Improving Adhesive Bonding of Composites Through Surface Characterization

Austin Zukaitis, **Rita Olander**, Brian Flinn
University of Washington
Materials Science & Engineering, Seattle, WA

JAMS 2019 Technical Review
May 22-23, 2019

Improving Adhesive Bonding Through Surface Characterization

- Principal Investigators & Researchers
  - Brian D. Flinn (PI)
  - Austin Zukaitis
  - Rita Olander
- FAA Technical Monitor
  - Ahmet Oztekin
- Other FAA Personnel Involved
  - Larry Ilcewicz, Cindy Ashforth
- Industry Participation
  - Epic Aircraft
  - Textron Aircraft
  - The Boeing Company
  - Henkel

Tasks

- Detection of Amine Blush & Bond Quality
  - Map and characterize conditions (time, temperature, humidity) that cause amine blush and *try to quantify amount of amine blush*
  - ***Investigate the influence of amine blush on bond quality***
  - **Investigate methods to mitigate amine blush**

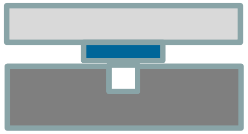
CECAM center of excellence for composites and advanced materials

JAMS JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

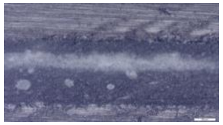
A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

Detection and Effect of Amine Blush in Paste Adhesive Bonds

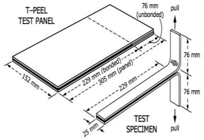
- Motivation and Key Issues
  - Bond failures have been attributed to amine blush
- Objective
  - What are the conditions for amine blush and how to measure blush?
  - What are the effects on bond quality?
  - Prevention & Mitigation
- Approach
  - Previous work:



Wet adhesive FTIR

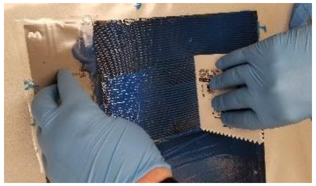


Bondline microscopy

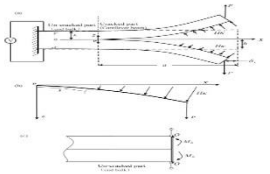


T-peel testing

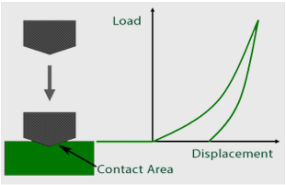
  - Current work:



Mitigation Techniques

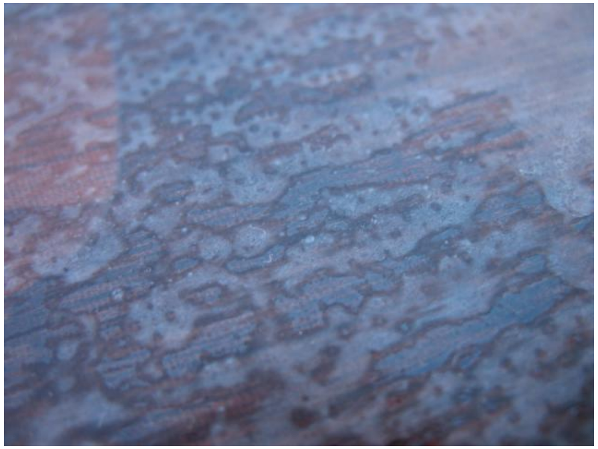


DCB

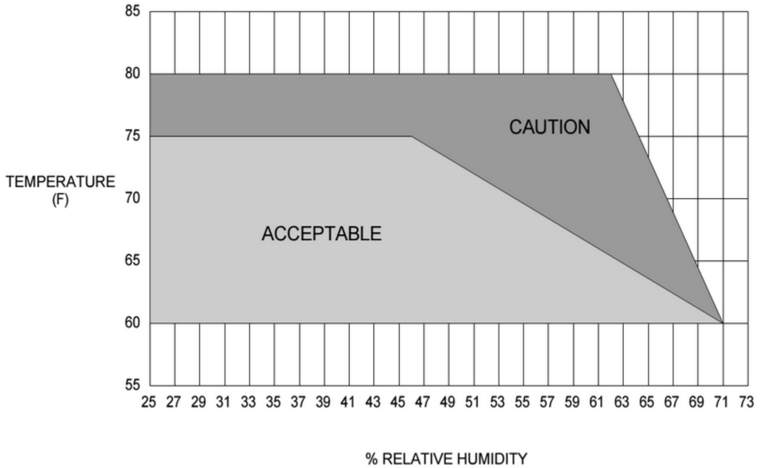


Nano indentation

Introduction



Source: AMT composites, amtcomposites.co.za

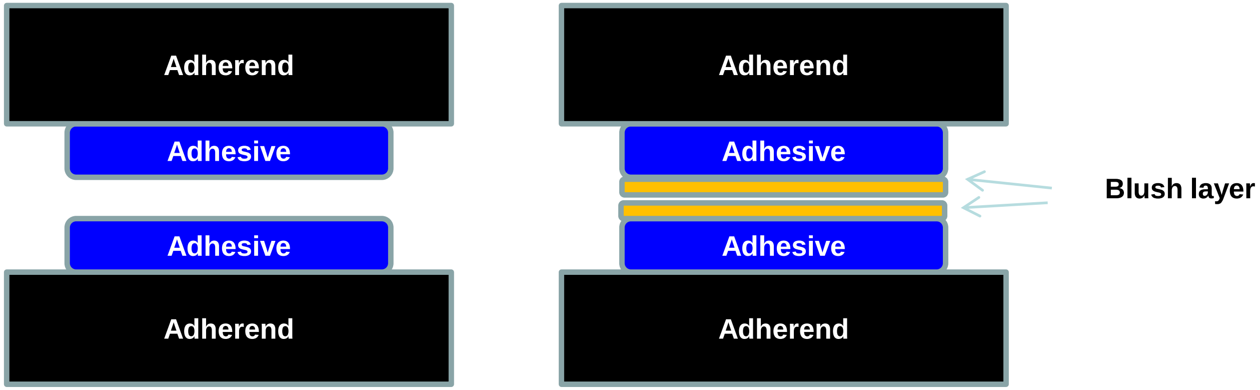


Environmental Bonding Requirements per Cirrus SR22T SRM

- 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

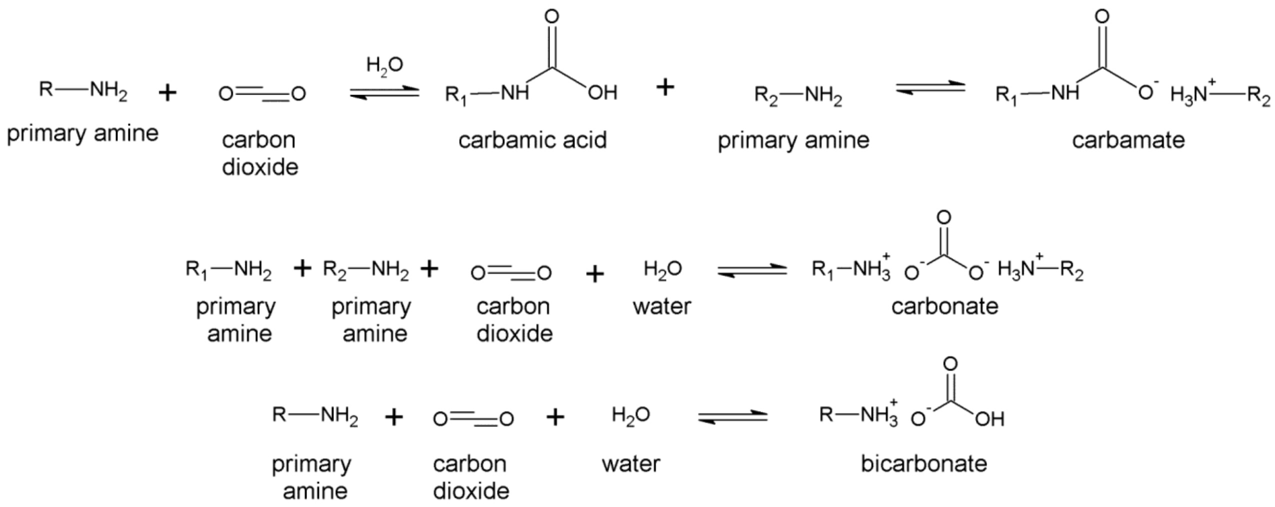
CECAM JAMS AMTAS

Introduction



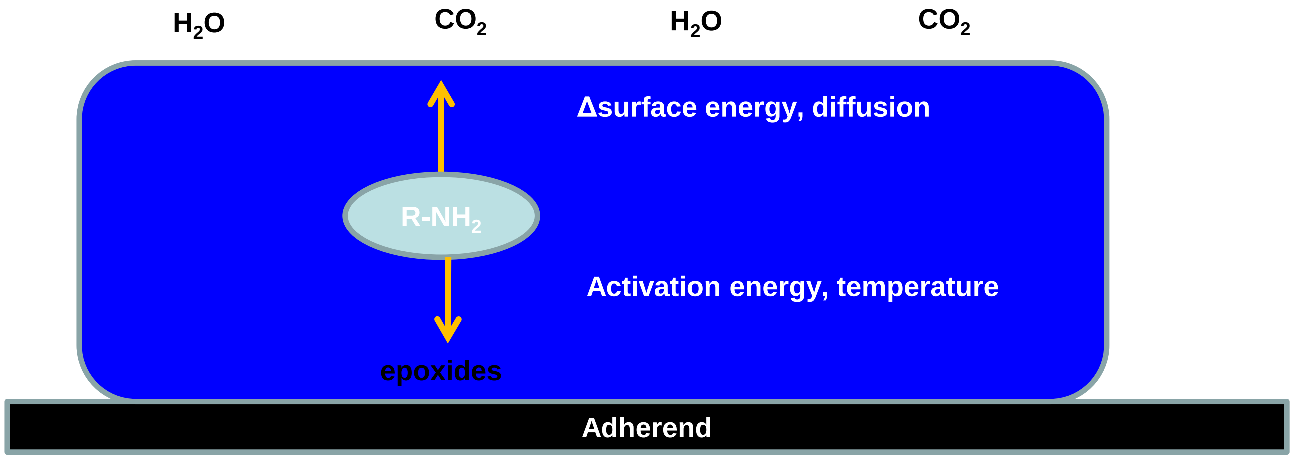
- Amine blush in paste adhesives leads to lowered bond strength – potential for kiss bonds & delaminations
- 2010 – Wing disbond/fuel leak attributed to amine blush in bonded structure – FAA Airworthiness Directive issued

Introduction



- Proposed reactions for amine blush
- Primary amine reacts with CO_2 to form carbamate (salt, network)
- Carbonates and bicarbonates also proposed

Introduction



- Primary amine in mixture can:

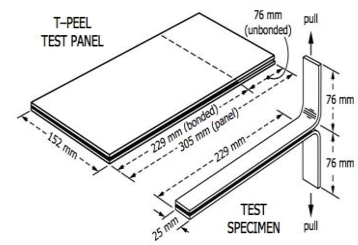
1. Diffuse to surface (ΔSE)
   – React with CO_2, H_20
2. React with epoxide (reactivity)

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
4. Effectiveness of Mitigation Techniques

Introduction



Mixing → Spreading → Close-out

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

Outline

- Methods
  - FTIR
  - DCB bond strength test
  - Mitigation techniques
- Model systems blush studies
  - Mitigation techniques
- Commercial system blush studies
  - Mitigation techniques
  - DCB testing

Outline

- Methods
  - FTIR
  - DCB bond strength test
  - Mitigation techniques
- Model systems blush studies
  - Mitigation techniques
- Commercial system blush studies
  - Mitigation techniques
  - DCB testing

Methods - FTIR

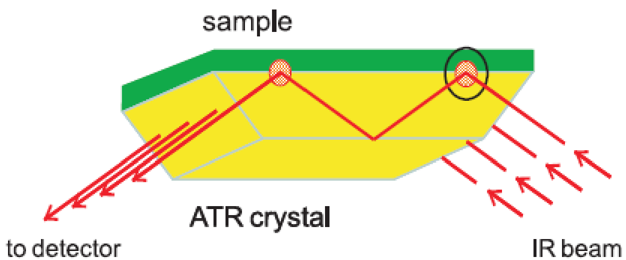
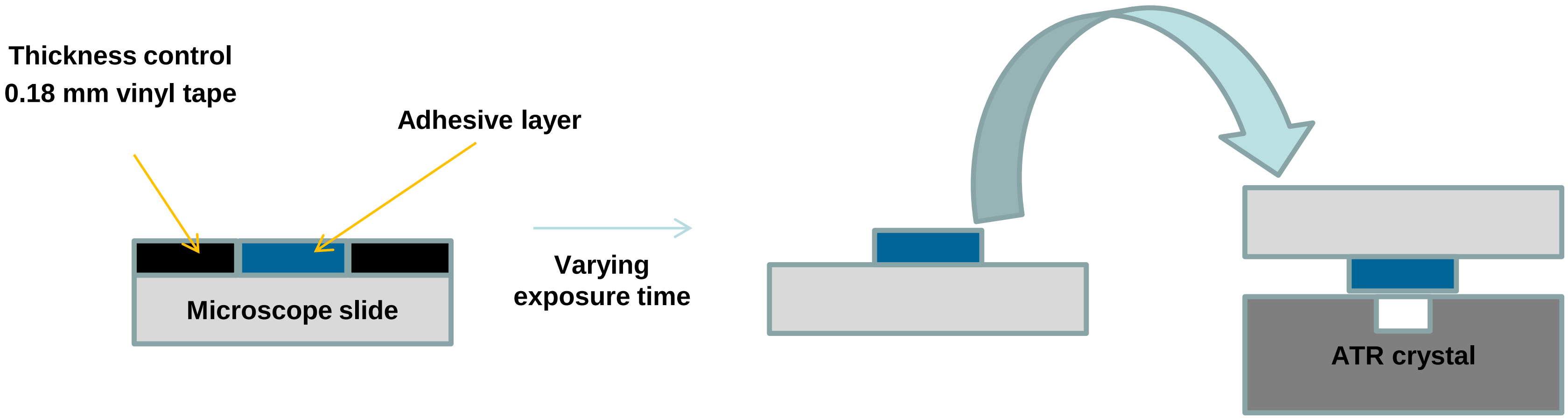


Figure 2: ATR principle

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

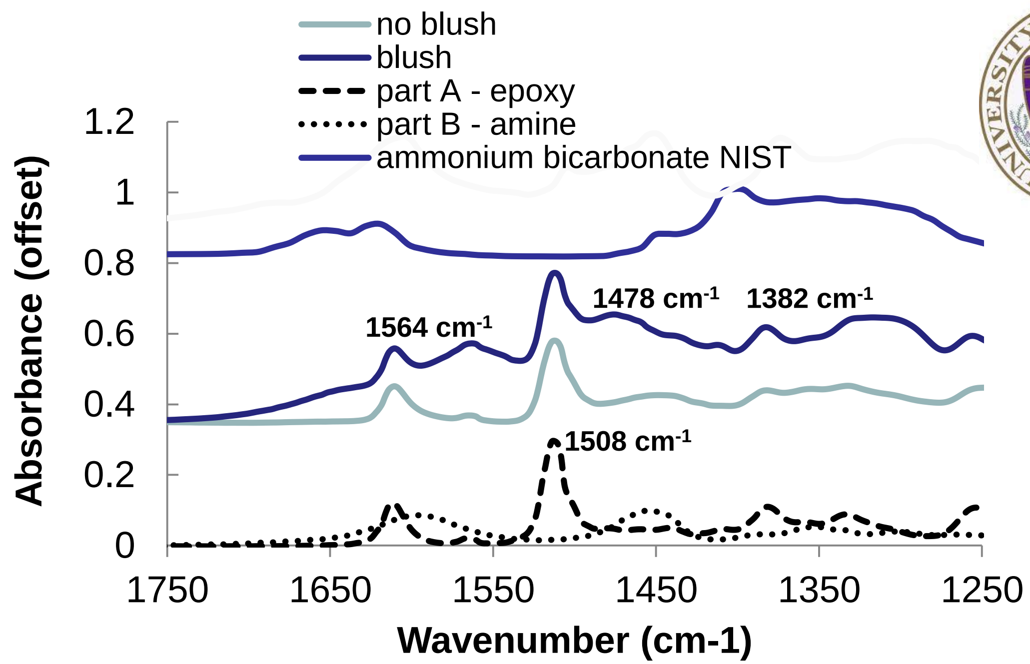
Methods – FTIR – Wet adhesive study



- Apply .18 mm adhesive layer to microscope slide
- Collect IR spectra from surface using ATR, after varying exposure time

Methods - FTIR

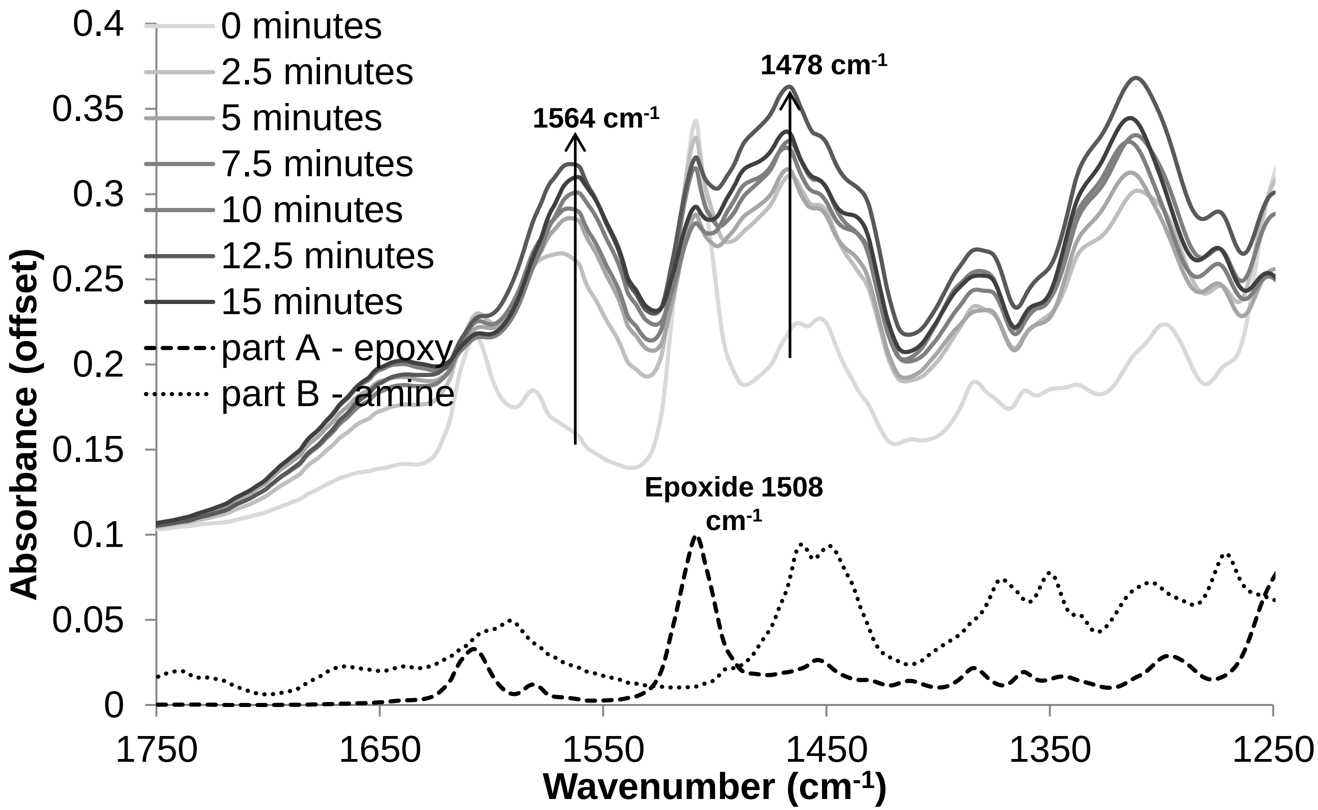
Species, bond type	IR peak (cm^{-1})
Epoxide, aromatic	1508
Carbamate, asymmetric	1550-1610
Carbamate, symmetric	1450-1350
Carbamate, stretch	1300-1260
Protonated amine	1479-1474



- FTIR studies of amine blush indicate carbamates form
- Epoxide aromatic 1508 cm^{-1} as a reference; asymmetric carbamate ~1560 cm^{-1} as blush indicator

$$blush\ ratio = \frac{A_{1564}}{A_{1508}}$$

Methods – FTIR – Wet adhesive study



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

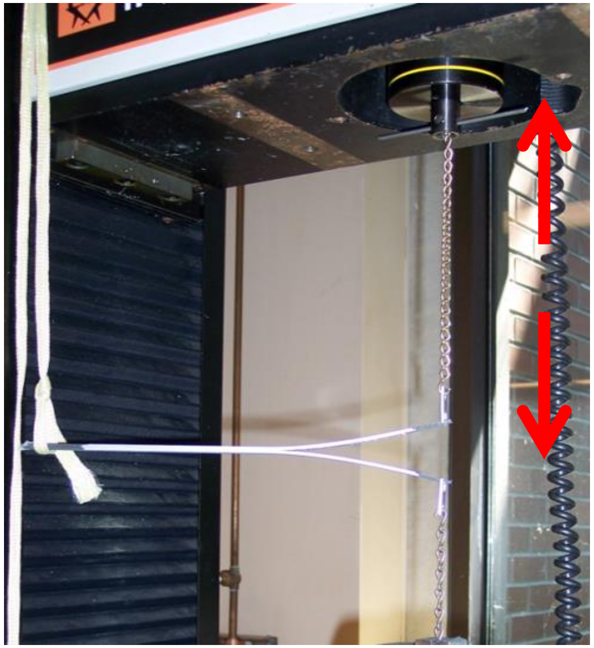
- Use epoxide as reference peak

$$blush\ ratio = \frac{A_{1564}}{A_{1508}}$$

Methods – DCB Testing

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

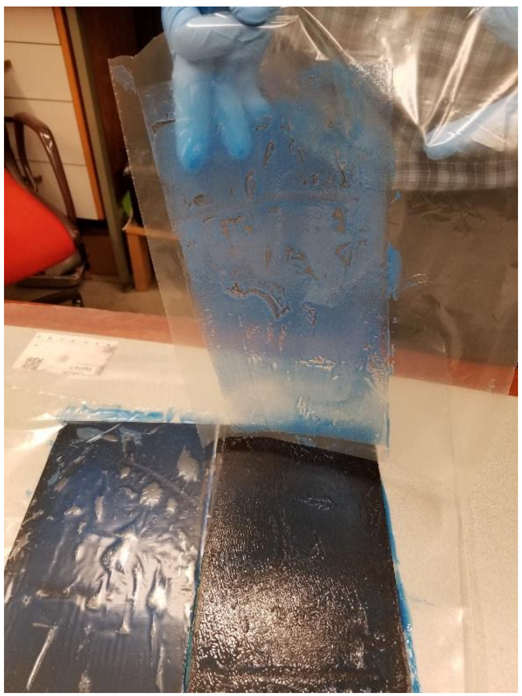
$$G_{IC} = \frac{E}{A \times B}$$



DCB Test

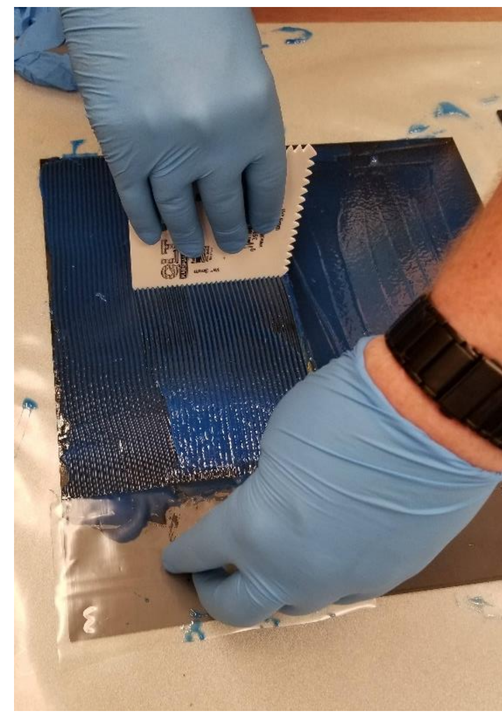
Methods – Mitigation Techniques

FEP removal



VARTM mesh removal

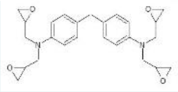
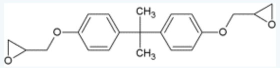
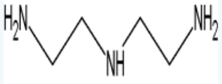
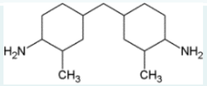
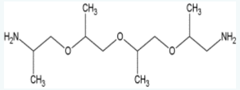
Comb



Outline

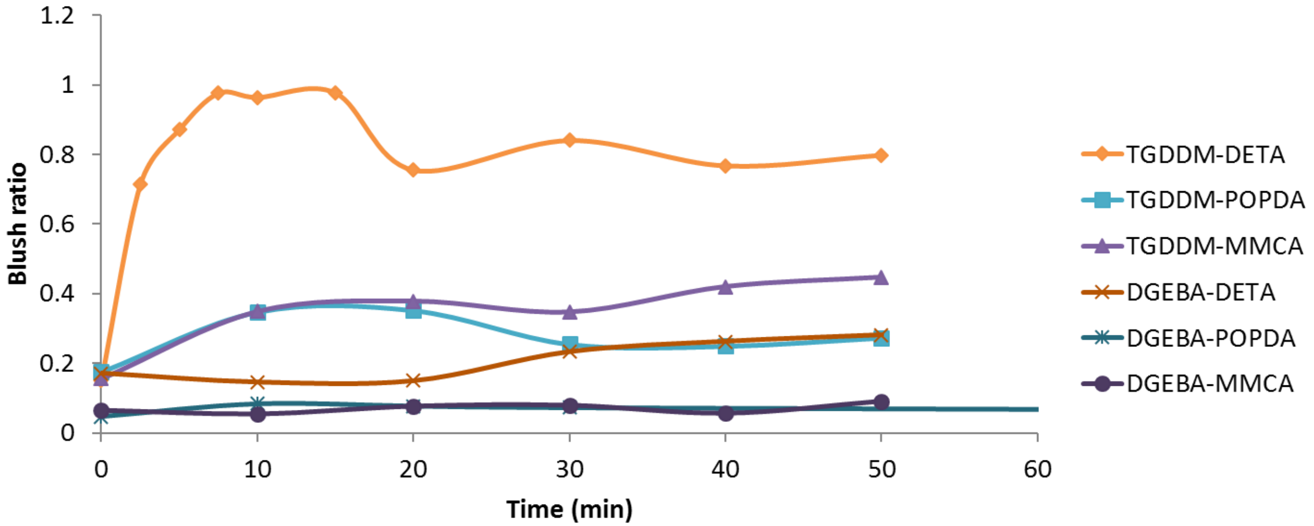
- Methods
  - FTIR
  - DCB bond strength test
  - Mitigation techniques
- Model systems blush studies
  - Mitigation techniques
- Commercial system blush studies
  - Mitigation techniques
  - DCB testing

Model Formulations

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

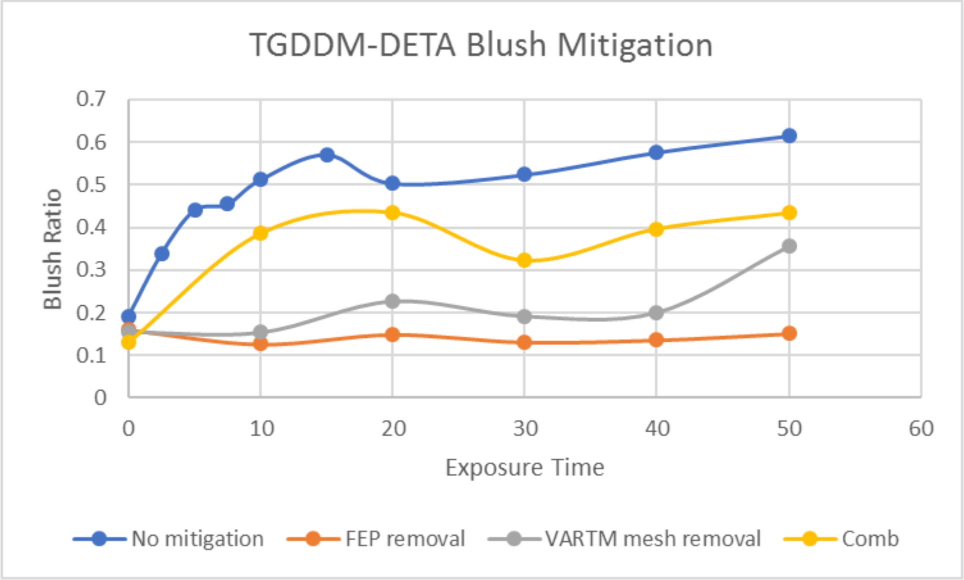
- 2 standard epoxies and 3 standard curing agents

Model formulations



- Fastest-forming, most extensive blush in TGDDM-DETA
- Little blush in other TGDDM-containing formulations
- No blush in DGEBA-containing formulations

Amine Blush Mitigation

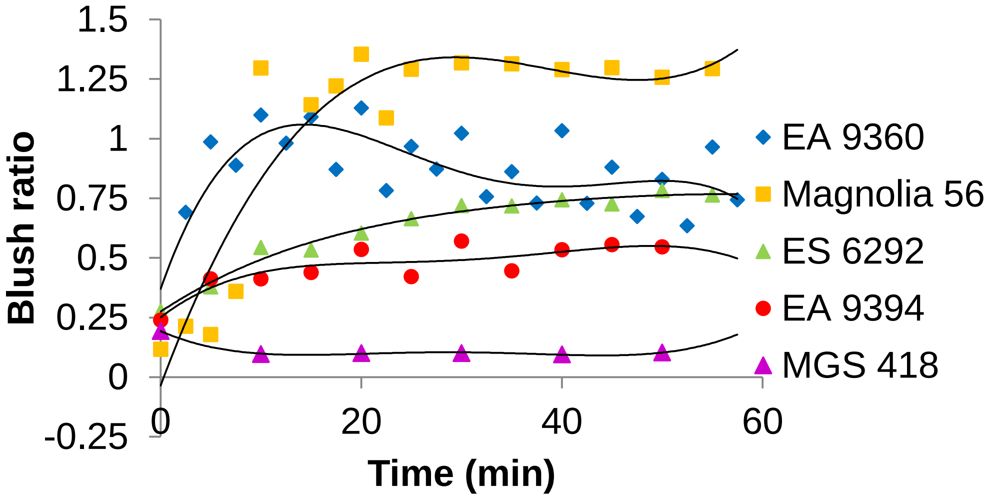


- Mitigation techniques reduce amount of amine blush present
- Highly dependent on operator use
- Amount of adhesive removed by mitigation needs to be accounted for

Outline

- Methods
  - FTIR
  - DCB bond strength test
  - Mitigation techniques
- Model systems blush studies
  - Mitigation techniques
- Commercial system blush studies
  - Mitigation techniques
  - DCB testing

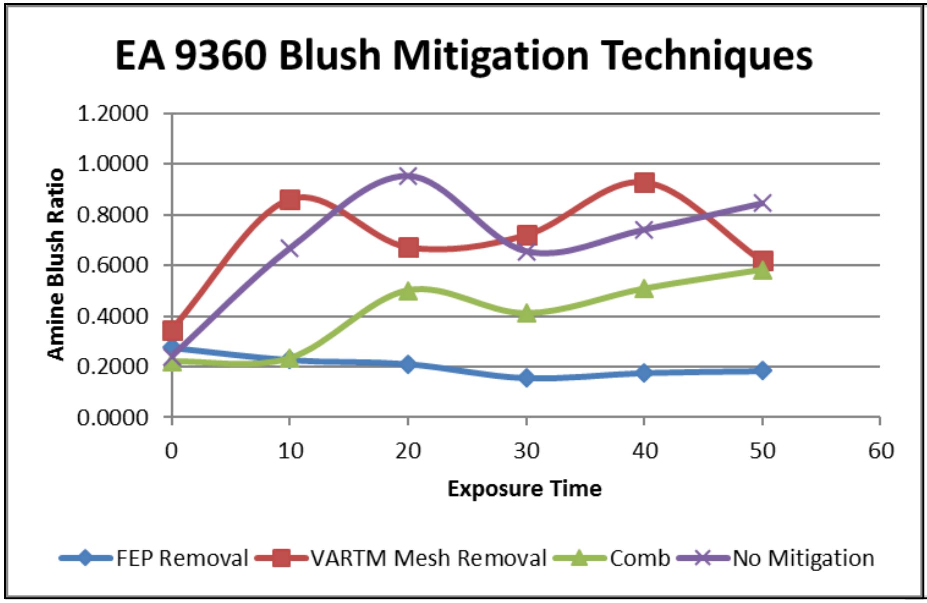
Commercial systems

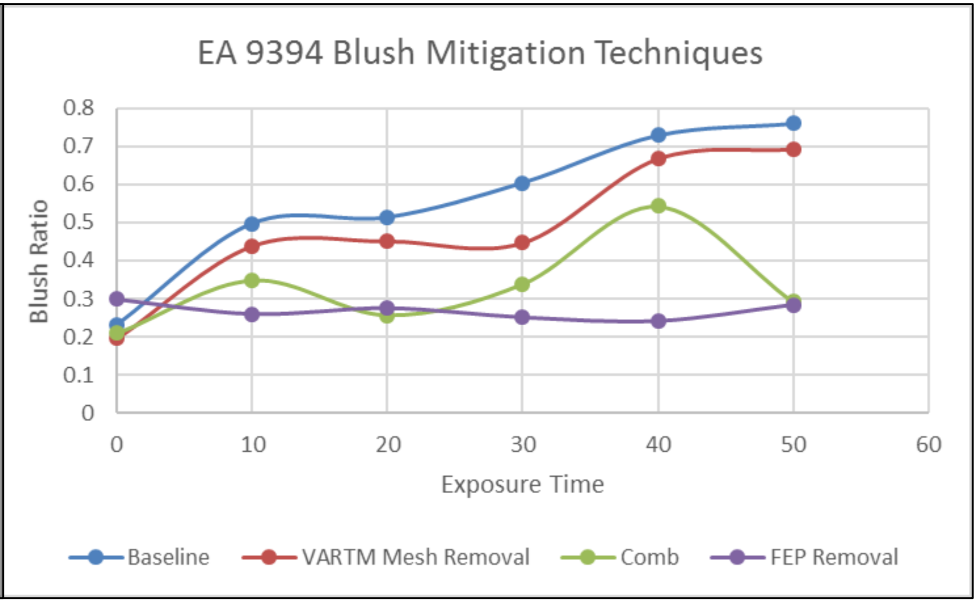


Adhesive	Δ blush ratio (min^{-1})	RT Pot life (min)
Magnolia 56	.070	180
EA 9360	.055	50
ES 6292	.0082	40-50
EA 9394	.0046	90
MGS 418	-.0013	300-360

- 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
- Slow : Hexion MGS 418

Commercial Adhesives Blush Mitigation

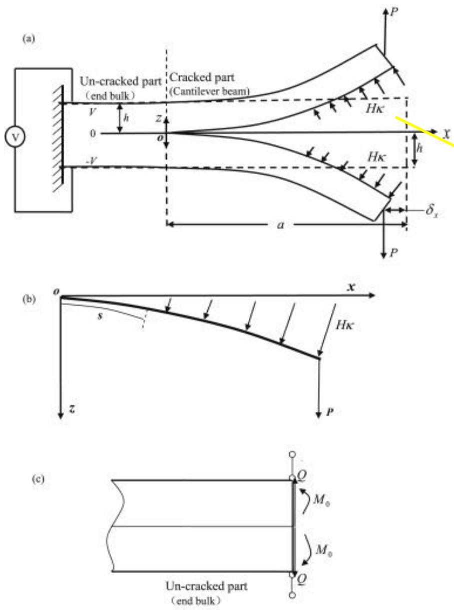


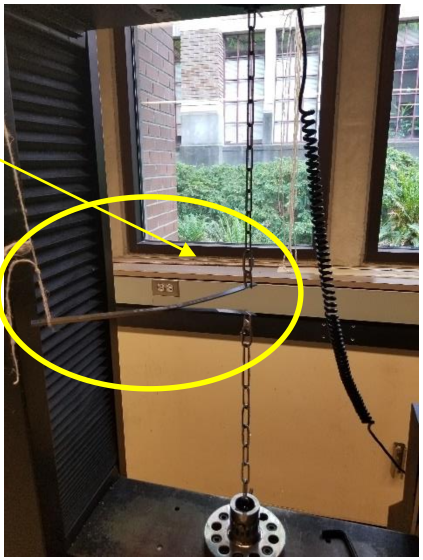


- FEP removal most effective technique
- Comb and VARTM mesh removal sensitive to operator technique
- Hypothesis: FEP prevents blush formation and VARTM mesh removal and combing break up blush layer

DCB Manufacturing & Testing

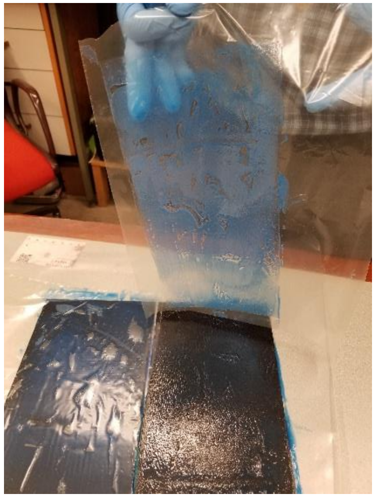
- Bond line thickness control
  - Spacer beads
- Perform mitigation techniques before close-out of DCB samples (40 min exposure)
  - FEP
  - Surface combing
- Panels cured and machined

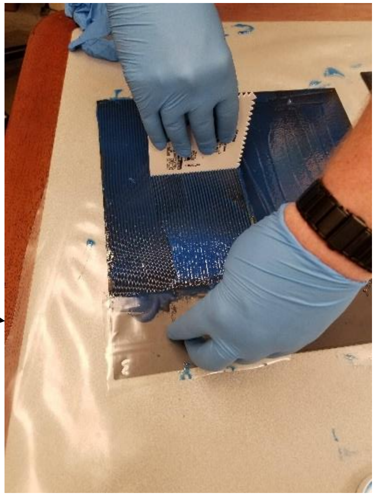
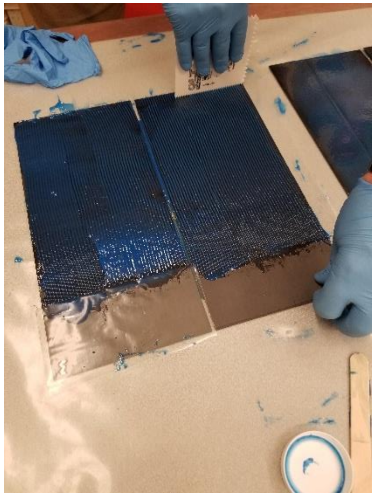




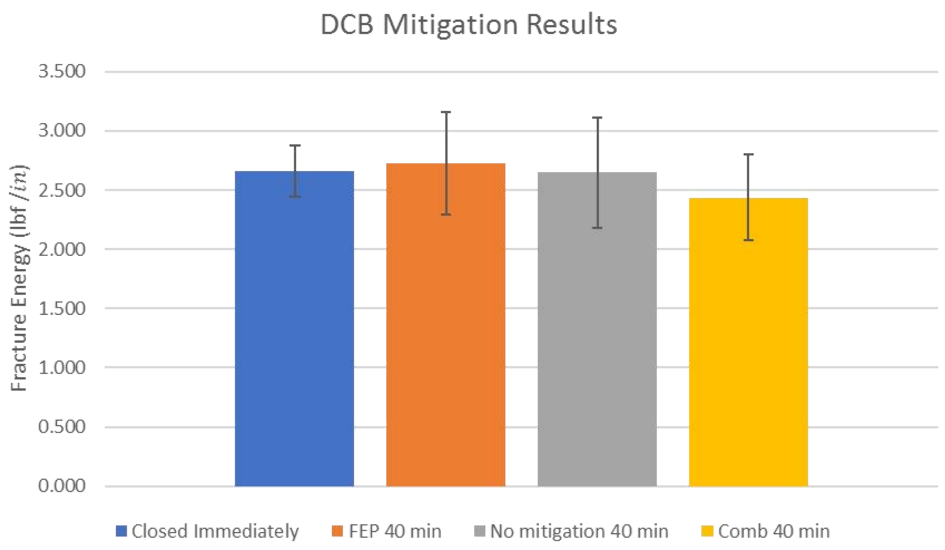
DCB Panel Production

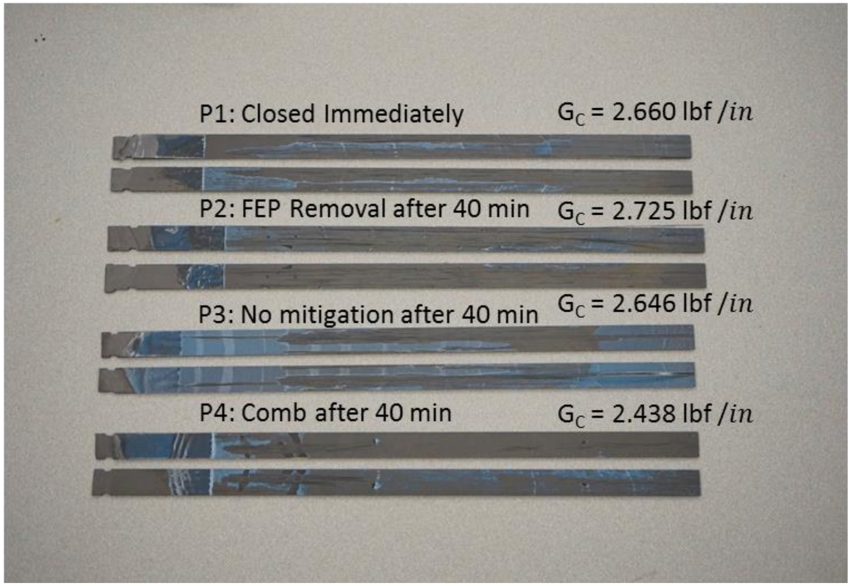
- P1: Closed Immediately
- P2: FEP removal after 40 min
- P3: No mitigation after 40 min
- P4: Comb after 40 min

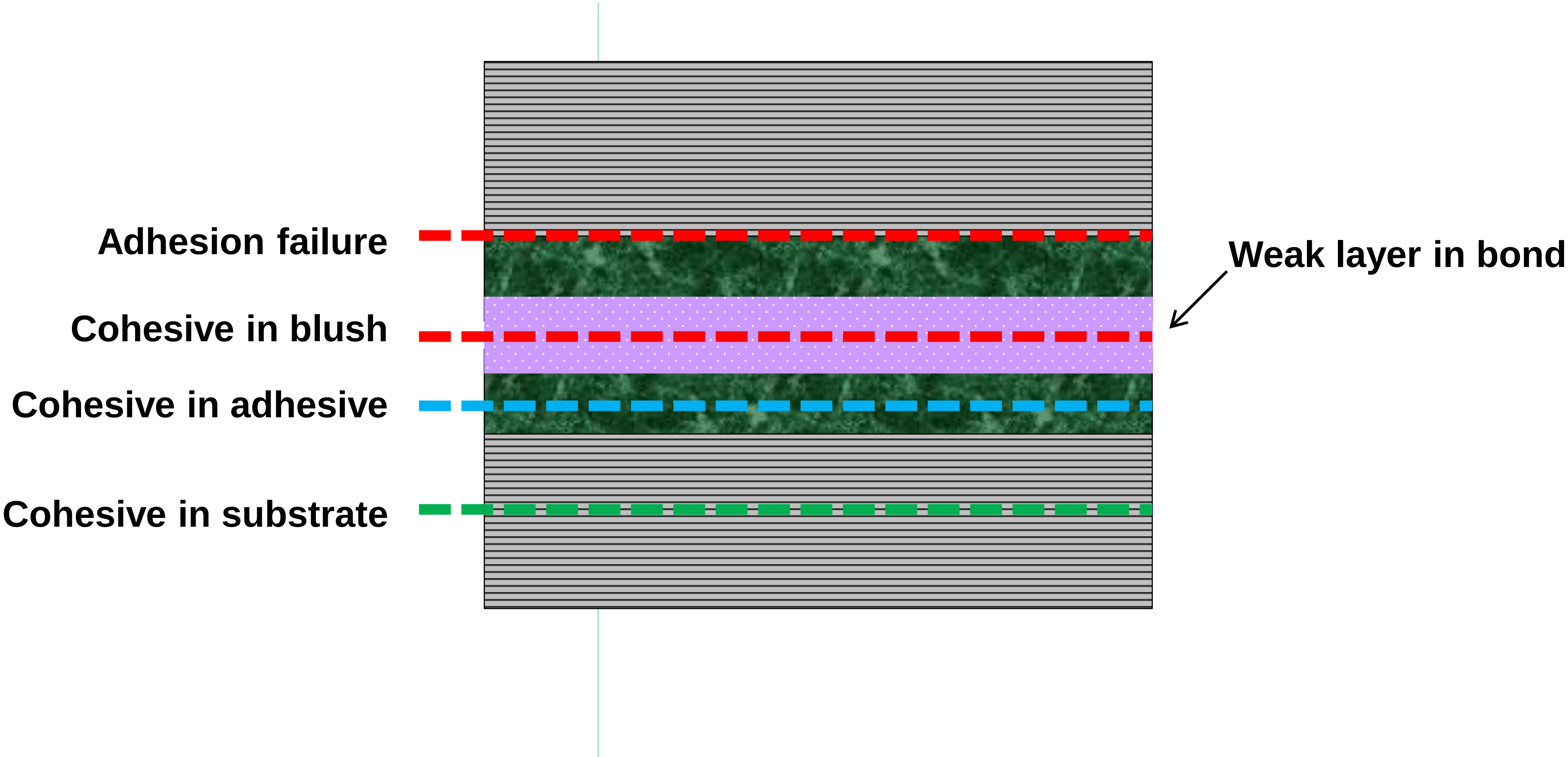

DCB Mitigation Results





- Average fracture toughness values are statistically the same
- Failure predominantly cohesive within the substrates for all four panels except P3
- P3 exhibited cohesive failure in the adhesive during crack initiation region, then mixed failure during propagation

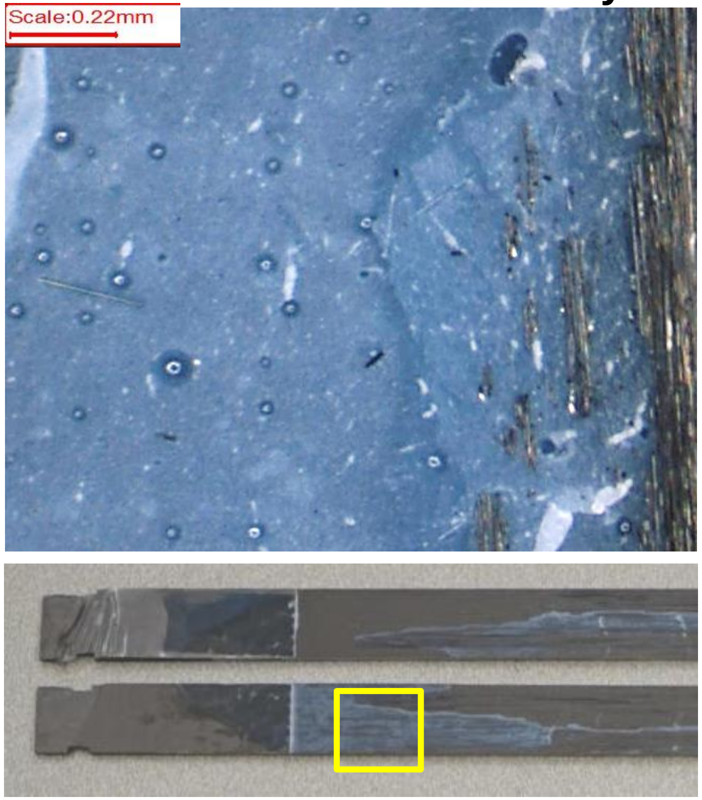
Paste Bond Failure Modes



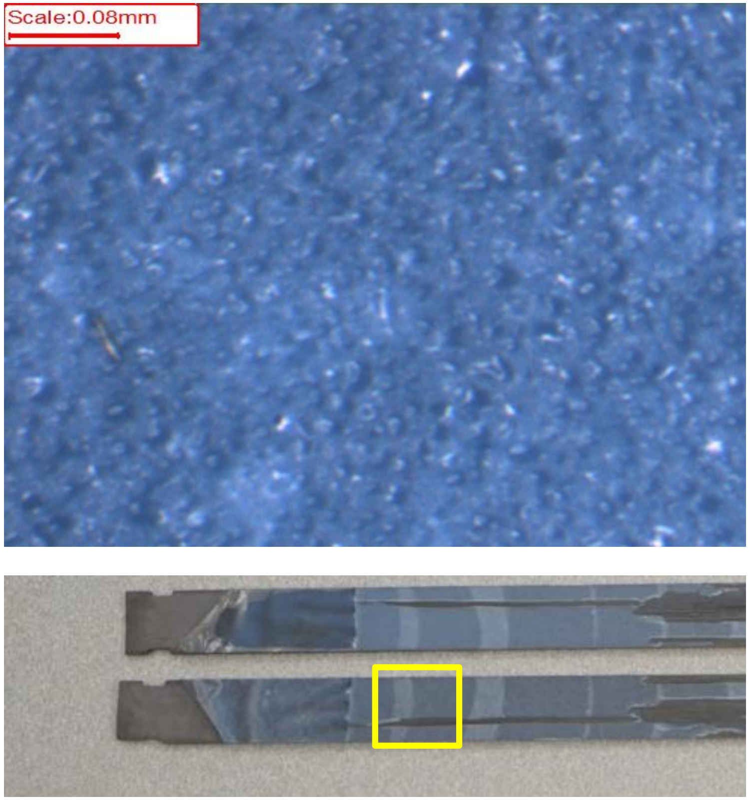
- Amine blush in paste adhesive can present additional undesirable failure mode

Failure Modes of DCBs

P1: Closed immediately



P3: No mitigation after 40 min



- Strain whitening present in P1 pre-crack initiation, characteristic of significant plastic deformation
- P3 has atypical surface, potentially due to failure in weak layer

Discussion of DCB Results

- Cracks predominantly propagated in substrates
- Substrates were out of autoclave cured and had low fracture toughness
- G_c values representative of substrates not adhesive bonds
- Unexpected fracture mode in unmitigated panel
  - Potential fracture in weak blush layer
- Mitigation techniques were successful at influencing the mode of fracture
- More tests will be conducted using autoclave cured substrates

Conclusions

- Blush formation rates can be observed with FTIR analysis
- Three mitigation techniques evaluated
  - FEP removal
  - VARTM mesh removal
  - Combing
- Effect of mitigation techniques can be measured by FTIR analysis
- Fracture energy measurements were inconclusive due to substrate failures
- Fractography results showed differences between mitigated and unmitigated samples
- Mitigation techniques appear promising
- When working with paste adhesives, need to monitor for blush formation
- Mitigation techniques should be evaluated for effectiveness

Future Work on Amine Blush

- Explore effectiveness of mitigation techniques with stronger substrates
- Explore nanomechanical characterization of paste bonds with and without blush
- Prepare FAA technical report

Acknowledgements

- FAA, JAMS, AMTAS
- Boeing Company
- Epic Aircraft
- Textron Aircraft
- Airtech International
- UW MSE

Questions?

Don't forget to fill out the feedback form in your packet or online at www.surveymonkey.com/r/jamsfeedback

Thank you.

CECAM
center of excellence for composites and advanced materials

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures