Nanomechanical Characterization of Adhesive Bondlines

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Nanomechanical Characterization of Adhesive Bondlines

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- Industry Participation
  - The Boeing Company

Outline

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- Acknowledgements

Background

Adhesive Aging Effects

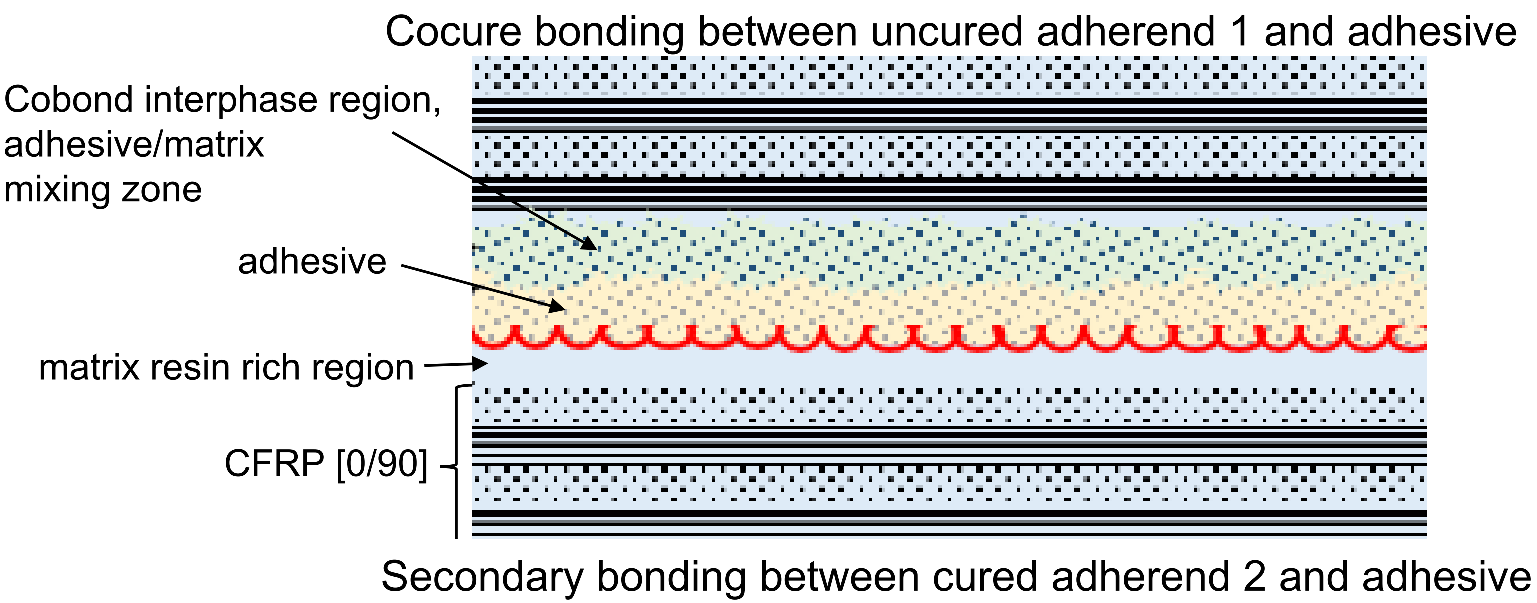
- Composite joints undergo thousands of service hours under environmental conditions (ie. hot-wet, fuel, hydraulic fluid, etc. exposure)
  - Diffusion of moisture → hydothermal aging
  - Cyclic loading → ratchet and fatigue
  - Oxygen-rich and elevated temperatures → thermo-oxidative aging

- many unknowns with the aging differences between the adherend and adhesive
  - physical and chemical aging
    - Changes in mass density and toughness
    - Plasticize
    - Tg changes
      - Moisture adsorption, cross-link density, free volume

> ➢ Do regions within the bondline age differently?
>
> ➢ Are bond degrading, and if so are they degrading at different rates?

Background

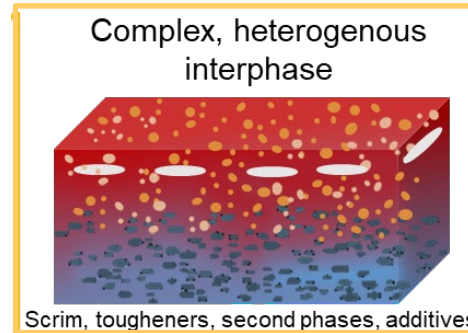
Bondline Regions within Cobond

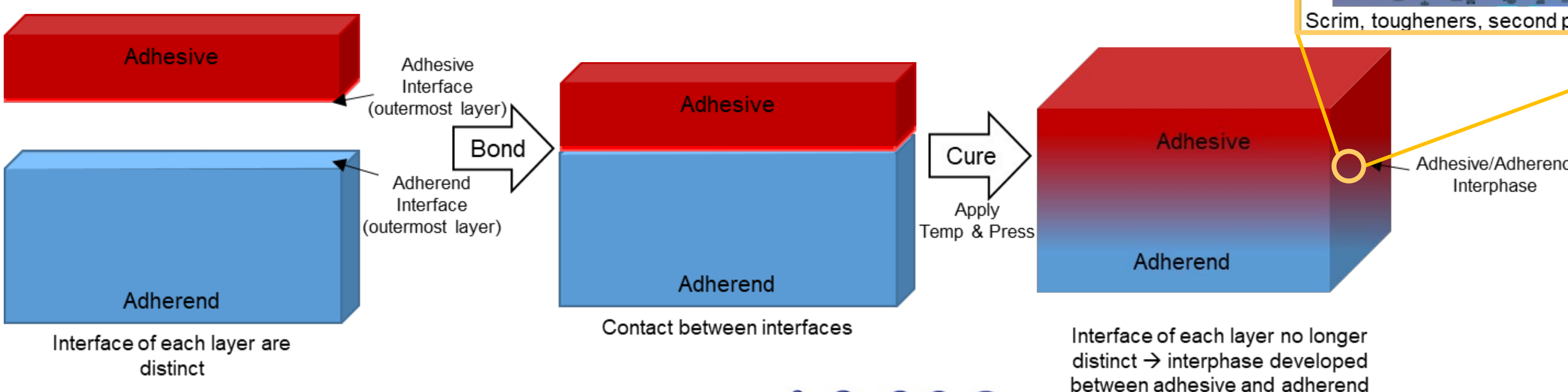


Background

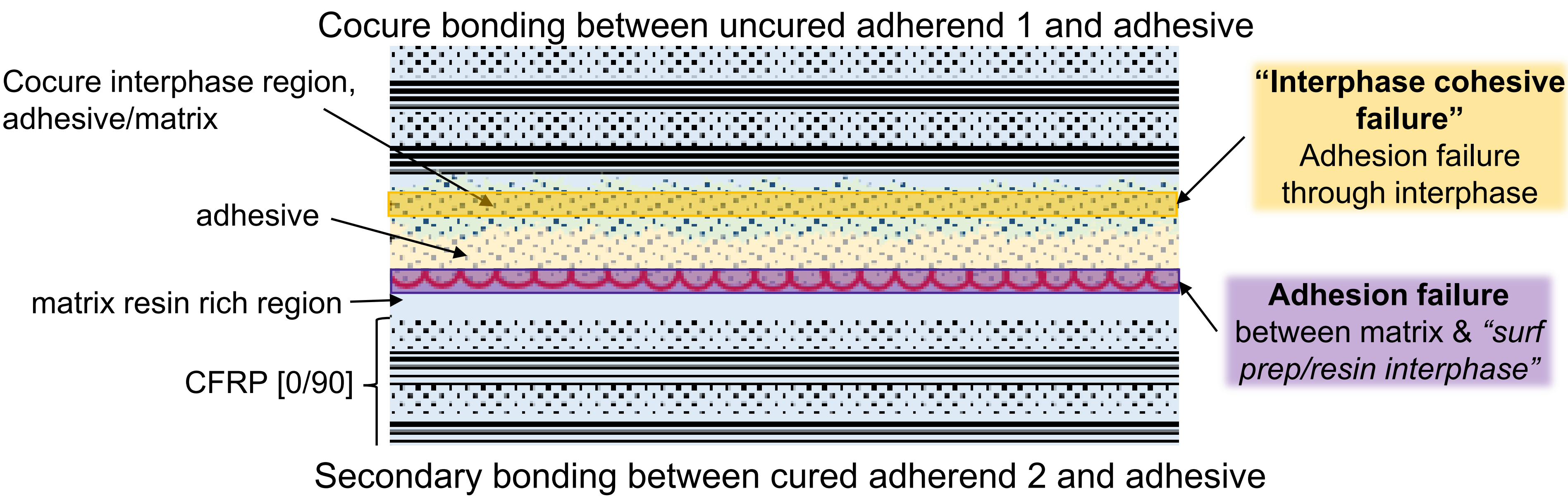
Interphase Characterization

- Bonding creates a mixing zone, or interphase, between two materials
  - Interphase can effect bond strength and durability
  - Interphase region involving an uncured adherend is significantly larger than other substrates (e.g. metal)
  - Factors influencing interphase development not fully understood
- The micron-scale regions within bondlines are difficult to characterize due to their size
  - Complex microstructures and chemistries different from bulk materials





Background
Aging Effects



- Will the interphase age differently compared to the bulk adhesive or bulk
- Will failure mode change? If so, is it changing to an unacceptable failure mode?

Can nanomechanical characterization detect changes?

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Background

Nanoindentation Methodology

- Equipment: Hysitron TriboIndenter 980
  - Diamond tip with Berkovich geometry
  - Indent surface from tens of nanometers to several micrometers deep
- Operated in load-controlled mode
- Load and displacement measured and graphed as indenter penetrates surface
- Hardness:

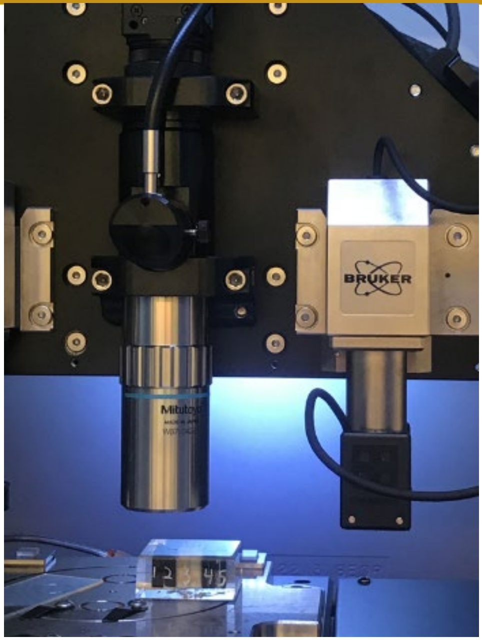
$$A_c = k_1 {h_c}^2 + k_2 h_c \qquad H = \frac{P}{A_c}$$

A_c = contact area of the indenter tip, k_1 and k_2 = fitted constants, P = the maximum load

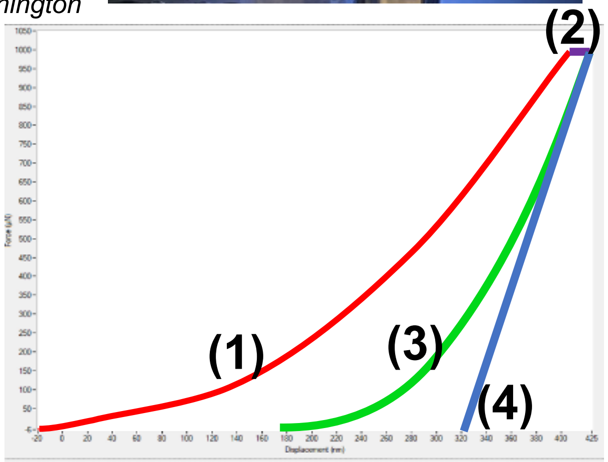
- Reduced modulus:
- Tangent of the unloading curve at instant point of unloading

$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A}} \qquad \frac{1}{E_r} = \left.\frac{1 - v^2}{E}\right|_{sample} + \left.\frac{1 - v^2}{E}\right|_{indenter}$$

S= stiffness of unloading curve, A=projected contact area, v = Poisson's ratio



Hysitron TriboIndenter 980 at U. Washington



Force-Displacement curve featuring:
- loading (1)
- holding (2)
- unloading (3)
- unloading tangent used to find *Er* (4)

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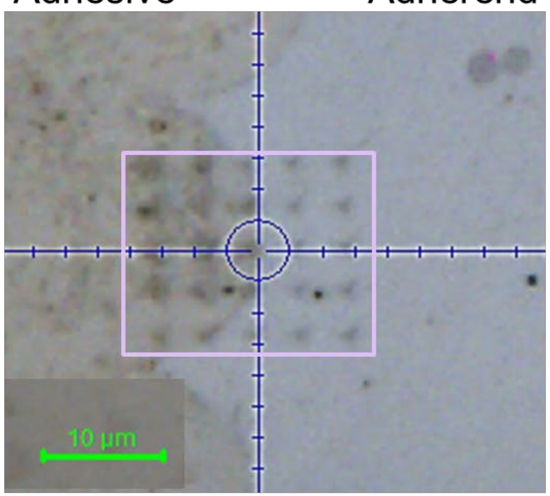
Background
Nanoindentation Characterization

Extreme Property Mapping (XPM)

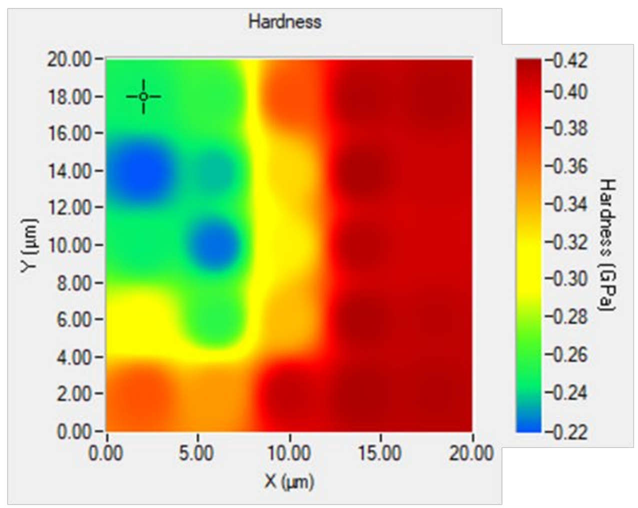
- Quick nanoindentations performed within specified array
- H and Er measured at every indent
- Mapped on X-Y graph using color gradients to illustrate changes in mechanical properties

Adhesive Adherend

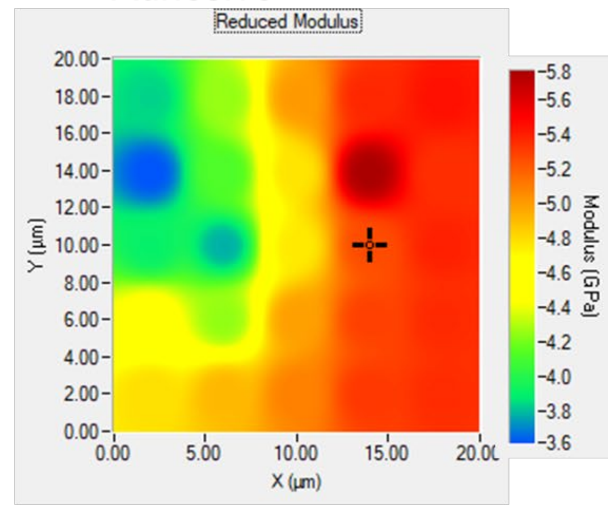


XPM array of epoxy

Adhesive Adherend



Adhesive Adherend



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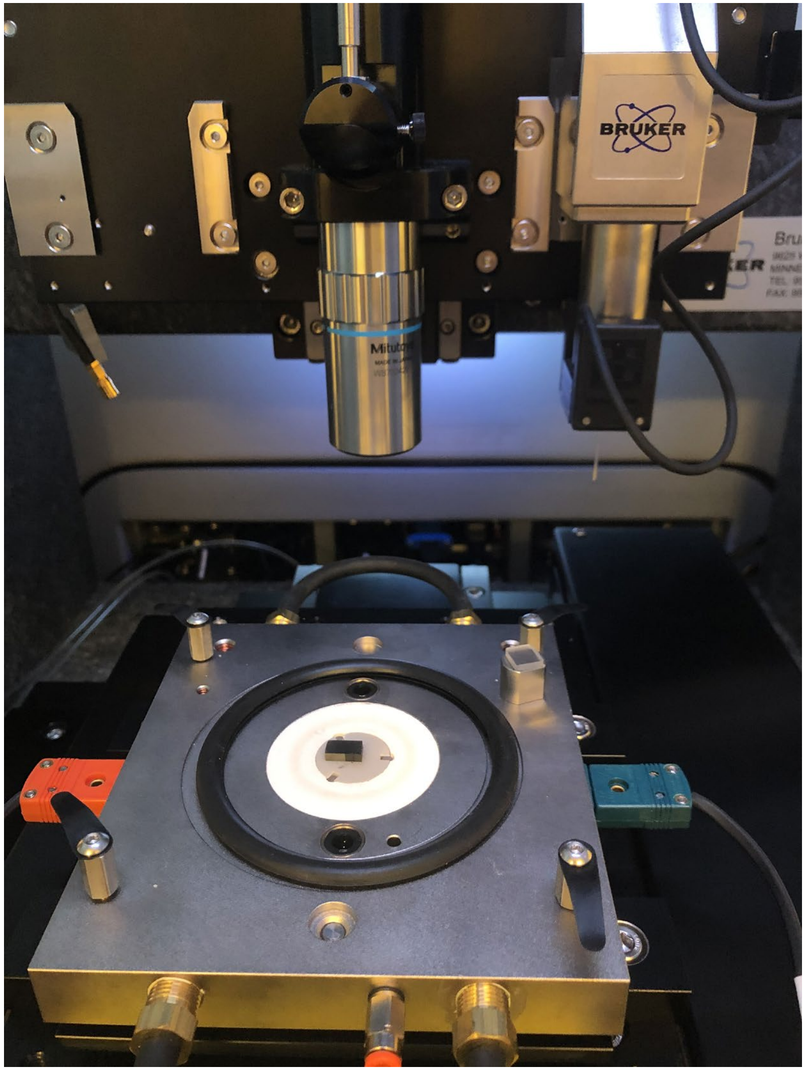
Background
Nanoindentation Characterization



Heated stage attachment of Hysitron TriboIndenter 980

NanoDMA

- Nanodynamic mechanical analysis on a submicron scale
  - → Oscillating force applied to nanoindenter tip
  - → sinusoidal stress is applied
  - → strain of the material is measured
  - → Measures viscoelastic properties of the material

$$\text{Tan(delta)} = \frac{E''}{E'}$$

E" = loss modulus (measuring viscous response)
E' = storage modulus (measuring elastic response)
Independent of indenter tip to sample contact area

- Heated stage used to vary temperature
  - → show variations in the moduli
  - → Determine the glass transition temperature (Tg) range

Value to Industry

- Potentially reduce representative testing to support qualification for existing or new bonding systems
  - Characterize interphases within systems and how they relate to macro mechanical performance
    - Bulk properties vs. Interphase properties
    - Evaluate effect of toughening particles, scrim, additives, etc.
    - Evaluate lifecycle health of bonding systems
  - Enable new systems development through new screening tests and creating a database for model based engineering (MBE)

- Understand fundamental science of matrix/adhesive interactions

Tasks

1. Understand the long term effects of moisture saturation and aging on the various regions of bondlines (structure and properties)

2. Understand the influence of additives, tougheners, and scrim found in adhesives (and not matrix resins) on structure and properties of aged bondlines

3. Identify potential long term aging model relationships between matrix resins and adhesives

4. Identify and develop accelerated aging protocols that mimic the effect of long term service (if time and budget permits)

Nanomechanical Preliminary Study

Bonding Systems

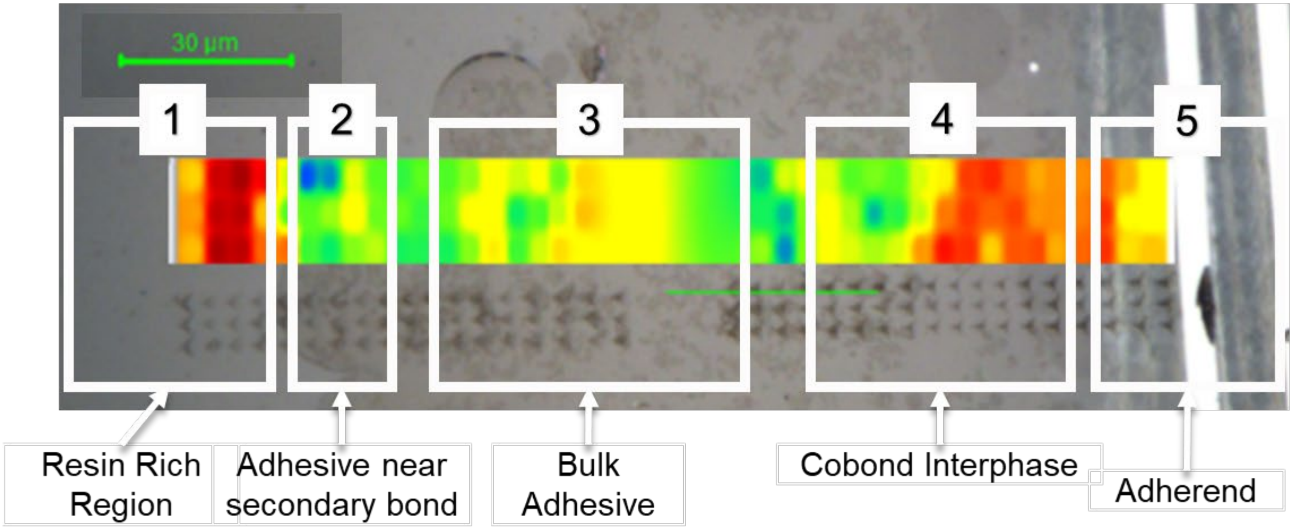
	Bond Type	Adherend	Surface Preparation (cured adherend only)	Adhesive
Bonding System 1	Cobond	BMS8-276 Toray T800S/3900 resin [F1]	BMS8-308 Ty IV Diatex 1500EV6 woven polyester peel ply [F2]	BMS5-160, Ty I 3M AF 555 polyester supported [F3]
Bonding System 2	Cobond	BMS8-276 Toray T800S/3900 resin [F1]	BMS8-308 Ty IV Diatex 1500EV6 woven polyester peel ply [F2]	BMS5-160 Ty II Solvay FM® 309-1 Knit or mat carrier [F3]
Bonding System 3	Secondary Bond	BMS8-276 Toray T800S/3900 resin [F1]	BMS8-308 Ty IV Diatex 1500EV6 woven polyester peel ply [F2]	BMS5-154 Cytec Metlbond® 1515-4 modified epoxy supported [F3]

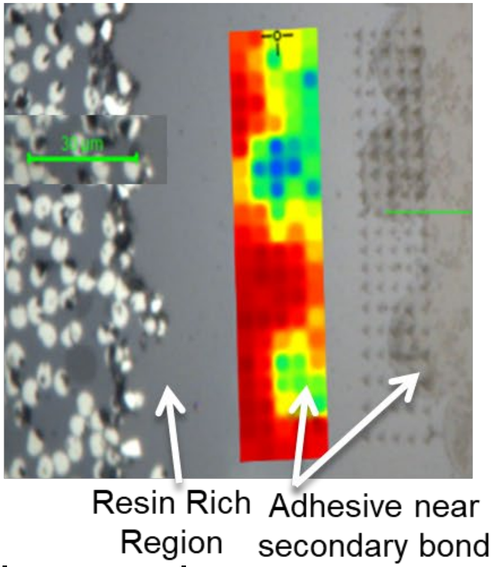
[F1] 350°F cured carbon fiber reinforced polymer matrix
[F2] Peel ply removed just prior to bonding
[F3] 350°F cured film adhesive

Nanomechanical Preliminary Study

Bonding System 1 - **AF555/3900** Cobond

- XPM arrays performed parallel to the bondline and normal to adhesive/cured adherend interphase
- Reduced modulus maps show distribution of properties (red = high blue = low)





- Matrix resin has highest values while adhesive has much lower values
- Interphase mixing zone can be observed
  - Approximately 40-50 µm thick but will vary along bondline (~30% of bondline)
- Well defined transition seen between matrix resin and adhesive

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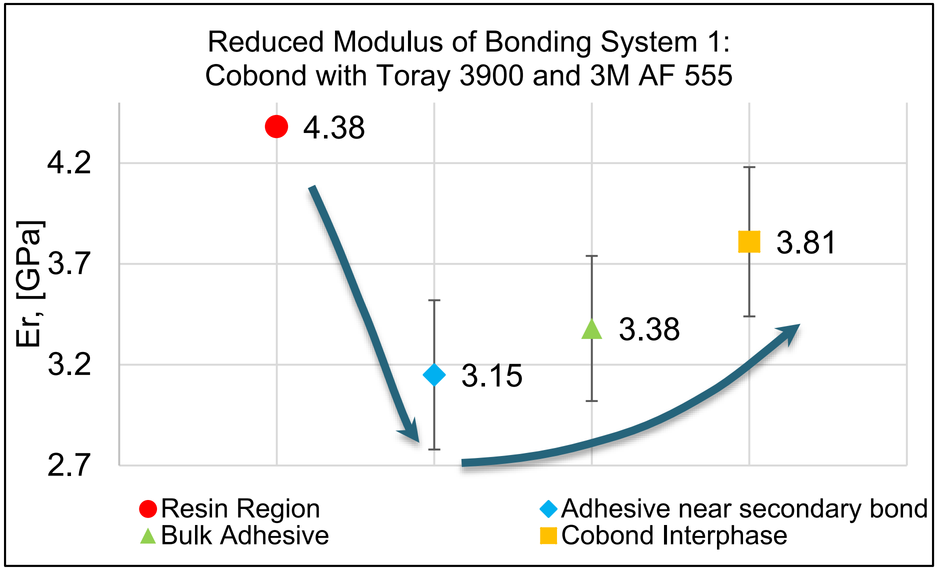
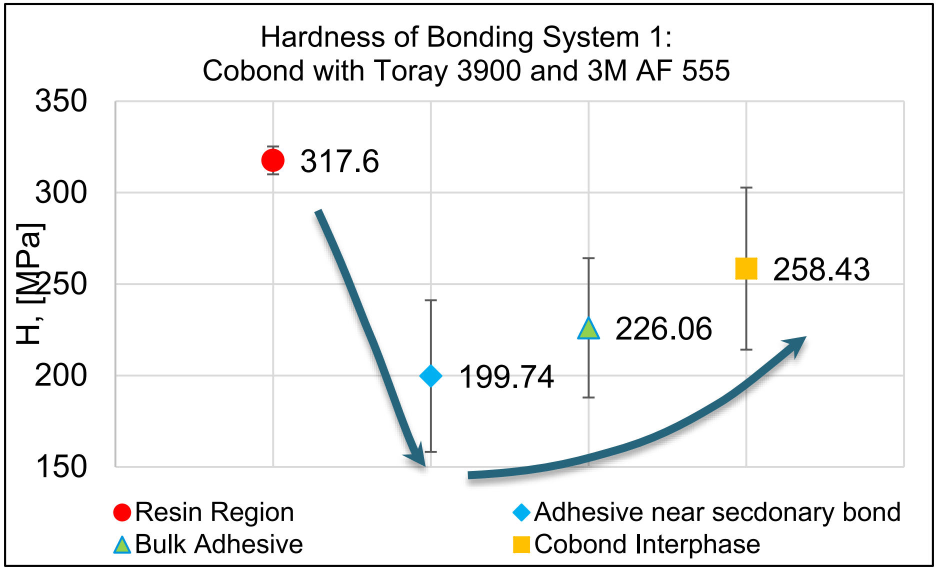
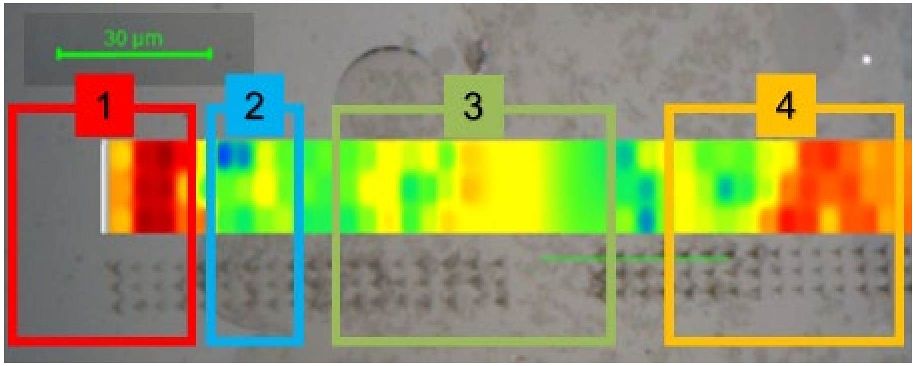
Nanomechanical Preliminary Study

Bonding System 1 - **AF555/3900** Cobond

Adhesive Property Mapping Trends







Example of regions within reduced modulus map of bonding system 1

Reduced modulus & hardness values within the adhesive exhibit a consistent trend

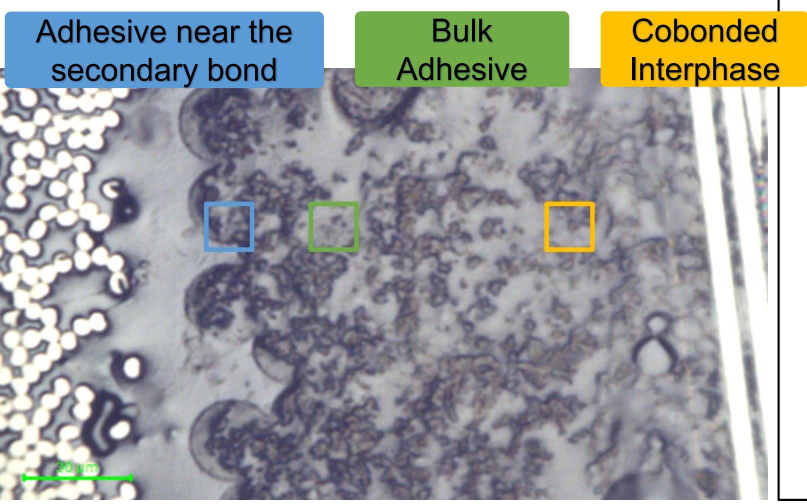
Resin regions (highest)
Cobond interphase
Bulk Adhesive
Adhesive near secondary bond (lowest)

Nanomechanical Preliminary Study

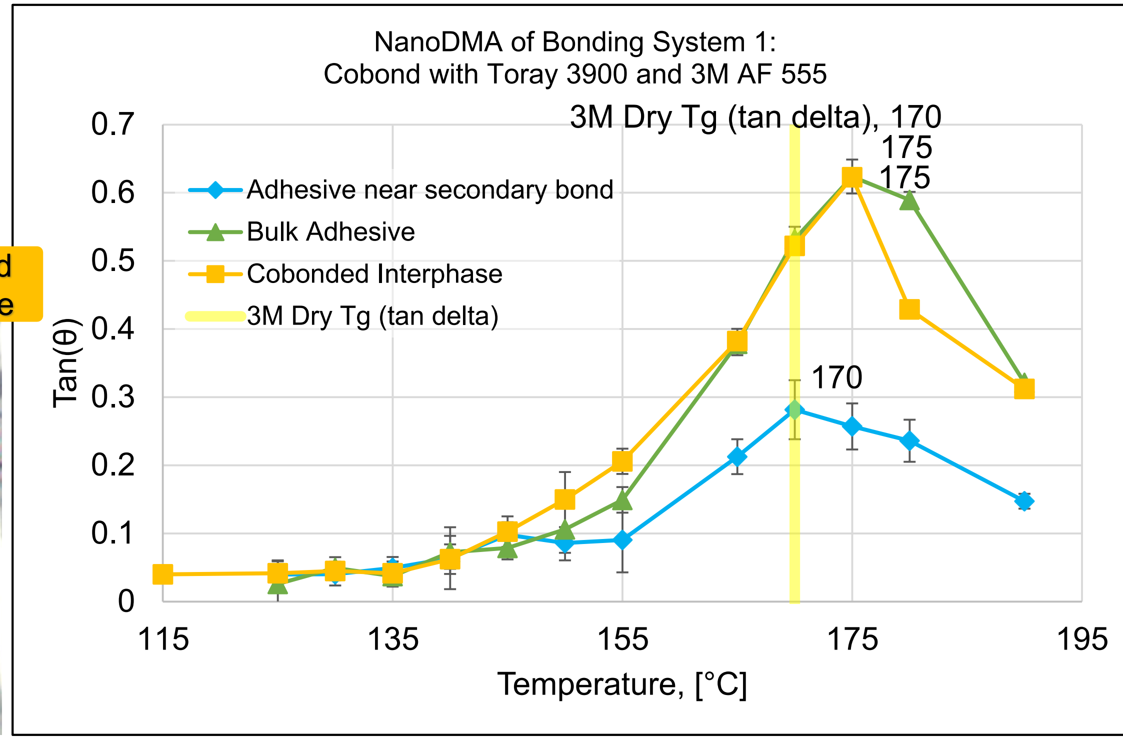
Bonding System 1 - **AF555/3900** Cobond

Adhesive Property Mapping Trends

Test Parameters	
Dynamic Frequency [Hz]	1
Peak Force [uN]	2000



Location of nanoDMA measurements



3M Technical Data Sheet – 170°C Dry Tg (DMA Tan delta peak) from neat adhesive, autoclave cured at 355°F for 120 min, 15-20 psi

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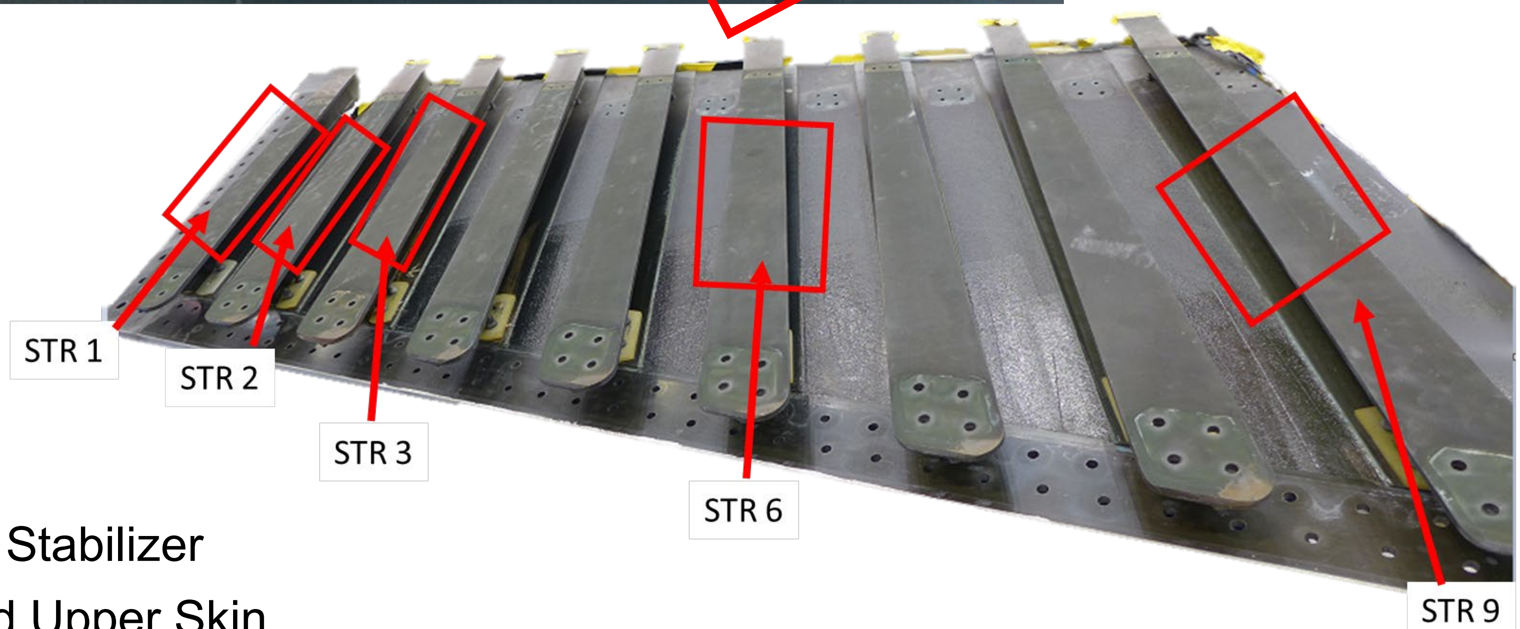
Nanomechanical Characterization of Aged Bondlines
Bonding Systems

	Bond Type	Adherend[F1]	Surface Preparation (cured adherend only)[F2]	Adhesive[F3]
"Pristine"/Baseline DCB Sample	Secondary Bond	Toray T800S/3900 resin	Diatex 1500EV6 woven polyester peel ply	Solvay Metlbond® 1515-4 modified epoxy supported
"Pristine"/Baseline DCB Sample	Cobond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
Lab Ambient 2008 "Aged" DCB Sample	Secondary Bond	Toray T800S/3900 resin	Diatex 1500EV6 woven polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
2012 Environmentally Aged Spare Stringer	Cobond	Toray T800S/3900 resin Toray FGF-108 29M	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
777-200 HSTAB Stringer (46,525 hours and 19,001 cycles)	Cobond	Toray T800S/3900 resin Toray FGF-108 29M	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported

[F1] 350°F cured carbon fiber reinforced polymer matrix
[F2] Peel ply removed just prior to bonding
[F3] 350°F cured film adhesive

Nanomechanical Characterization of Aged Bondlines

777-200 HSTAB Stringers



Horizontal Stabilizer

Right Hand Upper Skin

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Nanomechanical Characterization of Aged Bondlines
Approach

- Investigate surface preparation/matrix interphase and adhesive/adherend interphase on
  1. pristine, unaged bonds
  2. in-service aged structure samples
  3. artificially aged bonds using common industry accelerated aging methods (if time/budget permits)

Adhesive Characterization

- Nanomechanical Property Testing
  - NanoDynamic Mechanical Analysis (DMA)
  - Nanoindentation (modulus and hardness)
- MacroDMA
- Thermomechanical analysis (TMA)
- Differential scanning calorimetry (DSC)
- Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)
- Electron spectroscopy for chemical analysis (ESCA)
- Secondary ion mass spectrometry (SIMS)

Evaluate Bond Adhesion, Strength & Durability

- Mode I: Double Cantilever beam (DCB)
- Back-bonded DCB
- Metal Wedge
- Flatwise Tension
- Climbing Drum/Rapid Adhesion Test (RAT)
- Fracture Characterization

Acknowledgements

- FAA, JAMS, AMTAS
- Boeing Company
- UW MSE
- UW Molecular Analysis Facility
  - National Science Foundation (grant NNCI-1542101)
  - CEI

Questions?

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