MATERIALS SCIENCE & ENGINEERING
UNIVERSITY of WASHINGTON

Nanomechanical Property Characterization of Adhesive Bondlines

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A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

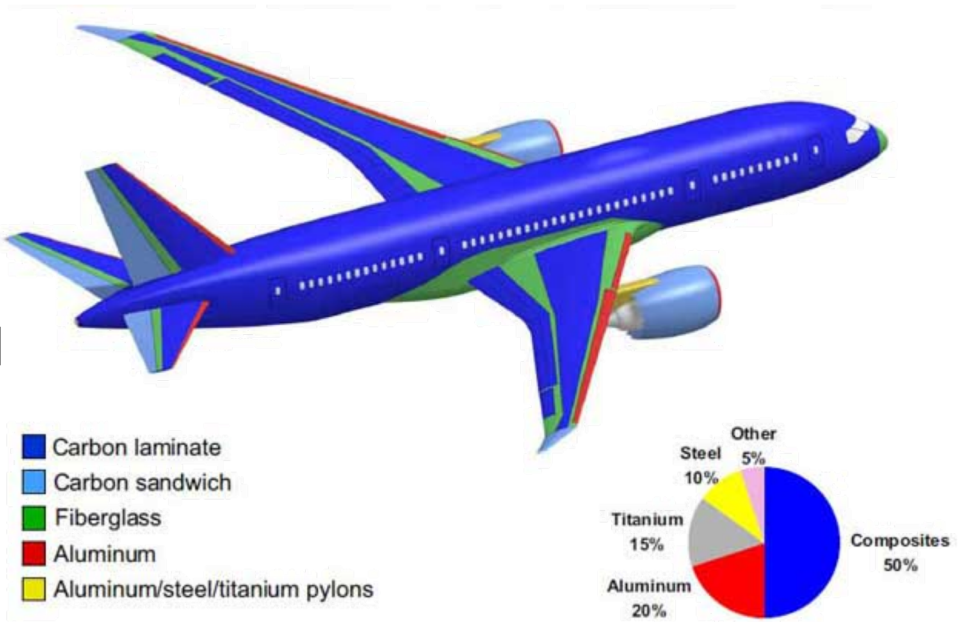
Outline

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

Motivation & Key Issues

Motivation & Key Issues

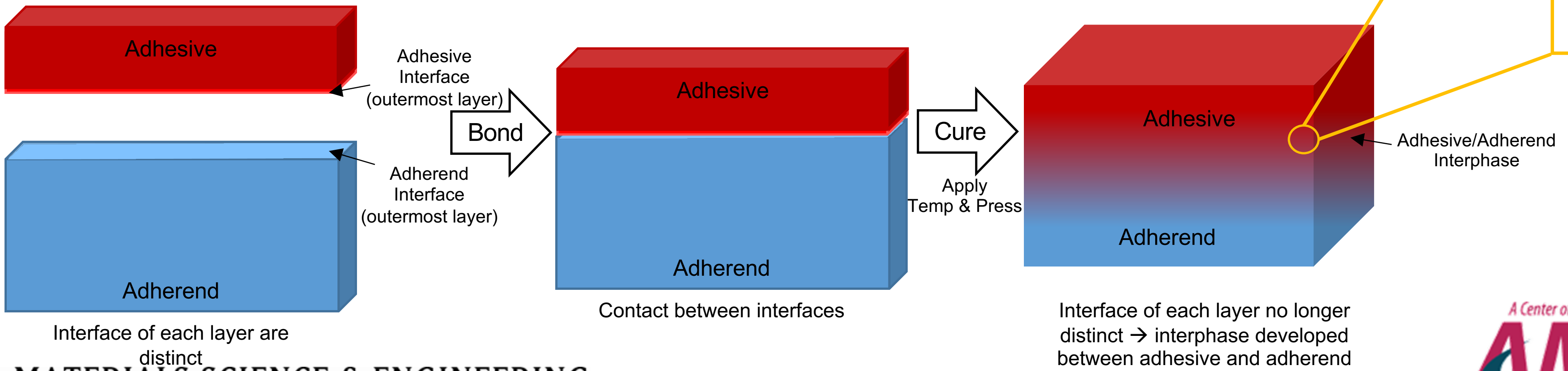
- Aerospace industry utilizes bonded joints in design and repair of composite structures
  - Reduces stress concentrations at joints
  - Reduces weight
  - Thousands of service hours under hot-wet environmental conditions
    - Service temperatures are limited by material properties (ie. glass transition temperatures (Tg))

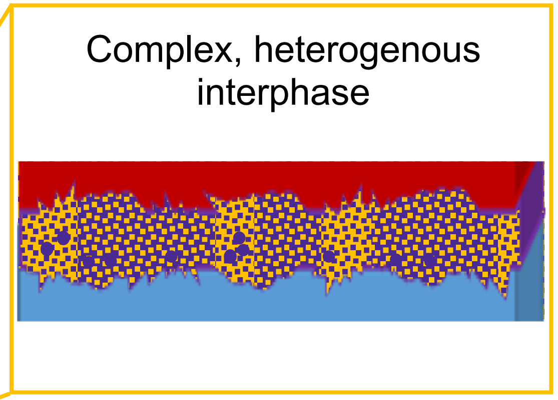


- A **bonding system** is composed of the substrate resin, adhesive, cure cycle, and surface preparation technique
  - Each has a significant impact on the bond quality of an adhesive joint
  - Important to understand how each contributes to the bonding system performance

Motivation & Key Issues

- Bonding creates an interphase between two materials
  - Interphase can effect bond strength and durability
  - 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
  - Many unknowns with the effects of aging on bondline durability

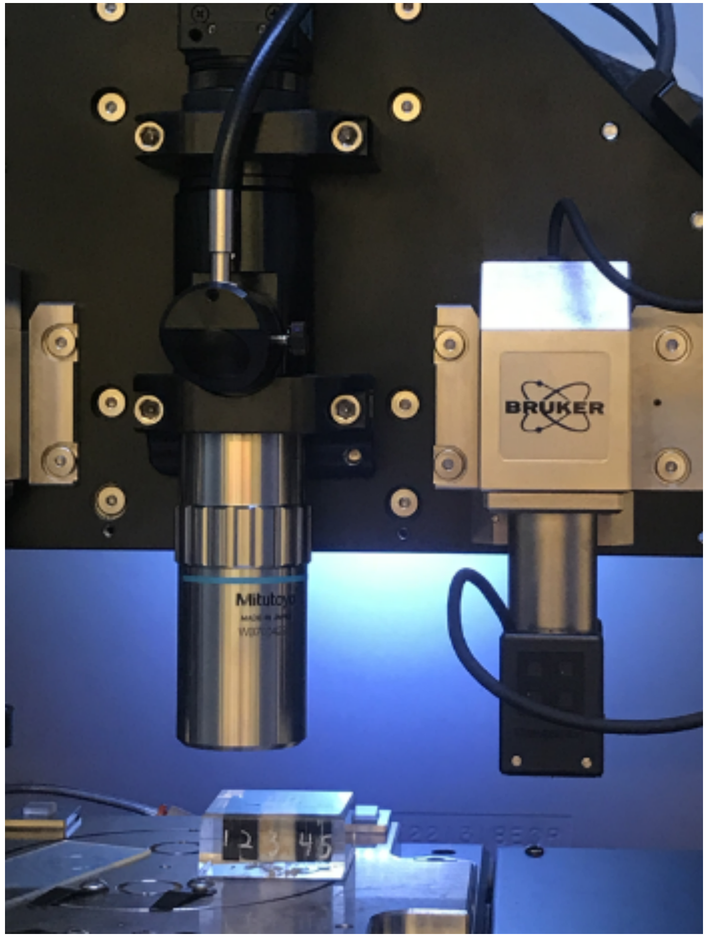




Methods and Materials

Nanomechanical Characterization

- Hysitron TriboIndenter 980 and diamond indenter tip with known geometry
- 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 (H) and reduced modulus* (Er) most commonly measured
- Capable of running different methods:
  - Single indentation (traditional methodology)
  - Extreme property mapping (XPM)
  - NanoDynamic Mechanical Analysis (NanoDMA)



*Er of nanoindenter tip and sample

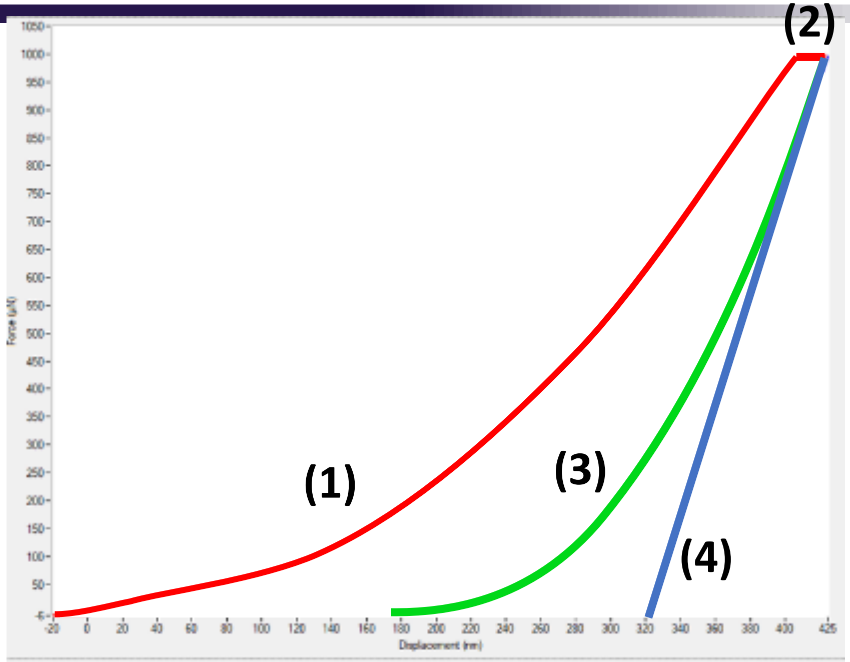
Nanoindentation Methodology

- Equipment: Hysitron TriboIndenter 980
  - Diamond tip with Berkovich geometry
- 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

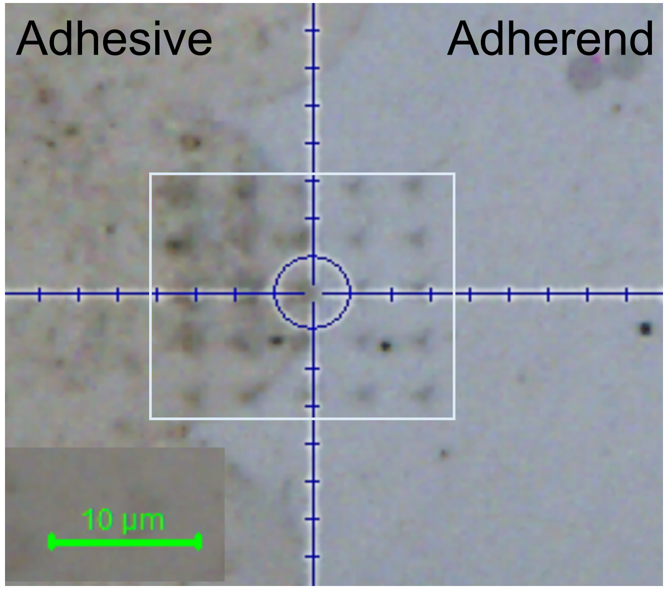


Force-Displacement curve featuring:
- loading **(1)**
- holding **(2)**
- unloading **(3)**
- unloading tangent used to find *Er* **(4)**

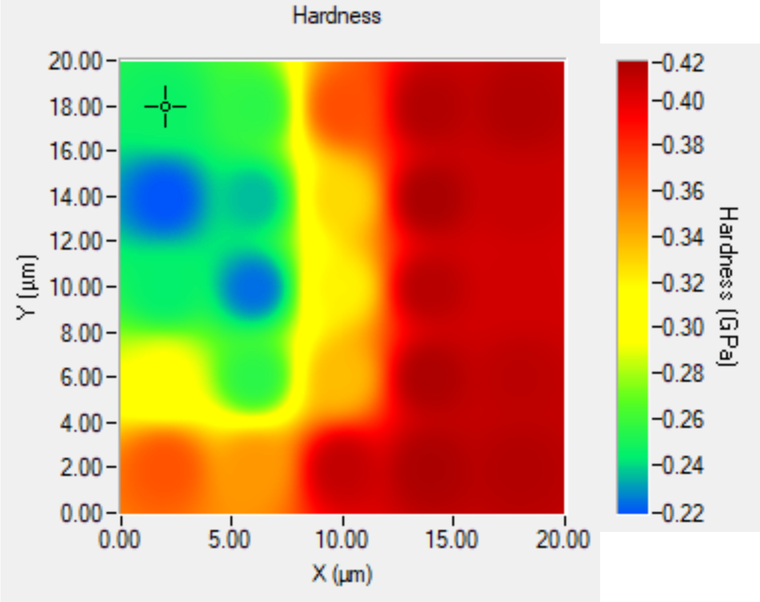
Nanomechanical Characterization

Extreme Property Mapping (XPM)

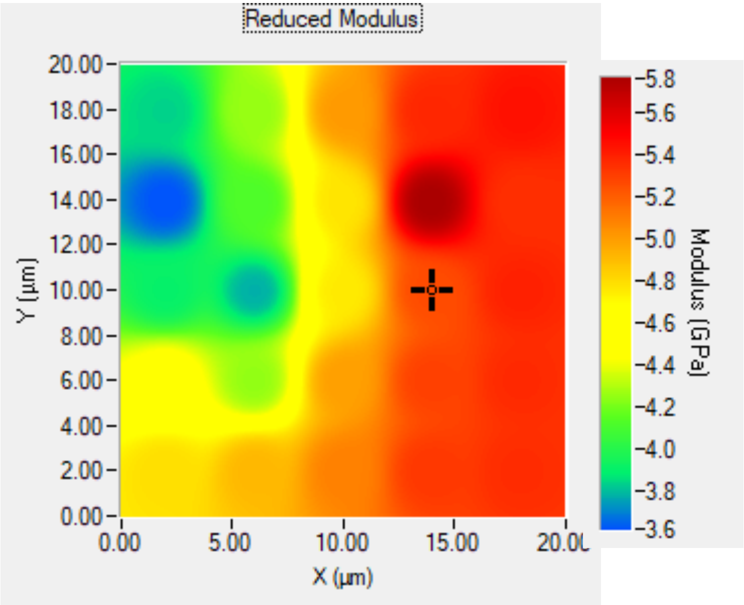
- Quick nanoindentations performed within specified array
- H and Er measured at every indent
- Mapped on X-Y graph using color gradients to illustrate changes in mechanical properties



Adhesive Adherend

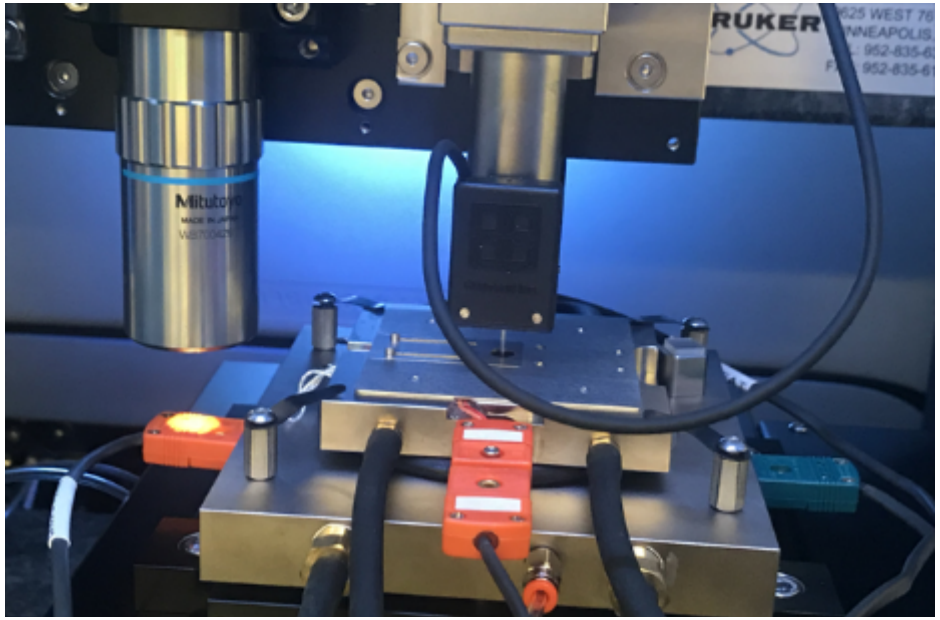


Adhesive Adherend



Nanomechanical Characterization

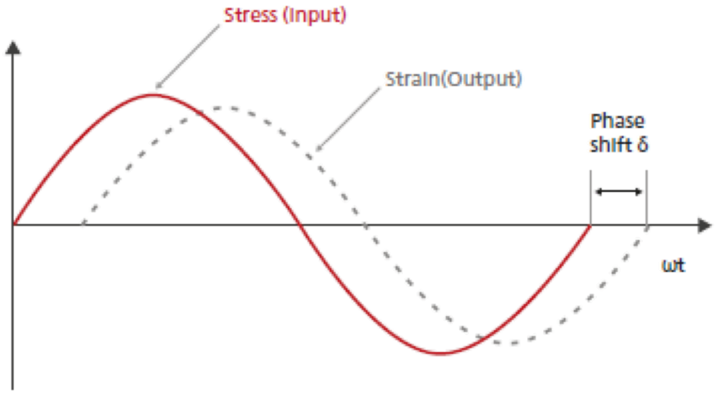
Nanodynamic mechanical Analysis - NanoDMA



- 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

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

E' = storage modulus (measuring elastic response)
E" = loss modulus (measuring viscous response)

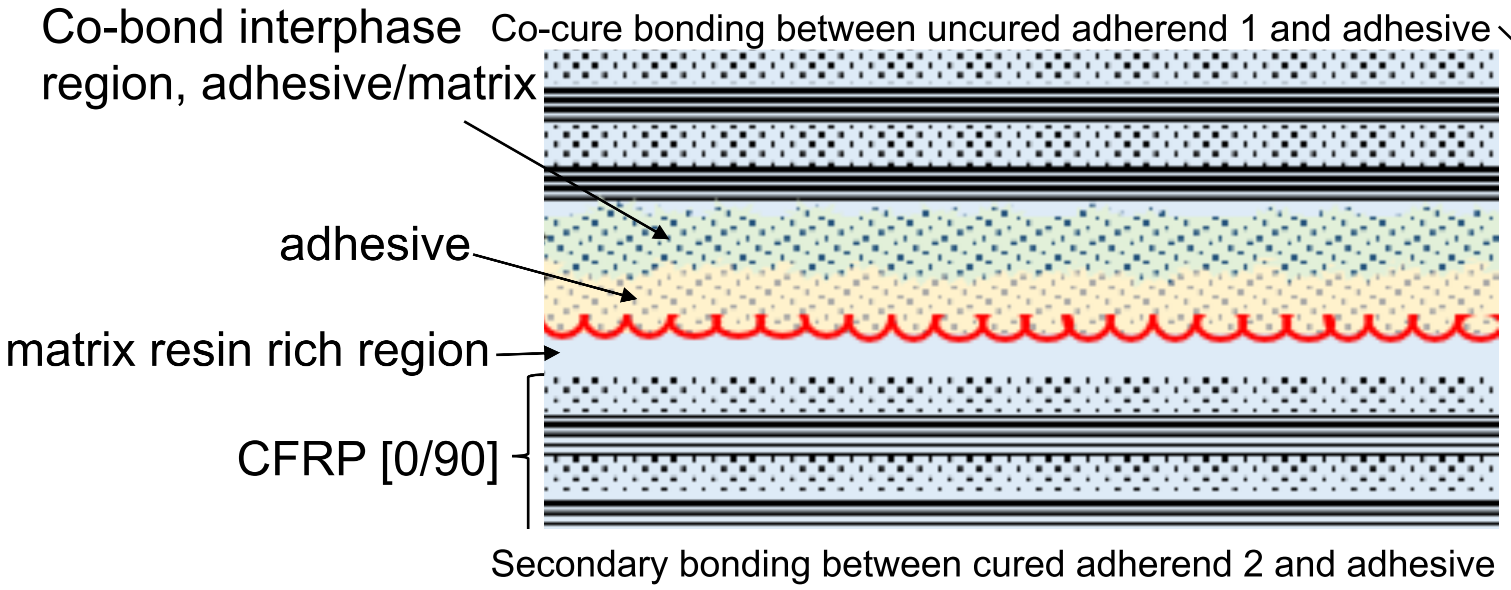


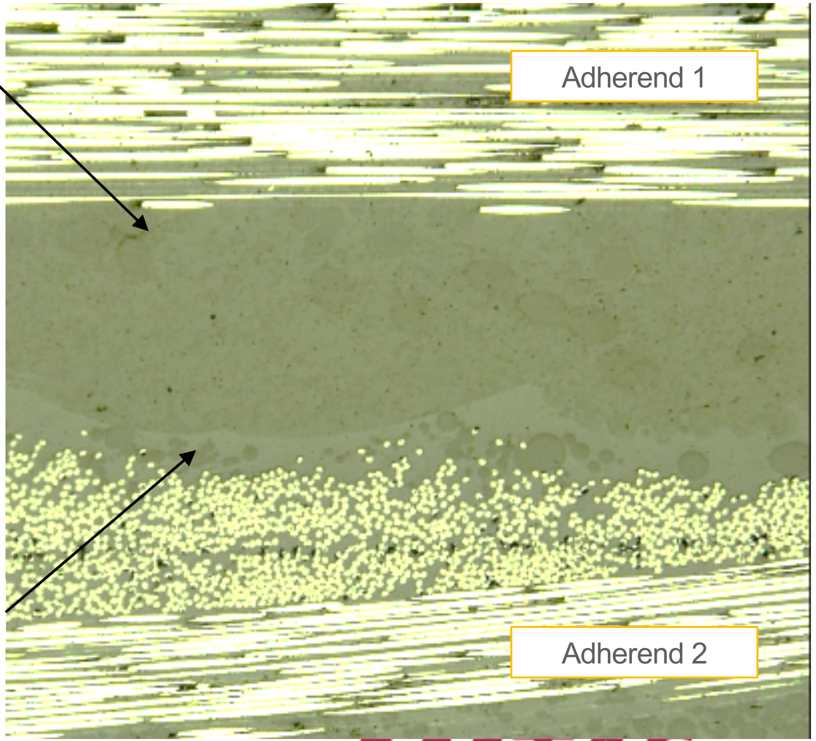
DMA - Measurement principle

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

Co-bonded Sample

- Toray T800S/3900 carbon fiber adherends
- Cured laminate treated with polyester peel ply
- 3M AF 555 scrim supported film adhesive

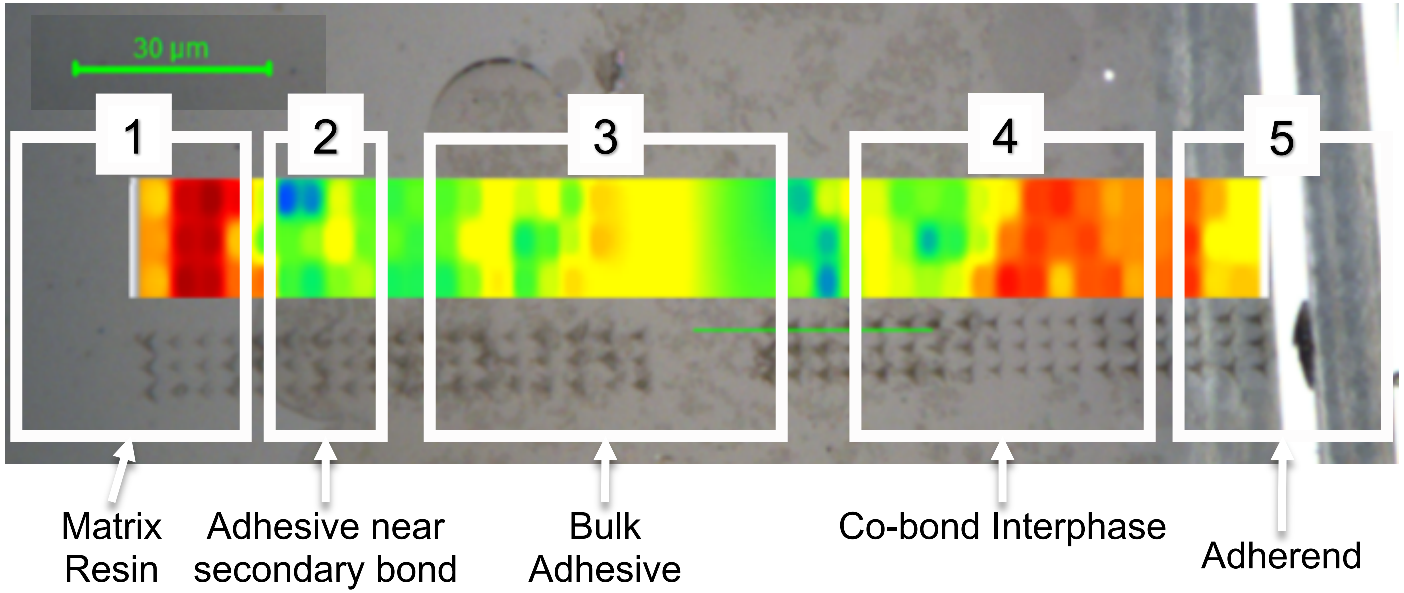


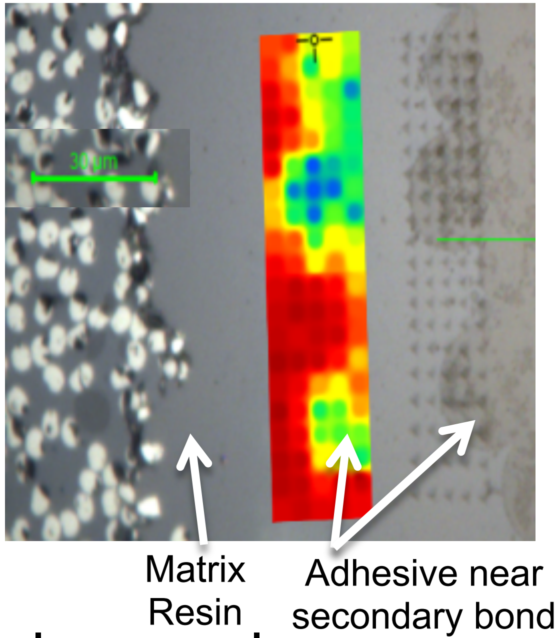


Preliminary Study Approach & Results

Bondline Property Mapping

- XPM arrays performed parallel and normal to adhesive interface
- Reduced modulus maps show distribution of properties (red = high blue = low)

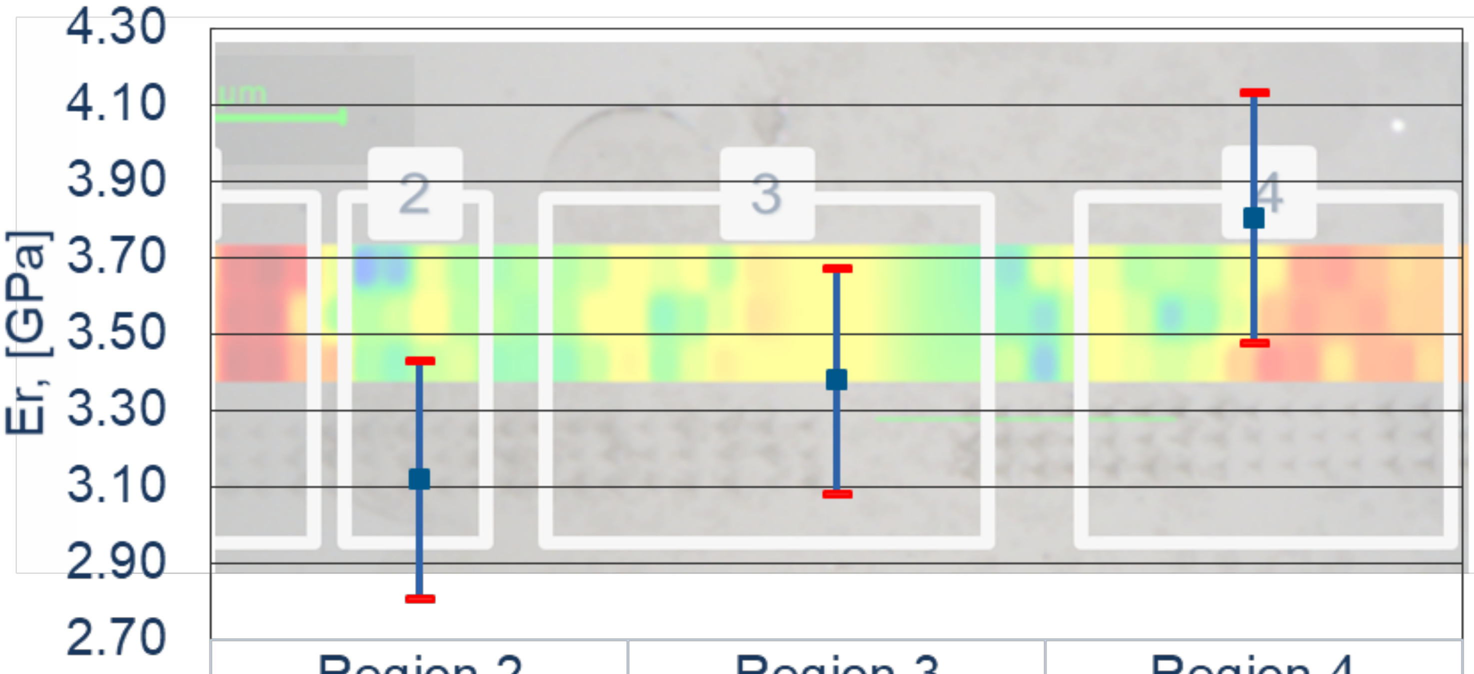




- Matrix resin has highest values while adhesive has much lower values
- Interphase mixing zone can be observed
  - Approximately 40-50 μm thick but will vary along bondline (~30% of bondline)
- Well defined interface seen between matrix resin and adhesive

Adhesive Property Mapping Trends

Reduced Modulus of Adhesive



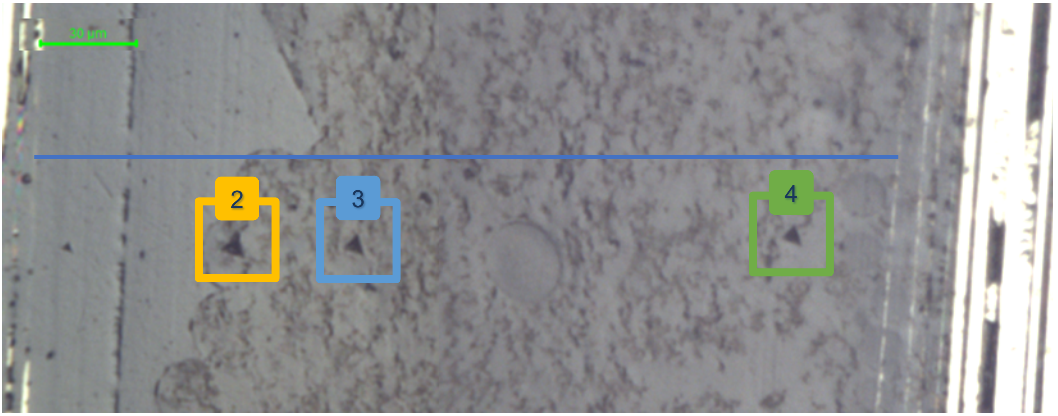
	Region 2	Region 3	Region 4
■ ave	3.12	3.38	3.81
– low	2.81	3.08	3.48
– high	3.43	3.67	4.13

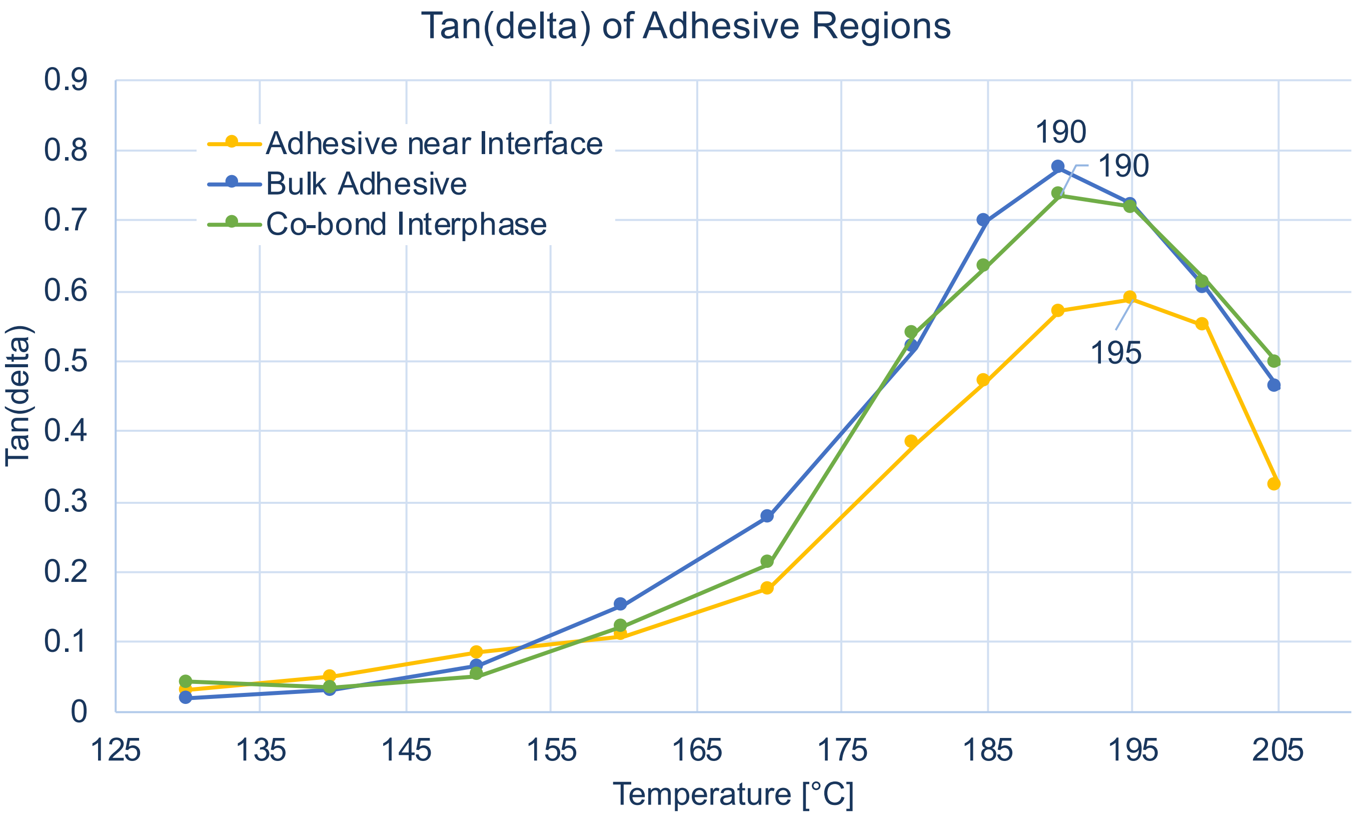
Region
(1) Matrix Resin
(2) Adhesive near secondary bond
(3) Bulk Adhesive
(4) Co-bond Interphase

NanoDynamic Mechanical Analysis (nanoDMA)

Adhesive Region Response Summary

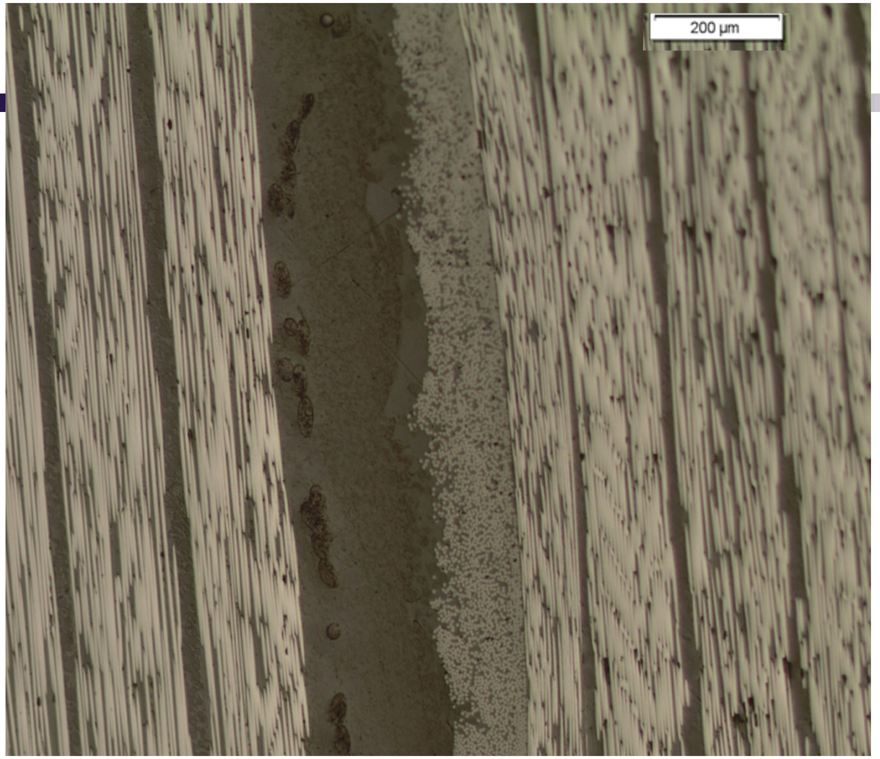
Test Parameters	
Dynamic Frequency [Hz]	101
Peak Force [uN]	2000
Quasi Dwell Time [s]	60





Regions within the adhesive have similar Tg values

Conclusion & Discussion



- XPM measurements show reduced modulus and hardness gradients within bondline
- XPM mode can quickly perform of indents in desired region
- Nanoindentation capable of characterizing adhesive regions at a micron scale
- Variation in measured properties support heterogenous nature of bondline
- T_g across the bondline can be estimated

→ Can characterize nanomechanical properties of bonded structures at unprecedented resolution

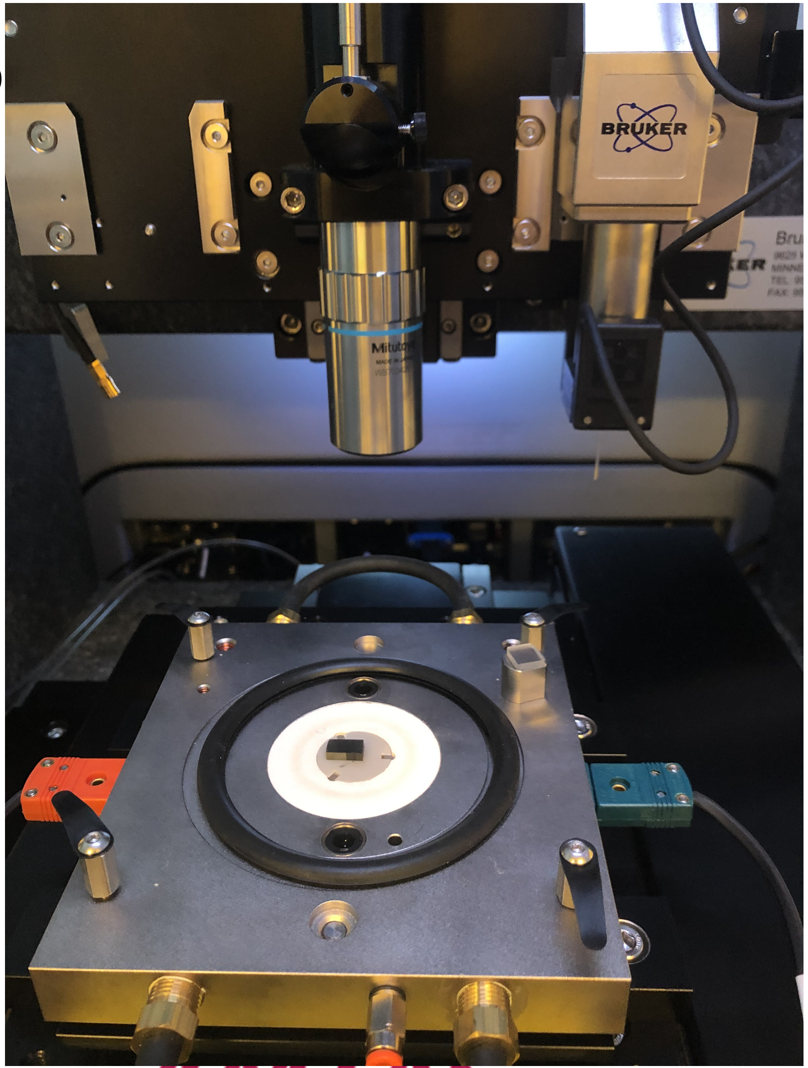
→ Provide additional insight of the behavior of composite bondlines

- Characterize the effects of aging, surface preparations, and environmental exposures

→ Potential method to characterize thermoplastics, AFP, additive manufacturing

Limitations

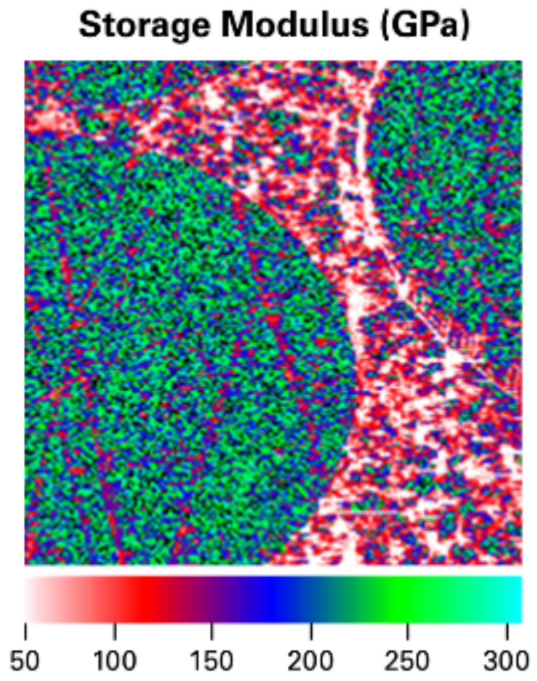
- Surface must be well polished to reduce roughness and flat to indenter tip
- Subsurface heterogeneity can influence measurements
- Relationship between macro and nanoDMA in-progress
- Thermal expansion of sample can effect DMA indent location
- Plastic zone around indentation can affect nearby measurements
  - Increasing spacing can prevent plastic zone interactions but results in lower spatial resolution



Future Work

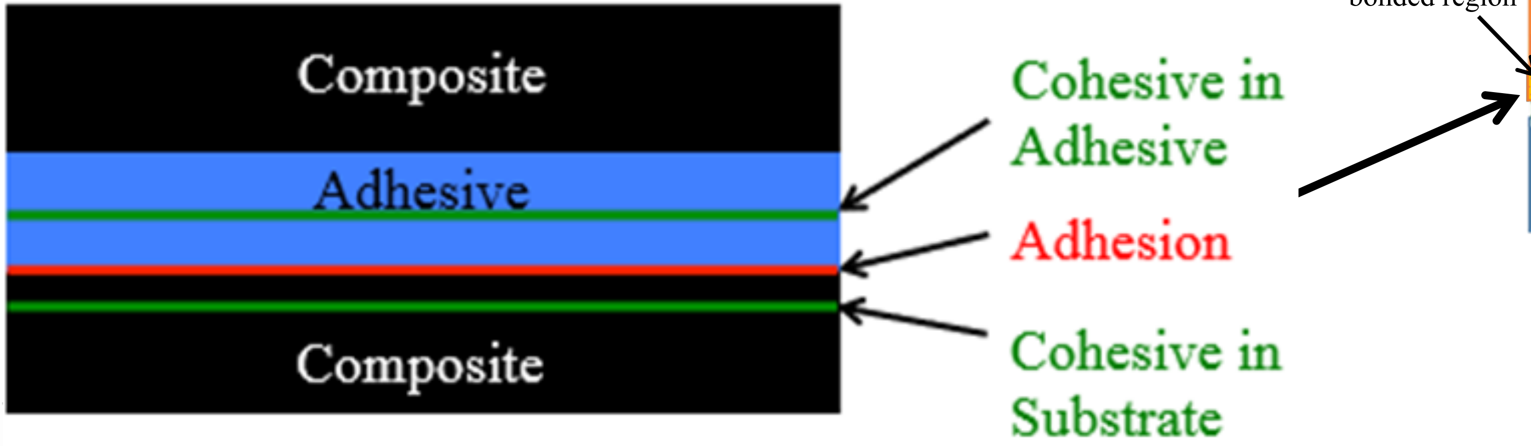
Future Work

- Nanoindentation experiments on bonding systems with ideal and suboptimal bonding surfaces
  - Characterize effect of surface preparation on bondline development
- Characterize and compare multiple bonding systems
  - Compatible adhesives for specific matrix resin systems
  - Secondary bonding
  - Wet peel ply surface preparations and resulting resin mixing zones
- Characterize the effects of different environments on bondlines
  - hot-wet environmental conditions
  - Accelerated aging
  - long term effects of environmental aging on the adhesive, the *surface preparation/matrix interphase*, and the *adhesive/bonding surface interphase*

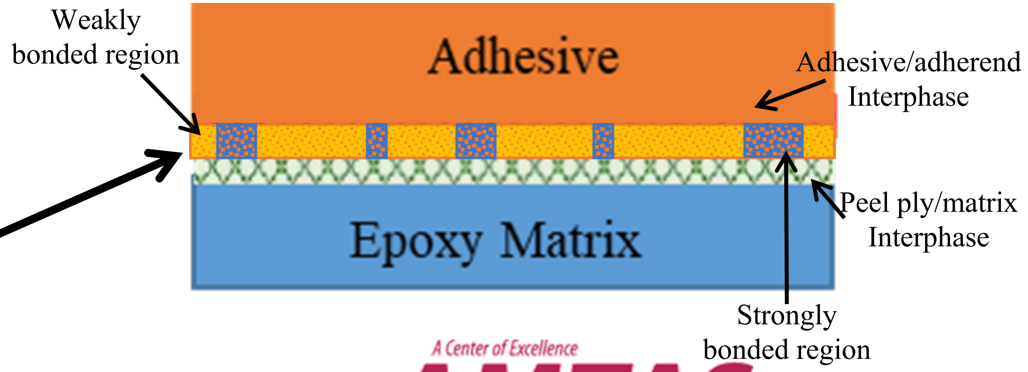


Future Work

- Composite joints are exposed to hot-wet environmental conditions for thousands of service hours
  - diffusion of moisture into the resin → hydrothermal aging
  - oxygen-rich and elevated temperature → thermo-oxidative aging
- Bulk Resin and Adhesive Physical & Chemical Aging
  - Change in mass density and toughness
  - Plasticize
  - Tg Changes
    - Moisture adsorption, Cross-link density, Free volume



Adhesion failure through interphase
"Interphase cohesive failure"



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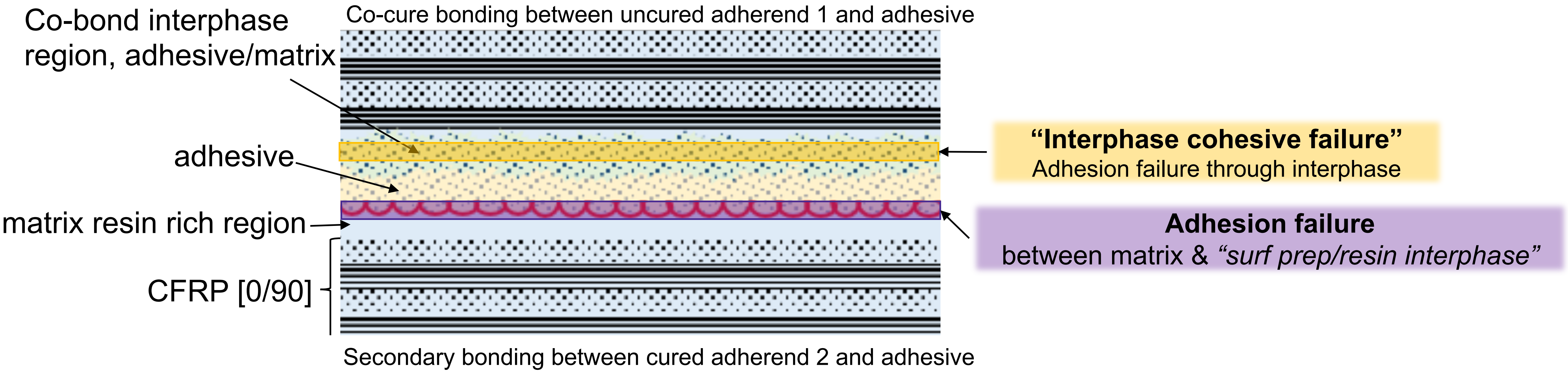
Future Work



→Will interphase age differently compared to the bulk adhesive or bulk resin?

→Will failure mode change?

change to unacceptable failure mode?

Future Work

Objectives:

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 and tougheners 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

Future Work

Materials & Approach:

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

1. pristine, unaged bonds
2. artificially aged bonds using common industry accelerated aging methods
3. in-service aged structure samples of each

Characterize Interphase	Evaluate Bond Quality & Durability
NanoDMA, nanoindentation Dynamic/destructive XPS/ESCA SIMS, iGC, CA, FTIR	Mode I: DCB, back-bonded DCB Flatwise Tension, Climbing Drum Fracture Characterization

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  - Material Science & Engineering
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Questions?

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Back-Up

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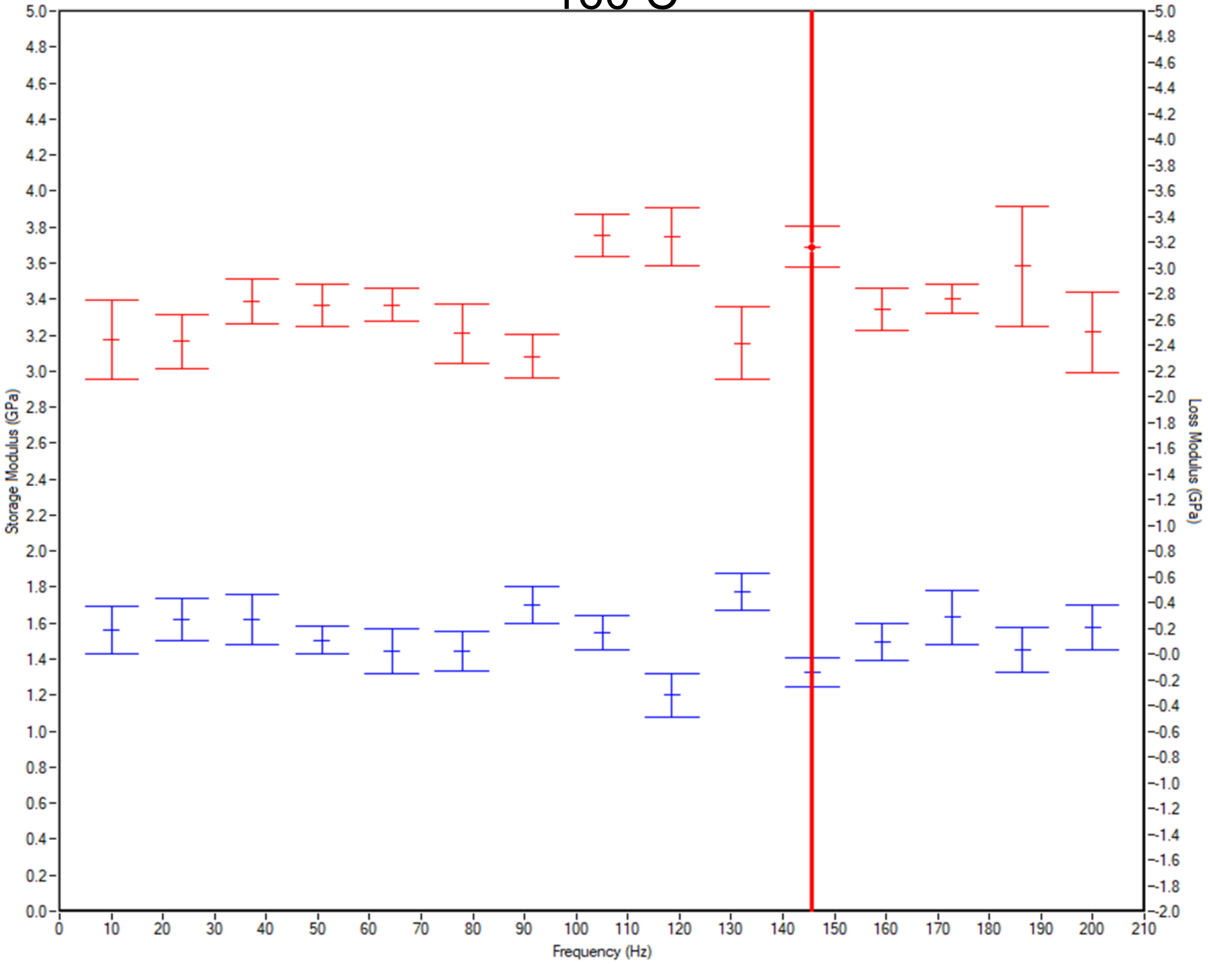
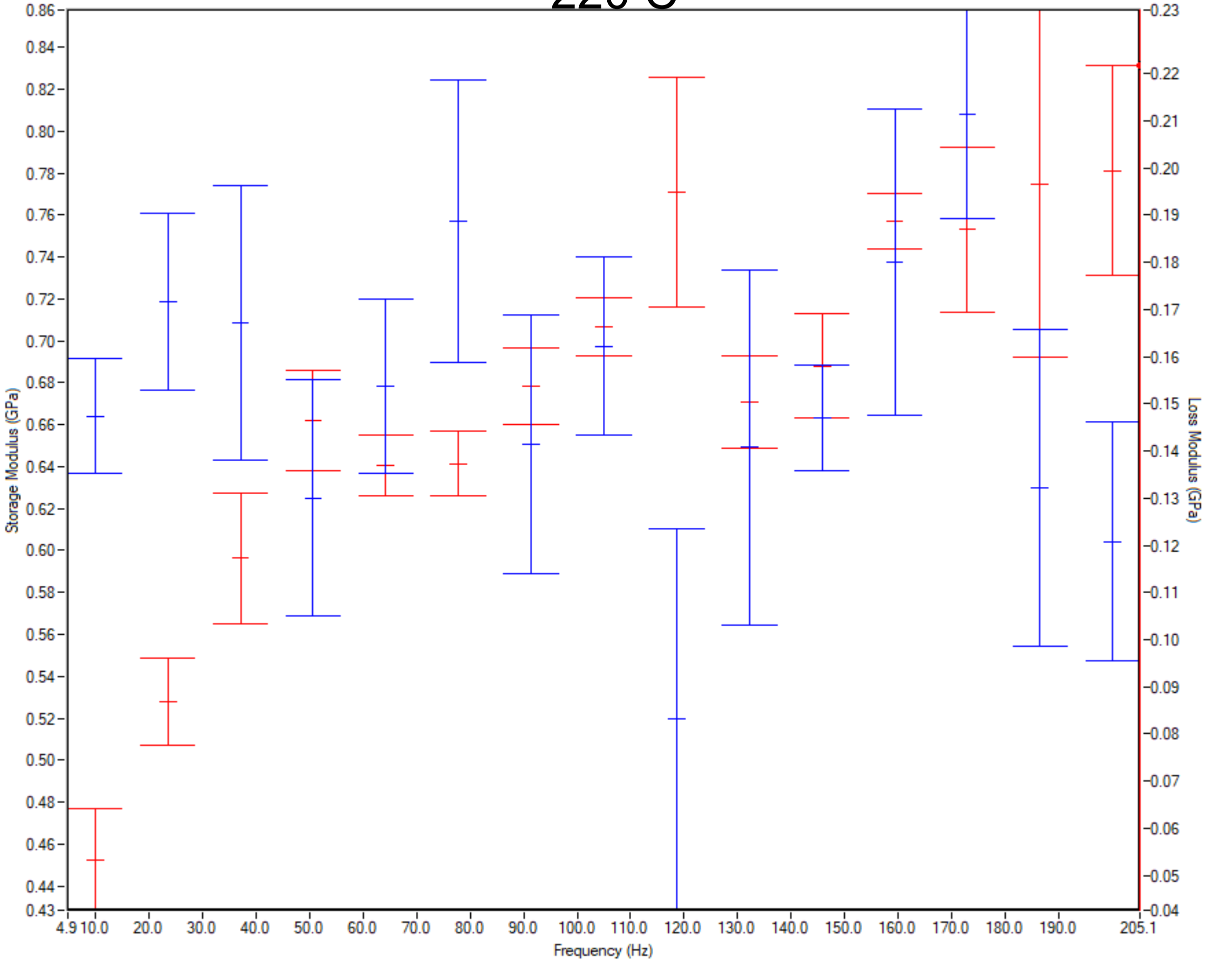
Tg Frequency Dependence

Matrix Resin Freq. Sweep

160 C



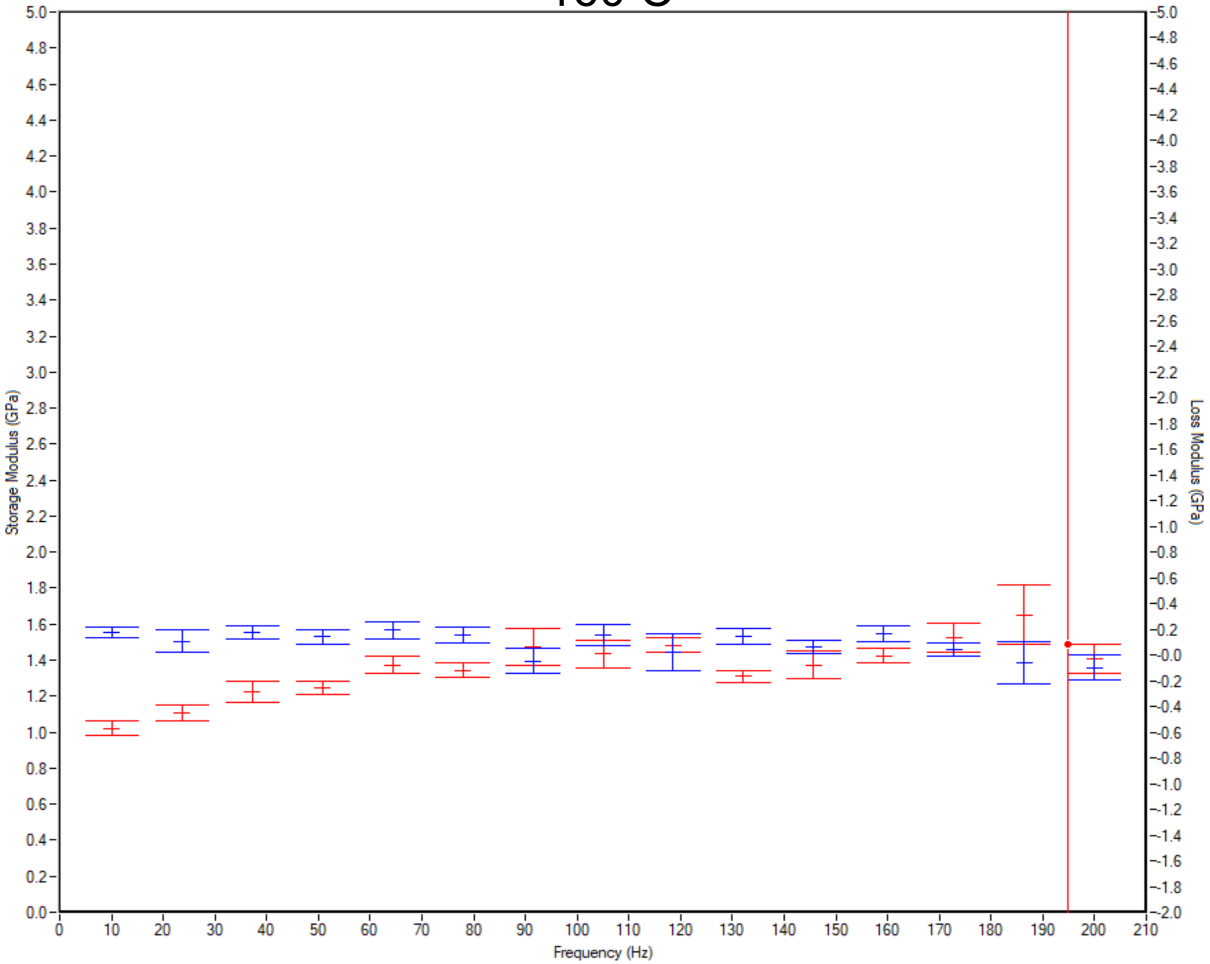
220 C



Tg Frequency Dependence

Adhesive Freq. Sweep

160 C



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