Improving Adhesive Bonding of Composites through Surface Characterization

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Participants

- Federal Aviation Administration
  - Ahmet Oztekin, Cindy Ashforth, David Westland, Curtis Davies
- Center of Excellence in Advance Materials in Transport Aircraft Structures (AMTAS)

- The Boeing Company
- Epic Aircraft
- Textron

- University of Washington Department of Material Science & Engineering
  - Dr. Brian Flinn, Principal Investigator
  - Marc Staiger , Ryan Toivola, Shawn Baker, Amy Chiu, Alex Gray (Blush)
  - Rita Taitano Johnson (iGC)

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Two Tasks

1. Surface Characterization using Inverse Gas Chromatography (iGC) Methods
   - Characterization of Adherend Surfaces
     - Effect of surface preparation on bond quality

2. Amine Blush in Epoxy Paste Adhesives
   - Characterization of Bondline
     - Effect of bonding environment on bond quality

Introduction

Questions:

- What are the conditions for blush formation?
- What are the effects on bond quality?
- Can blush be mitigated?

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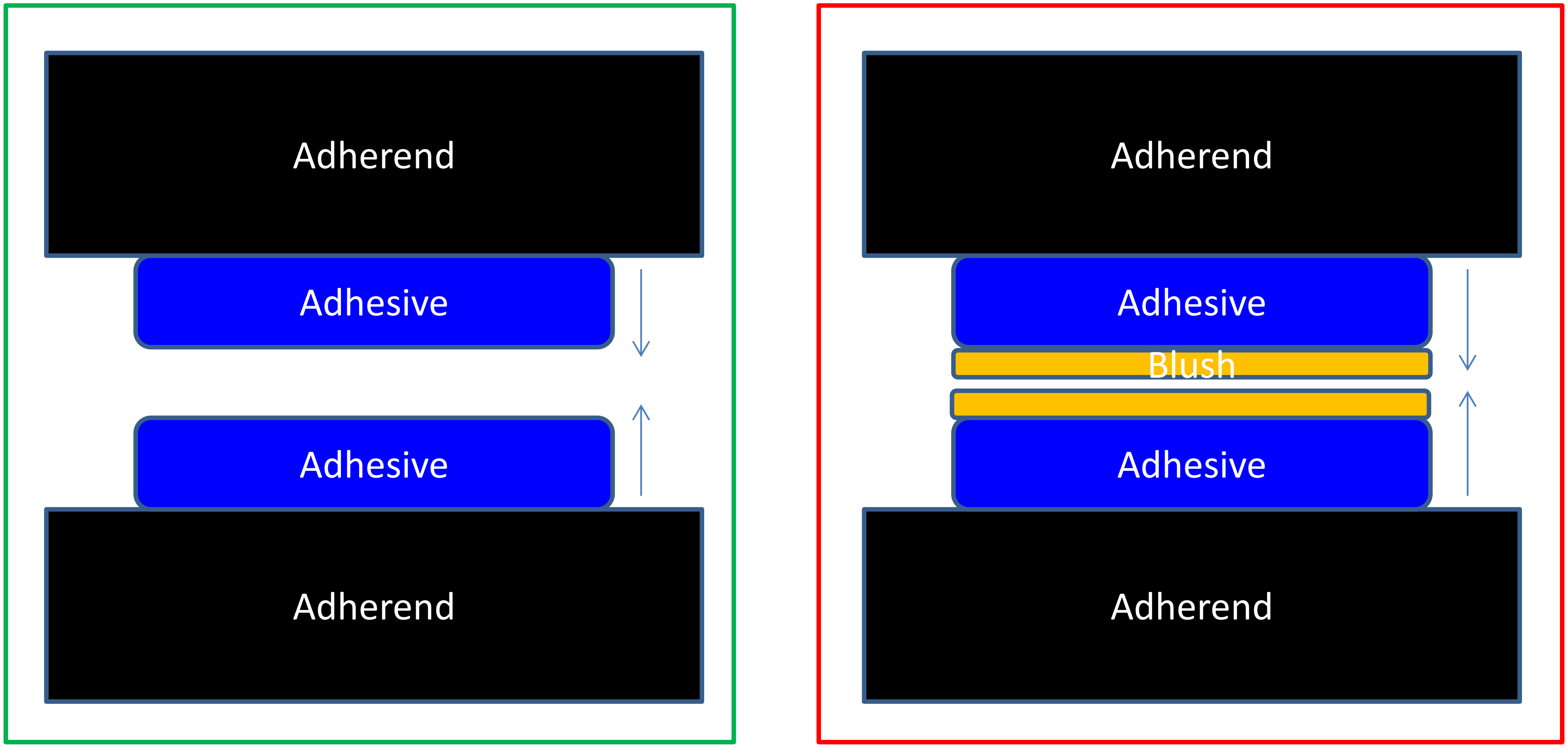
Amine Blush



- Amine blush is a surface phenomenon in amine-cured epoxy adhesives
- Blush layer forms interface between adhesives, leading to lower strength, hard-to-detect 'kiss bonds'

Amine Blush Formation

$$R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NH^+COO^-$$

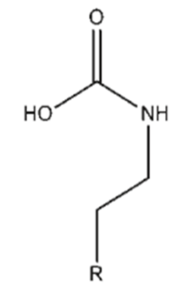
Primary or secondary amines — Carbamic acid zwitterion

$$R_1R_2NH^+COO^- + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \quad *$$

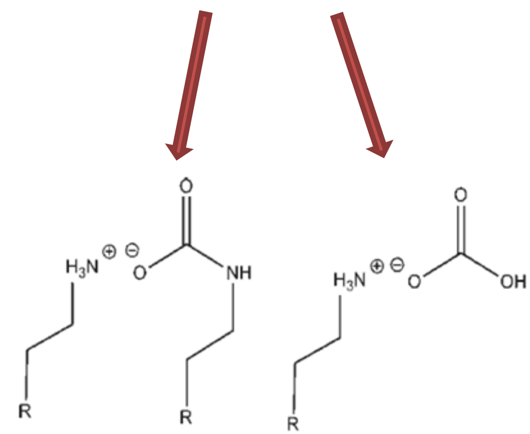
zwitterion — an ammonium carbamate

$$R_1R_2R_3N + CO_2 + H_2O \rightleftharpoons R_1R_2R_3NH^+ + HCO_3^- \quad **$$

tertiary amine — an ammonium bicarbonate



Carbamic Acid Formation (unstable)



* Carbamate Formation

** Bi-Carbonate Formation

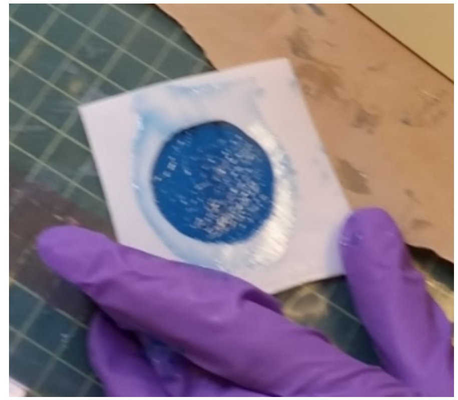
- Bloom – Mobile amine component diffuses to the surface creating greasy, tacky layer.
- Blush - The amine rich layer reacts with the atmosphere to potentially form carbamic acid, carbamates, carbonates, or bicarbonates.
- The bloom/blush process degrades the overall quality of the desired epoxy-amine crosslink reaction.

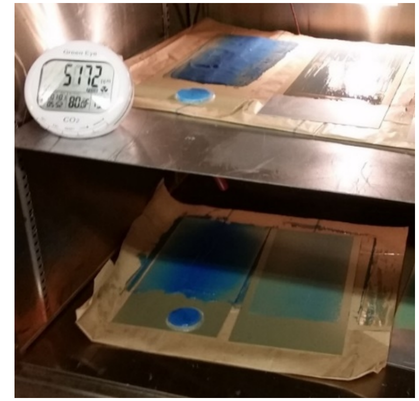
Mitigation Techniques

Surface scraping

- Environmental Controls
- Incubation Time
- Surface Combing/ Scraping
- Protective Film
- Limit amine mobility
  - Bulky amine molecular structure
  - High resin system viscosity

Previous Work





- **DOE focused on 4 variables:**
  - Exposure time after mixing
  - Temperature
  - Humidity
  - CO2
- **Mechanical Strength Measurement**
  - T-Peel (ASTM D1876)
- **Surface Characterization**
  - FTIR (ATR)

- Samples placed in a conditioning chamber at predetermined conditions.
- Pressed in a hydraulic press.
- Post cured after 48 hrs.
- Samples cut on a waterjet

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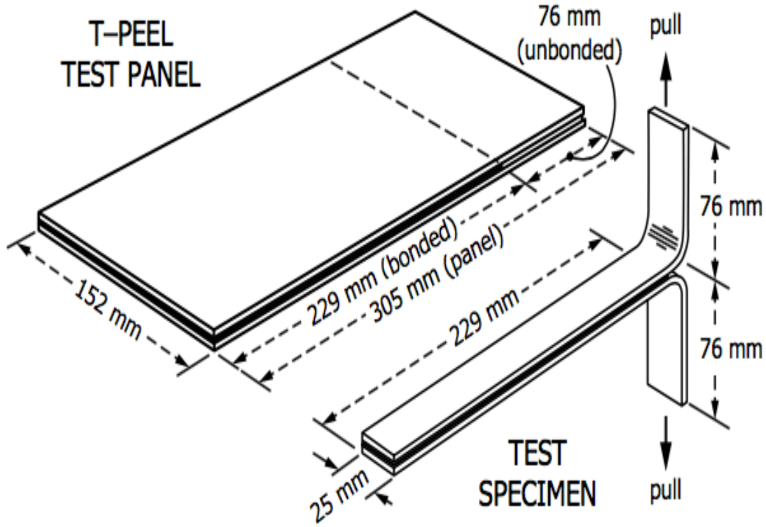
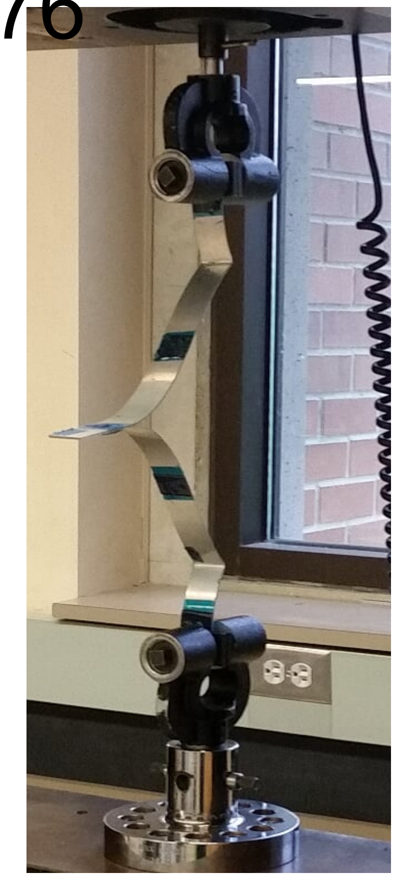
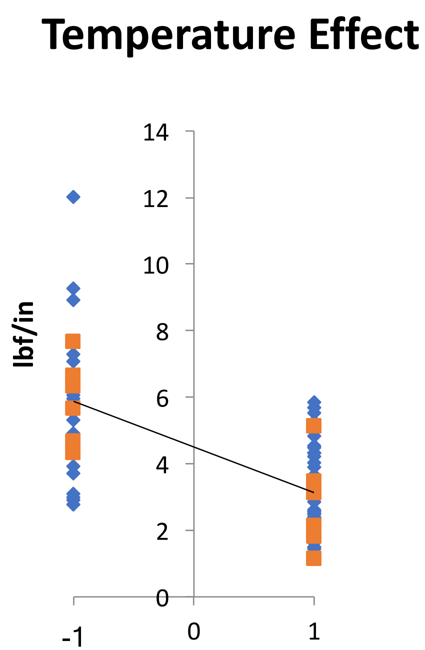
T-Peel Test – ASTM D1876



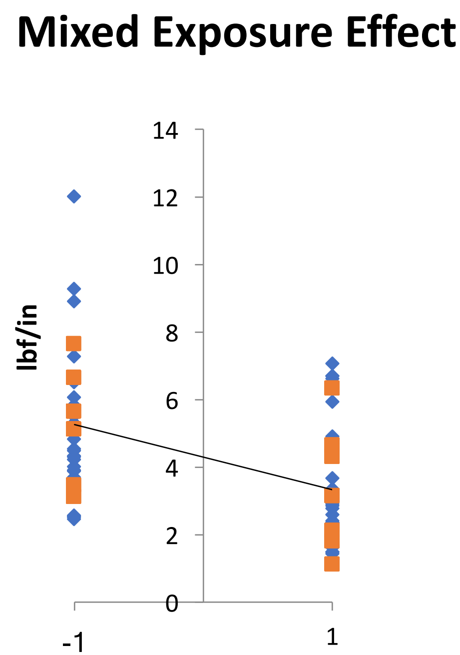


- Aluminum substrates (primed)
- Bond does not extend full length of substrates
- After bonding, non-bonded substrate ends bent to a 90º angle
- Ideal failure is mode 1 - cohesive

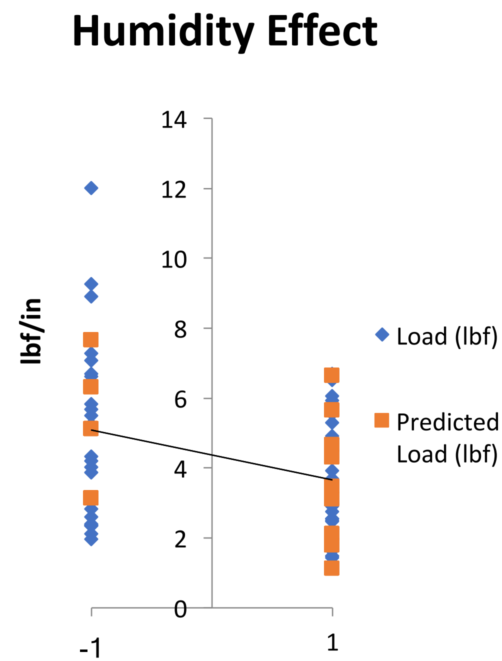
Previous Work – Mechanical Results



High – 80 °F
Low – 60 °F



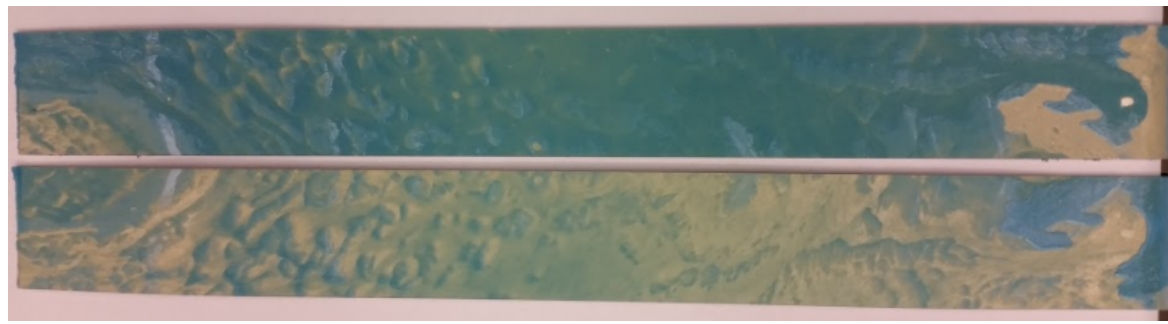
High – 45 min
Low – 15 min



High – 85 %RH
Low – 40 %RH

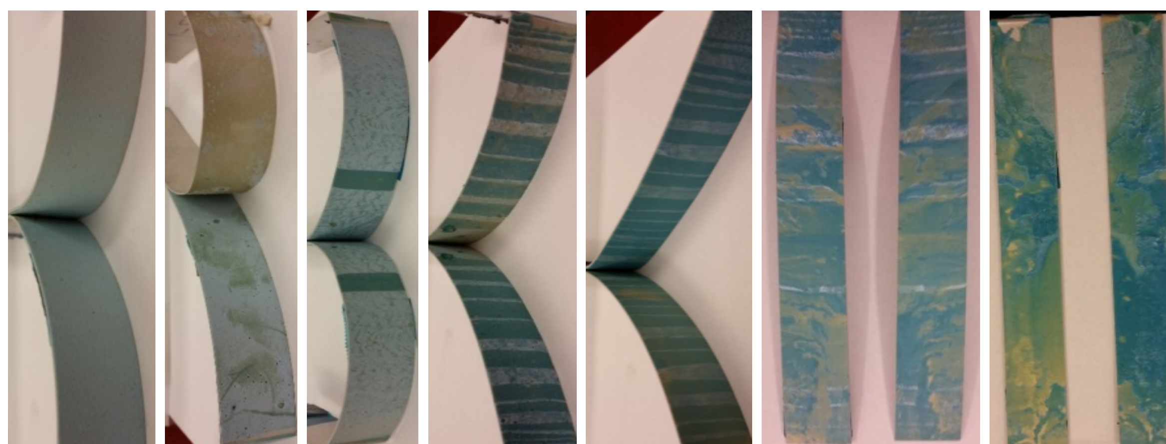
- Exposure time, humidity and temperature had the most effect on T-peel strength

Previous Work – Failure Mode



High Strength Bonds

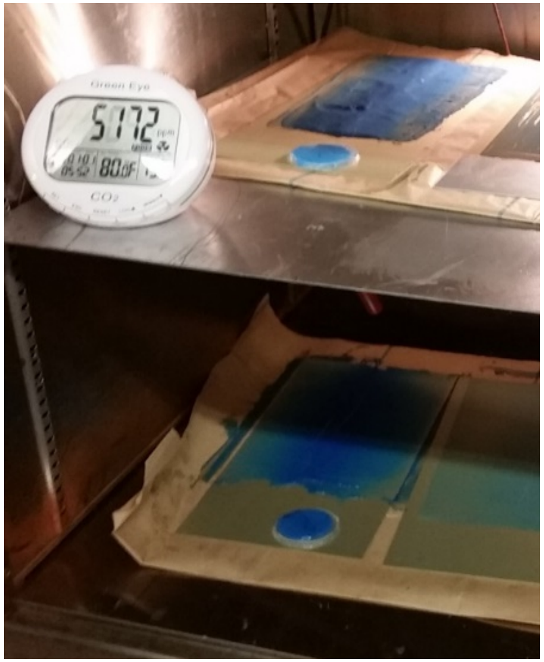
- Unexposed bond
- Fracture travels through the bulk adhesive

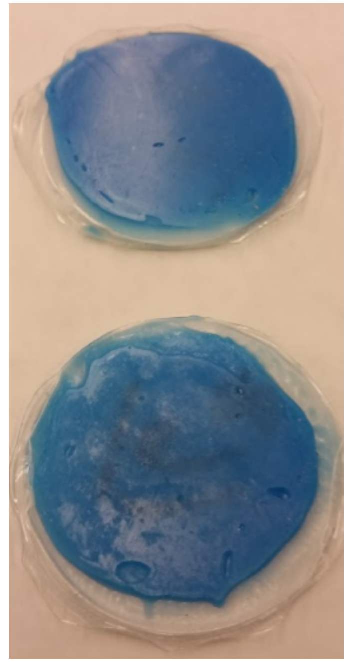


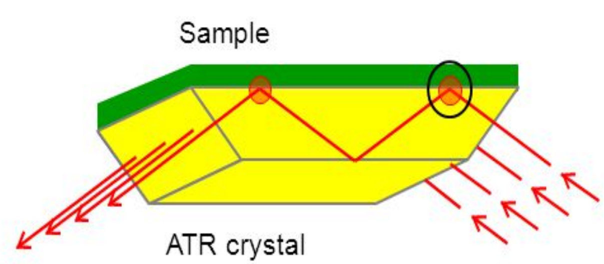
Low Strength Bonds

- High exposure Conditions
- Fracture travels through the bondline interface
- Flow lines from squeeze-out are visible

FTIR Surface Characterization







- Attenuated Total Reflectance (ATR) FTIR sampling used to characterize surface chemistry changes.

- Measures surface absorption/ transmittance of IR energy
  - 1^{st} 0.5 to 5 microns.

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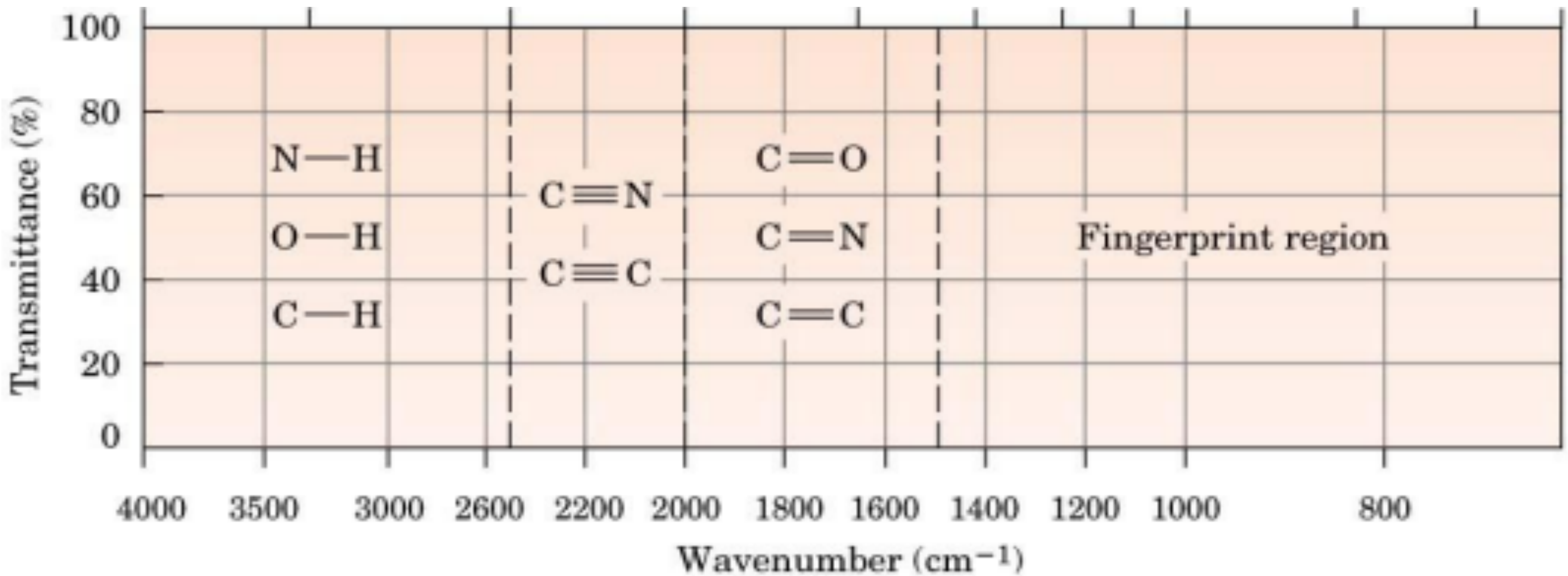
FTIR Surface Characterization



- Vibrational frequencies of bonding groups are determined through a spring and mass model. Where k = bonding stiffness and m = atomic mass.

$$\omega^2 = \frac{k}{m}, \quad \omega = \sqrt{\frac{k}{m}}$$

Epoxy Network IR Vibrational Absorbance

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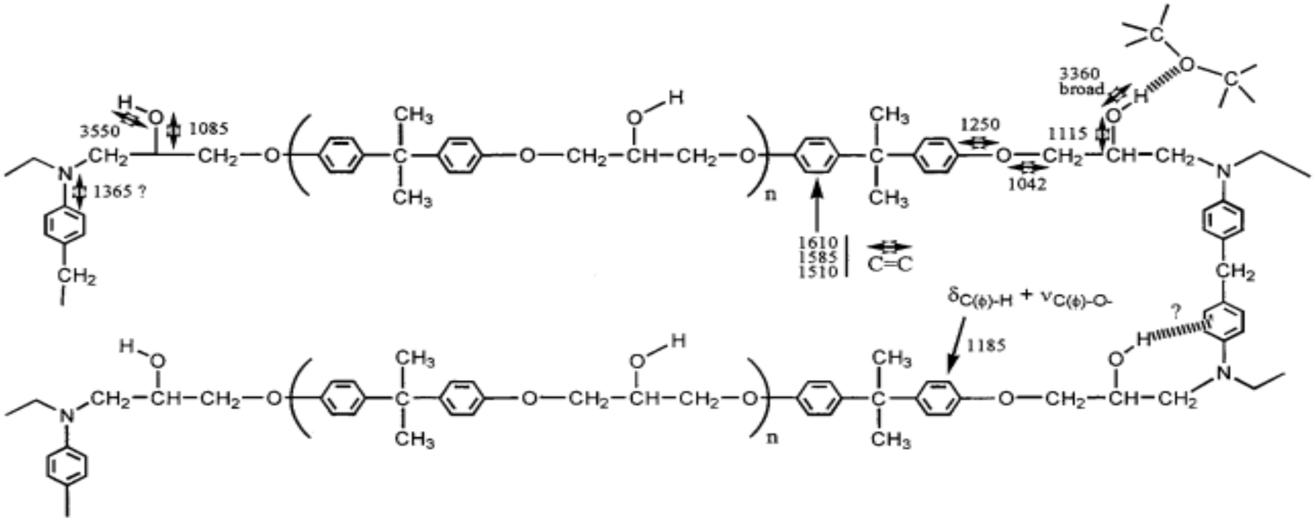
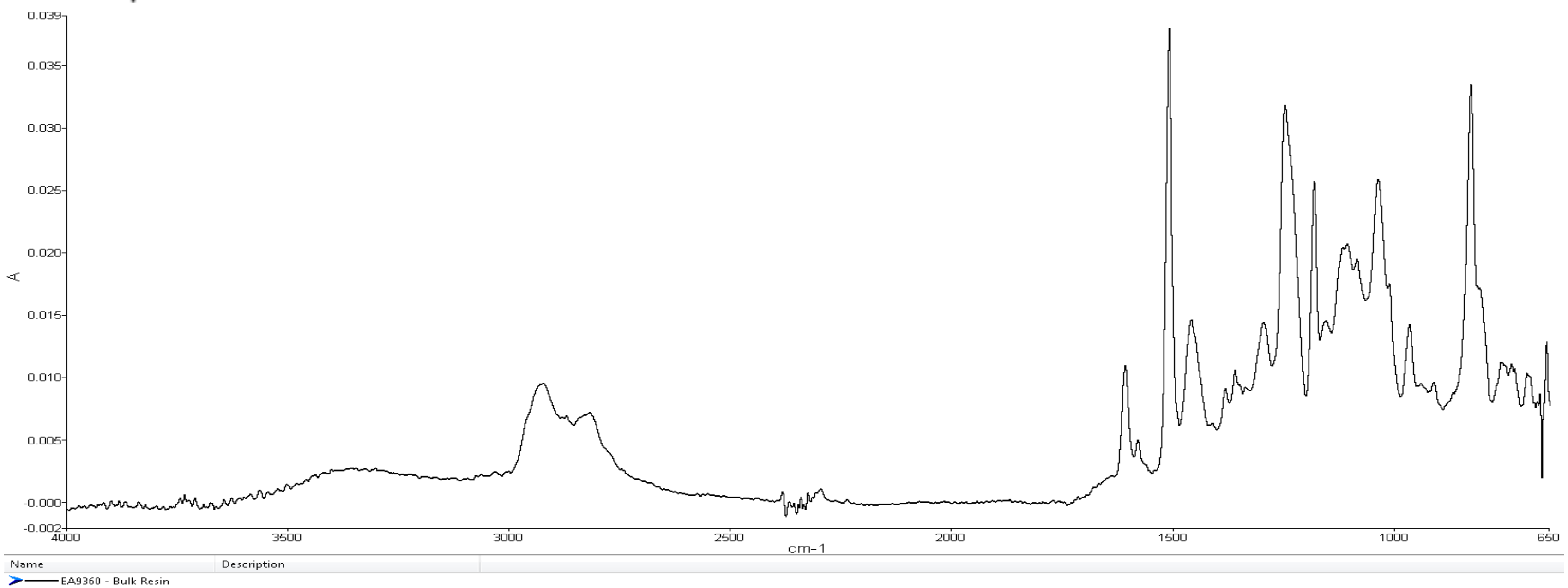


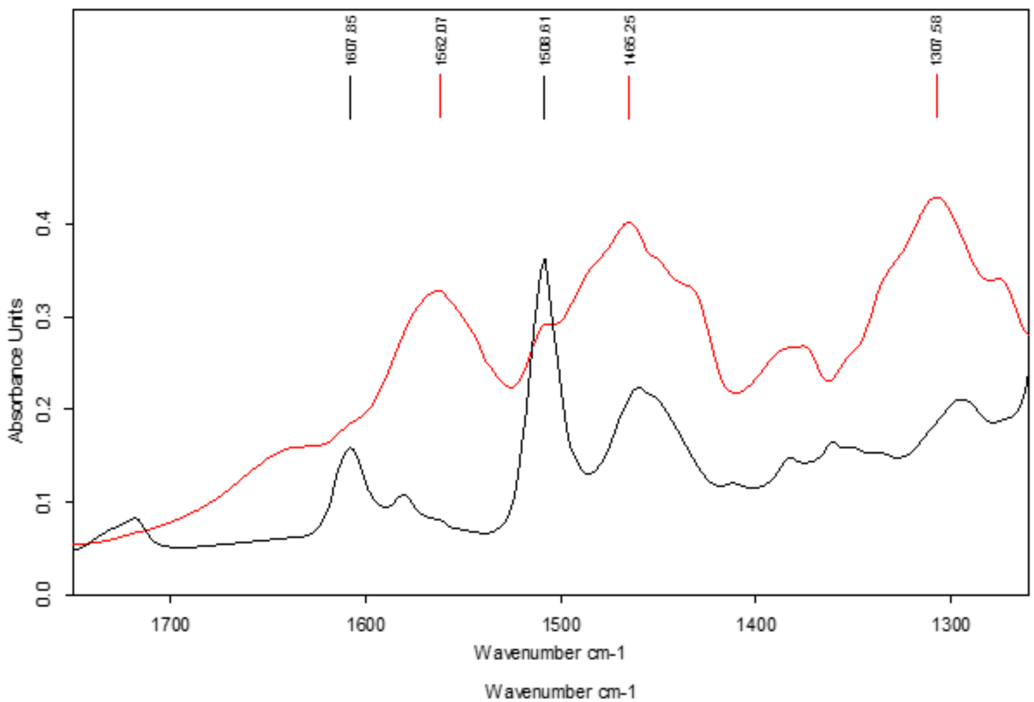


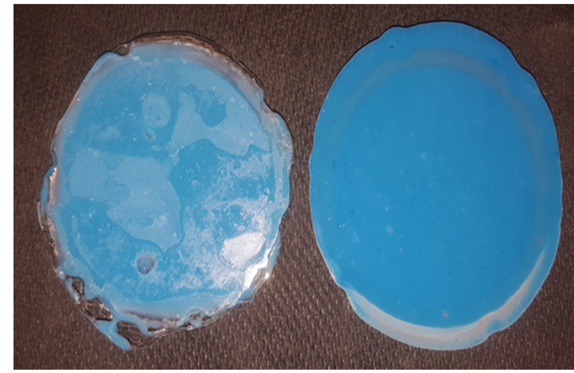
C-H, N-H and O-H Stretching

Double and Triple Carbon Bond Bending

Single Carbon Bonds and Functional Group Bending/ Vibrational Modes. (Finger Print Region)

Previous Work – FTIR Analysis

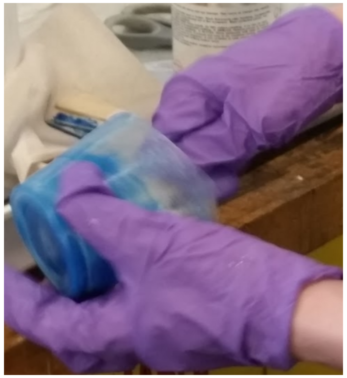


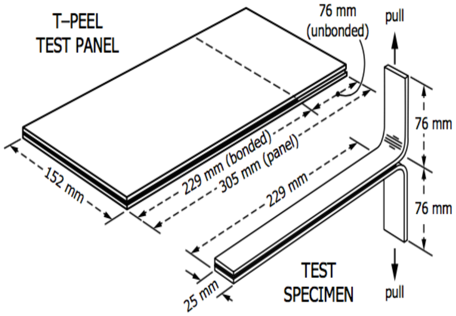


- Identified the important peaks corresponding to amine bloom/blush/salt formation
- Confirmed with FTIR measurements of “traveler” coupons
- Arrows indicate growth of blush/bloom related peaks

Current Research Plan

- Examine FTIR traveler coupons made of <u>uncured</u> epoxy bond lines rather than epoxies after cure.
- Examine bonds with lower exposure times than studied in previous research.
- T-peel specimens with varying times between spreading and close-out
- Examine environmental conditions for post-spreading exposures and correlate with FTIR.





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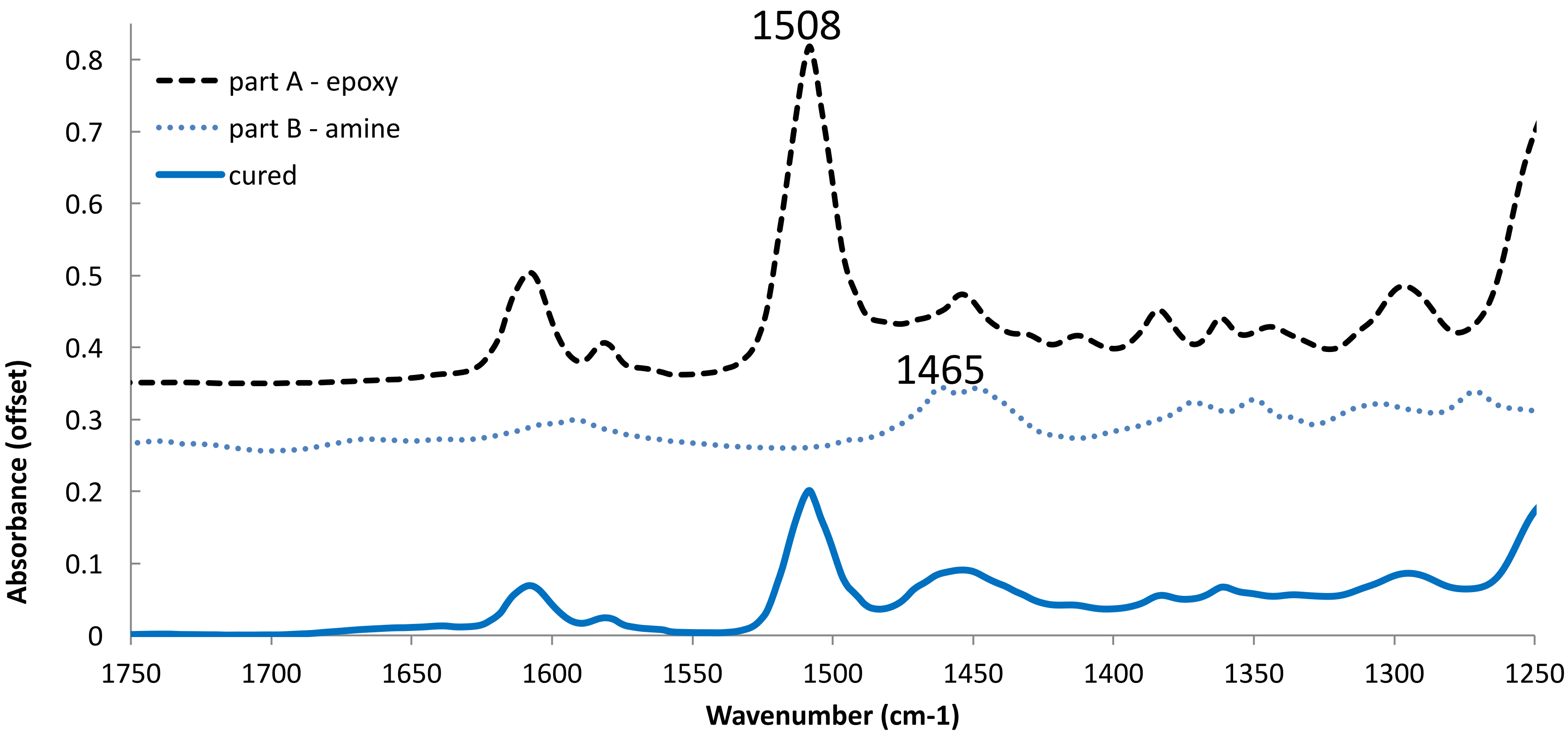
FTIR results



- Characterization of amine blush: Close examination of 1750-1250 cm^{-1} spectral region
- Assign 1508 cm^{-1} peak to aromatic ring of epoxy monomer (reference peak intensity)
- 1465 cm^{-1} peak assigned to amine monomer
- Both peaks present in fully cured adhesive
- Nothing in region 1510-1575 cm^{-1} in either monomer or cured adhesive

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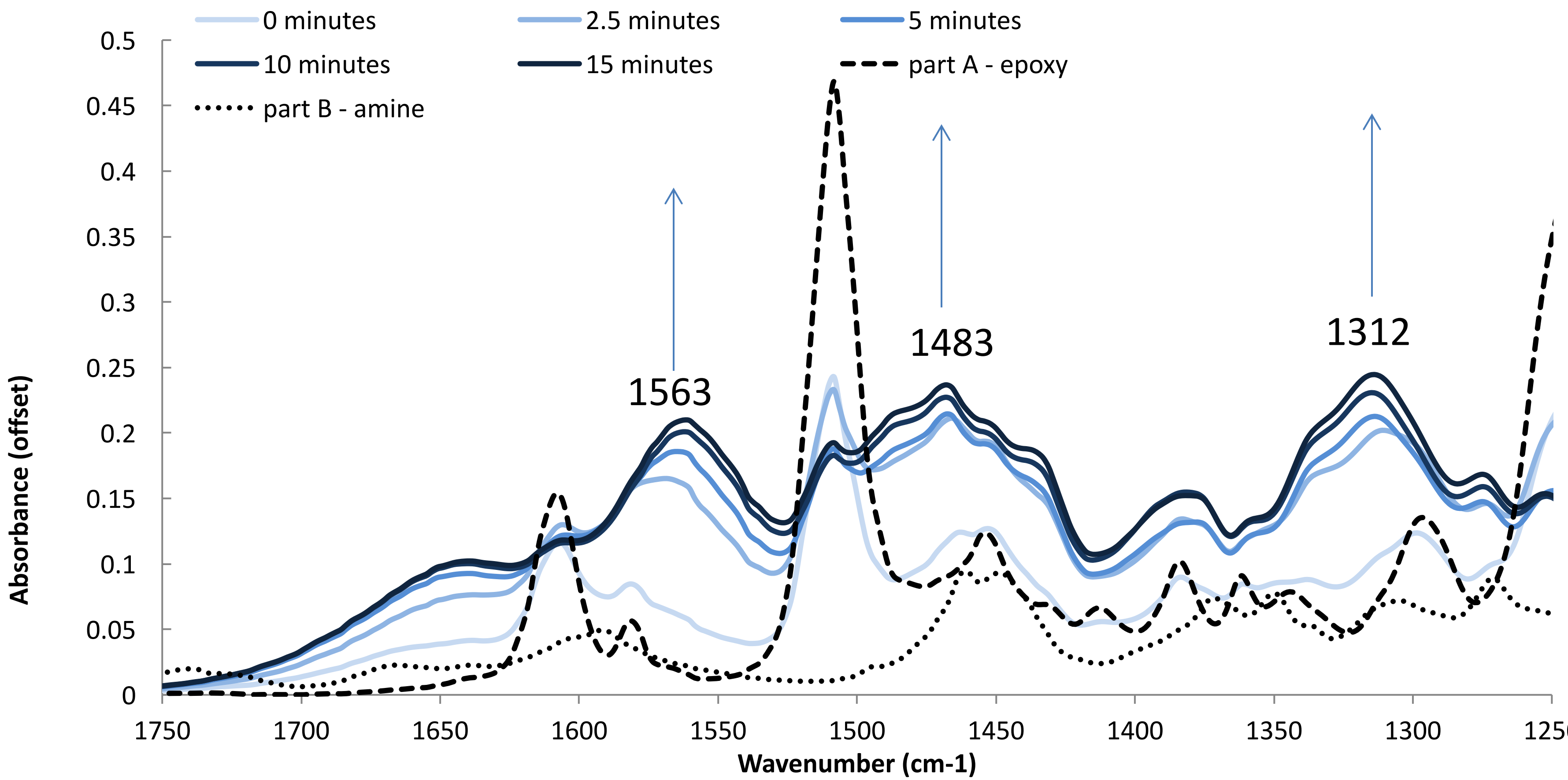
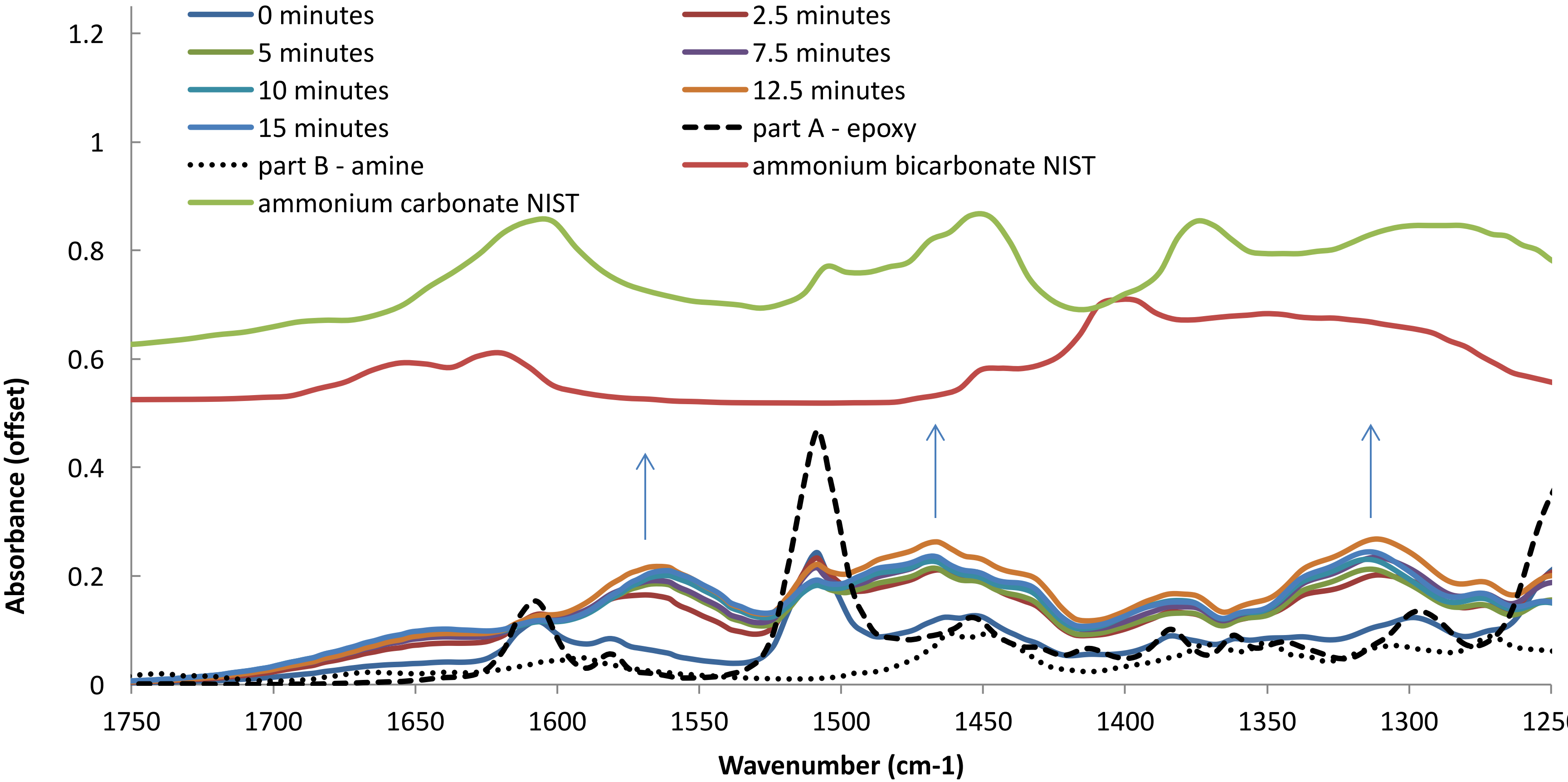
FTIR Results



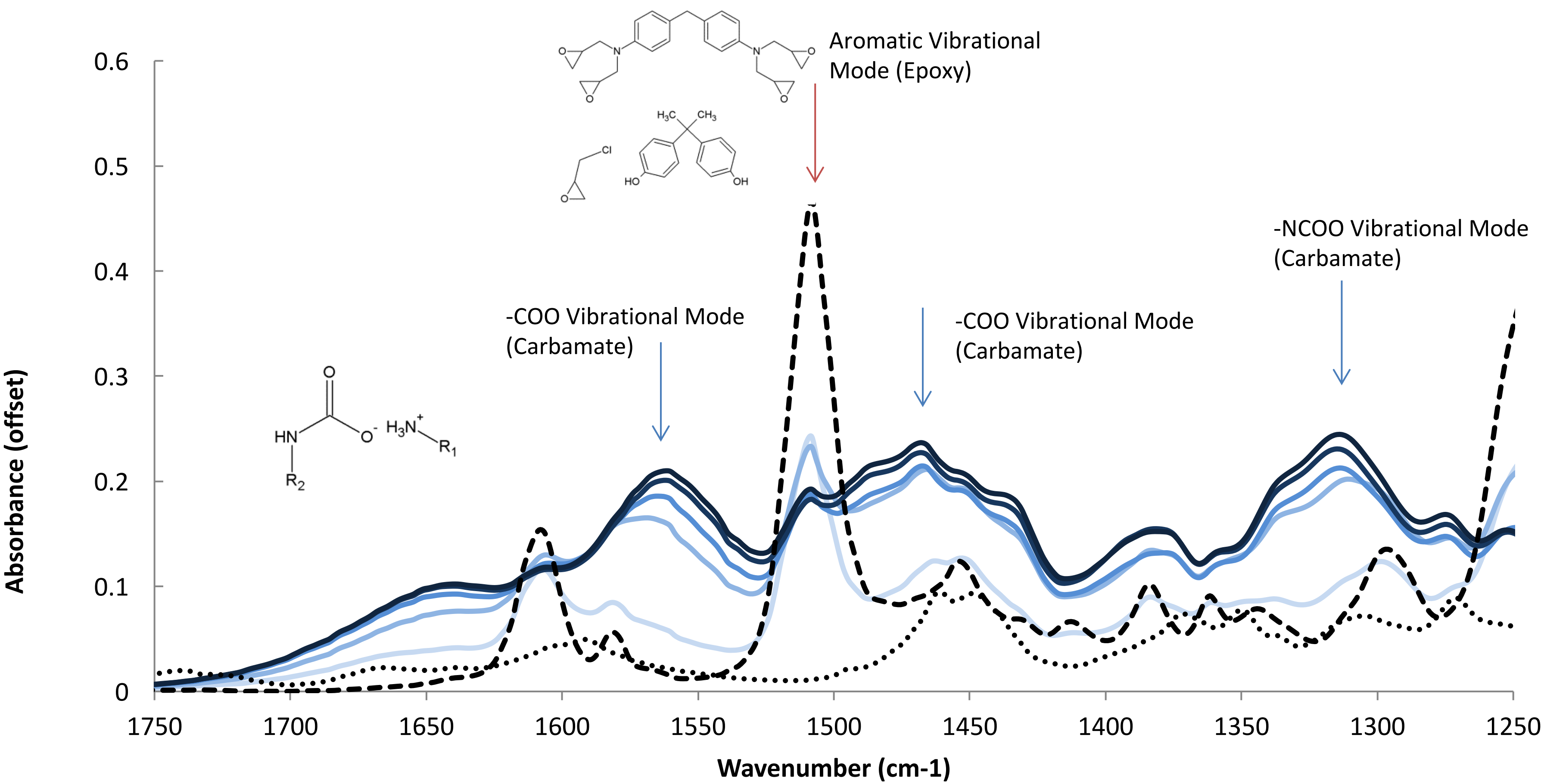
- Exposure time after spreading of adhesive at RT, in 7mil thickness.
- Obvious new species represented by 1563 cm^{-1} peak, growing over time

FTIR Results



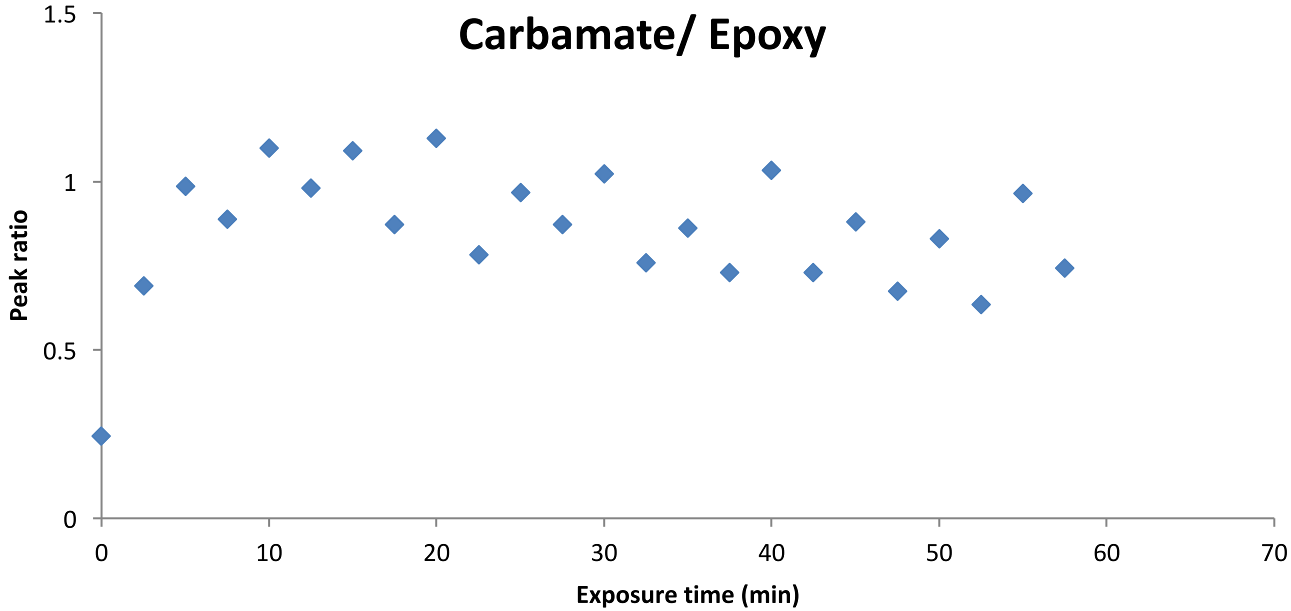
- Comparison with NIST standards suggests new species is not ammonium carbonate or bicarbonate
- Carbamate is likely based on previous literature
- 1563, 1483, and 1312 cm^{-1} FTIR signature consistent with IR-absorption peaks of carbamate reported in literature.

FTIR Results



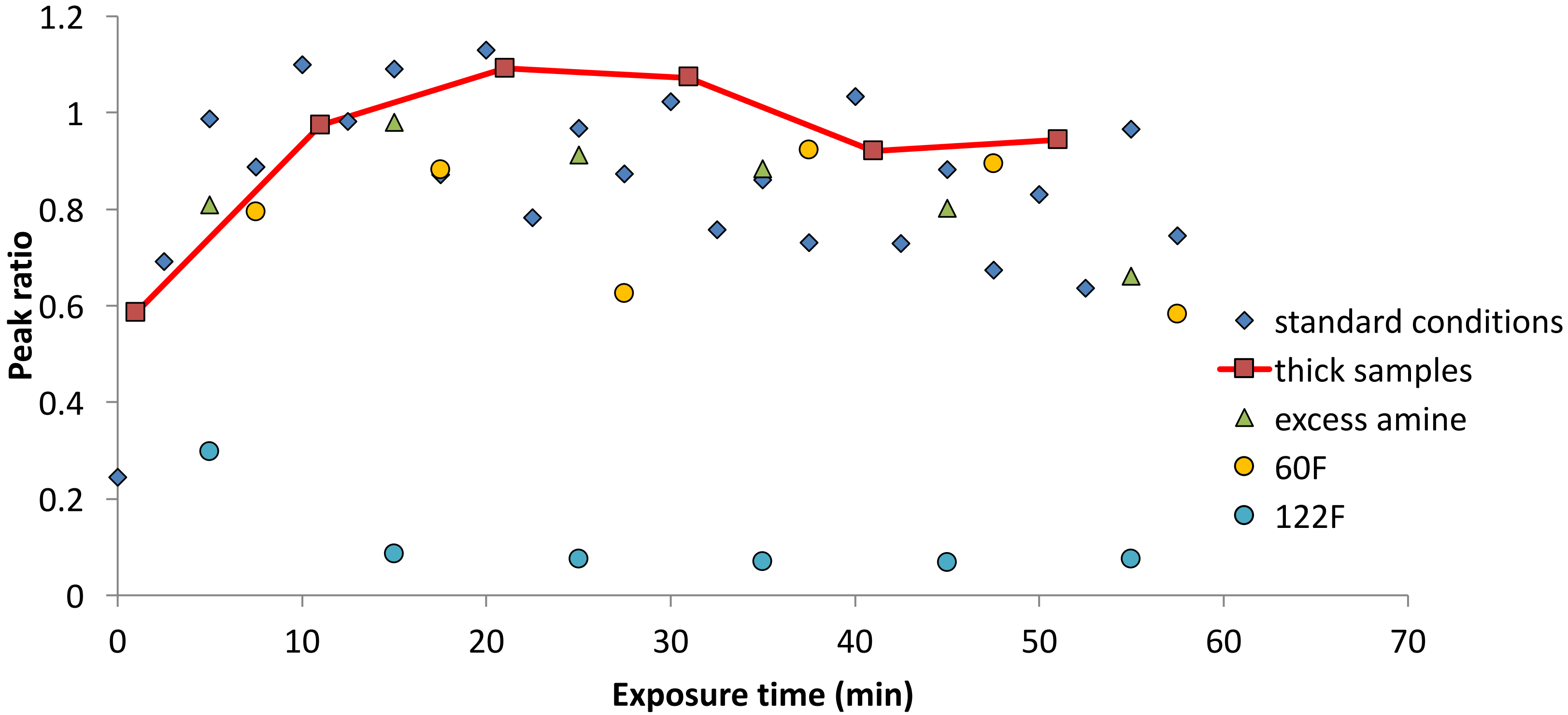
- Analysis: Use aromatic ring from epoxy as a reference, since it does not participate in amine blush or cure.
- Plot ratio of suspected carbamate peak, and suspected amine peak, to this reference over time

FTIR Results



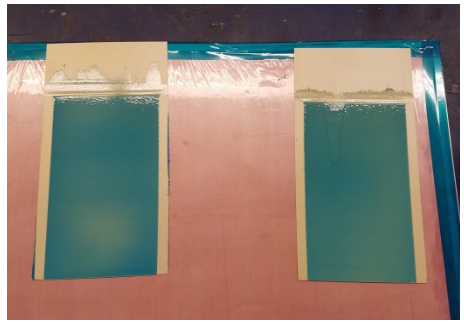
- Using aromatic epoxy ring (1508cm^{-1}) as reference, plot changes vs time.
- Rapid increase, peaking at 15min exposure time, then stable or slight decrease.
- Suggests rapid conversion of amine upon reaching surface.

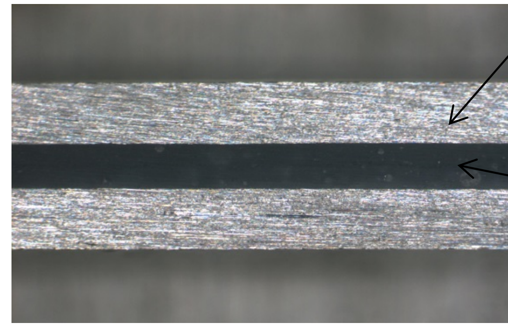
FTIR Results



- Behavior unchanged by – stoichiometry (50% excess amine), 10x thickness, lower temp to 60 °F
- Increasing exposure temperature to 122 °F prevented blush formation, probably by consuming amines in bulk before surface reactions could occur

T-Peel Results



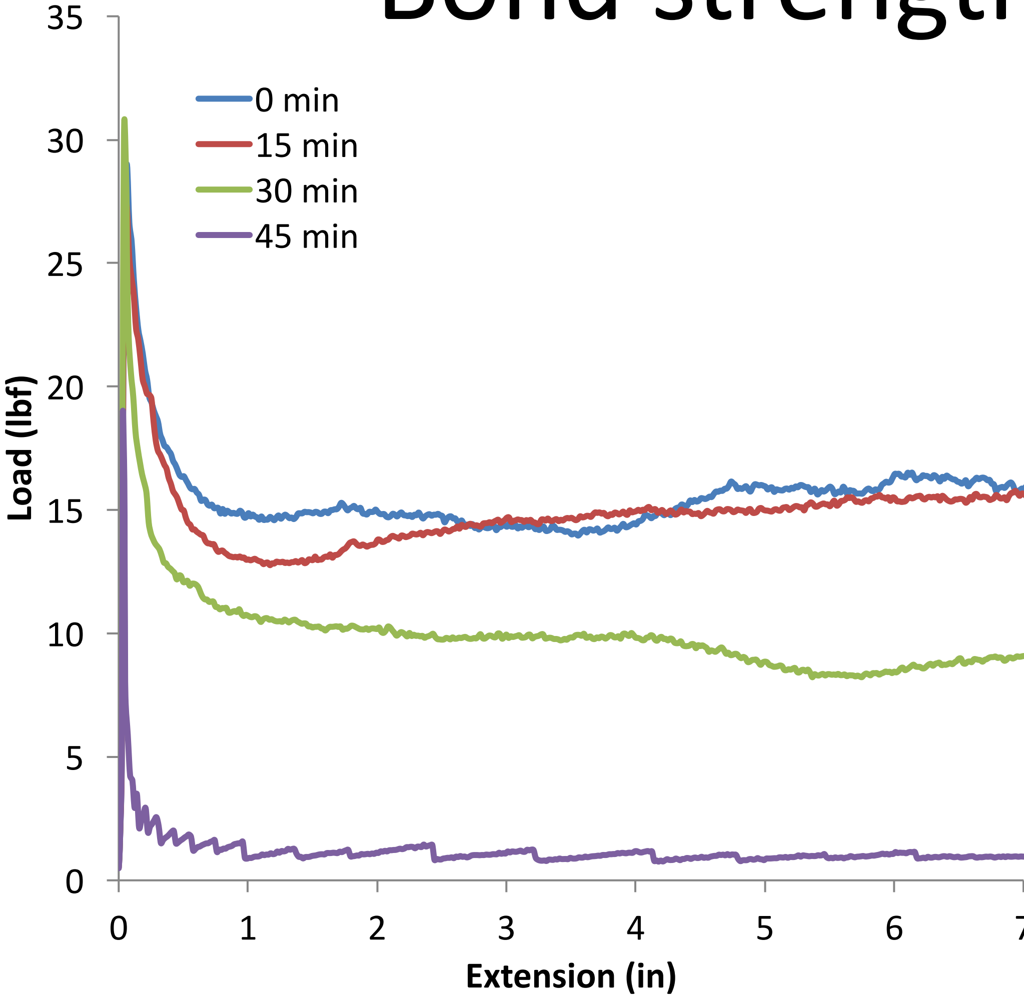


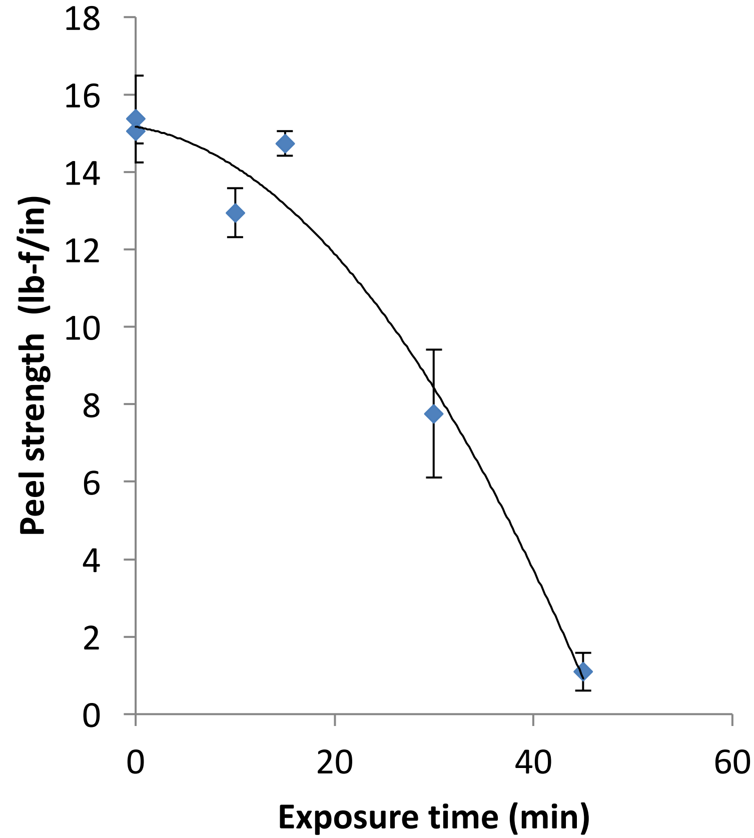
.020” PAA Al

Adhesive bondline

- Studied effect of post-spread time on peel strength
- Adherends: .020” anodized aluminum. Conditions: 70°F, 41% RH
- Made T-peels with varying exposures, closed, cured under 10psi at 150F 1hr, 150F 1hr ramped post cure
- Spread .020” adhesive per adherend, compressed to .010” feeler gauges
- Resulting bondline thickness ~.015”

Bond strength testing





- Bond strength is affected by post-spread exposure
- Consistent with FTIR data on blush formation vs time
- Note: samples designed to form blush and results maybe conservative

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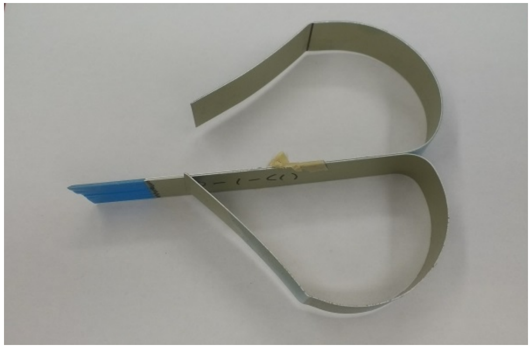
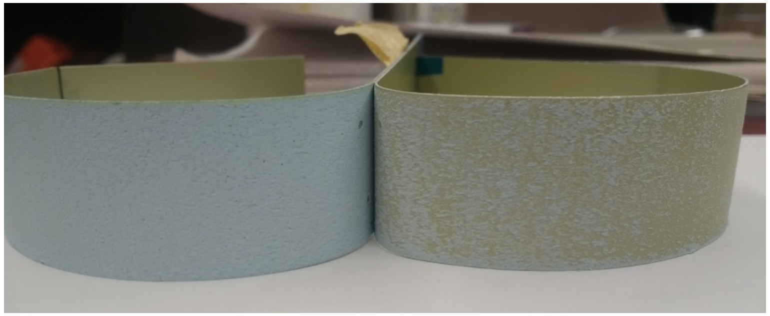
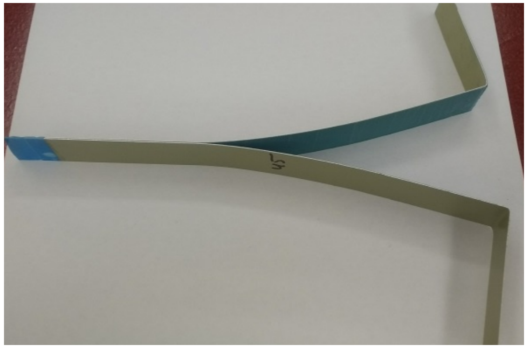
Bond strength testing

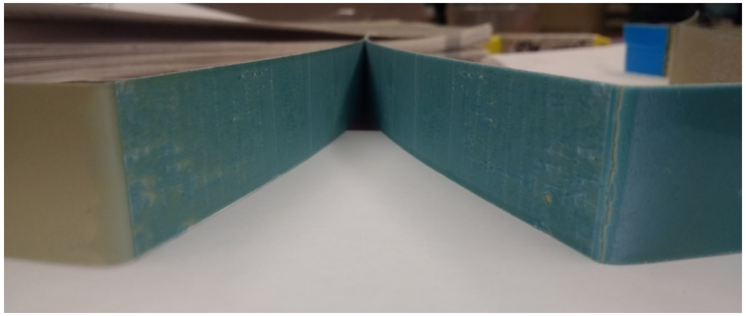
0 exposure strong bond





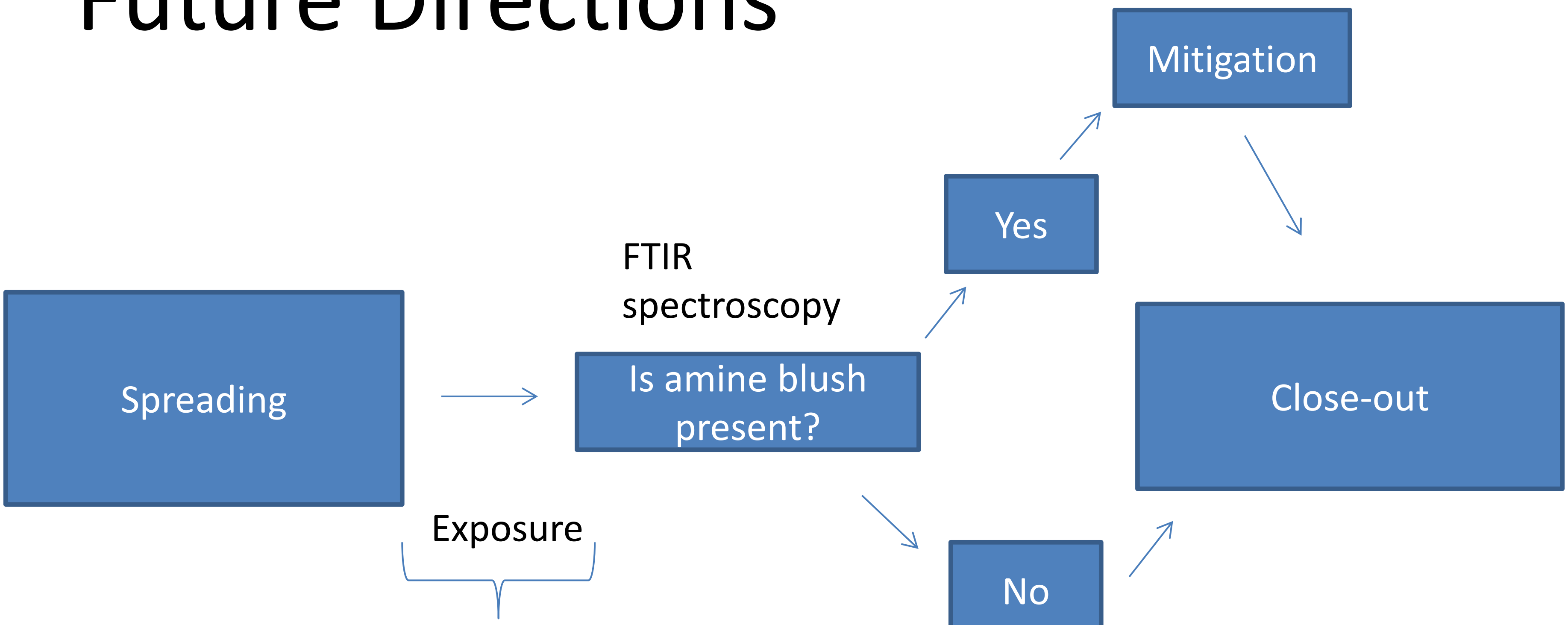
45min exposure weak bond





- Adherends and fracture surfaces of 0 exposure (top) and 45min exposure (bottom)
- In strong bond, failure at adhesive-primer interface (old anodized surface)
- In weak bond, failure at bondline (blush layer)

Future Directions



- It may not be possible to close out bonds in 15 minutes or less
  - Blush will form in most environments with this adhesive.

- Mitigation strategies should be pursued to “undo” effects of amine blush.
  - Surface combing/ scraping.
  - Adhesive squeeze-out.
  - Sacrificial/ protective films.

Conclusions

- FTIR on uncured 'traveler' coupons can monitor blush formation for post-spread exposures
- Short-time exposures after spreading can produce significant amine blush and can affect bond strengths
- T-peel testing continues to be a sensitive test for bond strength, but may not represent all bonding procedures and geometries

Deliverables

- A methodology for detection, quantification, and monitoring of amine blush formation in bonds before close-out
- A test for correlation between T-peel strength and amine blush formation

Future Work

- Correlate ATR-FTIR measurements of ‘traveler’ samples with T-peel strength measurements for short duration exposures in various environments

- Develop a methodology for generating a map of the environmental process space based on amine blush/FTIR measurements
  - Demonstrate methodology on EA 9360 adhesive system

- Explore possibility of hand-held ATR-FTIR + chemometric analysis as a predictor of bond strength based on IR changes

- Explore amine blush formation in other paste adhesive formulations

- Explore mitigation strategies –
  - High turbulence squeeze-out to ‘break up’ amine blush layer
  - FEP protective films, or “peel-ply” type removable layers to strip blush away immediately before close-out
  - Combing paste layer immediately before close-out

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