MATERIALS SCIENCE & ENGINEERING
UNIVERSITY of WASHINGTON

Nanomechanical Property Characterization of Adhesive Bondlines

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Research Collaboration FAA, Boeing, and UW

JAMS AMTAS A Center of Excellence Advanced Materials in Transport Aircraft Structures

BOEING

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Outline

- Motivation & Key Considerations
- Background
  - Bonding process, interfaces, and interphases
- Experimental Approach
  - Preliminary Study Experimentation via Nanomechanical Methodologies
- Preliminary Results & Discussion
- Future Work
- Acknowledgements

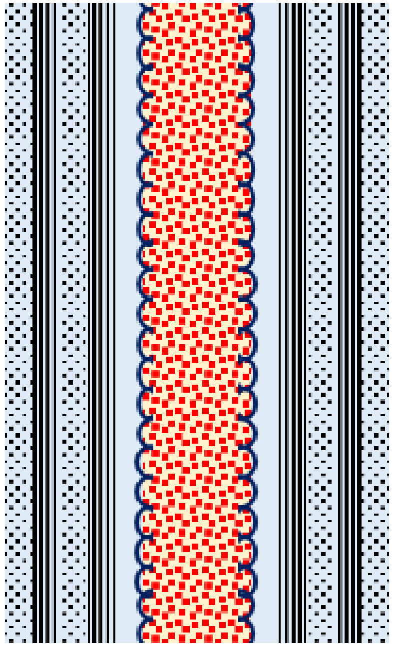
Motivation & Key Considerations

Background
Long-Term Exposure Effects

- Composite joints are designed to undergo thousands of service hours under environmental conditions (e.g. hot-wet, fuel, hydraulic fluid)
  - Diffusion of moisture → hygrothermal effects
  - Cyclic loading → ratchet and fatigue effects
  - Oxygen-rich and elevated temperatures → thermo-oxidative effects
- Better techniques for evaluating long-term exposure on bondline interphase and constituents are desired
  - Physical and chemical changes
    - Changes in mass density and toughness
    - Plasticize
    - Tg changes
      - Moisture absorption, cross-link density, free volume

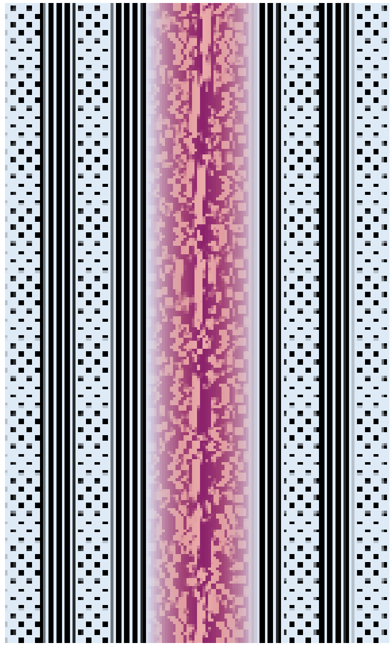
> ➢ Do regions within the bondline behave differently long-term?
>
> ➢ Are bonds changing, and if so, are they changing at different rates?

Composite Bond Architecture Types



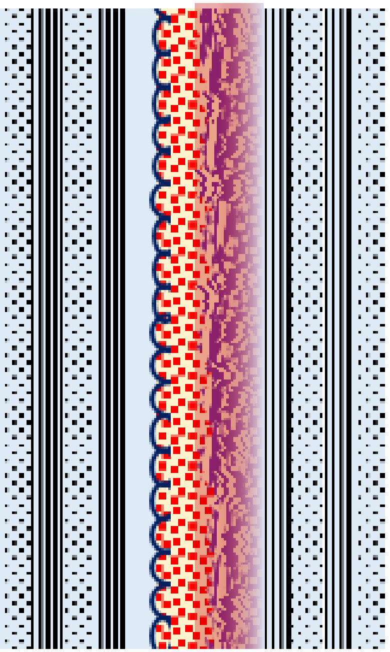
Secondary Bonding

- adherends 1 & 2 fully cured
- surface preparation on adherends 1 & 2
- bonded with adhesive



Cocure

- adherends 1 & 2 uncured
- Cured with green prepreg and adhesive
- Mixing with the adhesive and matrix resin from both laminates

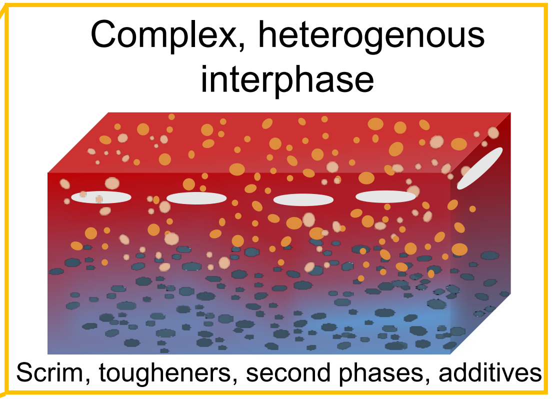


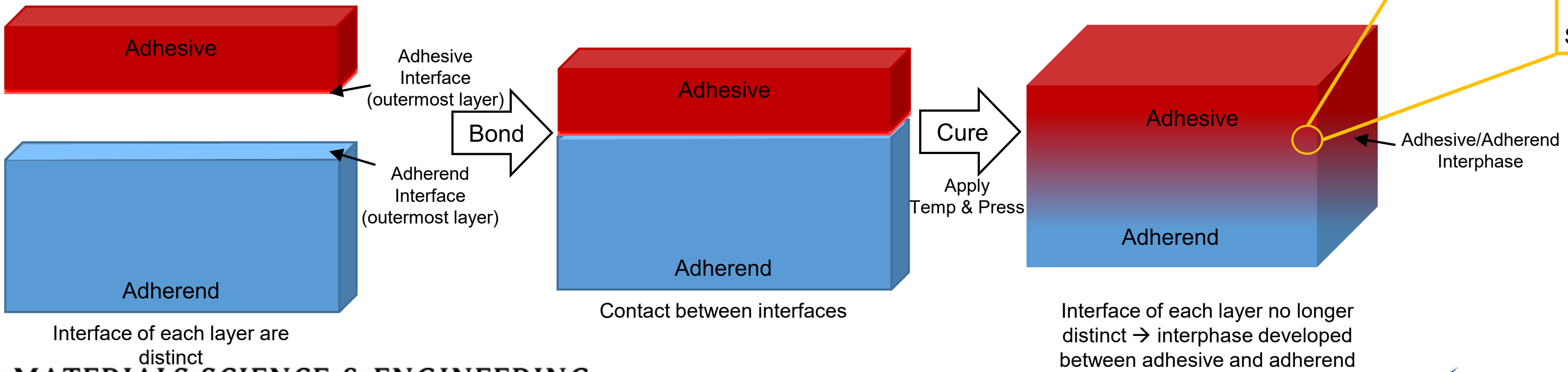
Cobonding

- adherend 1 fully cured (left), adherend 2 uncured (right)
- surface preparation on adherend 1 (left)
- bonded with adhesive

Motivation & Key Considerations

- Bonding creates an interphase between two materials
  - Interphase can affect bond strength and durability
  - factors influencing interphase development need further investigation
- Characterization of the micron-scale regions within bondlines is complex due to their size
  - Complex microstructures and chemistries different from bulk materials
  - Investigate effect of potential changes in microconstituents





Value to Industry

- Support evaluation of existing or new bonding systems
  - Characterize interfaces and/or interphases within systems
    - Bulk properties vs. Interface/Interphase proprieties
    - Evaluate effect of toughening particles, scrim, additives, etc.
  - Potentially act as screening tests for new systems
    - Process development
- Further understand the long-term exposure effects
  - Assessment of lifecycle of bonding systems
  - Micro level changes to bonding system

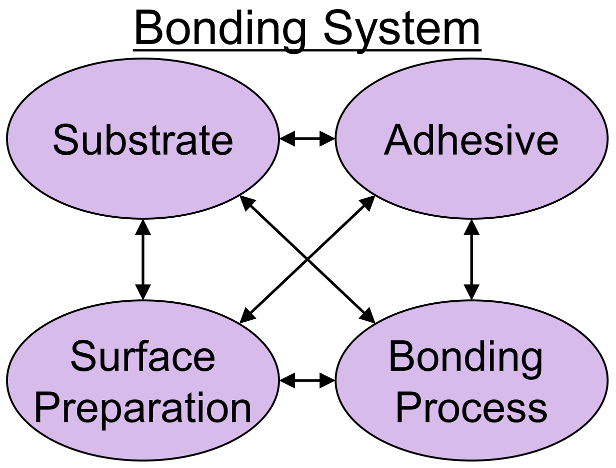


Figure adapted from Blohowiak, K.Y., et al., “Qualified Bonded Systems Approach to Certified Bonded Structure,” NATO Specialists’ Meeting AVT-266 on Use of Bonded Joints in Military Applications, STO-MP-AVT-266, Apr 2018

Understand fundamental science of matrix/adhesive interactions

Nanoindentation Limitations

- At this time, no relationship exists between nanomechanical characterization to any engineering properties used in the design, analysis and certification of bonded composite structures
- Subsurface heterogeneity can influence measurements
- Plastic zone around indentation can affect nearby measurements
  - Increasing spacing can prevent plastic zone interactions but results in lower spatial resolution

Research Objectives

- Understand the long term effects of in-service exposure and moisture saturation effects on the various regions of bondlines (structure and properties)
- Understand the influence of additives, tougheners, and scrim found in adhesives (and not matrix resins) on bondline properties with long-term exposure
- Identify potential long term exposure relationships between matrix resins and adhesives
- Future/unfunded: Identify and develop accelerated aging protocols that mimic the effect of long term service

Materials & Approach

Investigate *surface preparation/matrix interphase* and *adhesive/adherend interphase on*

1. baseline, unexposed bonds
2. Scrapped part samples
3. artificially aged bonds using common industry accelerated aging methods (future/unfunded)

Adhesive Bondline Characterization

- Nanomechanical Property Testing
  - NanoDynamic Mechanical Analysis (DMA)
  - Nanoindentation (modulus and hardness)
- MacroDMA
- Fourier-transform infrared spectroscopy (FTIR) Chemical Analysis
- 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)

Bonding Systems

	Bond Type	Adherend[F1]	Surface Preparation (cured adherend only) [F2]	Adhesive [F3]
Baseline DCB Sample[F4]	Secondary Bond	Toray T800S/3900 resin	Diatex 1500EV6 woven **Baseline**	Solvay Metlbond® 1515-4 modified epoxy supported
Baseline DCB Sample[F5]	Cobond	Toray T800S/3900 resin	60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
Lab Ambient 2008 Exposure DCB Sample[F5]	Secondary Bond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply **Environmental Exposure Only**	Solvay Metlbond® 1515-3 modified epoxy supported
2012 environmentally exposed Scrapped Cobond[F4, F6]	Cobond	Toray T800S/3900 resin Toray FGF-108 29M	60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
Scrapped Parts Cobond[F4, F6]	Cobond	Toray T800S/3900 resin Toray FGF-108 29M	Precision Fabric Group **Time, Stress, Environmental Exposure**	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
[F4] Samples produced by manufacturer
[F5] Samples produced by UW in lab setting
[F6] boneyard uncontrolled environment not maintained and exposed to the elements (e.g., standing water)

Coupon Considerations

Bondline variation observed through nanomechanical testing could be due to:

- Different material batches
  - Material changes at the supplier level
- Material changes (e.g. out time, storage conditions, moisture)
- Coupons were fabricated at different locations with different equipment
- Different autoclave cure runs, potentially years apart
  - Coupon level panels versus configured part manufacturing

Nanomechanical Analysis

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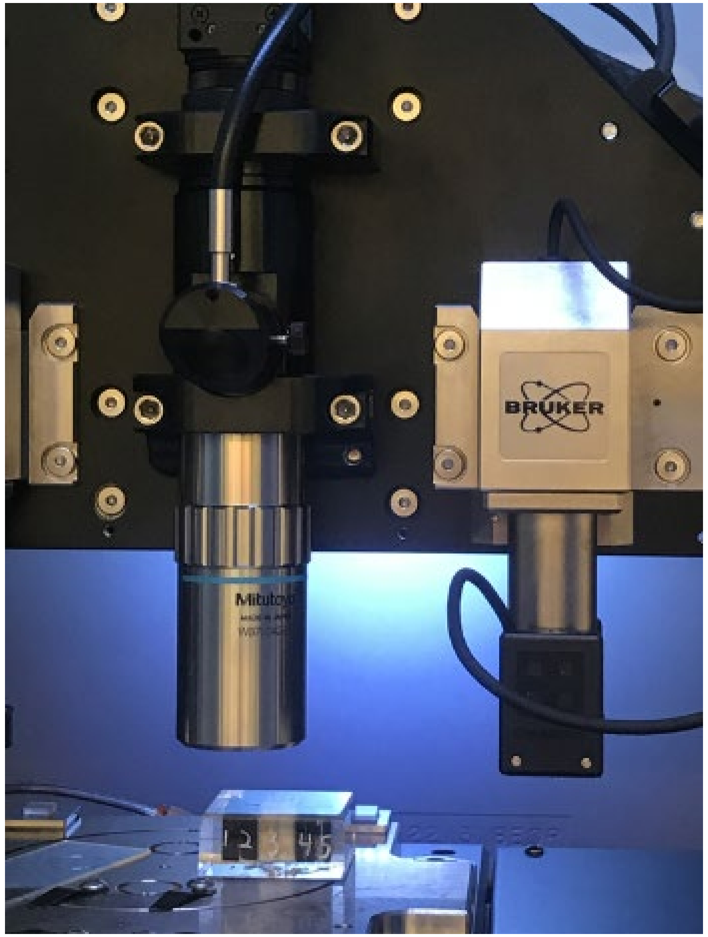
Nanomechanical Characterization

- Hysitron TriboIndenter 980 with Berkovich diamond indenter tip
- Indent surface from tens of nanometers to several micrometers deep
- Built-in digital microscope used to position indent
- High-precision transducers measures force & displacement
- Hardness and reduced modulus* most commonly measured

  (*Er includes nanoindenter tip and sample)
- Capable of running different methods:
  - Single indentation (traditional methodology)
  - Extreme property mapping (XPM)
  - NanoDynamic Mechanical Analysis (NanoDMA)



Hysitron TriboIndenter 980 at U. Washington

Nanoindentation Methodology

- Operated in load-controlled mode
- Load and displacement measured and graphed as indenter penetrates surface
- Hardness:

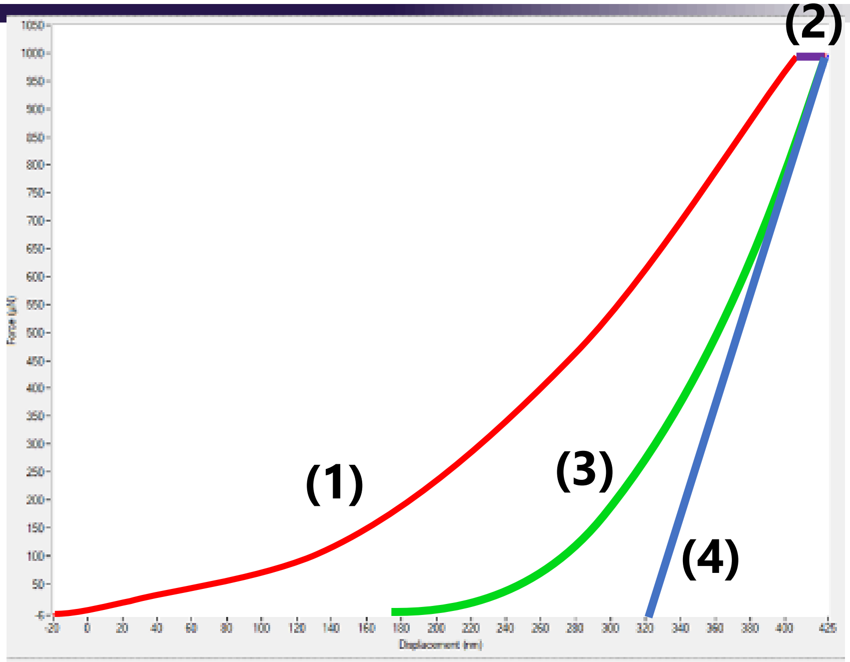
$$A_c = k_1 {h_c}^2 + k_2 h_c \qquad H = \frac{P}{A_c}$$

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

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

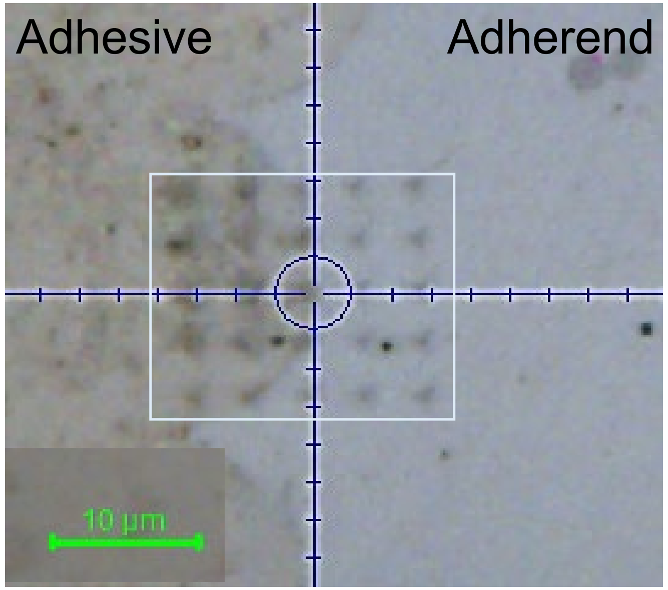
S= stiffness of unloading curve, A=projected contact area, v = Poisson's ratio



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

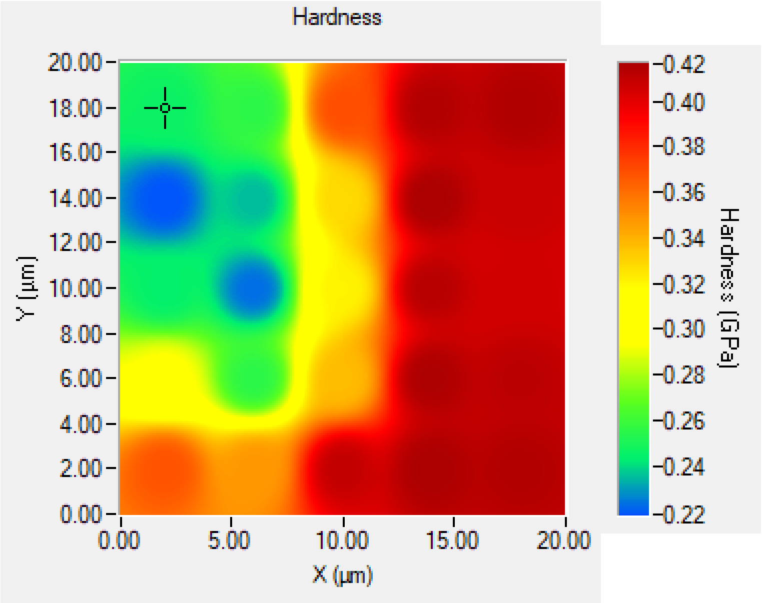
Nanomechanical Characterization
Extreme Property Mapping (XPM)

- 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

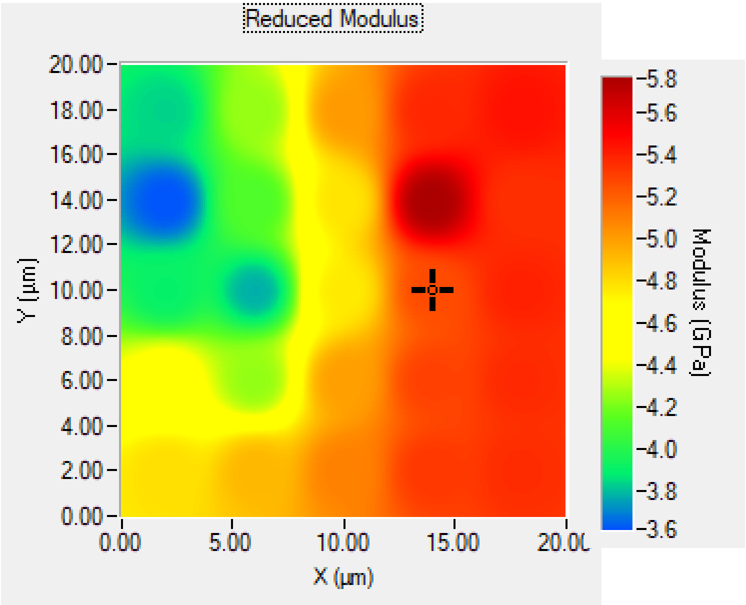


XPM array of epoxy

Adhesive Adherend



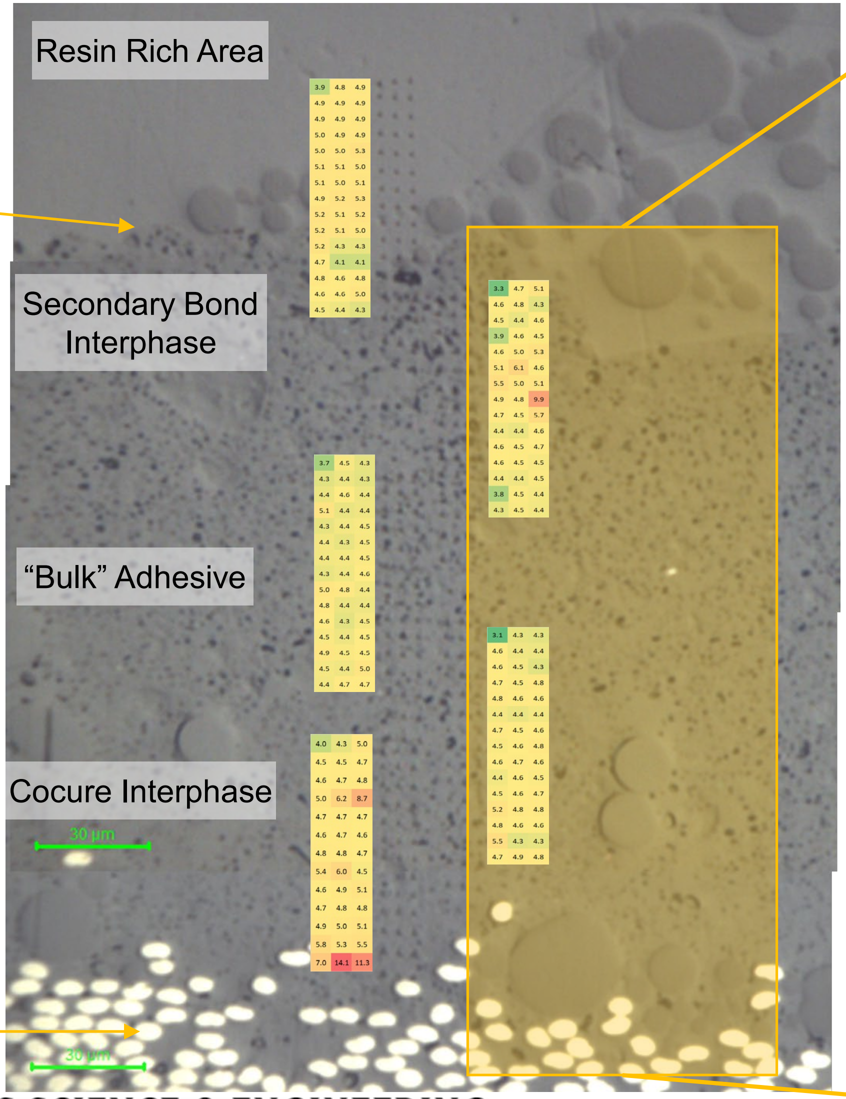
Adhesive Adherend



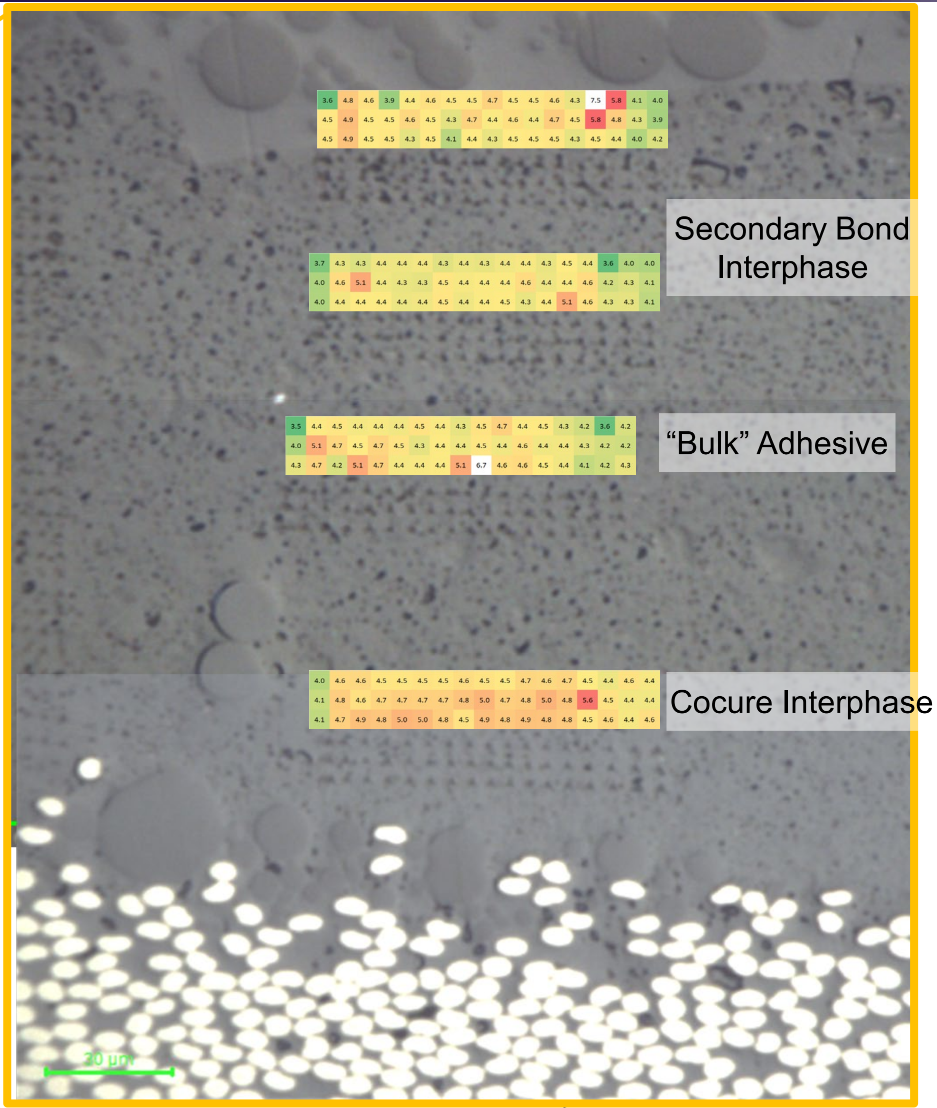
Nanomechanical Characterization

Extreme Property Mapping (XPM)

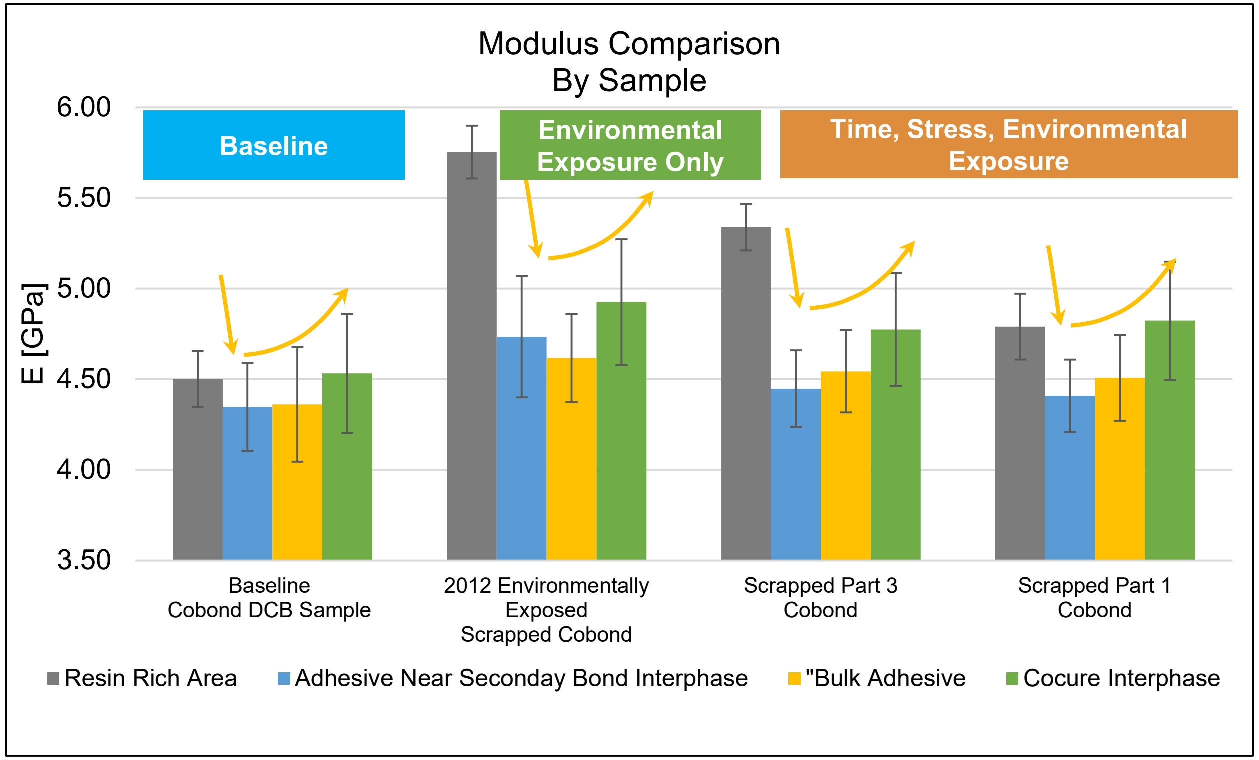
Peel Ply Surface Preparation

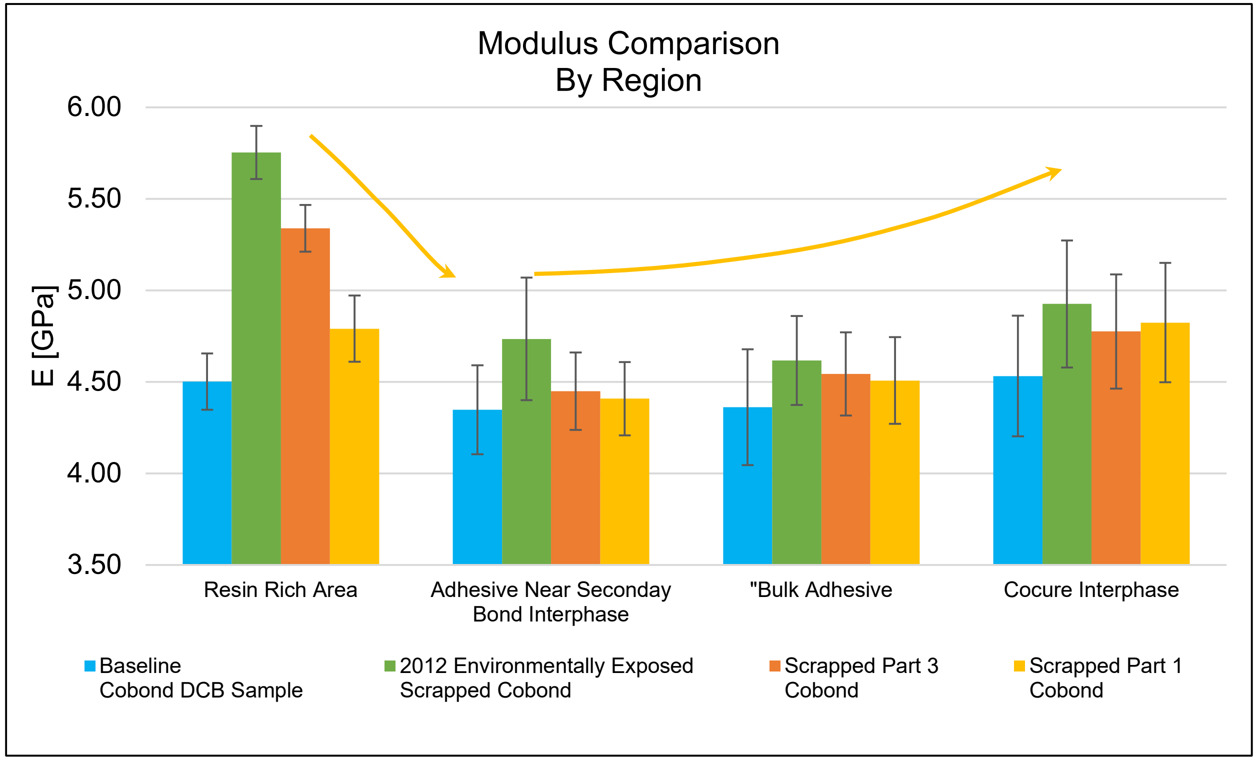


Carbon Fibers



Modulus Comparison





- Variation within region → highly heterogenous adhesive system
- Adhesive systems show emerging mechanical property trend:

  Resin > Cocure Interphase > Bulk Adhesive > Adhesive near Secondary Bond Interphase

Next Steps

- Macro and nano DMA to identify Tg of adhesive regions
- Perform chemical analysis of bondlines

Adhesive Bondline Characterization

• Nanomechanical Property Testing
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• MacroDMA
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Research Summary

- Nanomechanical properties of adhesive systems are showing unique regions and a specific trend:

  Resin Rich Regions (highest)
  Cocure Interphase
  “Bulk” Adhesive
  Adhesive Near Secondary Bond Interphase (lowest)

- Testing next steps:
  - Macro and nano DMA of adhesive bondlines
  - Perform chemical analysis of bondlines
- Compare bondline characteristics of “baseline”, “environmentally exposed”, and scrapped parts.

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  - Material Science & Engineering
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Questions?