Improving Adhesive Bonding of Composites Through Surface Characterization

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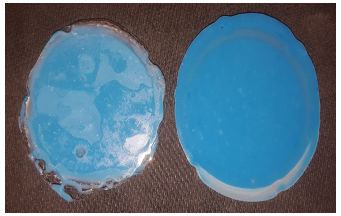
Advanced Materials in Transport Aircraft Structures

FAA Sponsored Project Information

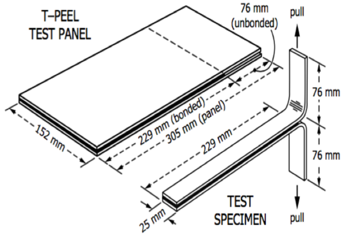
• Principal Investigator:	Brian Flinn
• Post-Doc Researcher:	Ryan Toivola
• Graduate Students:	Austin Zukaitis Rita Johnston
• FAA Technical Monitor:	Ahmet Oztekin
• Collaborators:	The Boeing Co. Henkel Epic Aircraft Textron

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:

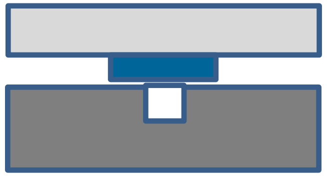


Cured “traveler” coupons

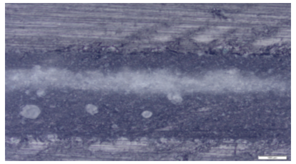


T-peel testing

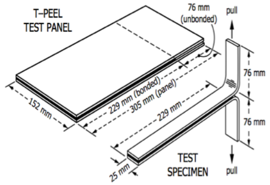
  - Current work:



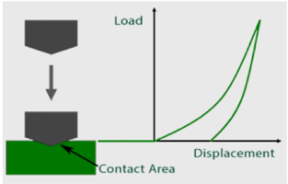
Wet adhesive FTIR



Bondline microscopy

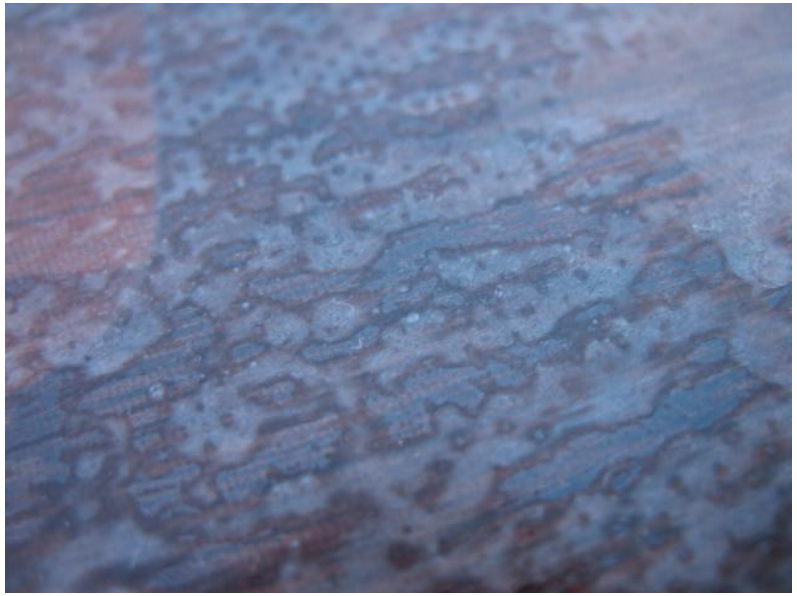


T-peel testing

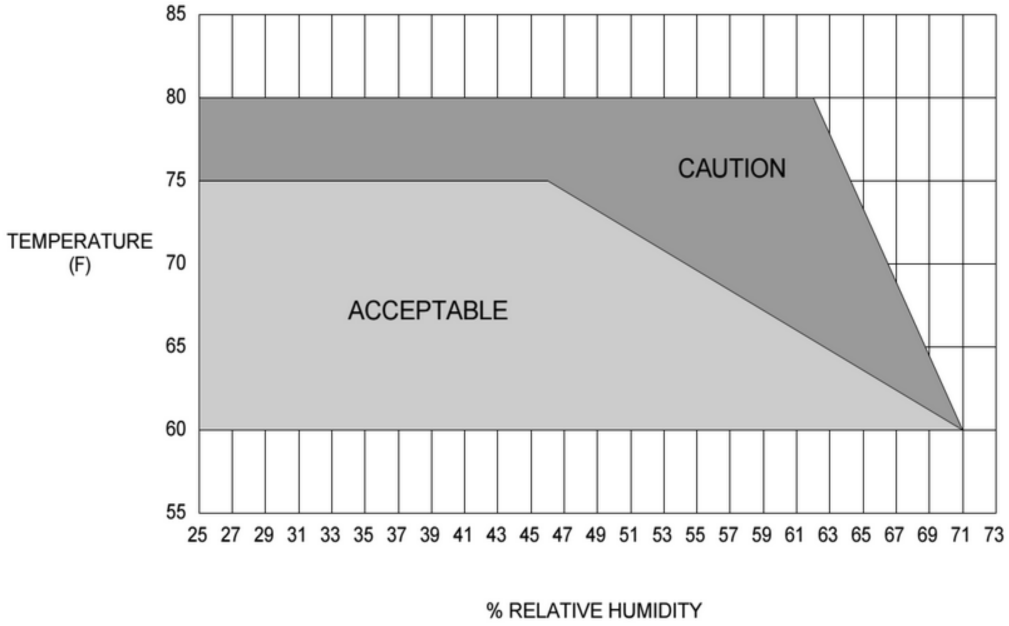


Nano indentation

Introduction



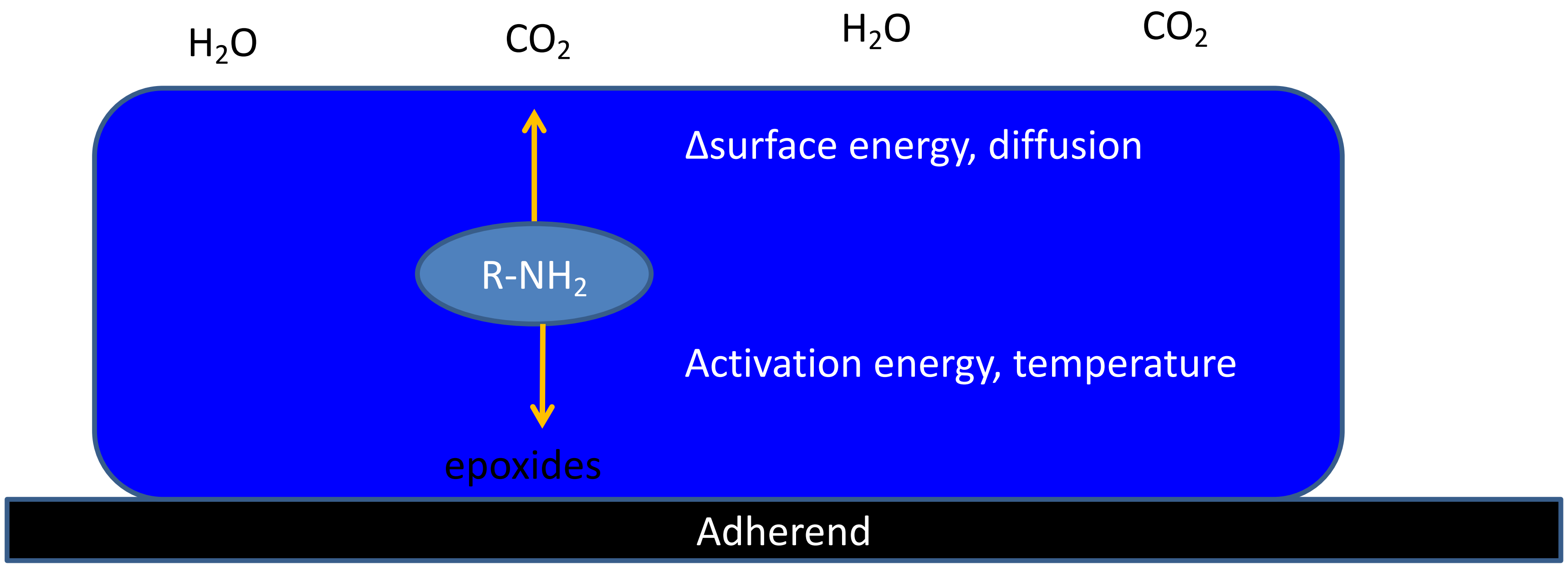
Source: AMT composites, amtcomposites.co.za



Environmental Bonding Requirements per Cirrus SR22T SRM

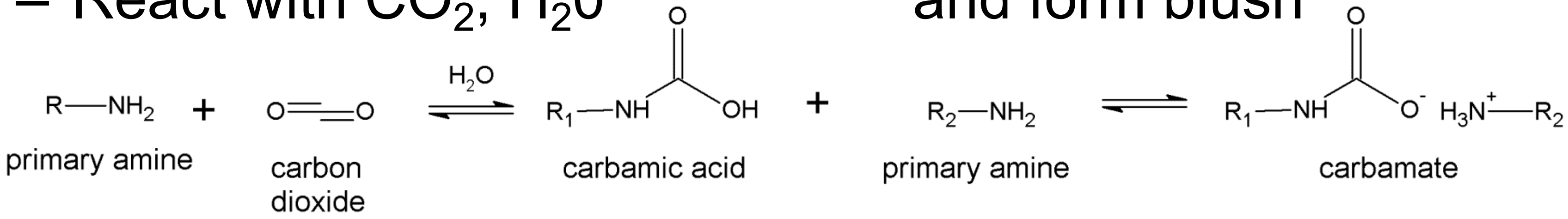
- Amine blush is a surface phenomenon in amine cured epoxy systems
- “Whitish, hazy, waxy, oily, soft, sweaty” surface coating
- Problematic in RT cure systems processed in high humidity environments
- Weak layer in bond

Introduction



Primary amine in mixed paste adhesive can:

- Diffuse to surface (ΔSE)
  - React with CO_2, H_20 and form blush



- React with epoxide (reactivity)

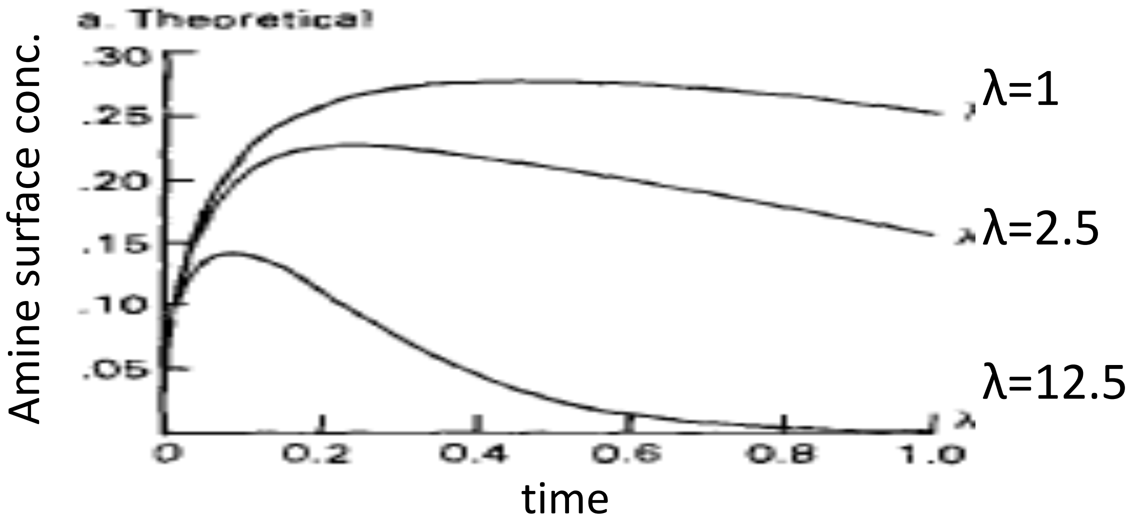
Introduction

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

$$k_1 = epoxy - amine\ reaction\ rate\ constant$$

$$\Gamma = Langmuir\ capacity \qquad a = Langmuir\ affinity$$

$$D = diffusivity$$



- Foister (J. Coll. Interf. Sci. 1984)
- Observed surface concentration of amines in a curing epoxy mixture
- Damkohler number λ: ratio of reactivity to diffusivity of primary amine. Low: amines stay at surface. High: amines cure with epoxy

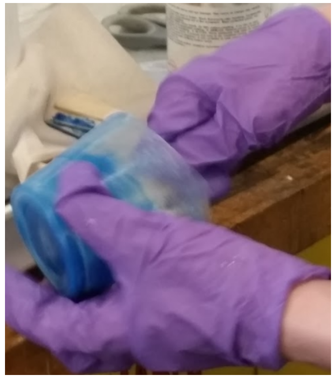
Introduction

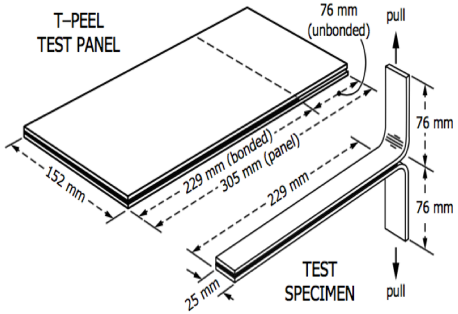
- Gaps in knowledge & understanding of amine blush:
- 1) How fast does amine blush form on adhesive surface?
  - Effect of temperature, humidity, adhesive formulation
- 2) Relationship between surface blush and blush layer thickness in adhesive bondlines
- 3) Relationship between blush layer thickness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





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

Methods - FTIR

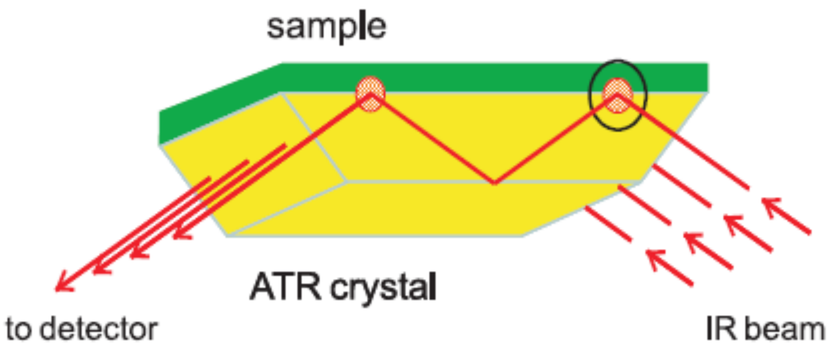
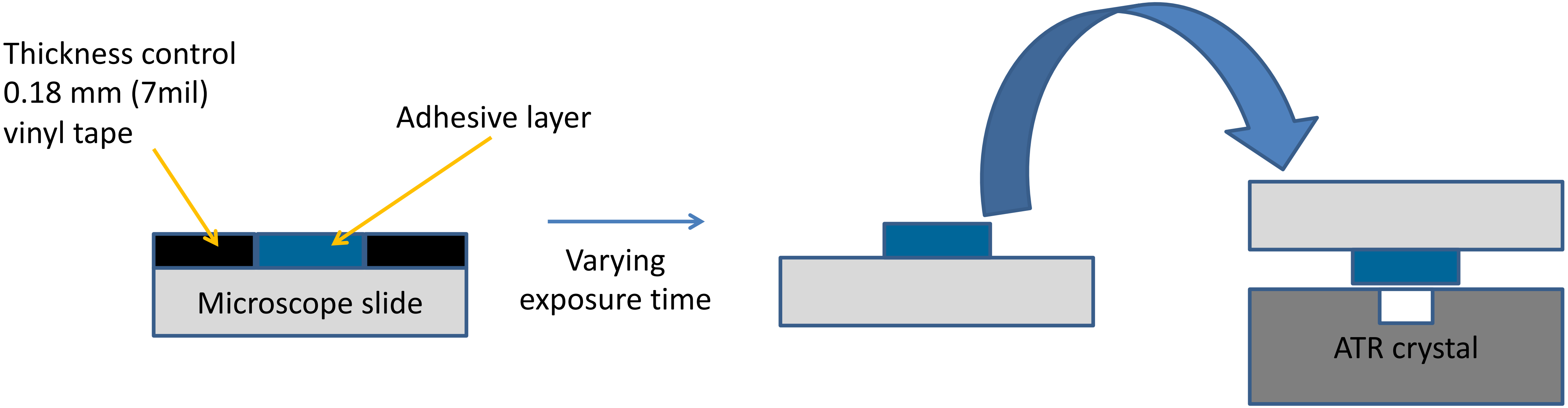


Figure 2: ATR principle

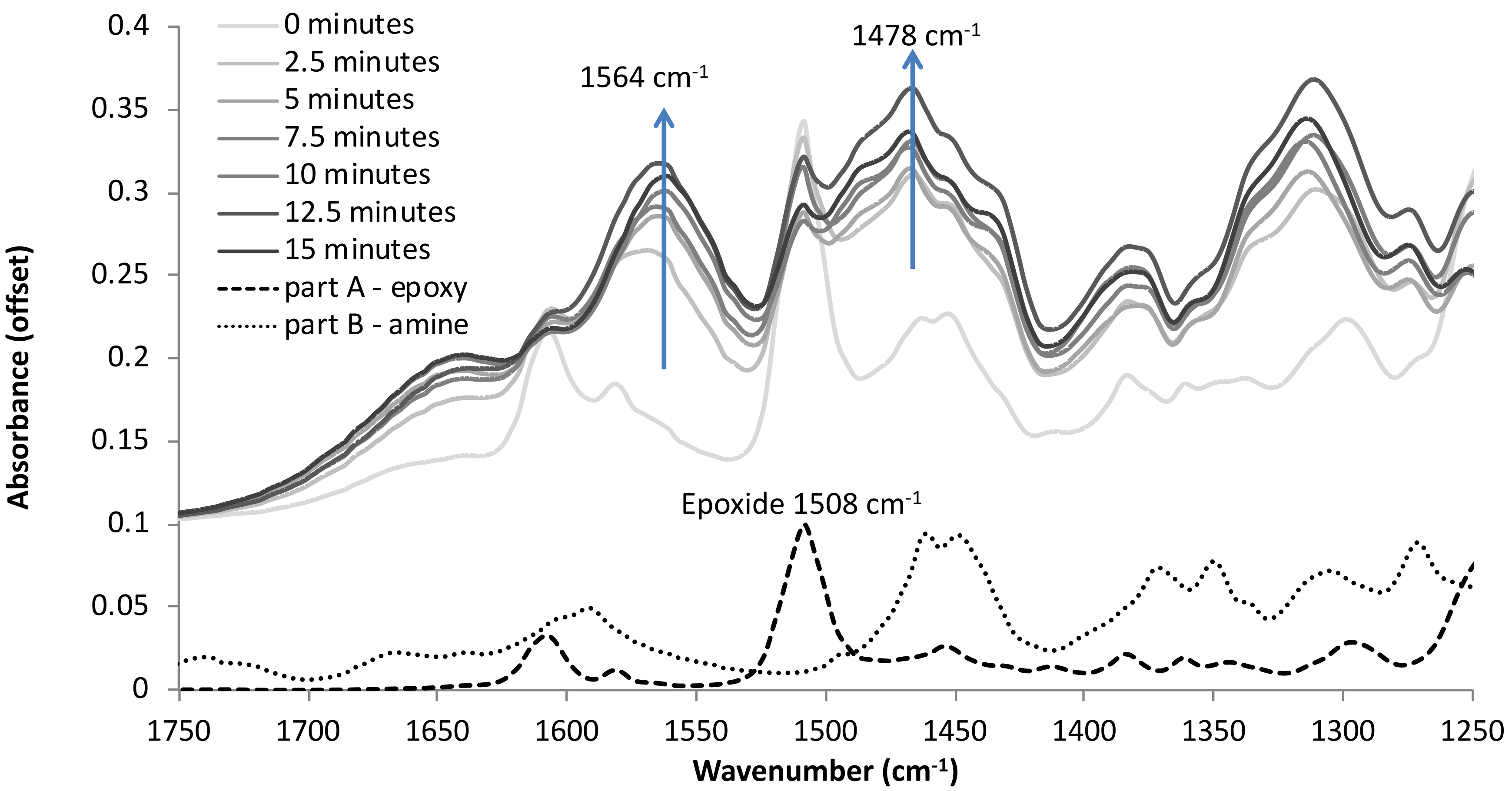
- Attenuated Total Reflectance (ATR) FTIR is ideal for analyzing surface effects
- IR beam penetrates ~0.5 -3 μm of sample depth

Methods – FTIR – Wet adhesive study



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

Methods – FTIR – Wet adhesive study



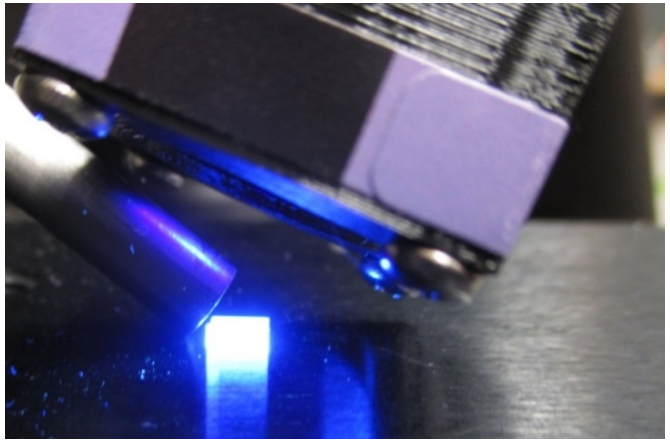
Carbamate peaks (1564 & 1478 cm^{-1}) increase as exposure time increases

- Use epoxide as reference peak

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

Methods – Visual analysis techniques

Amine blush. Courtesy of the author



- 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

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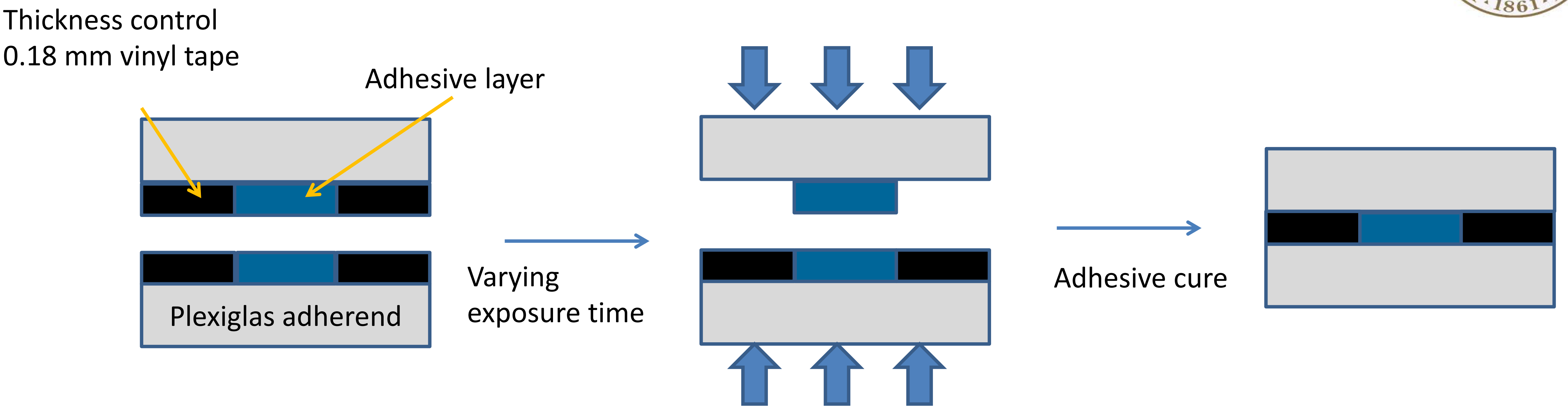
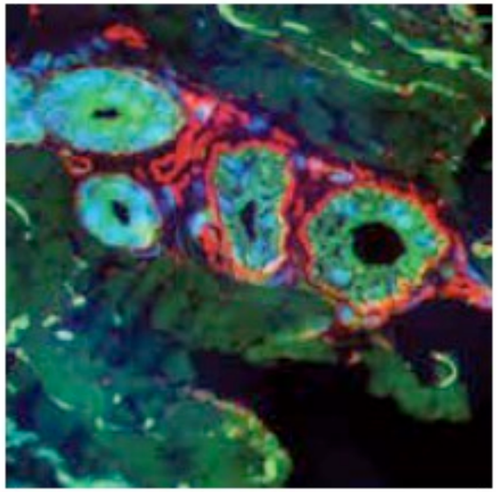
Methods - Microscopy



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

Methods – Fluorescence Microscopy

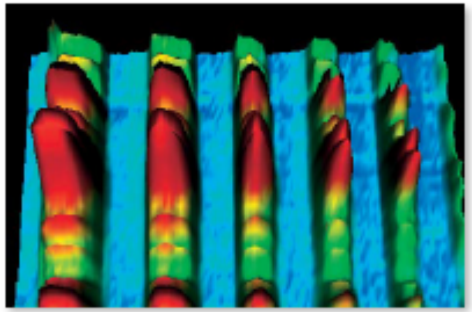


Dye	Excitation (nm)	Emission (nm)
DAPI	357	447
GFP	470	510
Texas Red	585	624

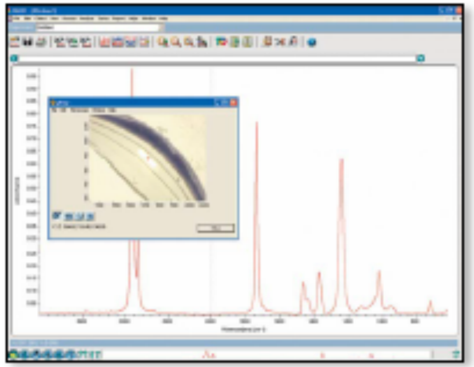
- Thermo EVOS FI Microscope
- Blue, green, red wavelengths & filters, designed for biological dyes
- Overlay single-color images to highlight subtle features
- Is blush more obvious with other wavelengths of light?

Methods – FTIR Microscopy

Infinity-corrected design and TruView optics allow sharp visible images to be seen while collecting IR data.

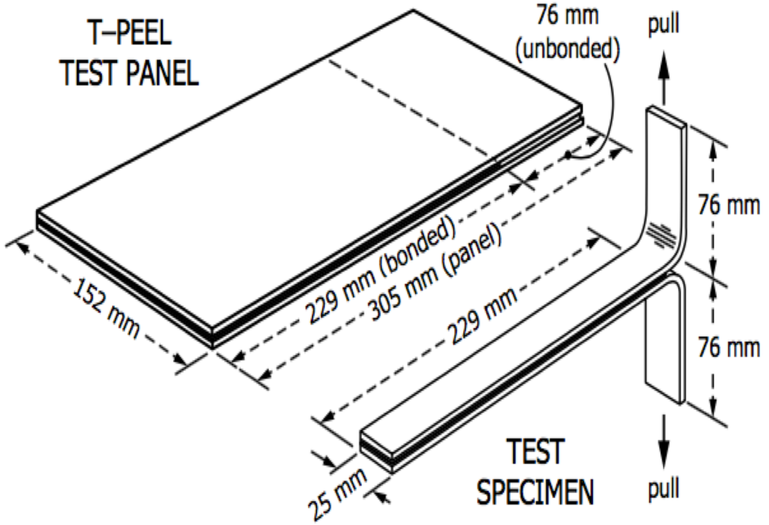


Spatial resolution achievable with the Slide-On TipATR Objective (Photoresist target. Latter profile <5 µm wide)



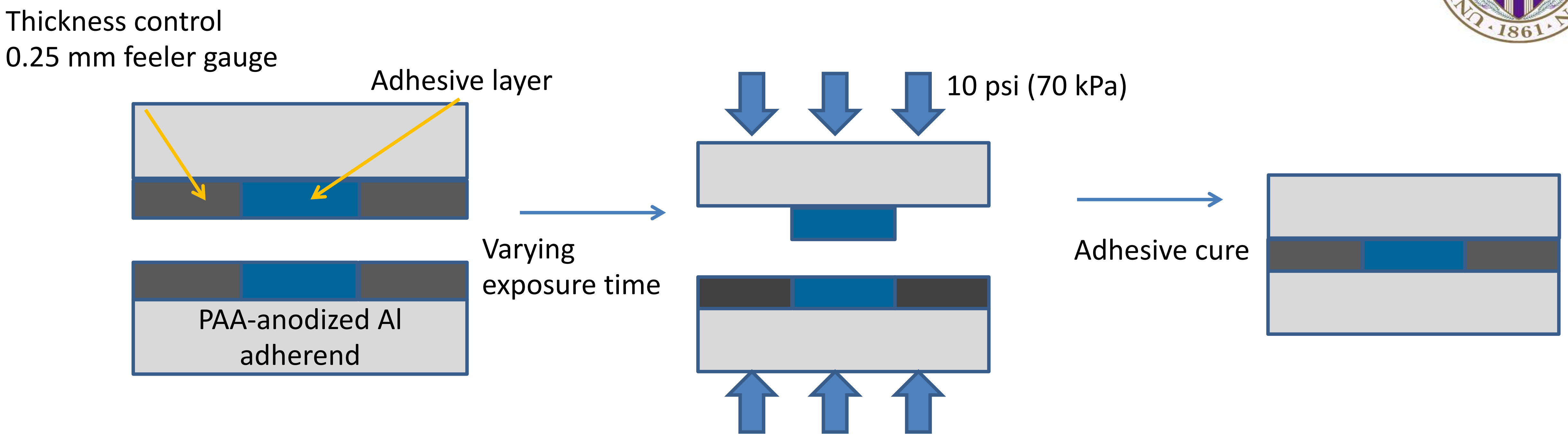
- Nicolet Continuum IR microscope
- Collect FTIR spectra from different sample locations
- 50 μm^2 areal resolution

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

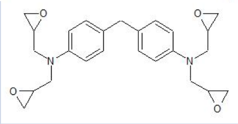
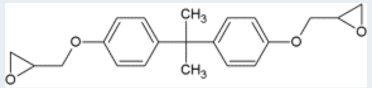
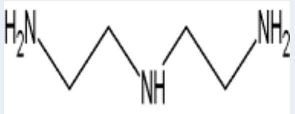
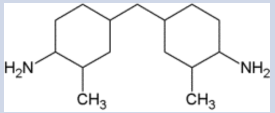
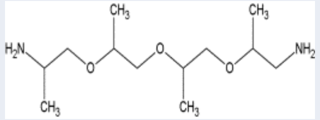


- T-peel sample manufacturing
- Dual .25 mm (10 mil) layers squeezed to single .25 mm (10 mil) layer
- Cut into 300 mm long T-peel specimens with 75 mm unbonded length

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

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

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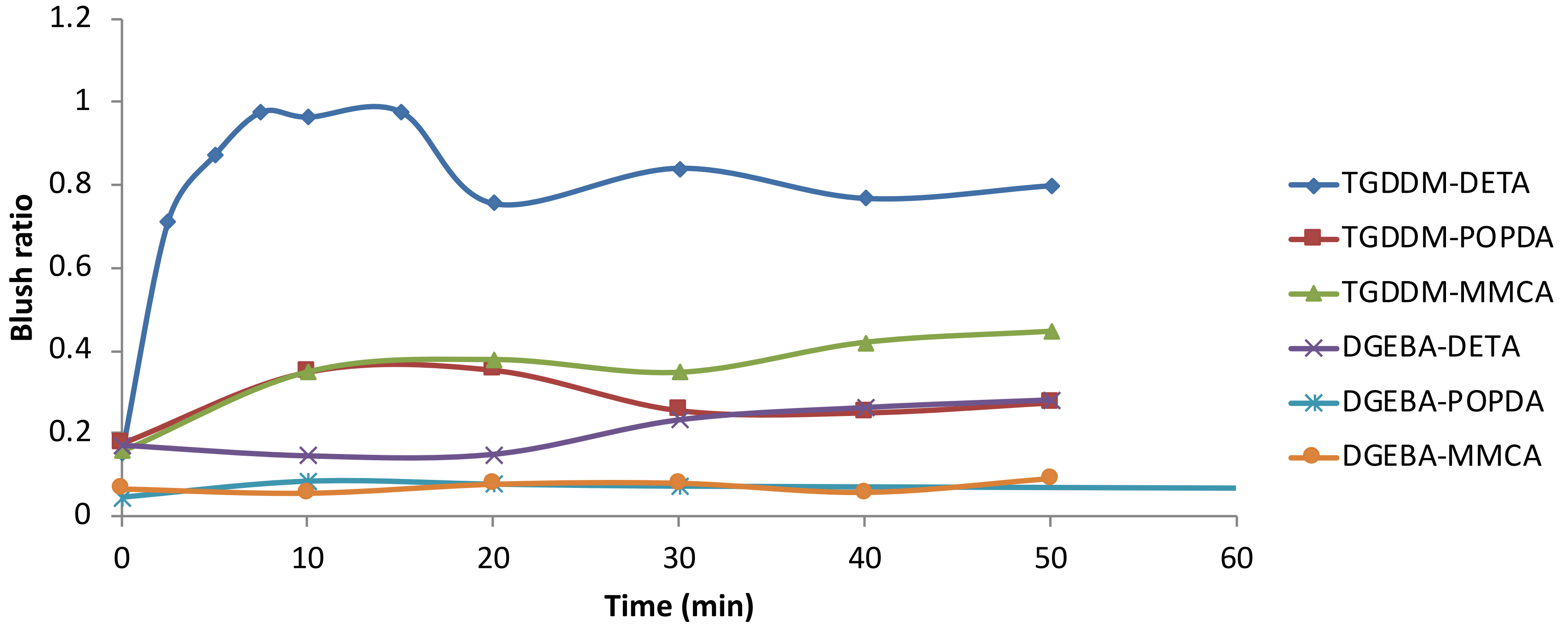
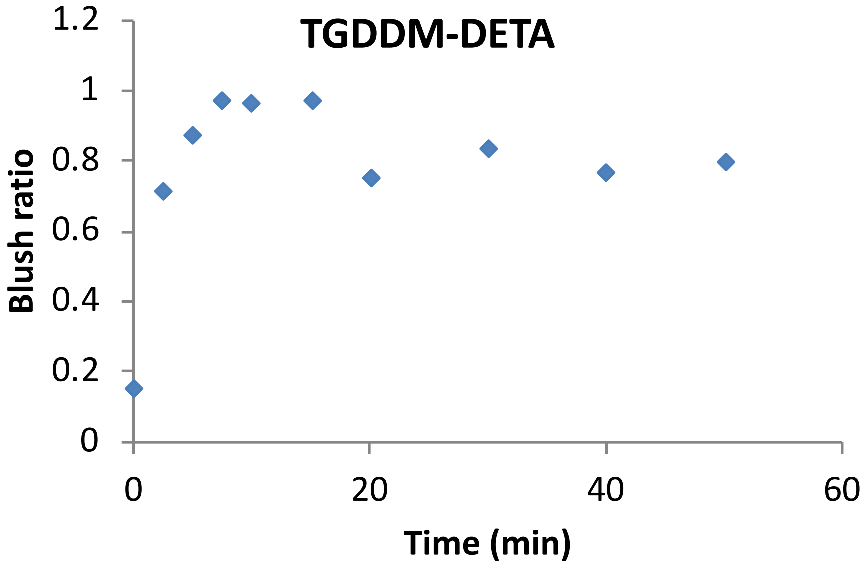
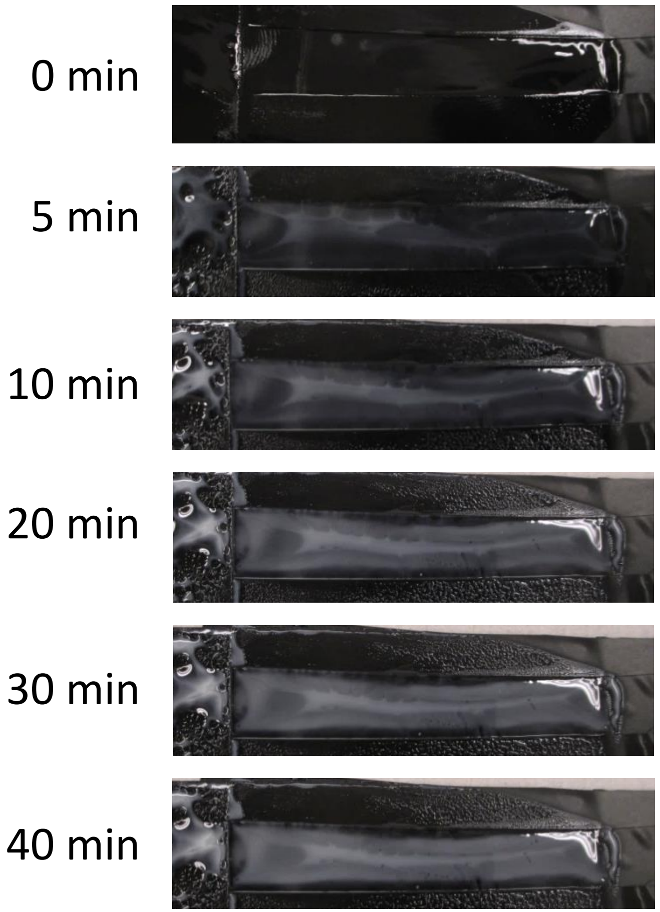
Model formulations



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

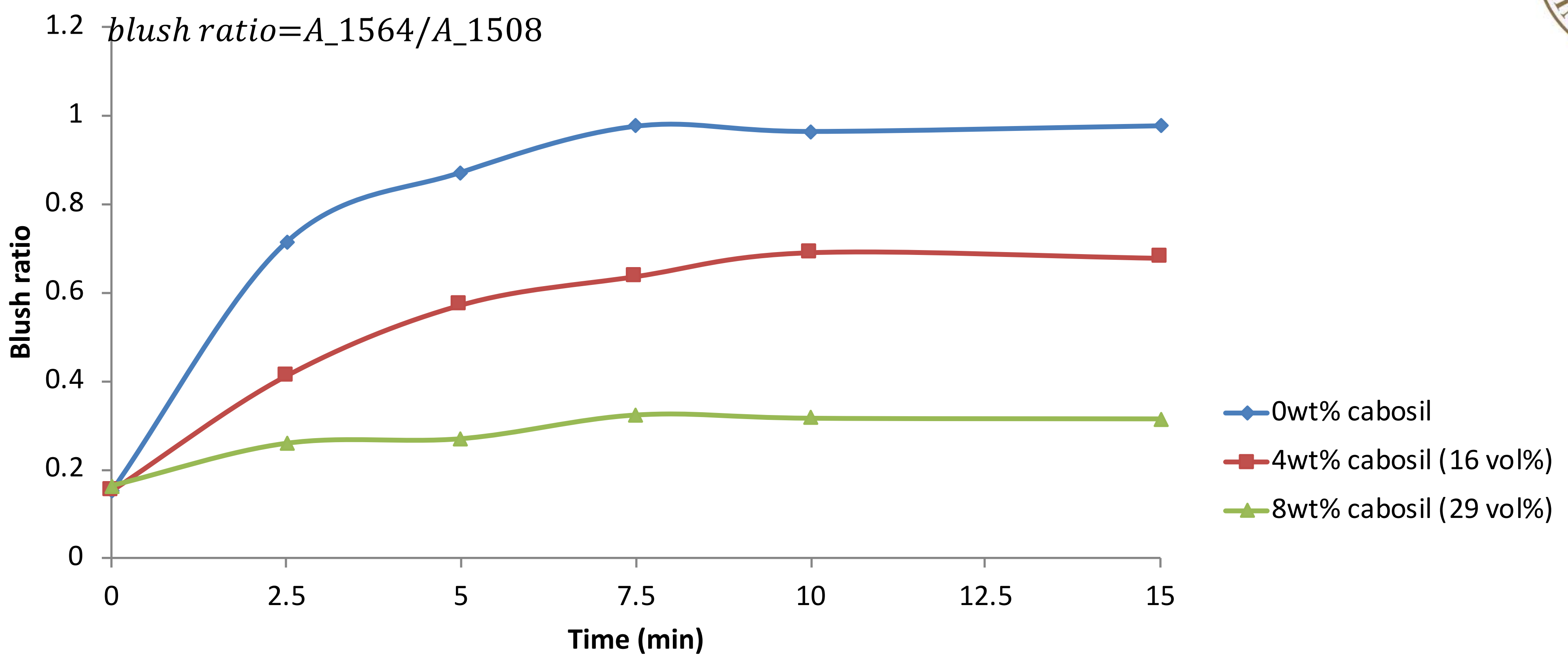
Model formulations – TGDDM-DETA





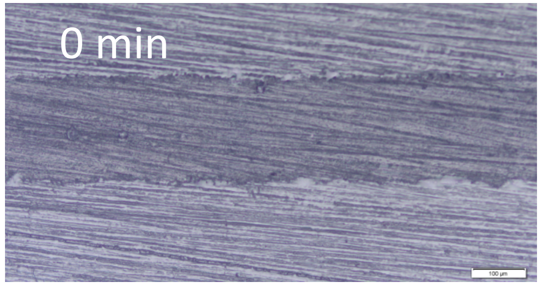
- Downselect to TGDDM-DETA for extended study
- Blush formation visible on same timescale as FTIR

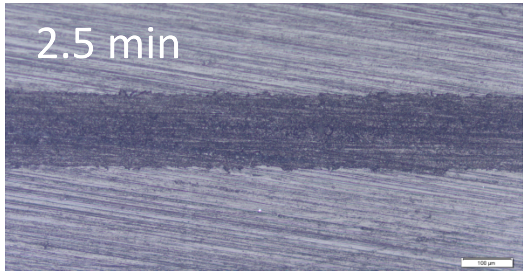
Model formulations – TGDDM-DETA FTIR

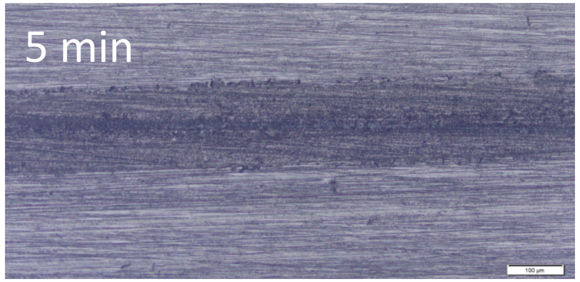


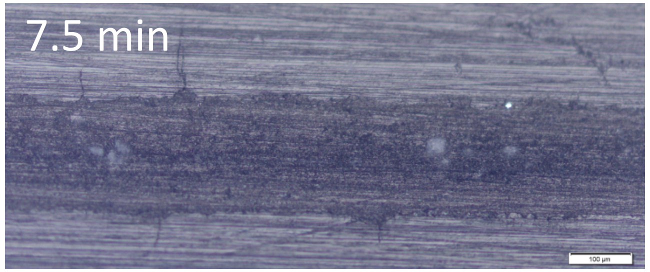
- Add fumed silica (Cab-o-sil) for closer approximation of paste adhesive
- Increasing wt% Cab-o-sil causes slower, less extensive blush
- Viscosity-based change to Damkohler number?

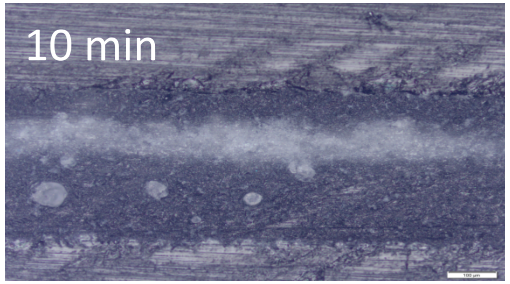
Model formulations – TGDDM-DETA microscopy

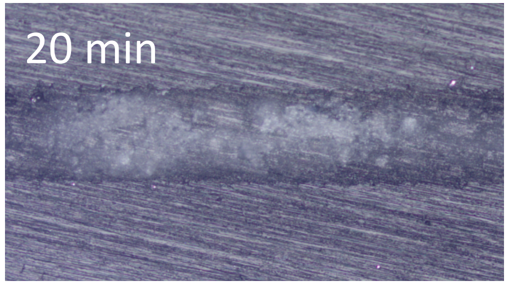


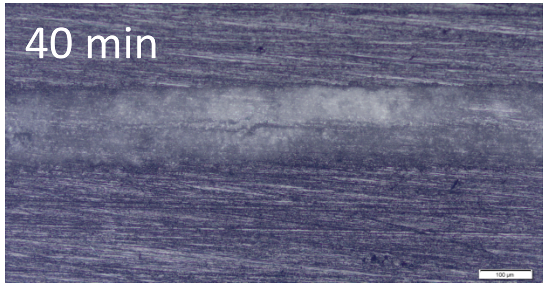






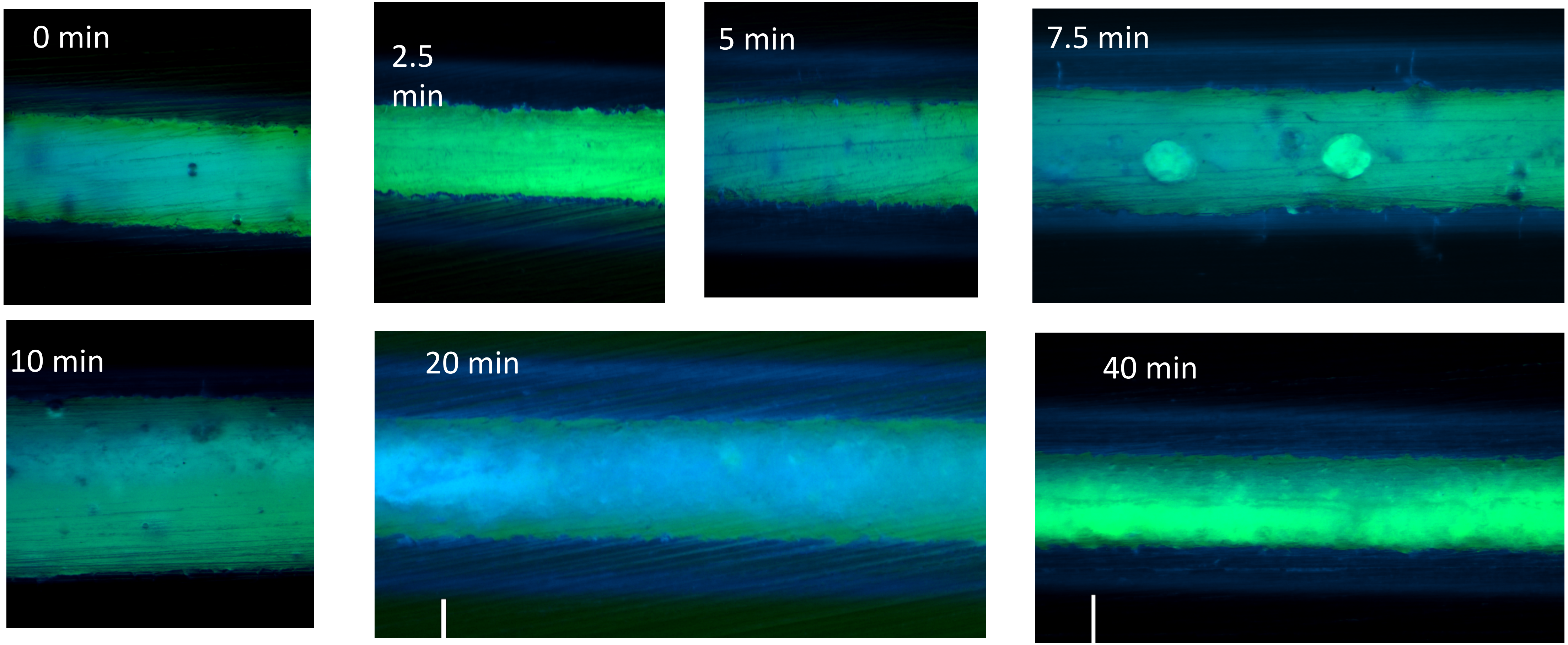






- Inclusions of amine blush visible at 7.5 min
- Full bondline presence at 10 min
- 20 min and 40 min extensive presence

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

Outline

- Methods
  - FTIR
  - Traditional and Fluorescence Microscopy
  - T-peel bond strength test
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  - Effect of stoichiometry
  - Effect of thickener concentration
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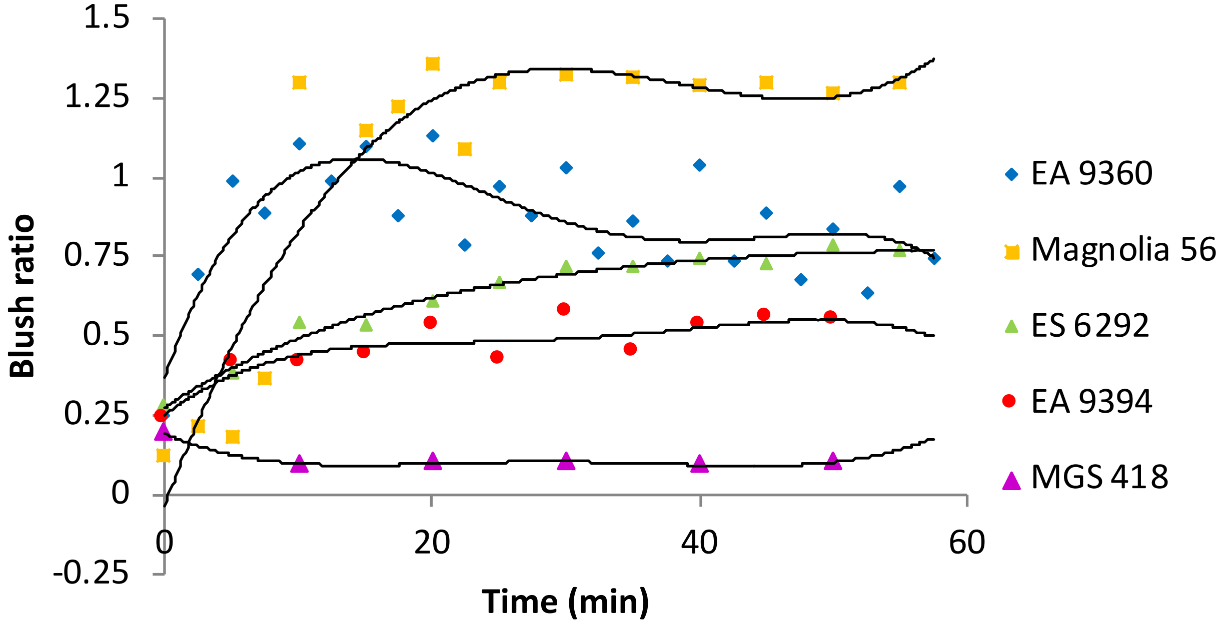
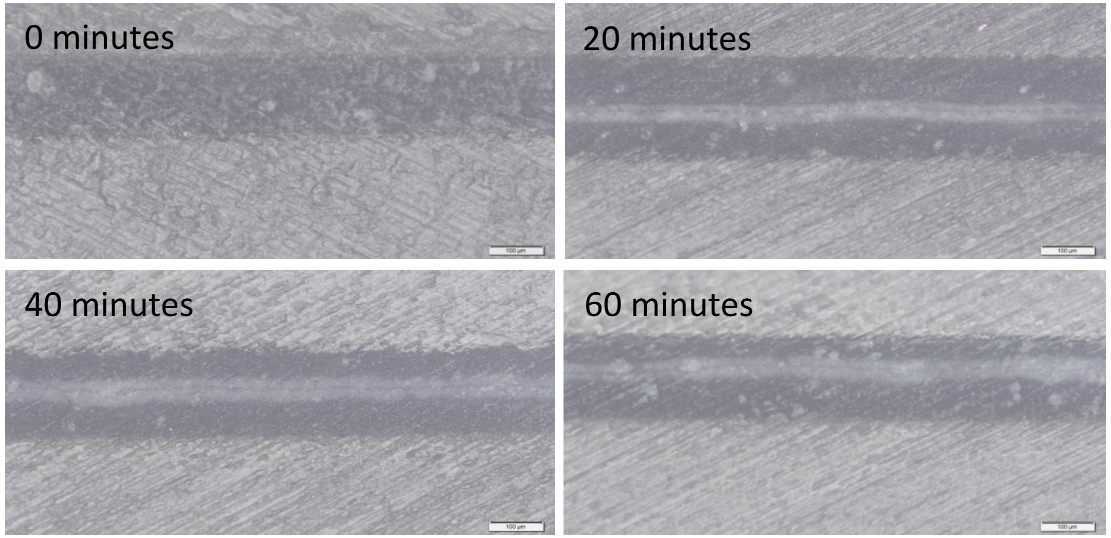
Commercial systems

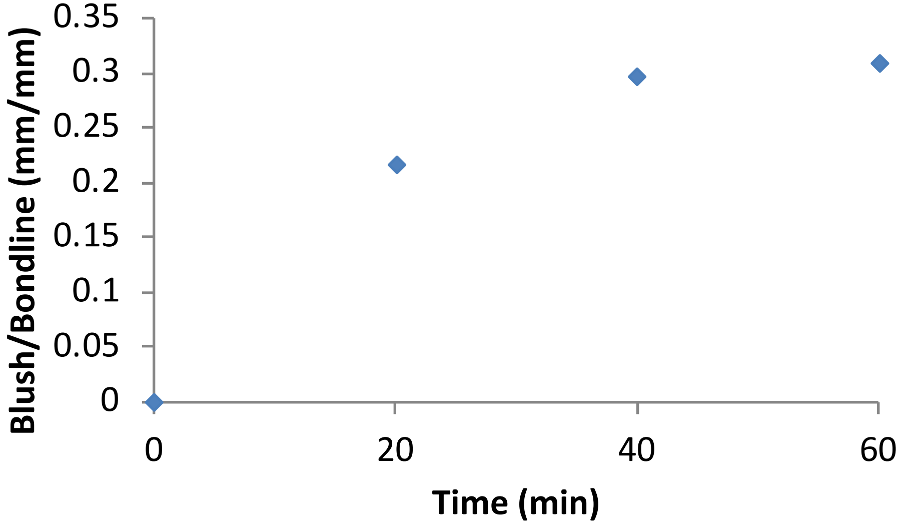


Adhesive	Δ blush ratio (min^{-1})	RT Pot life (min)
Magnolia 56	.070	180
EA 9360	.055	50
ES 6292	.0082	40-50
EA 9394	.0046	90
MGS 418	-.0013	300-360

- 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
- None: Hexion MGS 418

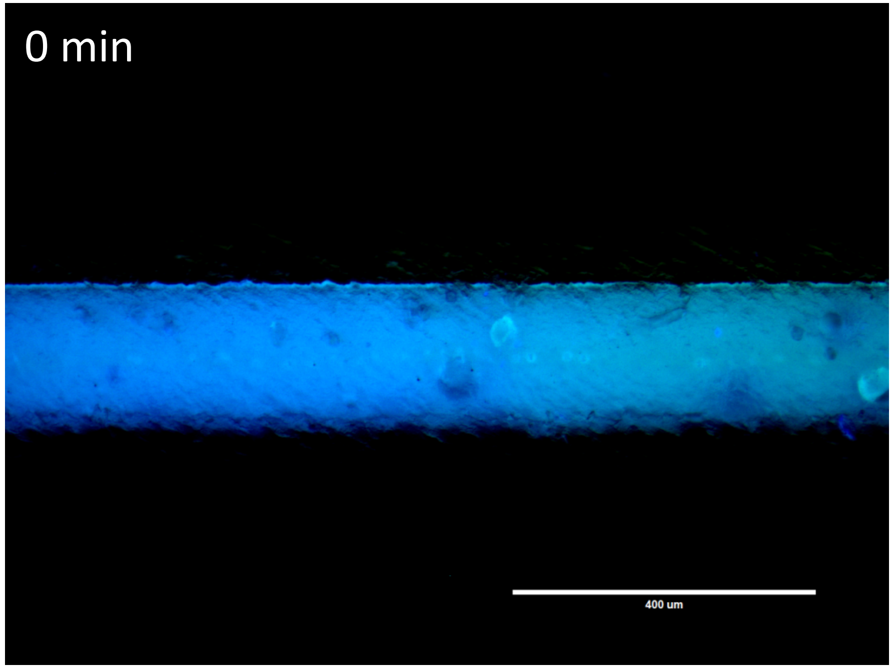
Commercial systems – EA 9360 microscopy

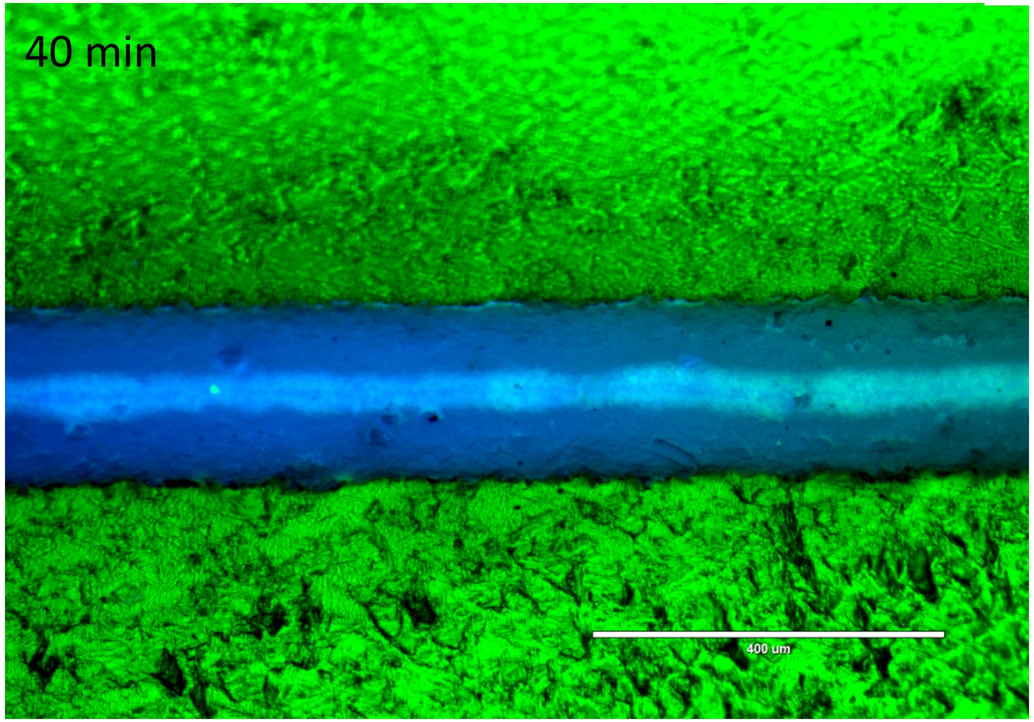




- Blush formation is visible in bondline after 20 minutes post-spread exposure
- Ratio of blush to bondline thickness increases, plateaus over time

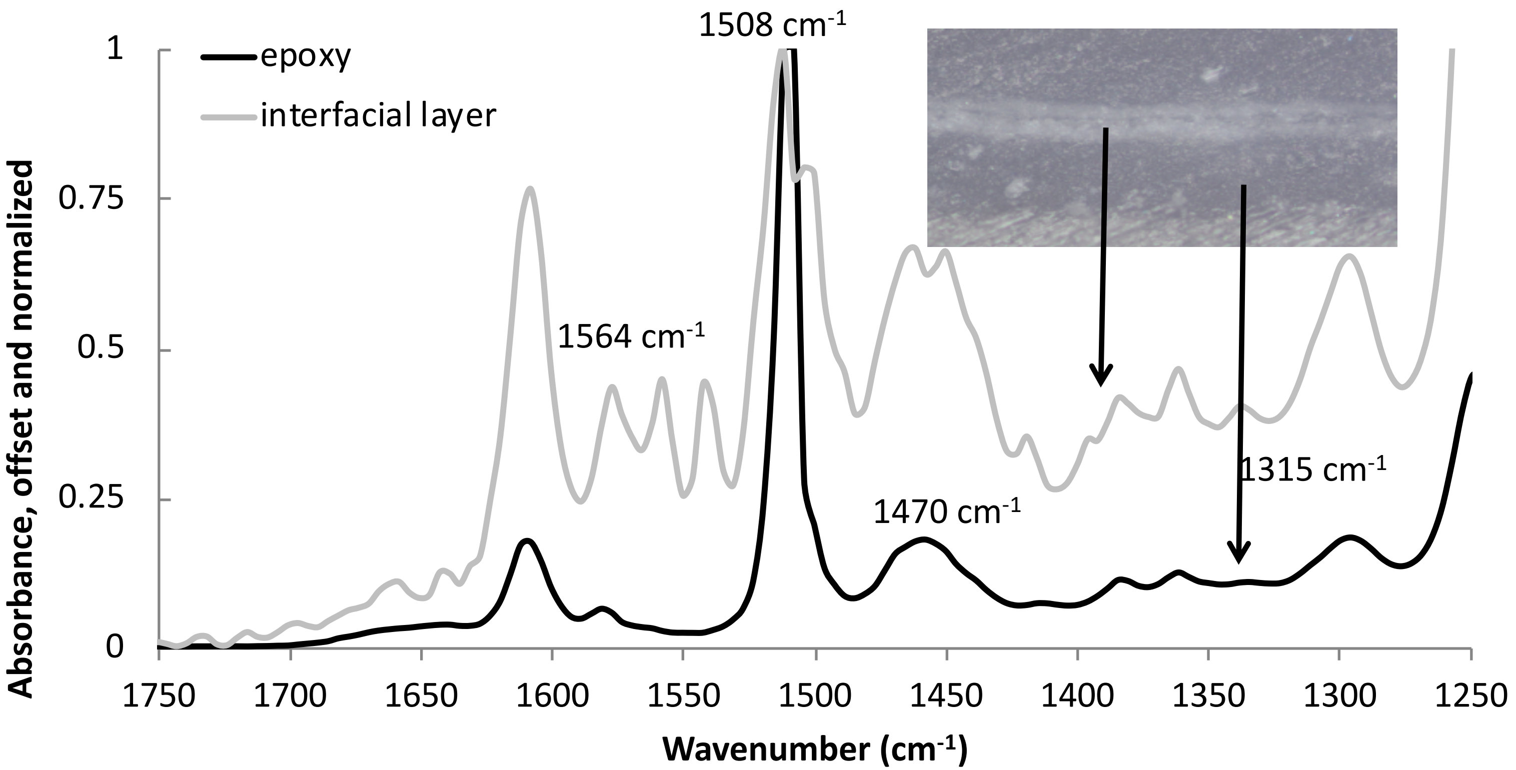
Commercial systems – EA 9360 Fluorescence





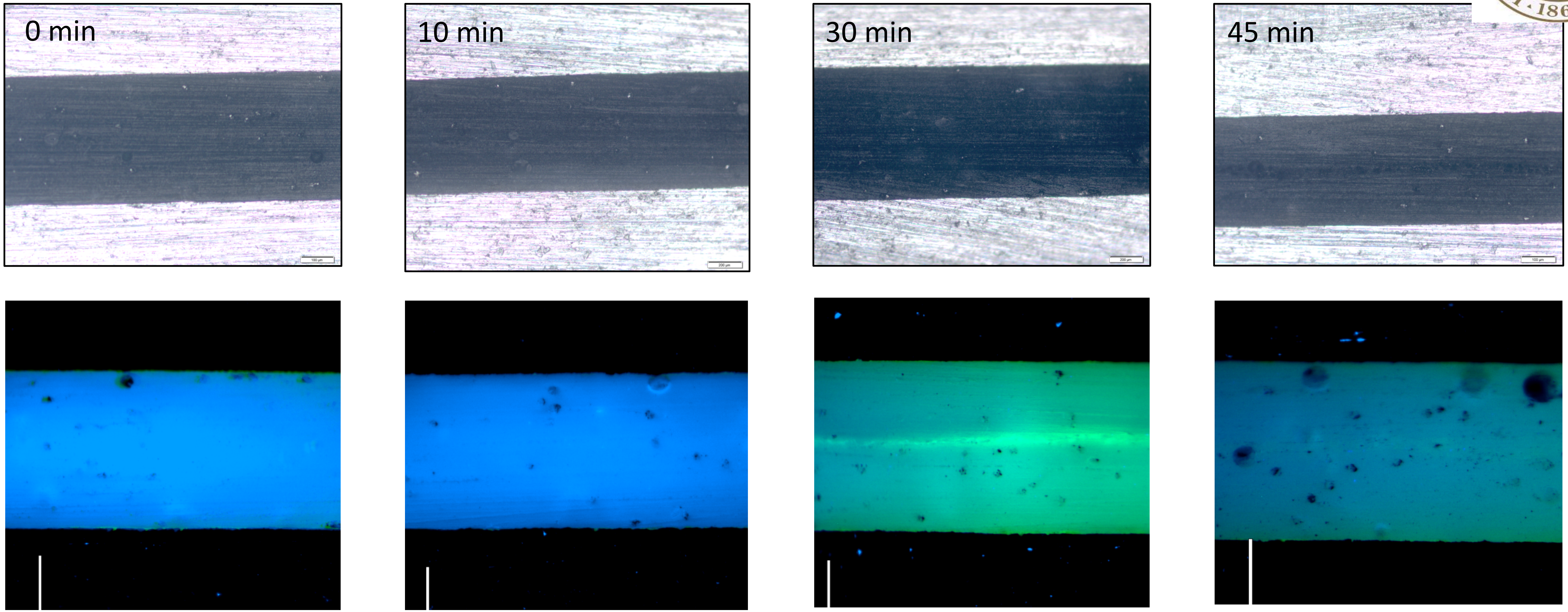
- Images using DAPI (blue) and GFP (green) filters
- Blush layer clearly visible

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

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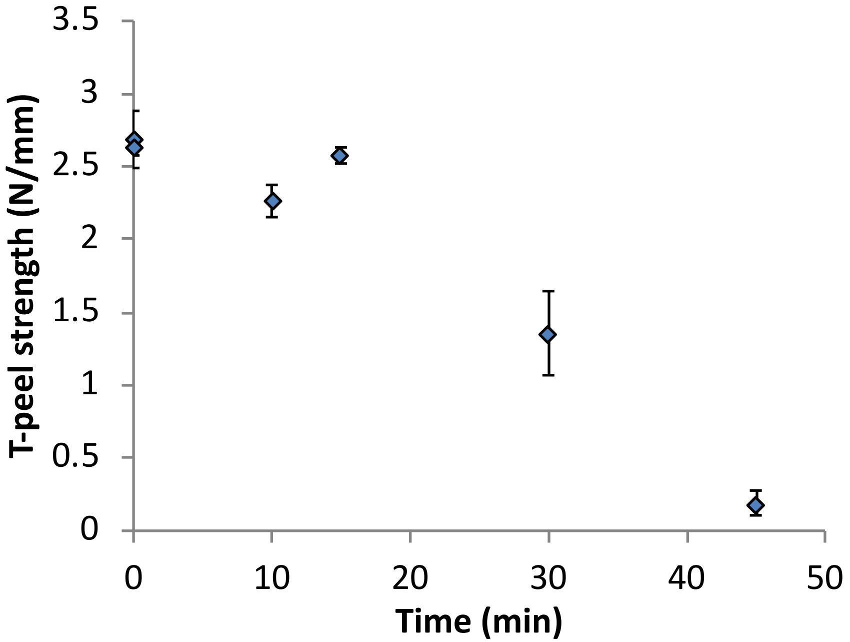
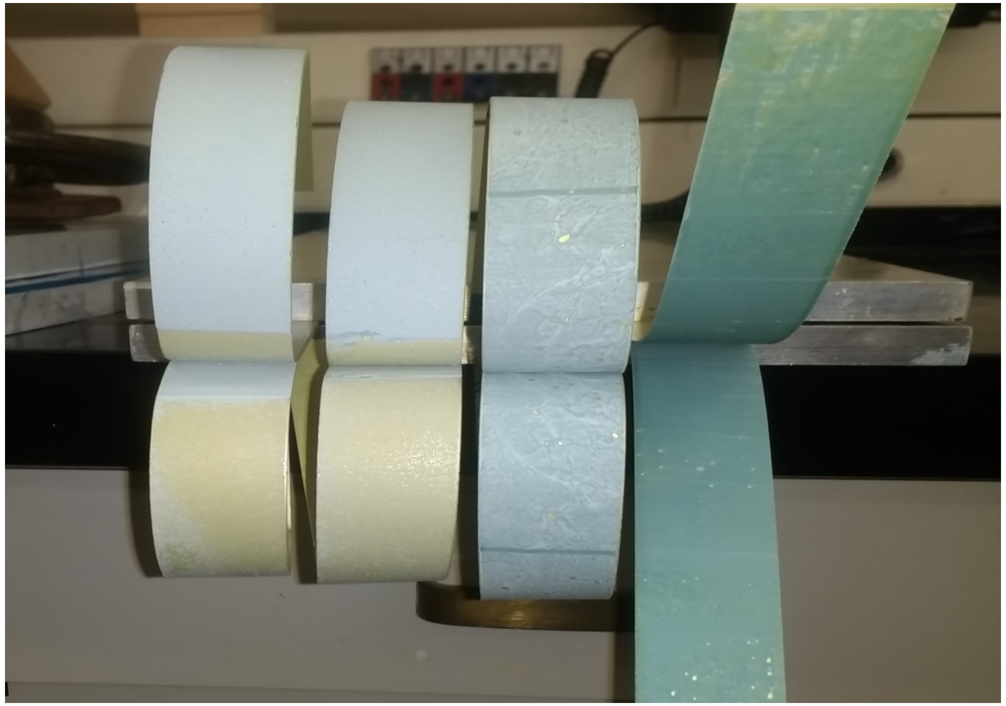
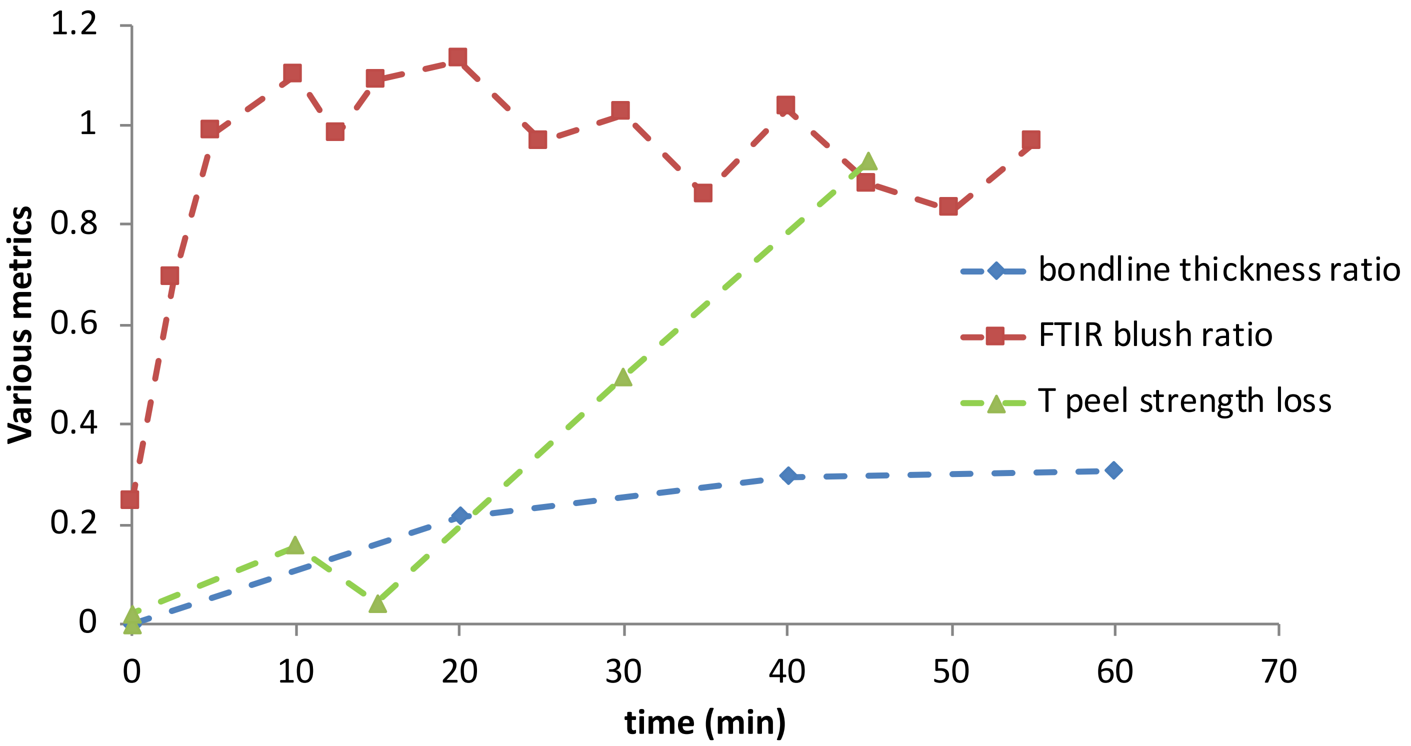
Commercial systems – EA 9360 T-peel strength





- 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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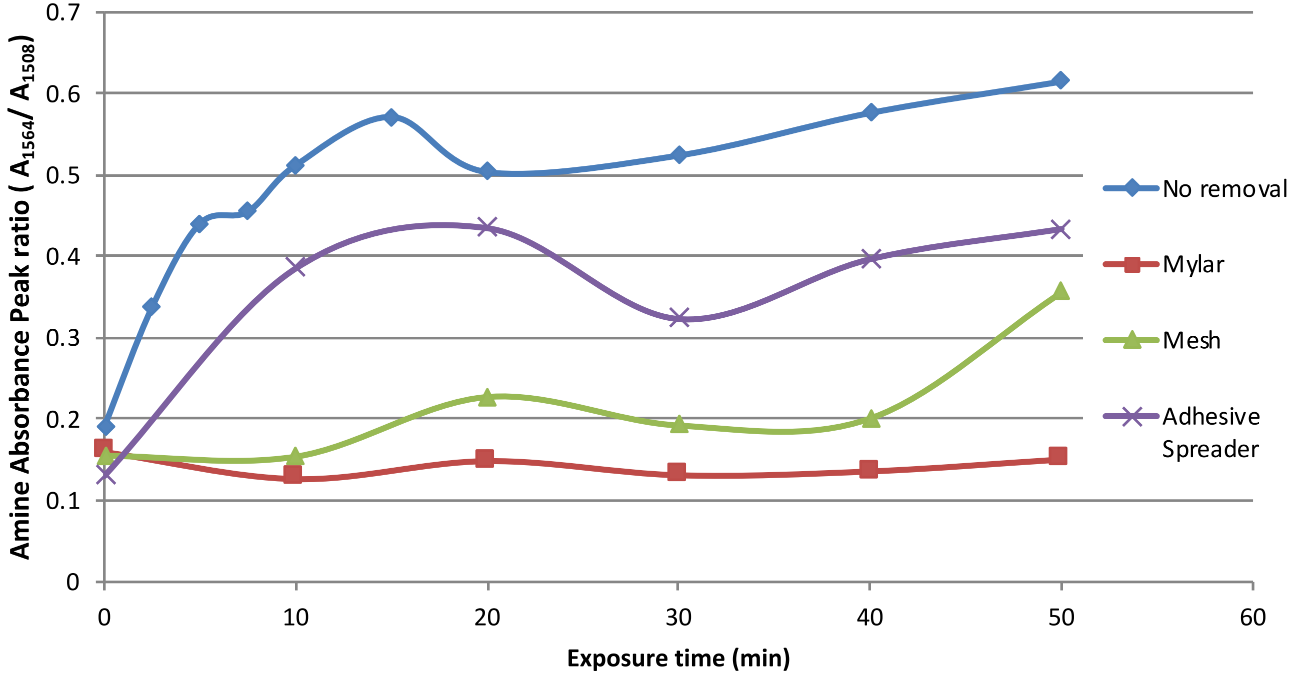
Amine Blush Mitigation

Surface Amine Blush Removal TGDDM-DETA 1-1 Ratio 4wt% cabosil



- 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

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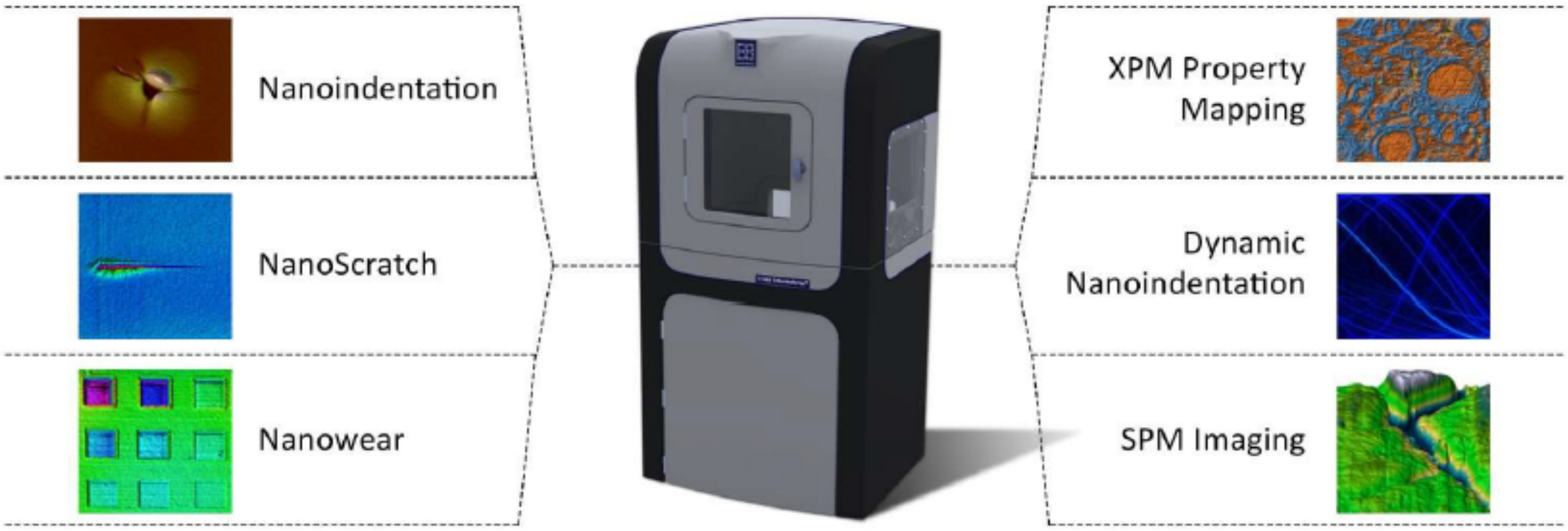
New UW capabilities for bonding research



The world's most comprehensive nanomechanical and nanotribological test system for all your material analysis needs

- 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

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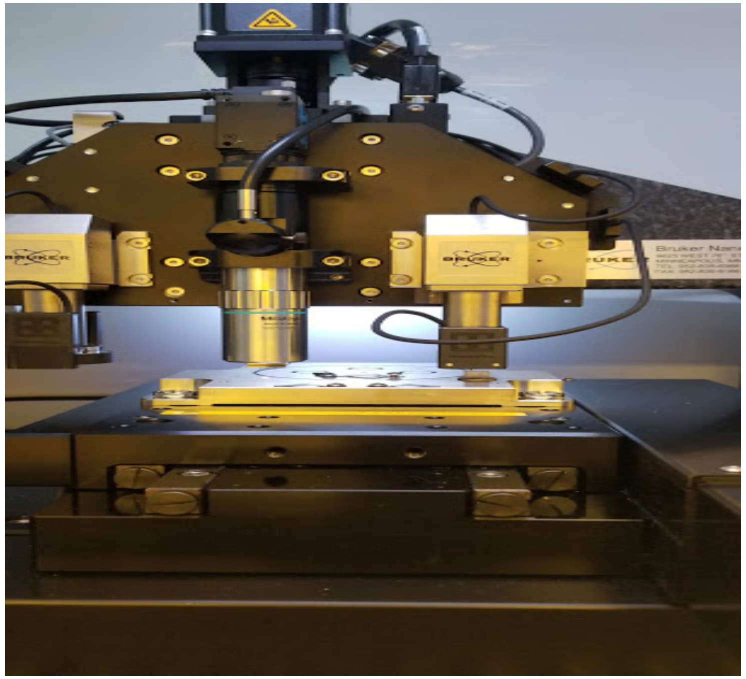
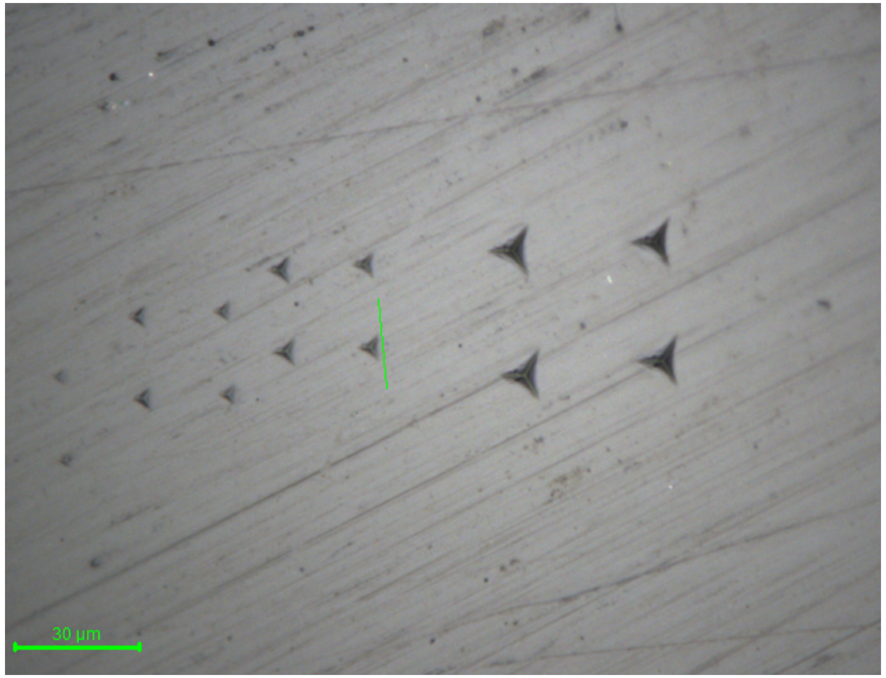
Nanoindentation

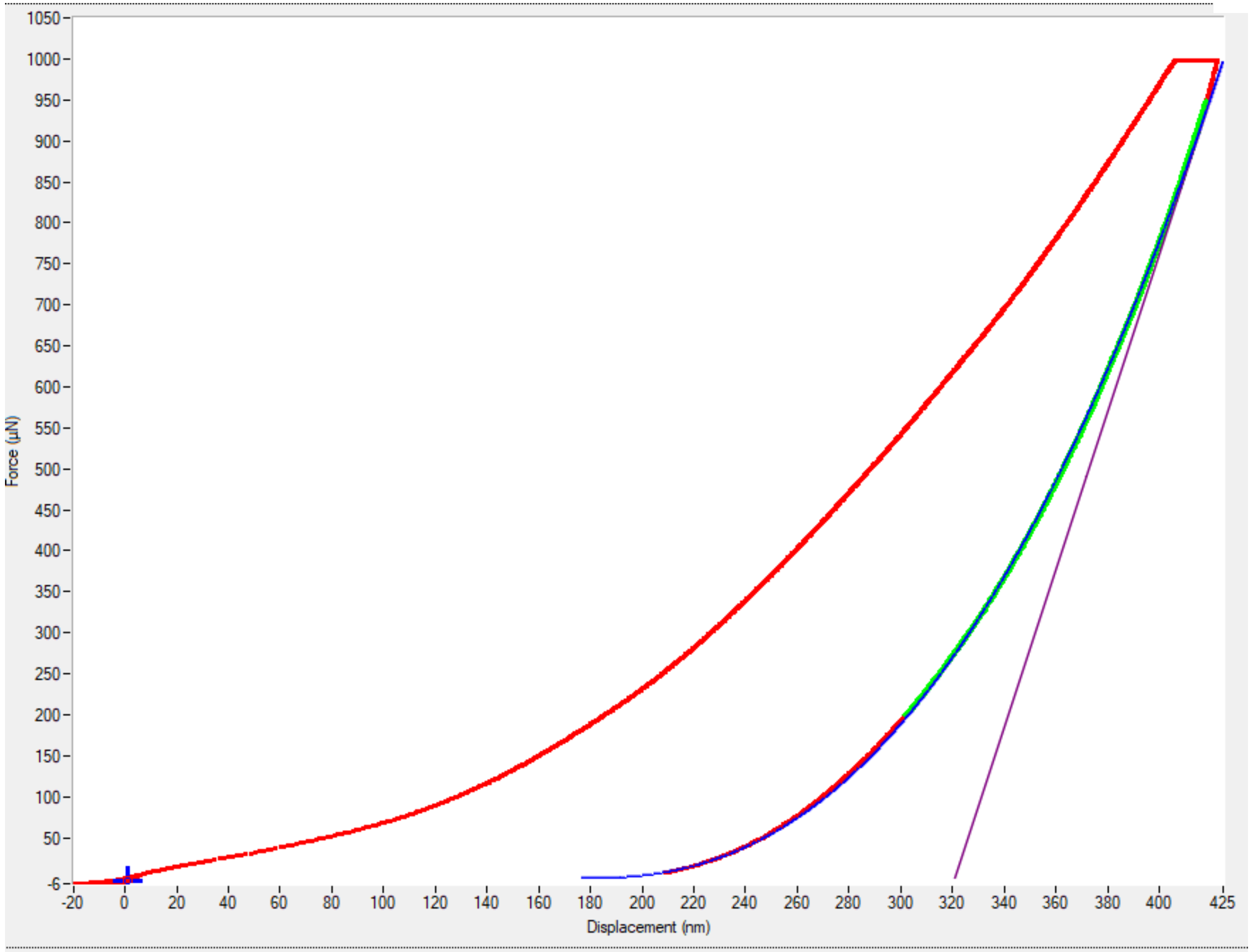




- Depth of penetration measured and area of contact is determined by indenter geometry (Berkovich tip)
- Hardness is found by dividing force by area of contact
- Reduced modulus is calculated based on slope of unloading curve

Load Control Mode

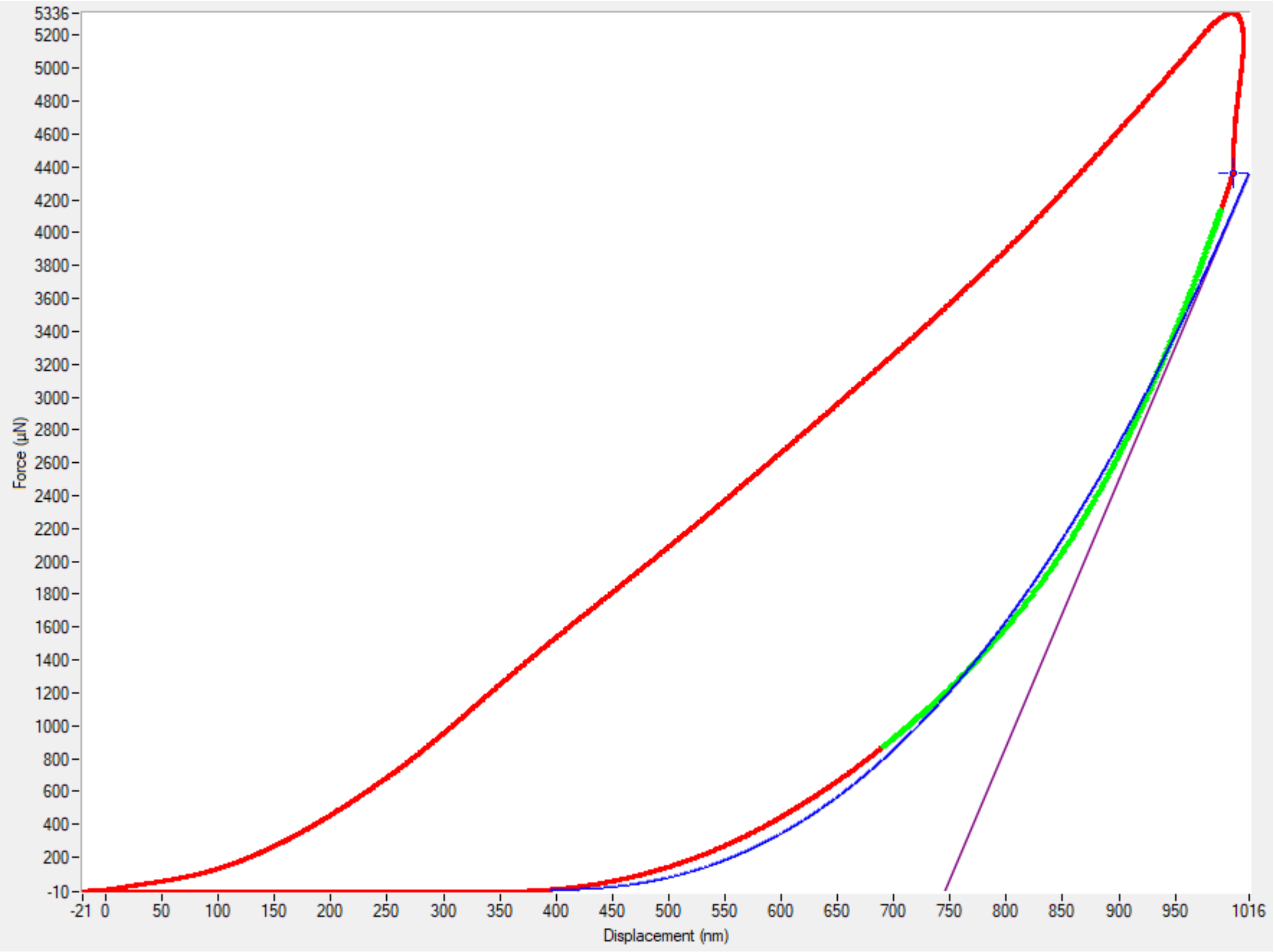
- Nanoindenter applies specified load and holds for several seconds, then releases load
- Force vs. Displacement curve generated
  - Viscoelastic behavior can be seen at the peak, as the material continues to deform while the 1000µN force is held for 5s



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

Displacement Control

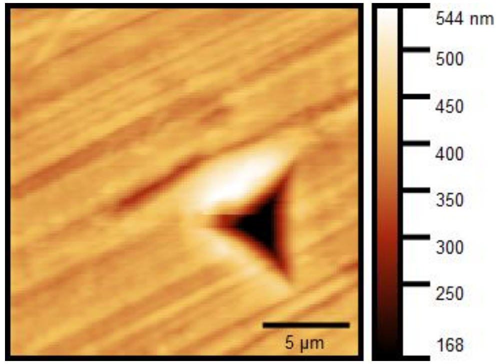
- Nanoindenter indents samples to a specified depth, holds for several seconds, then withdraws from sample
- Force vs Displacement curve generated
  - Stress Relaxation
  - load drops while displacement held constant

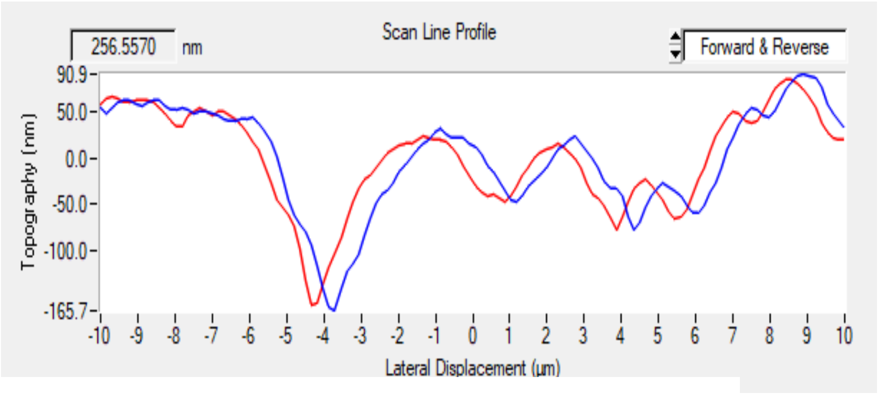


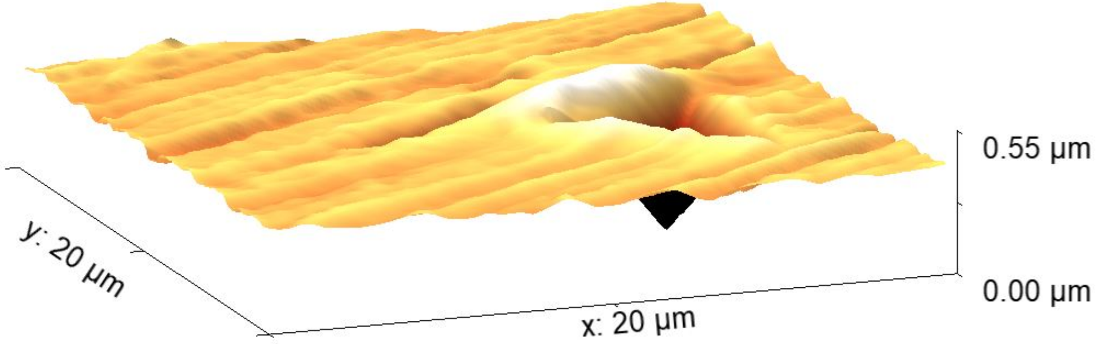
Acrylic adherend: 1000 nm deep indent applied at 100 nm/s, held for 5s, then removed at 100 nm/s

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

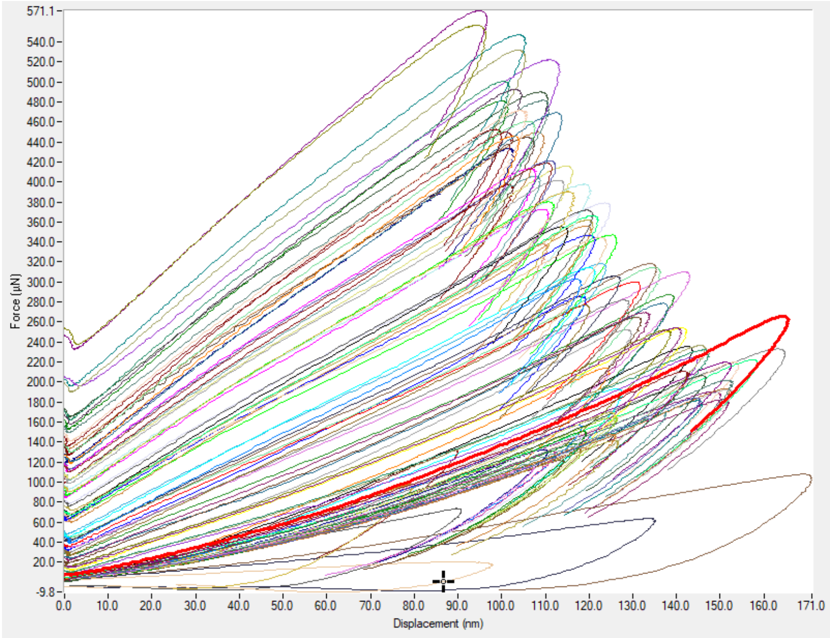


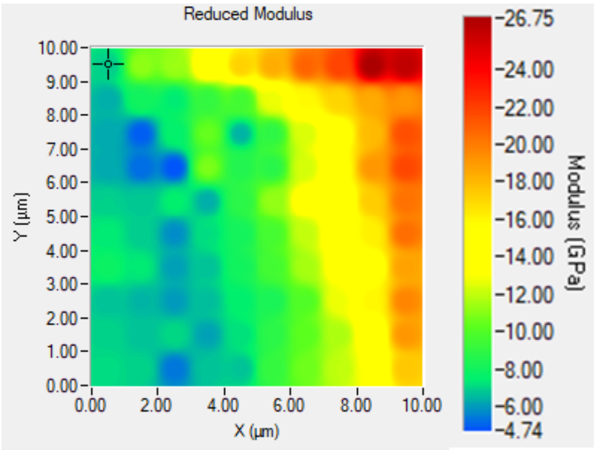


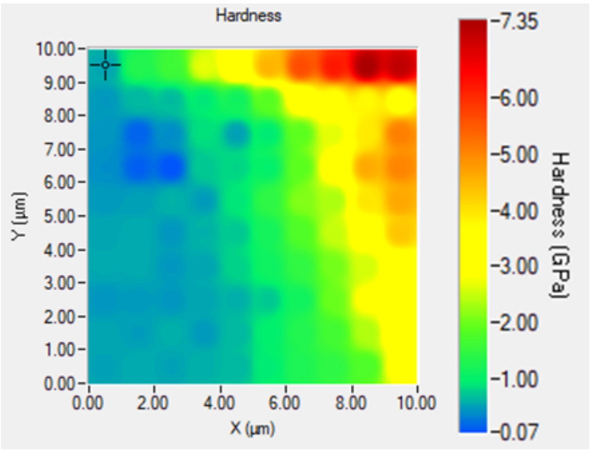


XPM (Accelerated Property Mapping)

- 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





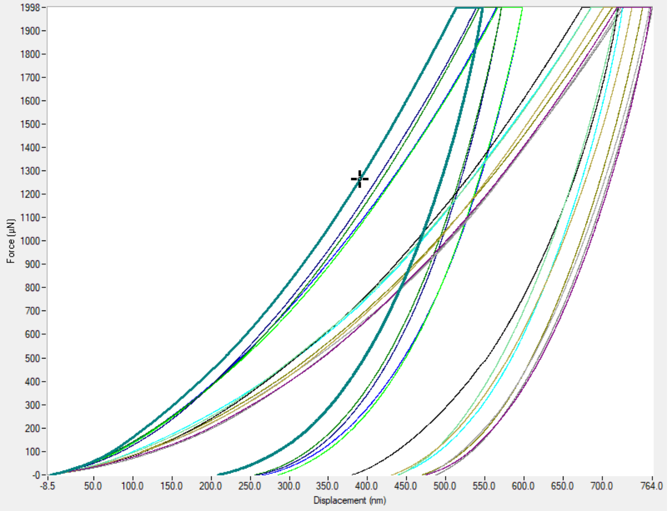


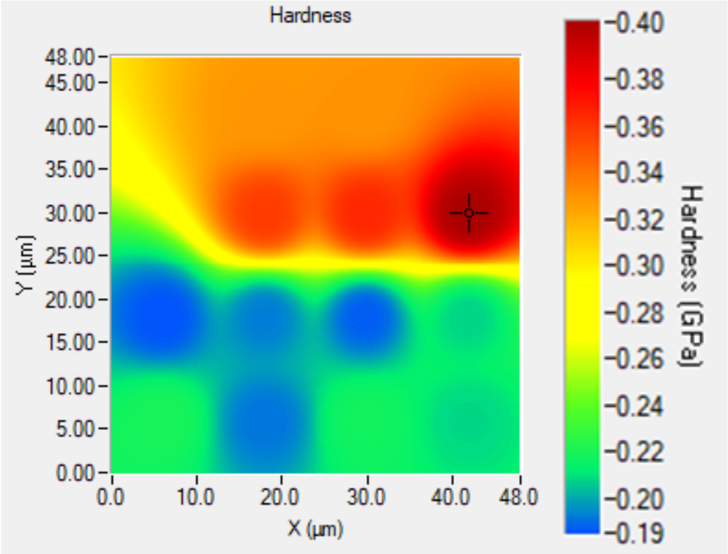
$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A}}$$

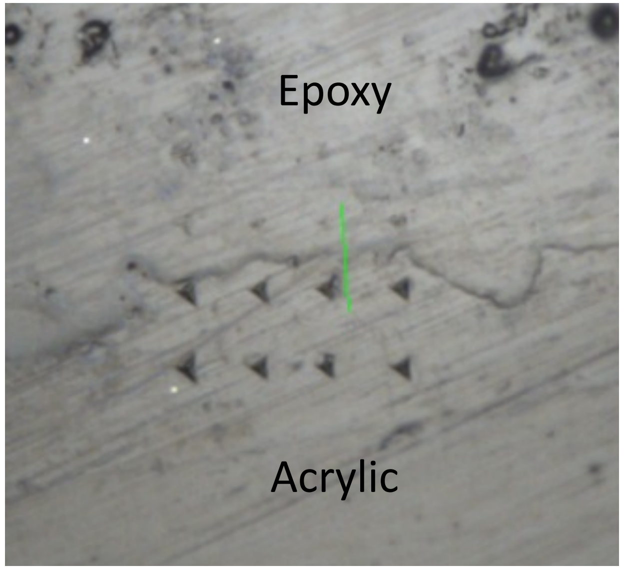
$$H = \frac{P_{max}}{A}$$

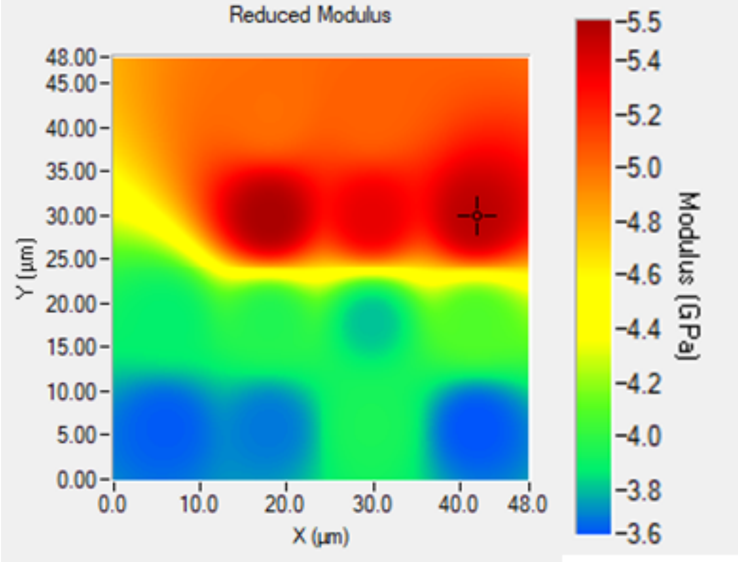
XPM on Bond Interface

- 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

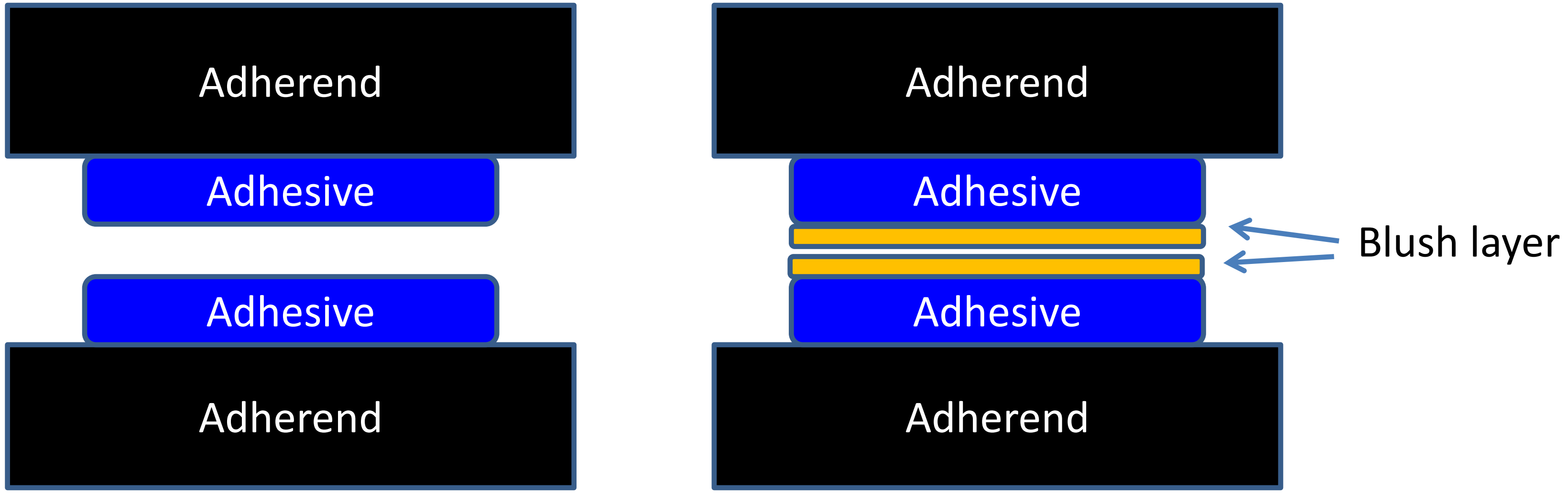
- **Benefit to Aviation**
- Better assurance that paste adhesives and use conditions will result in good bonds
- Establish a correlation between blush detection methods and bond strength for industry use

- **Future needs**
- Further study on several adhesive systems
- Standardized optical microscopy techniques
- Correlation with Nano-indenter mechanical property measurements

Thank you! Questions? Suggestions?

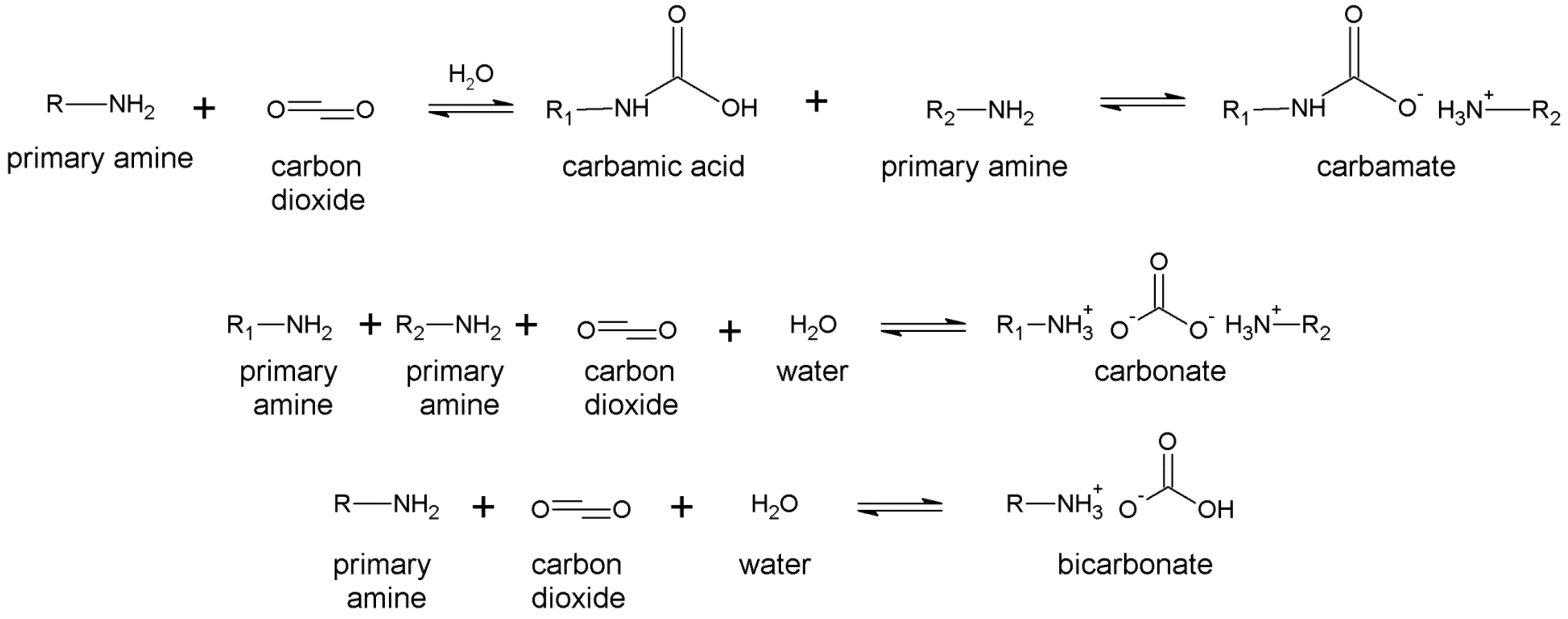
Other work slides

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

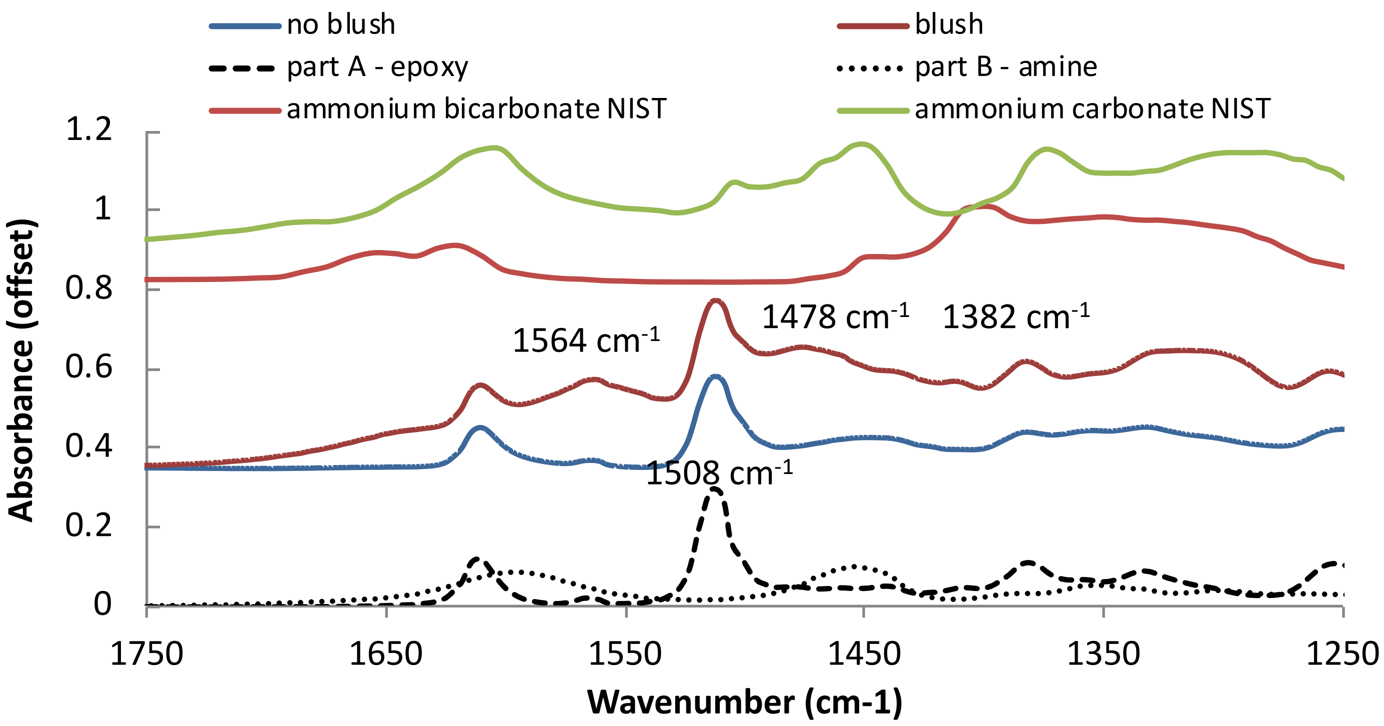
Introduction



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

Methods - FTIR

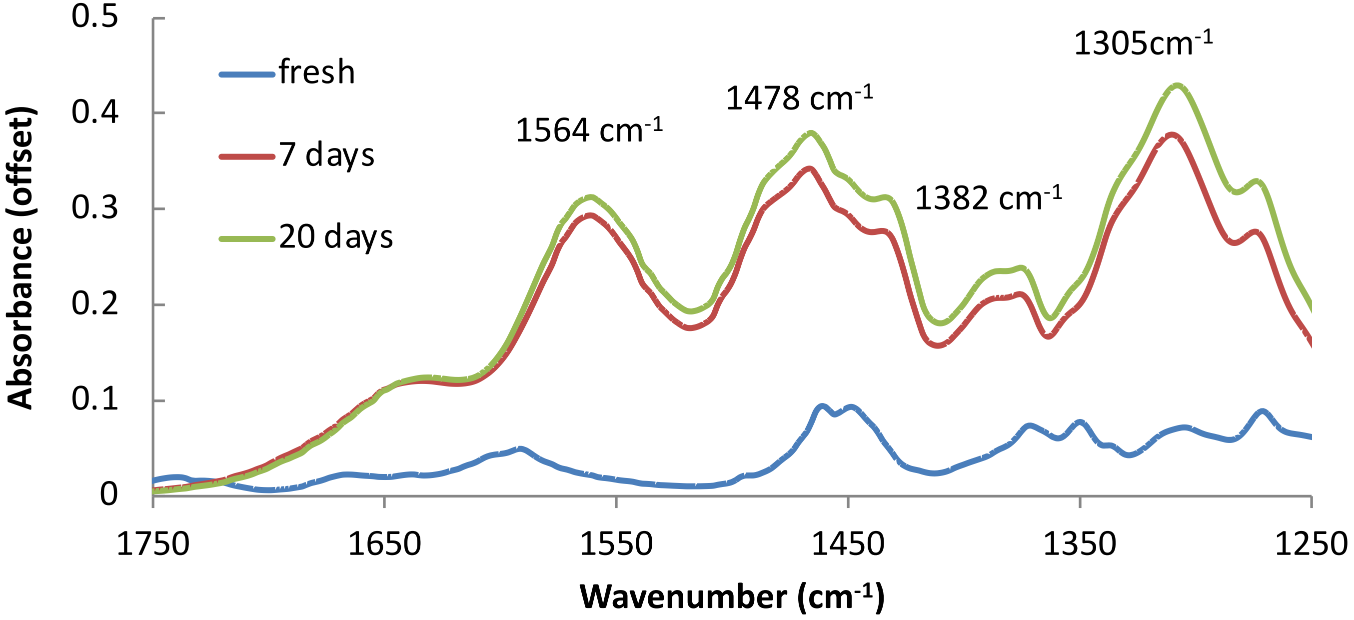
Species, bond type	IR peak (cm^{-1})
Epoxide, aromatic	1508
Carbamate, asymmetric	1550-1610
Carbamate, symmetric	1450-1350
Carbamate, stretch	1300-1260
Protonated amine	1479-1474



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

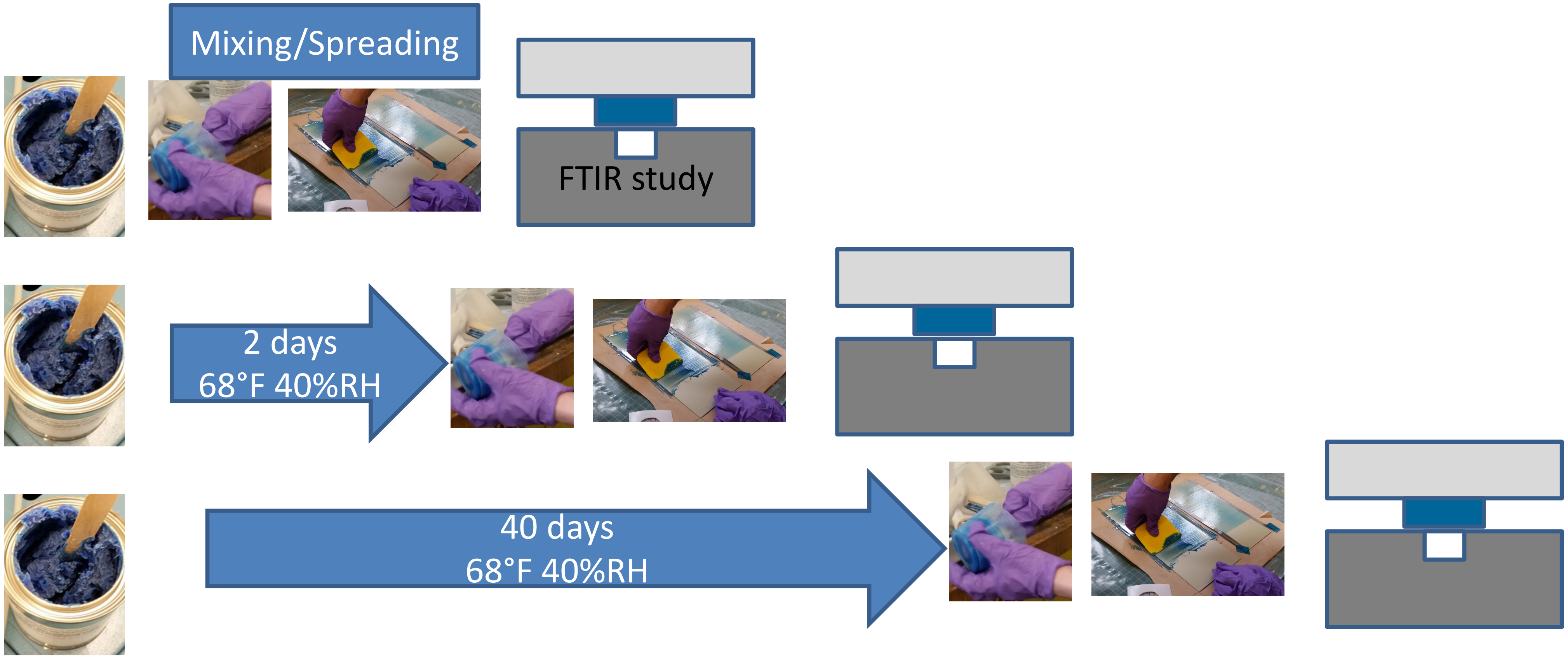
$$blush\ ratio = \frac{A_{1564}}{A_{1508}}$$

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-ai



- Samples of hardener exposed to ambient for 0-40 days
- Mixed with epoxy, spread for blush formation rate study

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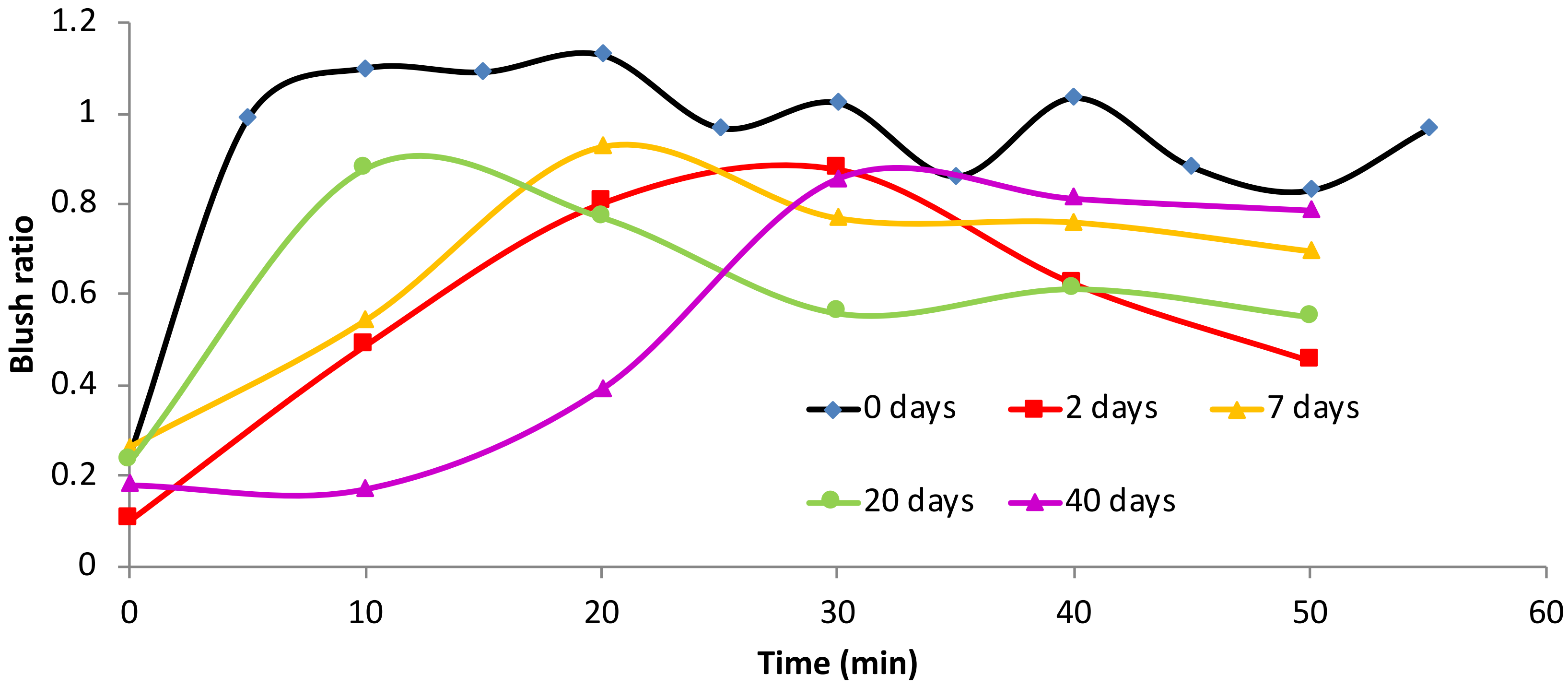
Commercial systems – EA 9360 hardener open-ai



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

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

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