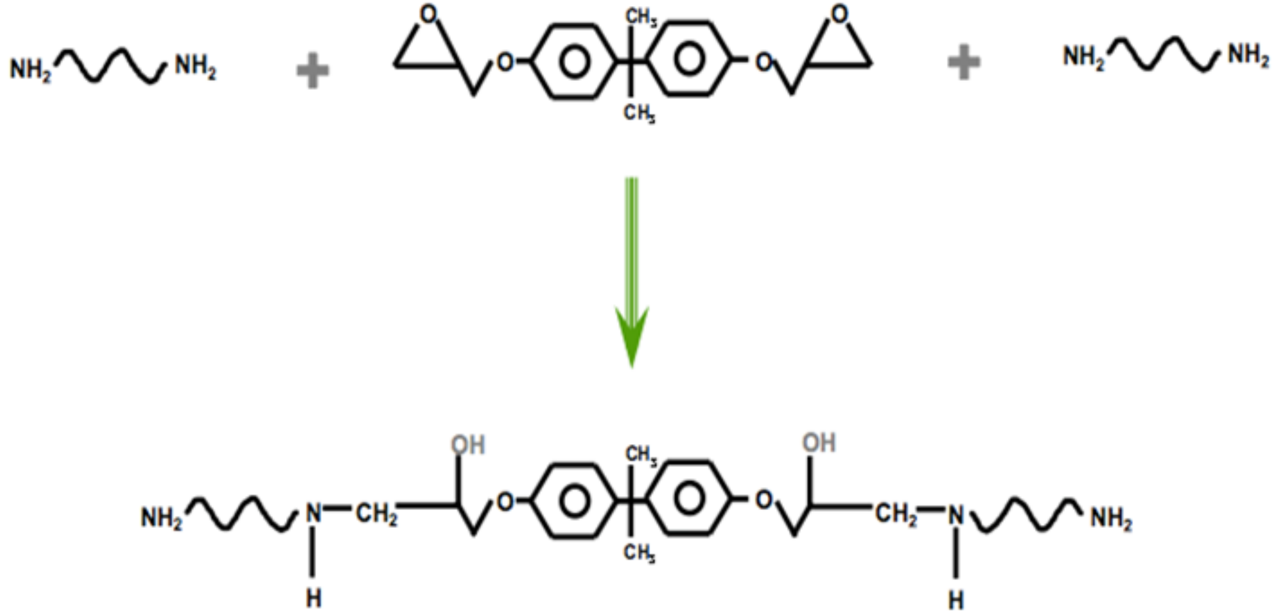
Amine Blush

What is supposed to happen to an adhesive?

- Linear Mw build-up....



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Amine Blush

What happens instead?

CO_2 + H_2O => H_2CO_3
From the atmosphere

H_2CO_3 + RNH_2 => $RNHCOOH$ + H_2O
Amine curing agent — carbamic acid

$RNHCOOH$ + RNH_2 => $RNH_3{}^{+-}OCONHR$
carbamate

Primary and Secondary Amines

↓

Ammonium Carbamate

Tertiary Amines

↓

Ammonium Bicarbonate

Problems:

-surface tackiness

-incomplete cure

-poor adhesion

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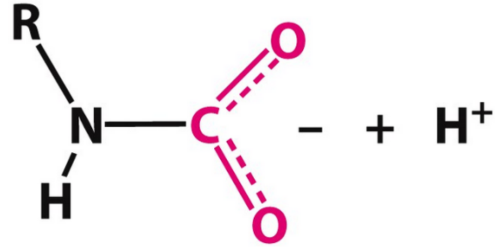
Detecting Amine Blush - FTIR Peaks

☆ Carbamate

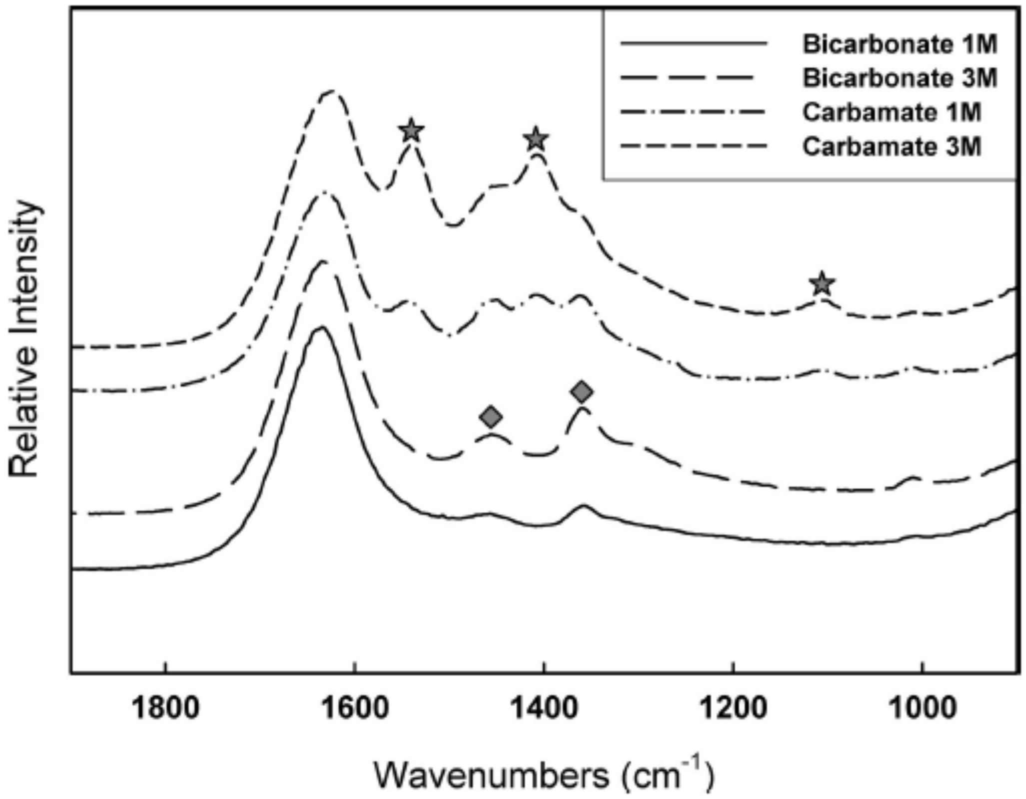
~1100 cm^-1 (C=O symmetric stretching)

~1400 cm^-1 (C-N stretching)

~1550 cm^-1 (C=O asymmetric stretching)



Carbamate



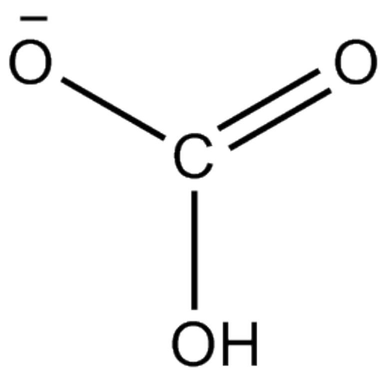
Analysis of the CO2 and NH3 Reaction in an Aqueous Solution by 2D IR COS. Formation of Bicarbonate and Carbamate, 2008.

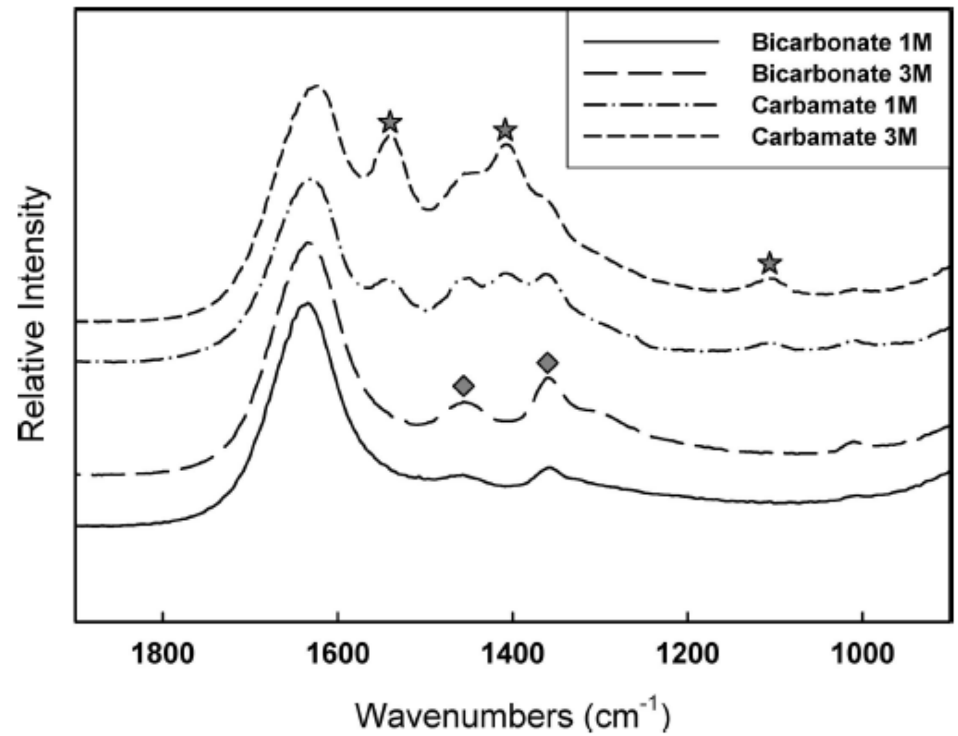
Detecting Amine Blush - FTIR Peaks

- 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

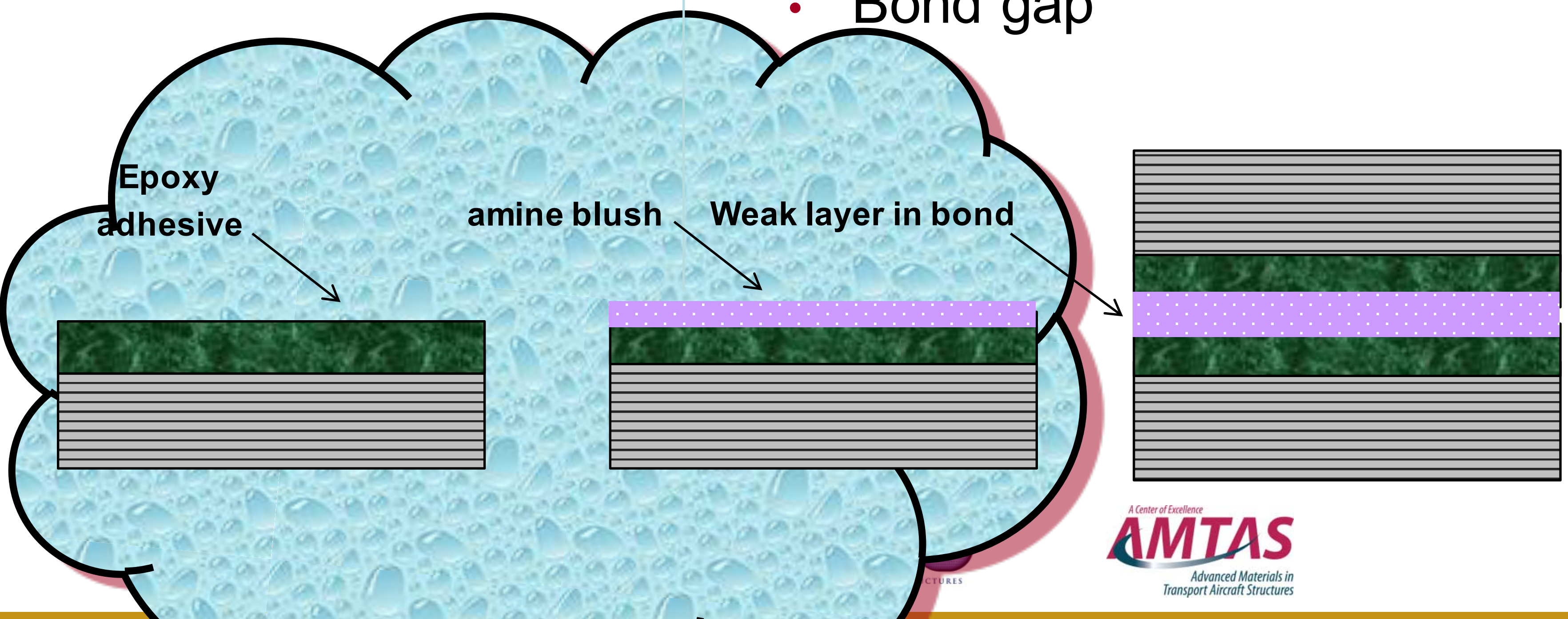
Blush Production

Intrinsic Factors

- Amine content
- Diluents
- Gel time
- Stoichiometry
- Compatibility

Testable Factors

- ✓ Temperature
- ✓ Humidity
- Induction
- ✓ Time after application
- Primer thickness
- Bond gap



Materials and Methods

- Toray T800/3900 laminates
  - DCB Unidirectional panels
  - Lap Shear $[0/+45/-45/0]_2$ 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

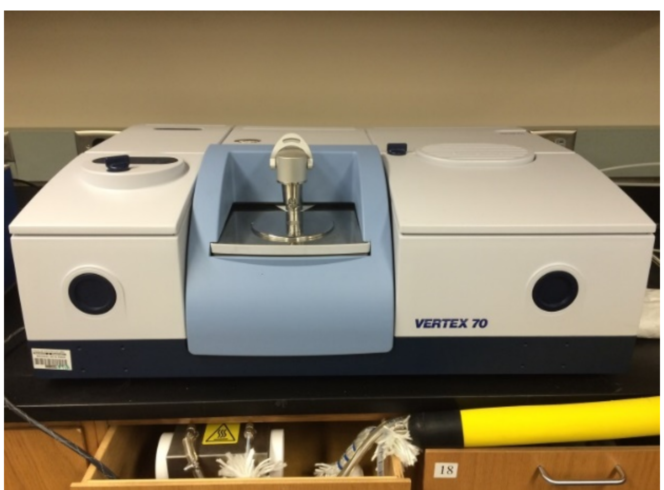
Adhesives

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

Blush Production and Detection

Equipment

- Hum/Temp Sensors
- Heratherm OGS100
- Litmus paper
- Bruker Vertex 70FTIR
  - ATR



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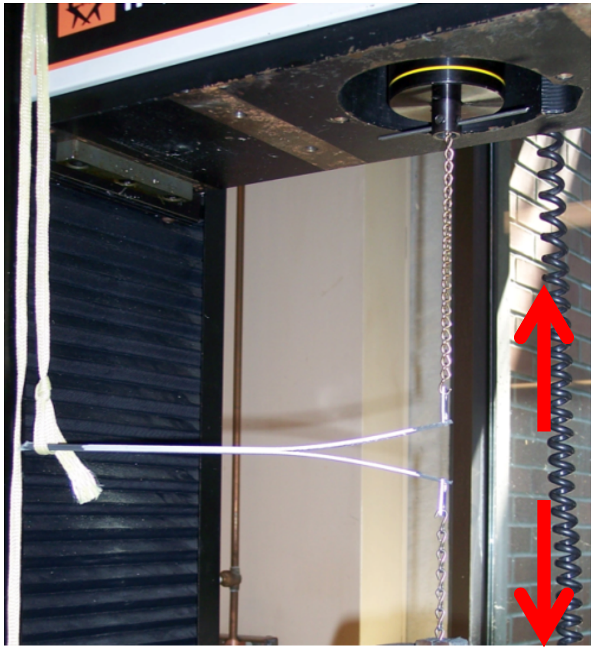
Bond Quality

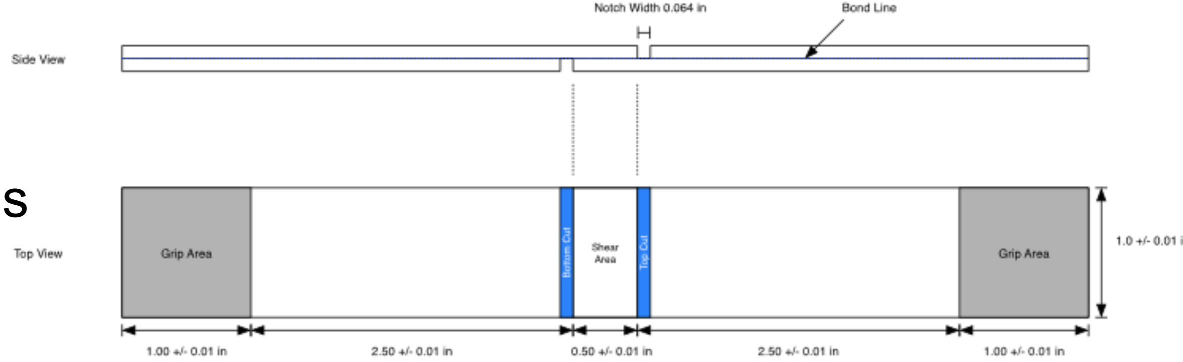
- DCB Mode I strain energy release rate (G_{IC}) and failure mode
  - 3 samples per condition
  - Area method for G_{IC} calculations
  - E: area of curve
  - A: crack length
  - B: specimen width

$$G_{IC} = \frac{E}{A \times B}$$



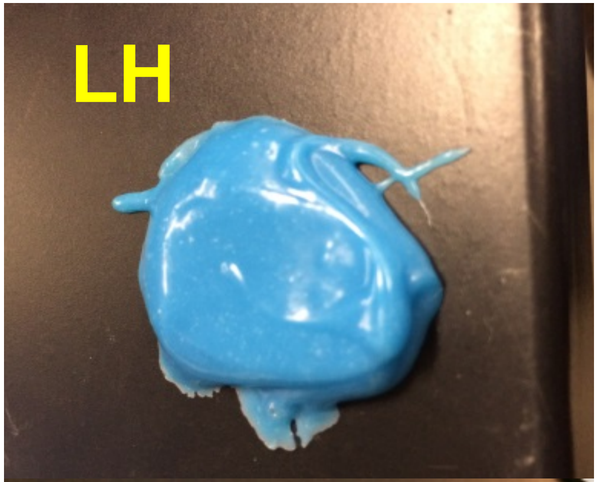
DCB Test

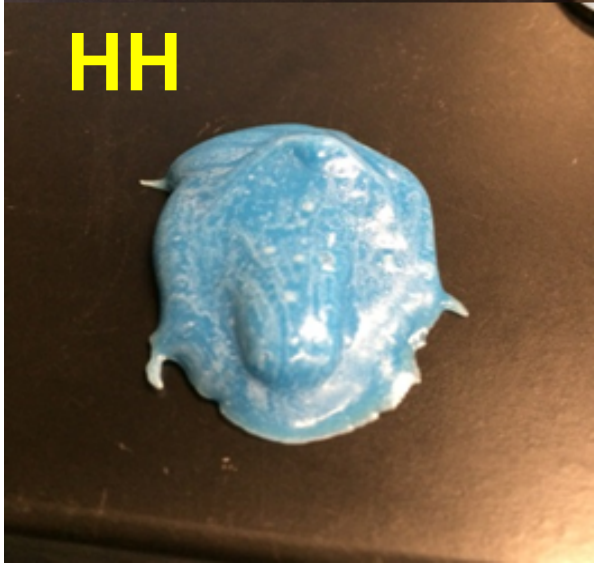
- Double Lap Shear
  - 5 samples per conditions



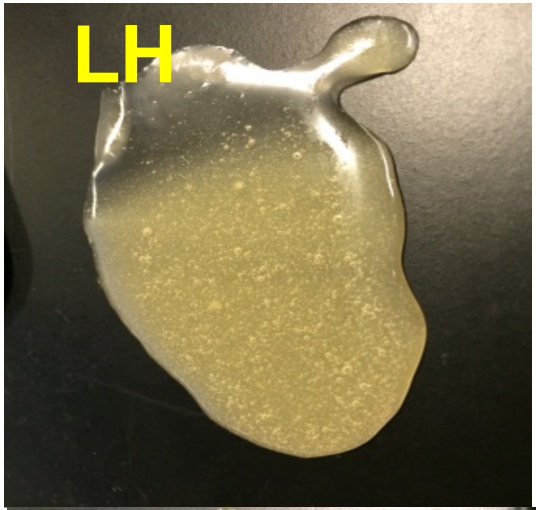
Visual Test Results

Henkel EA 9360





Henkel EA 956



Visual Test Results

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

30 mins

1 hour

2 hours

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pH Test Results -ProGlass 1300

Time (mins)	Humidity (%)	Temperature (F)	Proglas 1300
0	83	72	7
15	83	72	7
30	83	72	9
45	83	73	11
60	84	75	11
75	84	75	8.5
90	85	77	8.5
105	85	77	8
120	85	77	8

Amines are alkaline – high pH

Carbamates and carbonate are salts - more neutral

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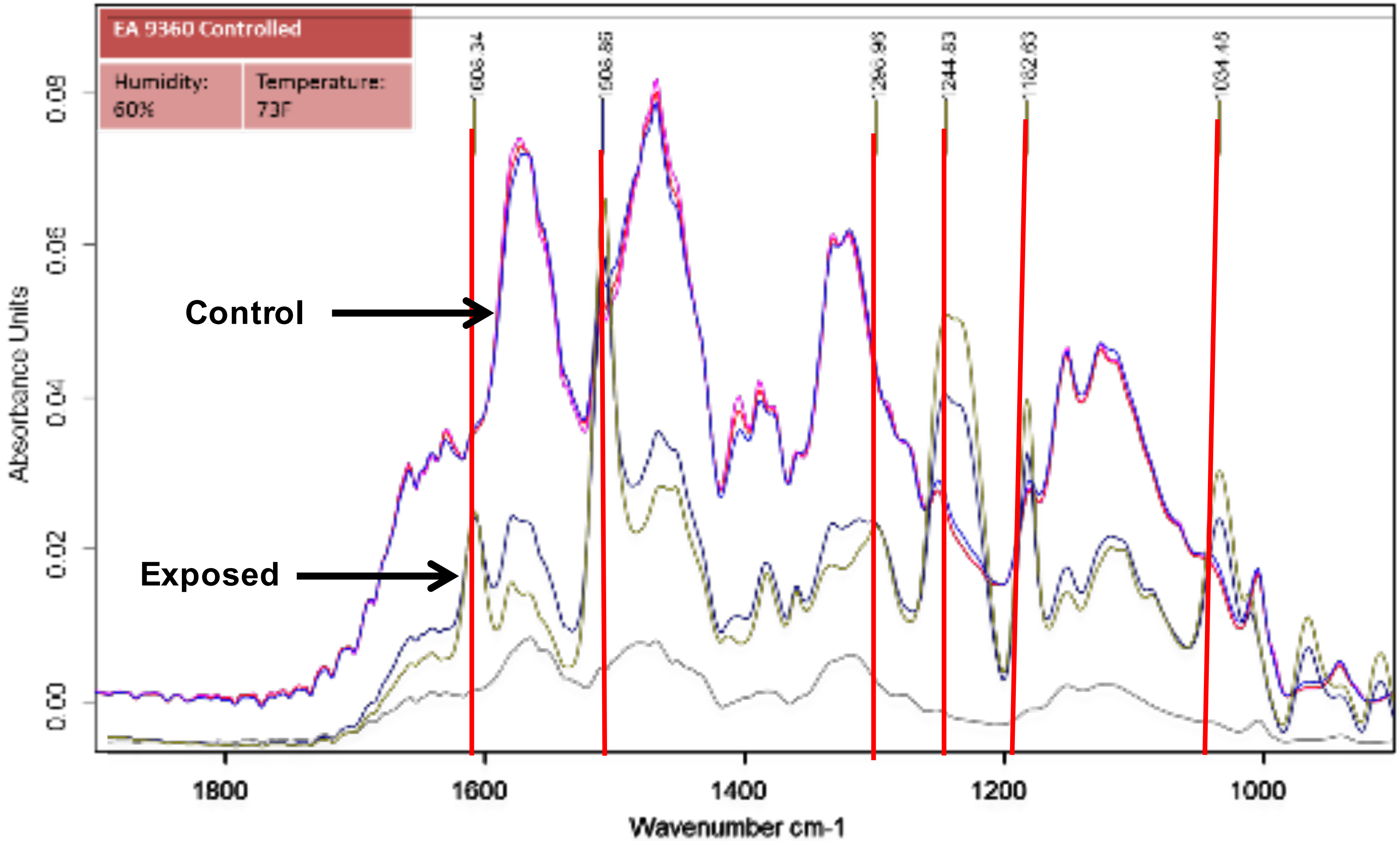
FTIR Results-Humidity Exposure



- **Carbamate and carbonate peaks develop with exposure**

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Summary of Surface Characterization

Blush Detection in Adhesives

Material	Visual	pH	FTIR
MGS L285/H-285	YES*	NA	YES
MGS L285/H287	retest	retest	retest
ProGlas 1300	YES*	YES	YES
Hysol 956	YES*	NA	YES
Hysol 9360	YES*	NA	YES

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

- **FTIR was most consistent in detecting all stages**

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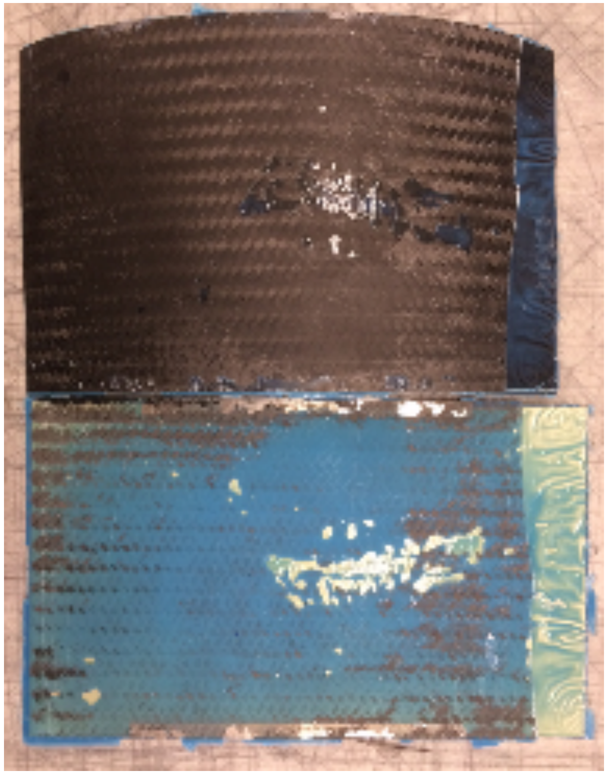
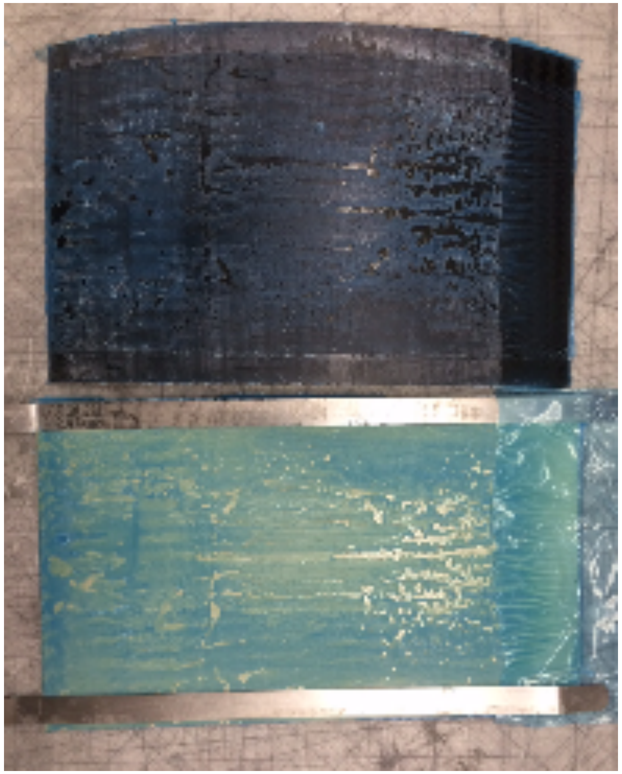
RAT Results-Humidity Exposure





Panel Specimens (1-9)	Failure Assessment
Controlled	Interlaminar/Cohesive
Low Humidity	Cohesive in Adhesive
High Humidity	Cohesive in Adhesive

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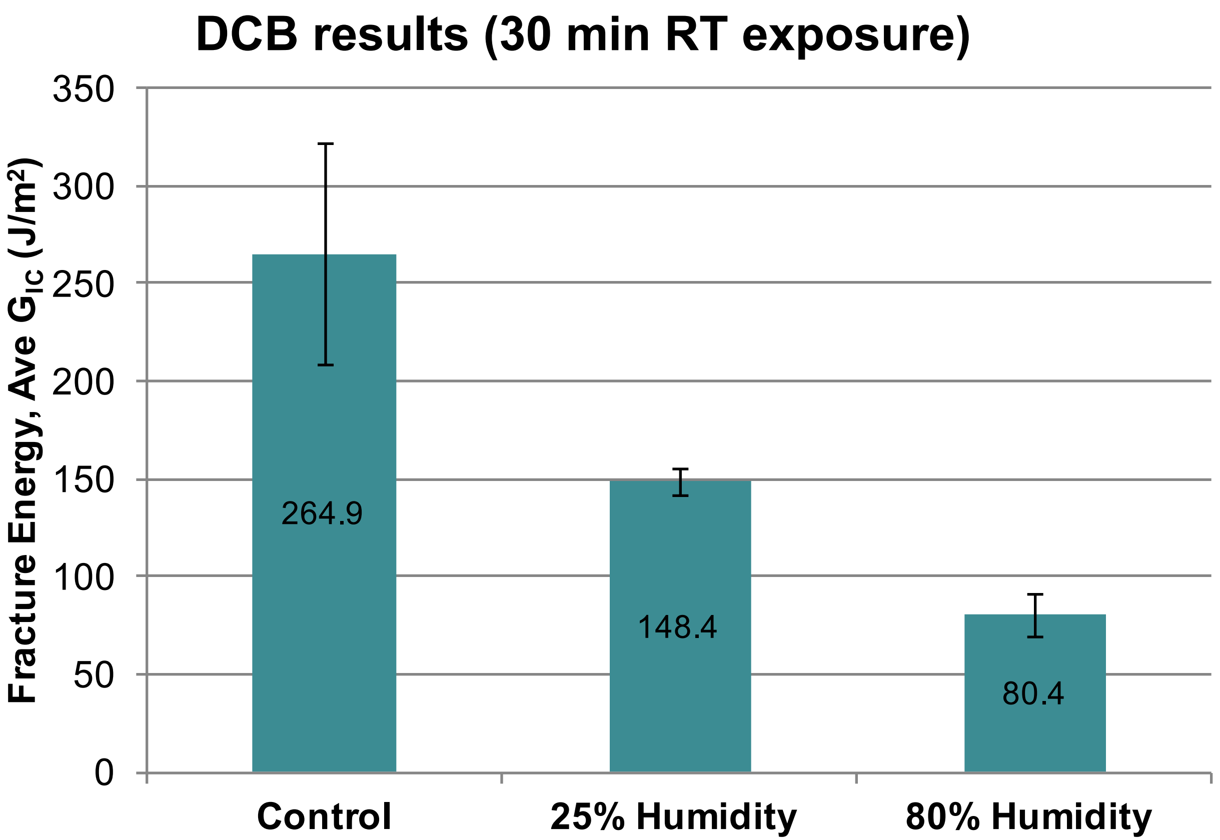
DCB Results-Humidity Exposure

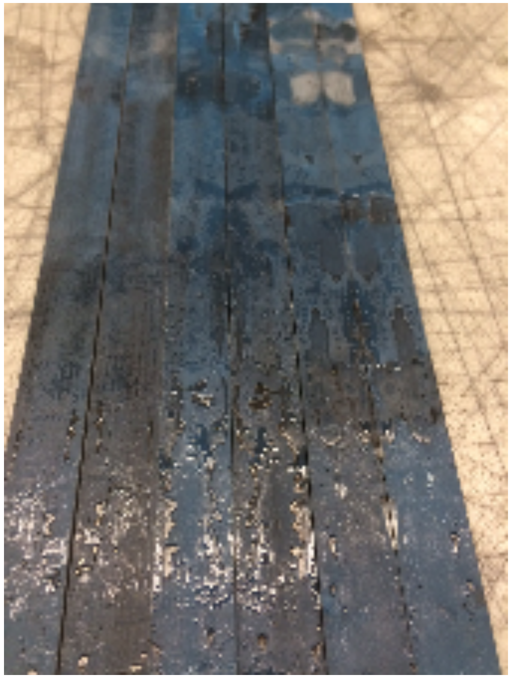


- G_{IC} values decreased significantly after 30 minute exposure to 25% and 80% RH
- Differences correspond with amine blush by surface characterization

DCB Results-Humidity Exposure

Control (left)

Low RH (center)



High RH (right)

- Fracture mode- Cohesive in adhesive- but different appearance
- Differences correspond with amine blush by surface characterization

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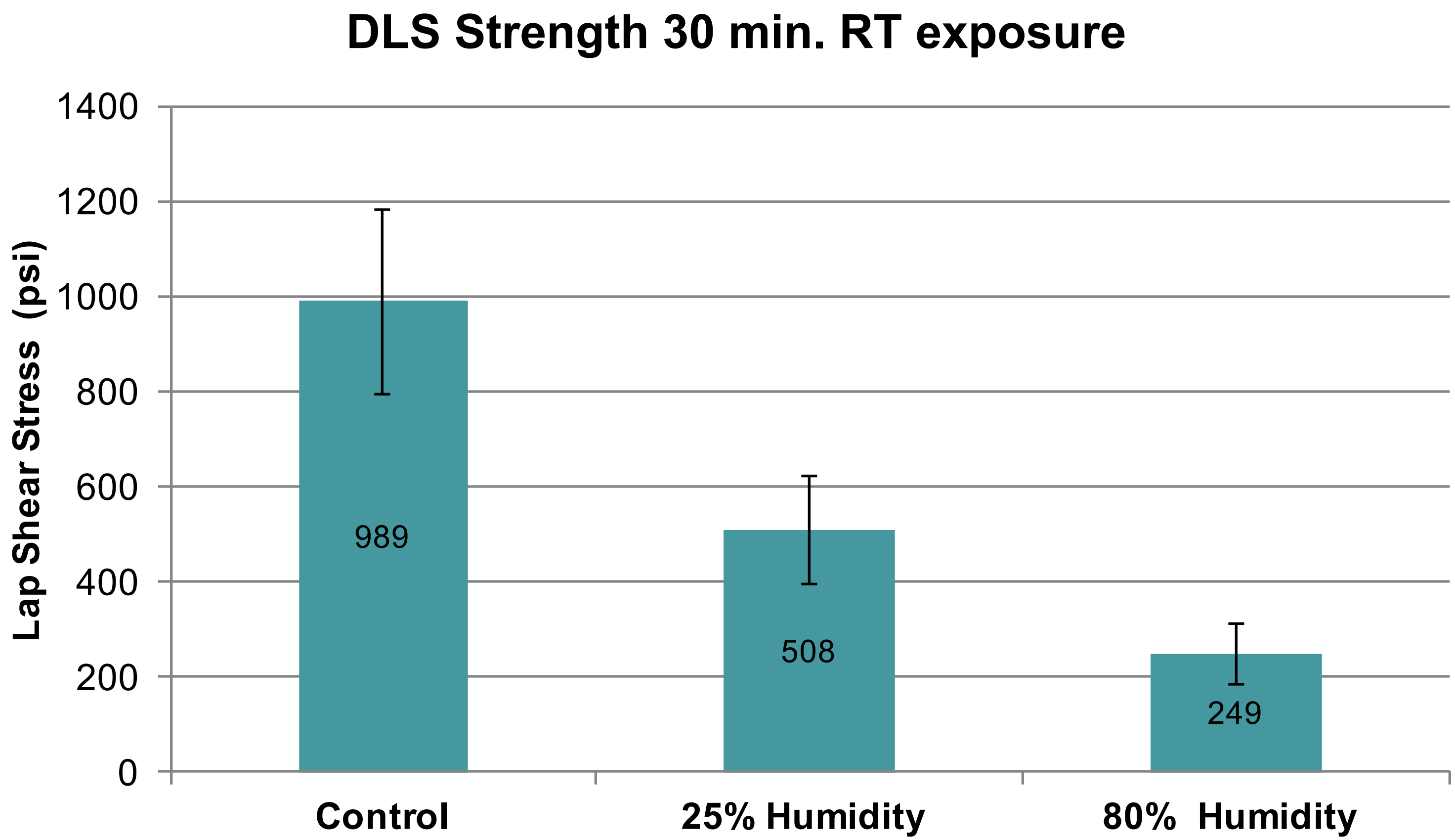
DLS strength Results-Humidity Exposure



- G_{IC} values decreased significantly after 30 minute exposure to 25% and 80%
- Differences correspond with amine blush by surface characterization

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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

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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

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- Boeing Company
  - Paul Vahey, Paul Shelley, John Osborn, Kay Blohowiak
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  - David Pate
- Textron Aircraft
  - Shannon Jones
- Precision Fabrics Group
- Airtech International
- UW MSE

Questions and comments are strongly encouraged.

Thank you.

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- 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

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