MATERIALS SCIENCE & ENGINEERING
UNIVERSITY of WASHINGTON

Nanomechanical Property Characterization of Adhesive Bondlines

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JAMS

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

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Outline

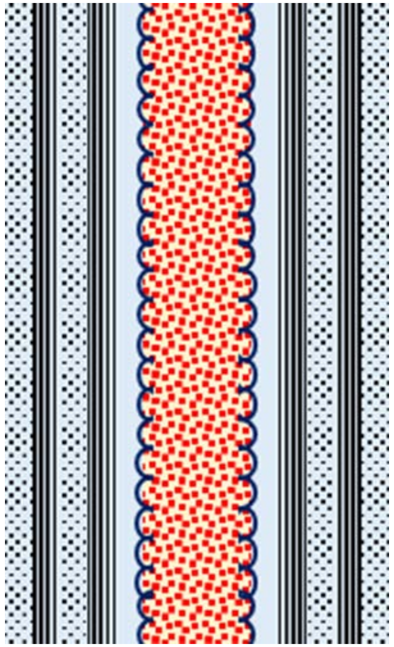
- Motivation & Key Considerations
- Background
  - Bonding process, interfaces, and interphases
- Experimental Approach
  - Experimentation via Nanomechanical and Nanochemical Methodologies
- Preliminary Results & Discussion
- On-going Work
- Acknowledgements

Motivation & Key Considerations
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

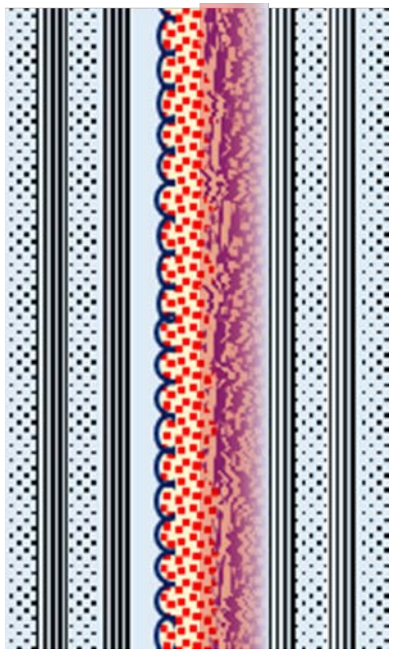
> ➢ Do regions within the bondline behave differently long-term?
>
> ➢ Are bonds changing, and if so, are they changing at different rates?

Composite Bond Architecture Types



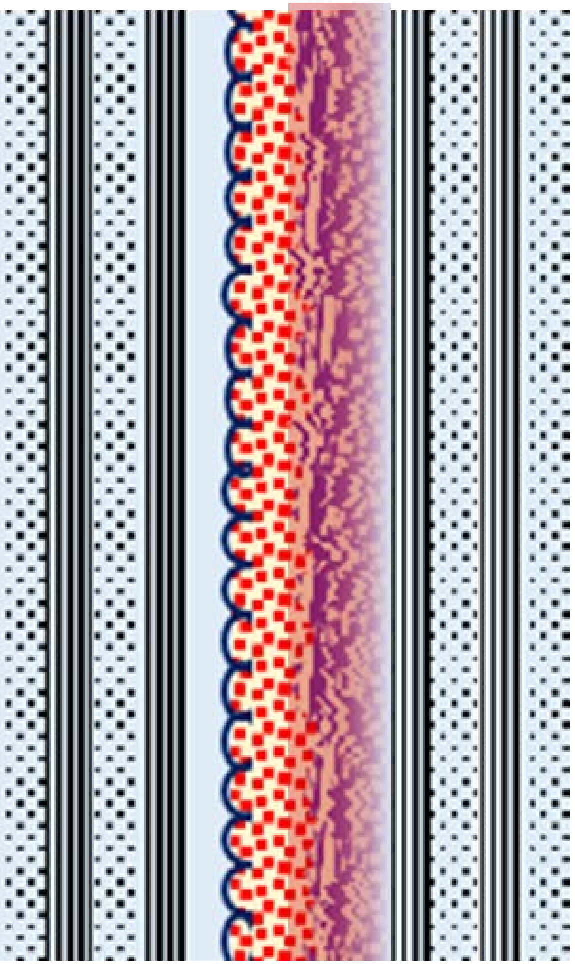
Secondary Bonding

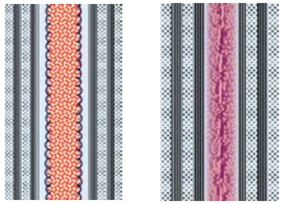
Cocure



Cobonding

Composite Bond Architecture Types





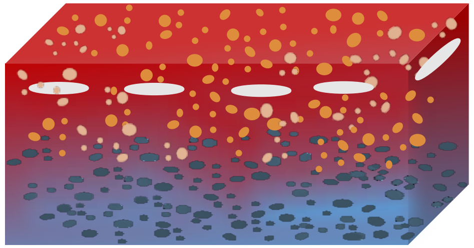
Cobonding

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

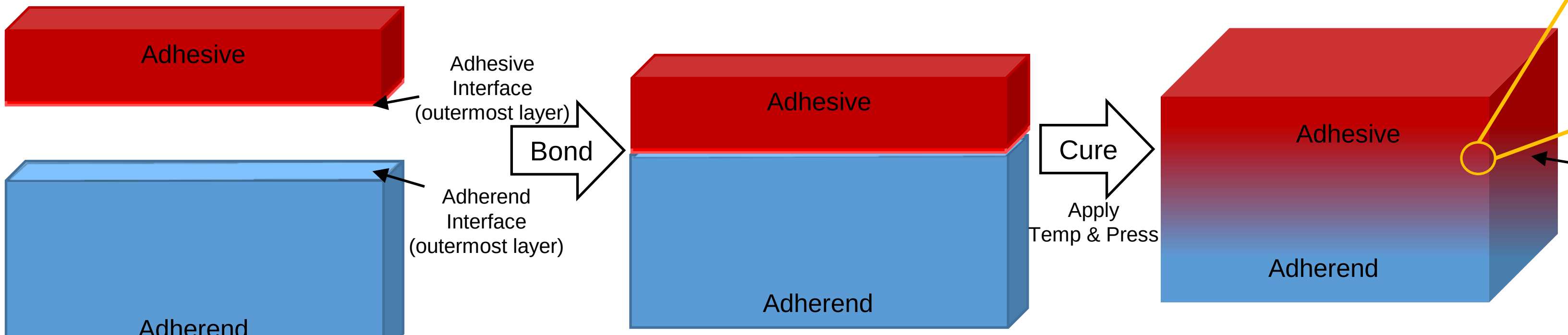
Motivation & Key Considerations

- 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

Complex, heterogenous interphase



Scrim, tougheners, second phases, additives



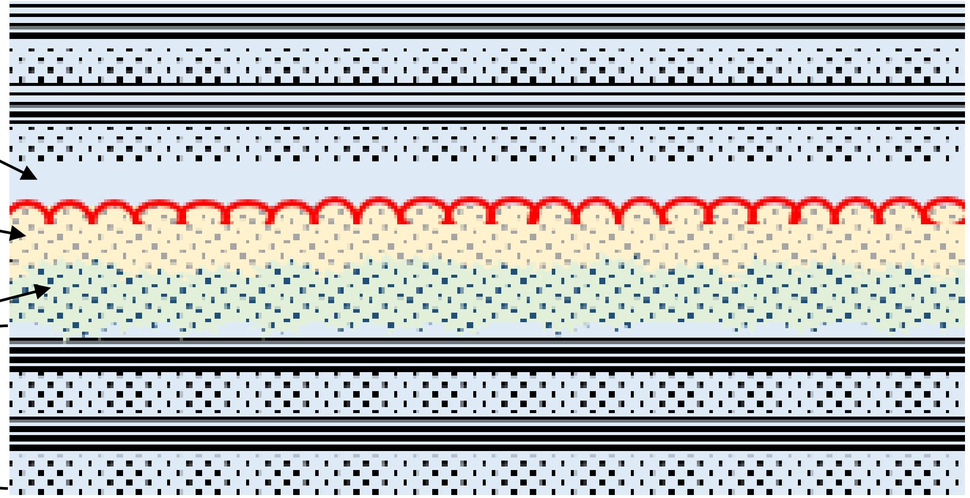
Interface of each layer are distinct

Contact between interfaces

Interface of each layer no longer distinct → interphase developed between adhesive and adherend

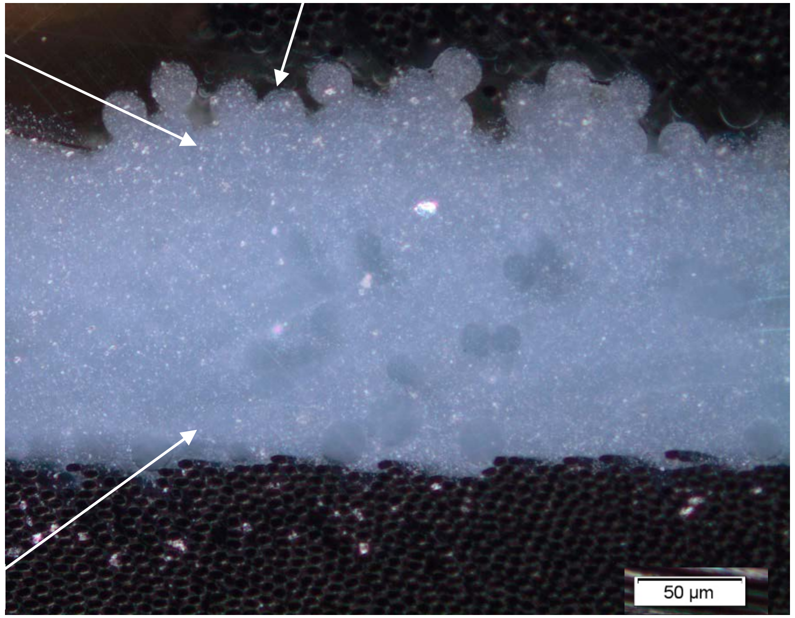
Regions within Cobonded Systems

Secondary bonding between cured adherend 2 and adhesive



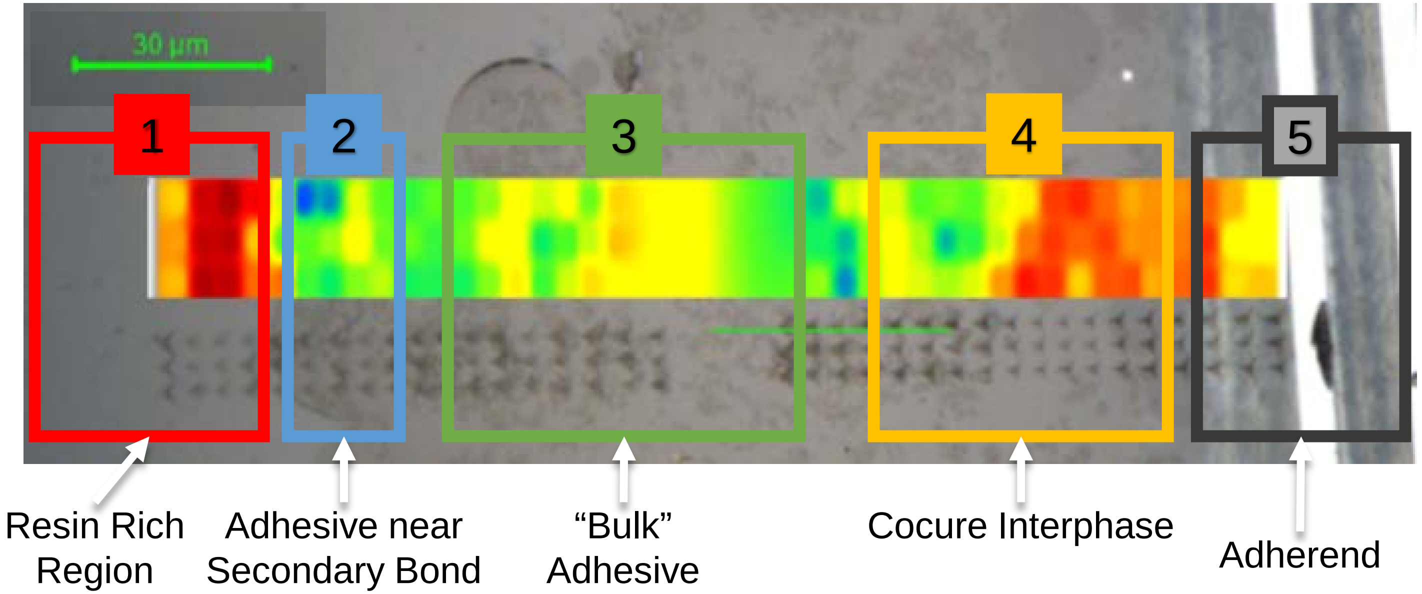
Cocure bonding between uncured adherend 1 and adhesive

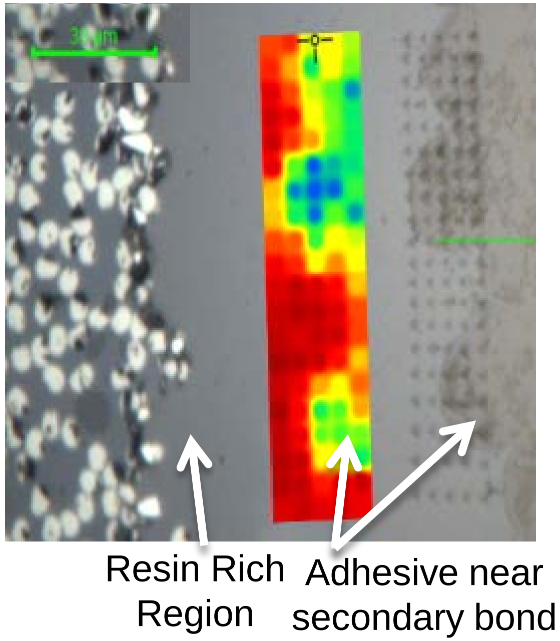
Peel Ply Surface Preparation for secondary bond



Preliminary Investigation

- Nanomechanical method to evaluate adhesive bondlines was developed
- Distinct bondline regions were detected





- Properties in distinct bondline regions were found to be statistically different

Develop nanomechanical and nanochemical methodology to evaluate interphase properties of cobonded systems

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

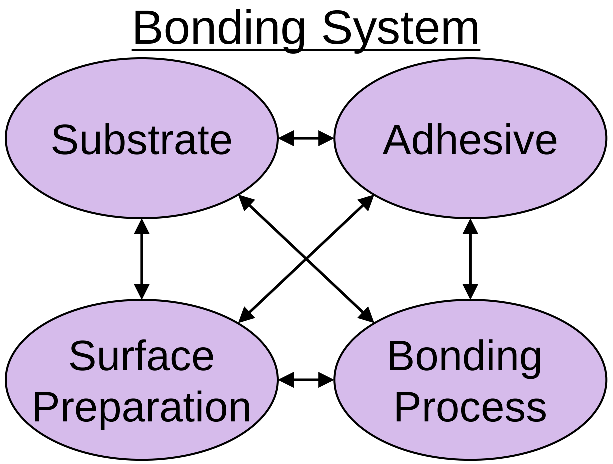


Figure adapted from Blohowiak, K.Y., et al., “Qualified Bonded Systems Approach to Certified Bonded Structure,” NATO Specialists’ Meeting AVT-266 on Use of Bonded Joints in Military Applications, STO-MP-AVT-266, Apr 2018

Understand fundamental science of matrix/adhesive interactions

AMTAS 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

Technical Approach

1. Development/application of new techniques to investigate interphases in structural adhesive bonding systems
   - Nanomechanical Methodology
     - Nanoindentation (property mapping)
     - NanoDMA – glass transition temperature ranges at nanoscale
   - Nanochemical Analysis – Photo-induced Force Microscopy (PiFM)

2. Development of model system to investigate degree of comingling
   - Controlled mixtures of bulk adhesive and bulk resin
   - "Cocure Interphase Mixtures" based on "Rule of Mixtures" Theory

3. Investigation of high temperature exposure effects on interphases in bondlines

Technical Approach

1. Development/application of new techniques to investigate interphases in structural adhesive bonding systems
   - Nanomechanical Methodology
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Secondary Bond Systems	Compare 2 adhesive systems
Cocure Systems	Compare 1 adhesive system to other types
Cobond Systems	Compare 3 adhesive systems
	“Cocure Interphase Mixture” Models

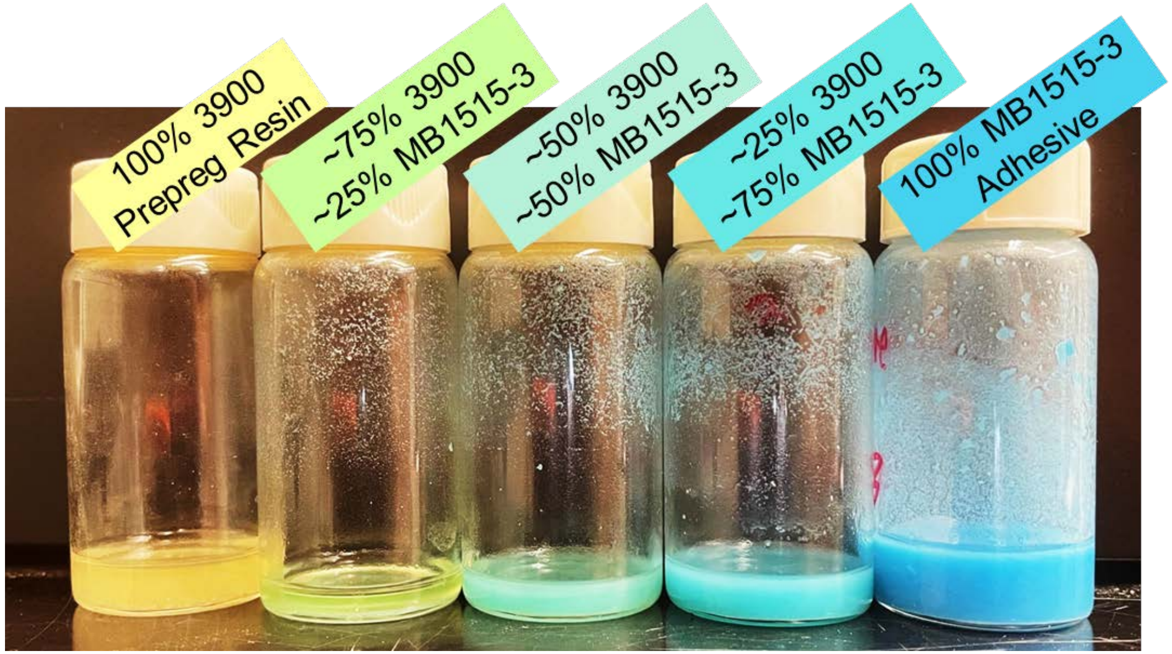
Adhesive Characterization

- Nanomechanical Property Testing
  - NanoDynamic Mechanical Analysis (DMA)
  - Nanoindentation (modulus and hardness)
- Photo-induced Force Microscopy (PiFM)
- MacroDMA
- Moduluated Differential scanning calorimetry (MDSC)
- Fourier Transform Infrared (FTIR)
- Free Volume Evaluation

Technical Approach

2. Development of model system to investigate degree of comingling
   - Controlled mixtures of bulk adhesive and bulk resin
   - “Cocure Interphase Mixtures” based on “Rule of Mixtures” Theory

Model #	Fabrication Method	Adherend Resin	Adhesive Resin
1	Acetone Extraction	Toray T800S/3900-2 Prepreg	Solvay Metlbond® 1515-3 modified epoxy supported
2	“Neat” Resin, FlackTek SpeedMixer®	Toray 3900-2 Same Qualified Resin Transfer Molding (SQTRM)	AF 555 unsupported film



Technical Approach

3. Investigation of high temperature exposure effects on interphases in bondlines

	Bond Type	Adherend[F1]	Surface Preparation (cured adherend only) [F2]	Adhesive [F3]
Baseline				
Baseline DCB Sample[F4]	Secondary Bond	Toray T800S/3900 resin	Diatex 1500EV6 woven polyester	Solvay Metlbond® 1515-4 modified epoxy supported
Baseline DCB Sample[F5]	Cobond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
Controlled High Temperature Exposures				
2hrs @ 330°F DCB Sample[F5]	Cobond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
1hr @ 400°F DCB Sample[F5]	Cobond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
30days @ 3300°F DCB Sample[F5]	Cobond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
Environmental Exposure Only				
Lab Ambient 2008 Exposure DCB Sample[F5]	Secondary Bond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
2012 environmentally exposed Scrapped Cobond[F4, F6]	Cobond	Toray T800S/3900 resin Toray FGF-108 29M	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
Time, Stress, Environmental Exposure				
Scrapped Parts Cobond[F4, F6]	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
[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 and Nanochemical Anaylsis

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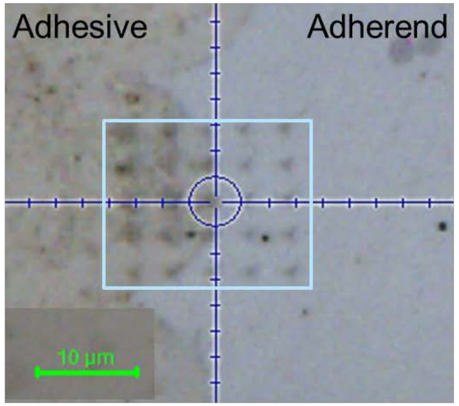
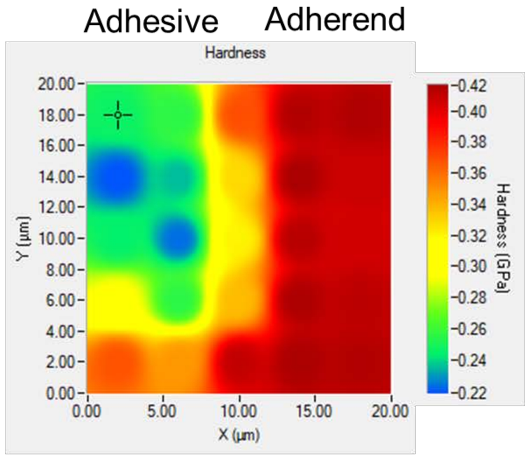
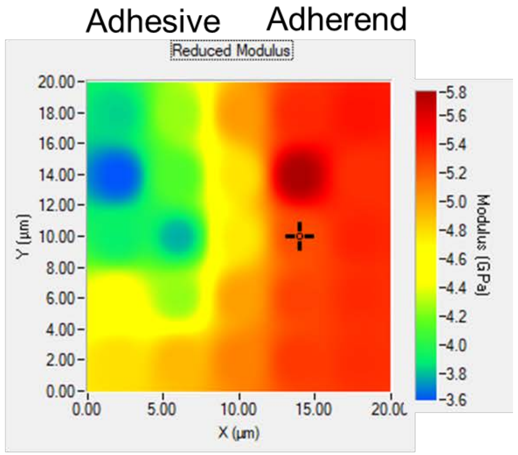
Nanoindentation Methodology

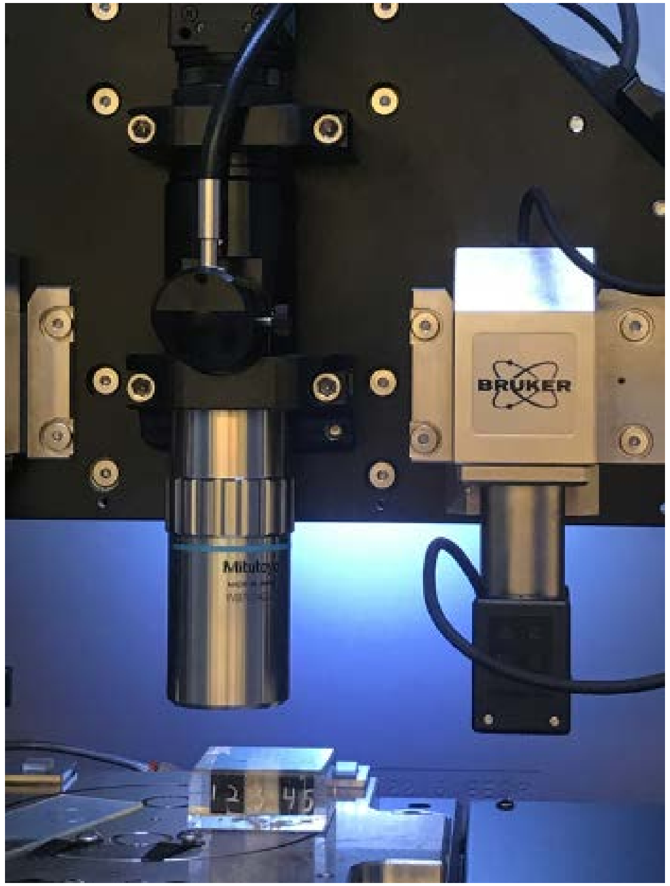
- Hysitron TriboIndenter 980 with Berkovich diamond indenter tip
- Indent surface from tens of nanometers to several micrometers deep
- Extreme Property Mapping (XPM™)
  - Hardness and reduced modulus mapped across bondline
- Nano-Dynamic Mechanical Analysis (NanoDMA)



XPM array of epoxy







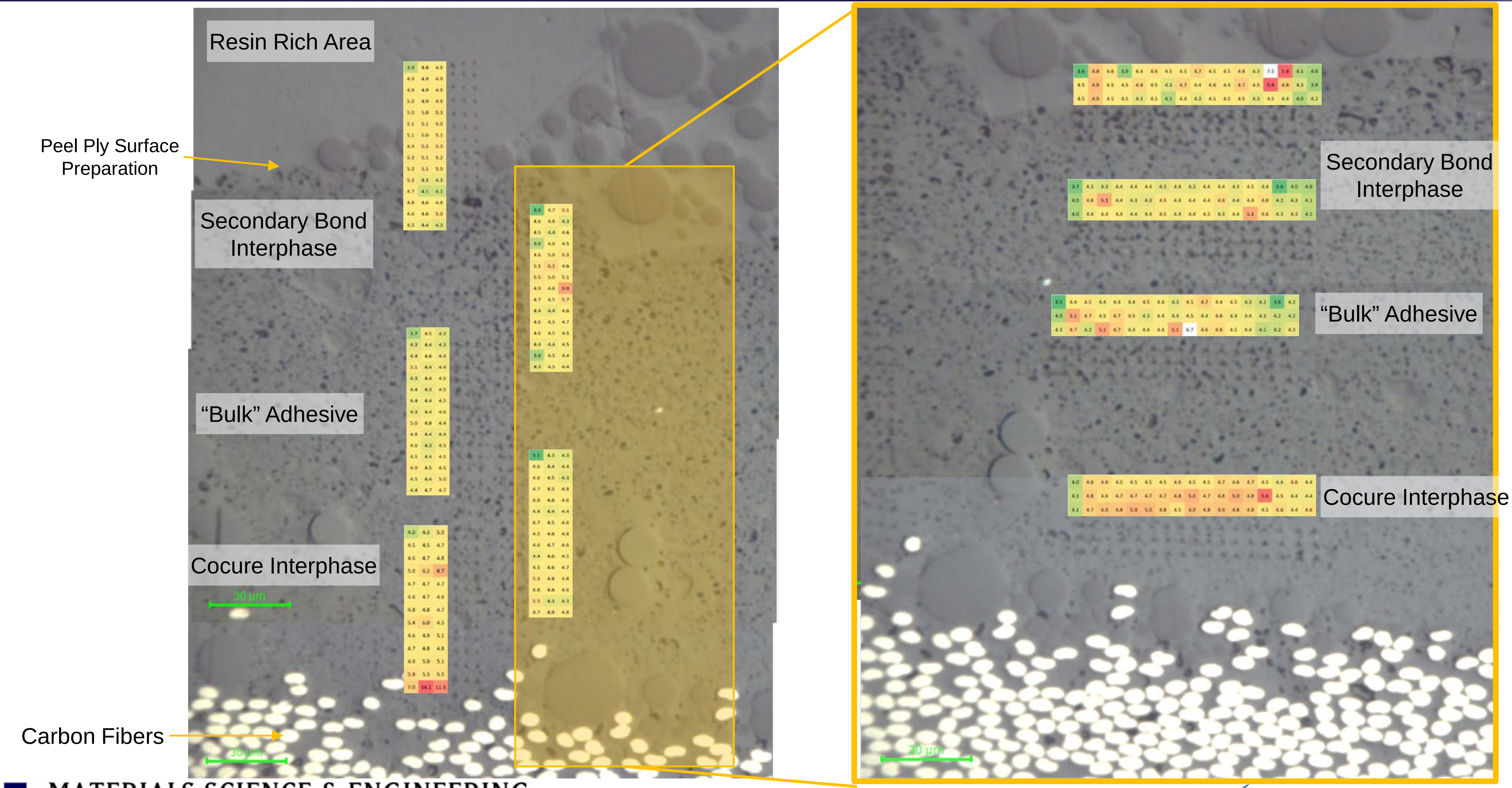
Hysitron TriboIndenter 980 at U. Washington

Nanoindentation Limitations

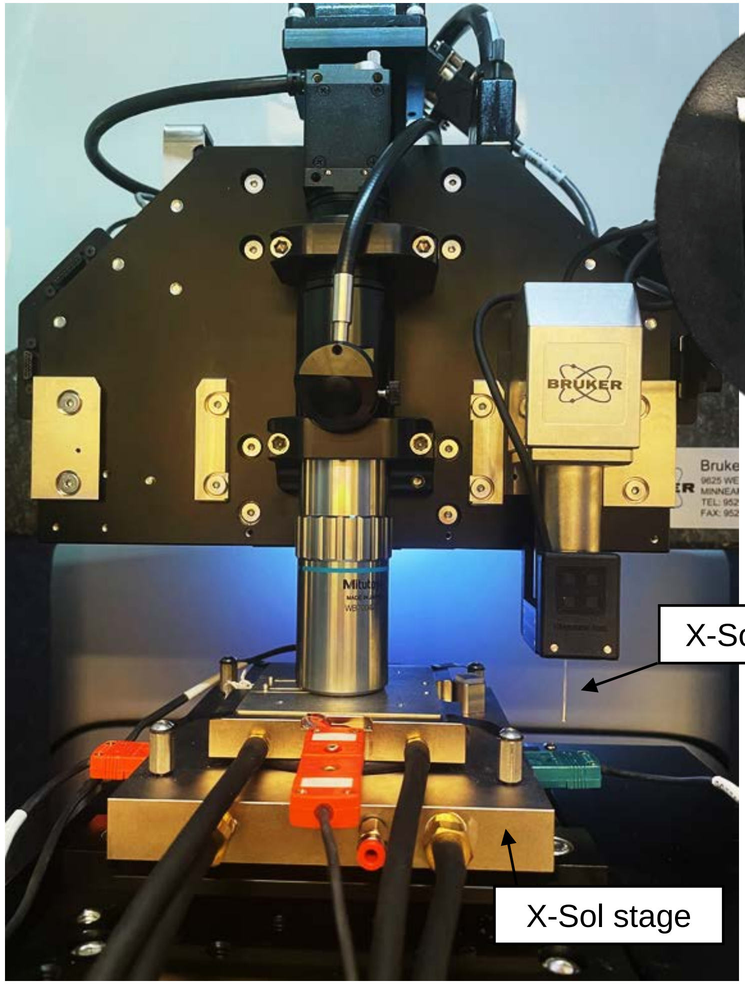
- At this time, no relationship exists between nanomechanical characterization to any engineering properties used in the design, analysis and certification of bonded composite structures
- Subsurface heterogeneity can influence measurements
- Plastic zone around indentation can affect nearby measurements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

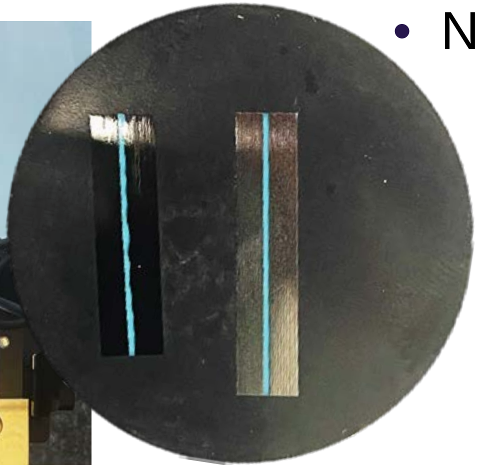
Nanomechanical Characterization

Extreme Property Mapping (XPM)



Nanomechanical Characterization
Nano-Dynamic Mechanical Analysis (NanoDMA)





Nanoindentation Sample Example

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

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

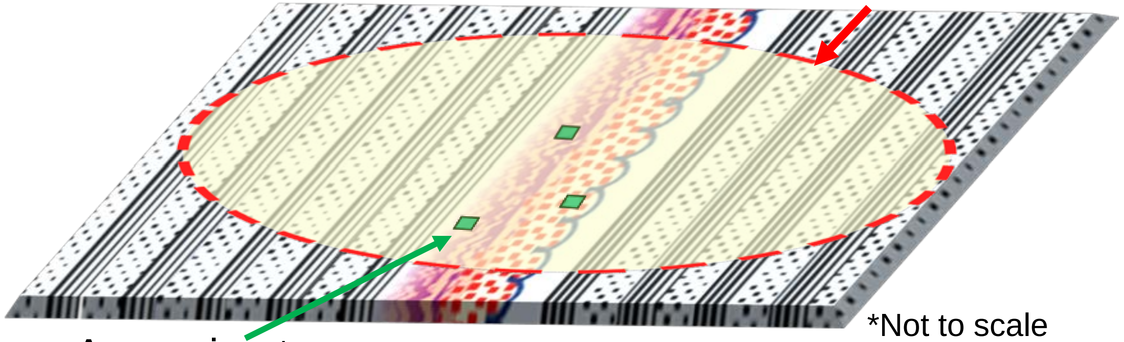
Nanochemical Characterization

Photo-induced Force Microscopy (PiFM)

- Non-contact AFM method relying on tip-sample force interactions [19,20]
- Highly localized field created by excitation laser focused on a metal coated AFM tip [19,20]
- Fixed-wavelength PiF images to map individual chemical constituents
- Identify characteristic absorptions specific to bulk materials and controls at room temperature
  - →Investigate degree of comingling
  - →Investigate effects of high temperature

Objective: Use characteristic absorptions to investigate degree of comingling and thermal stability

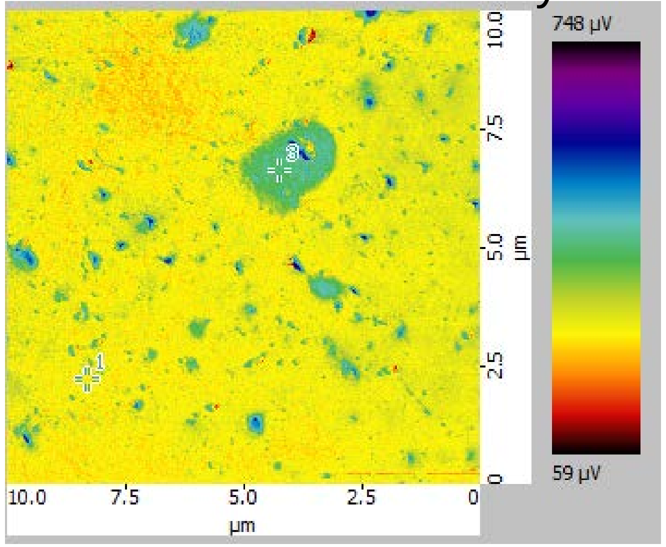
Approximate
Macro-FTIR Scan Area



*Not to scale

Approximate
PiF Scan Area

Adhesive near Secondary Bond



PiF at given wavenumber

Preliminary Results

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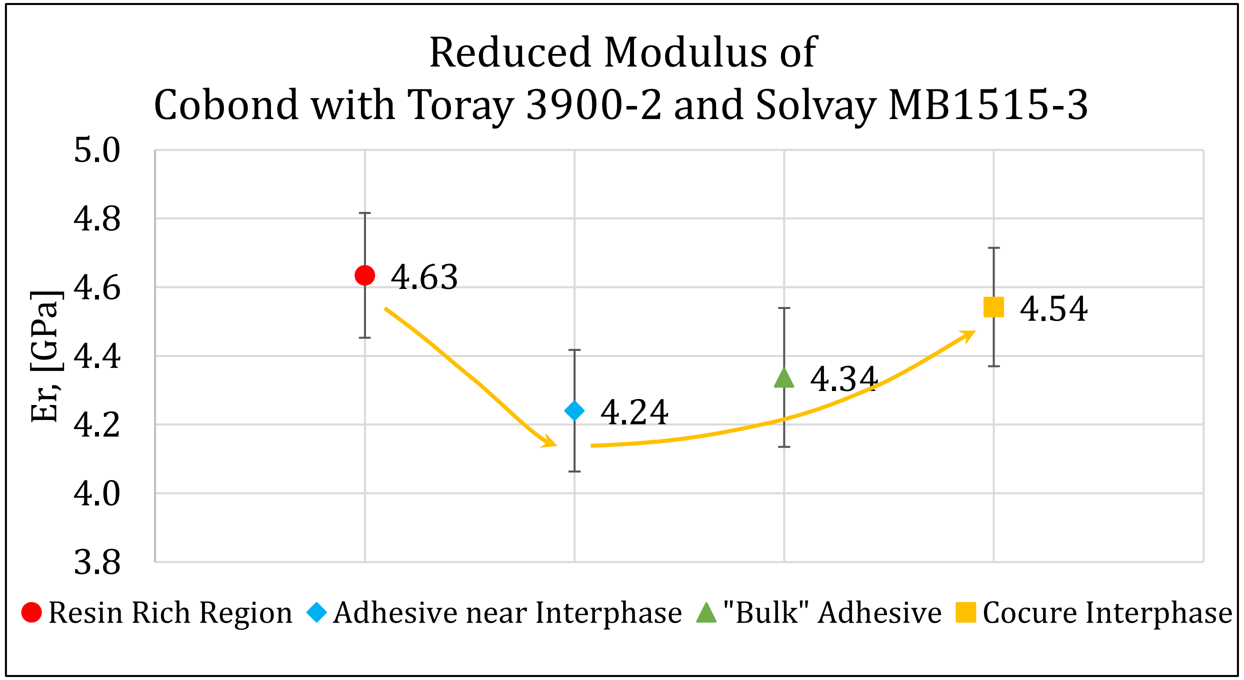
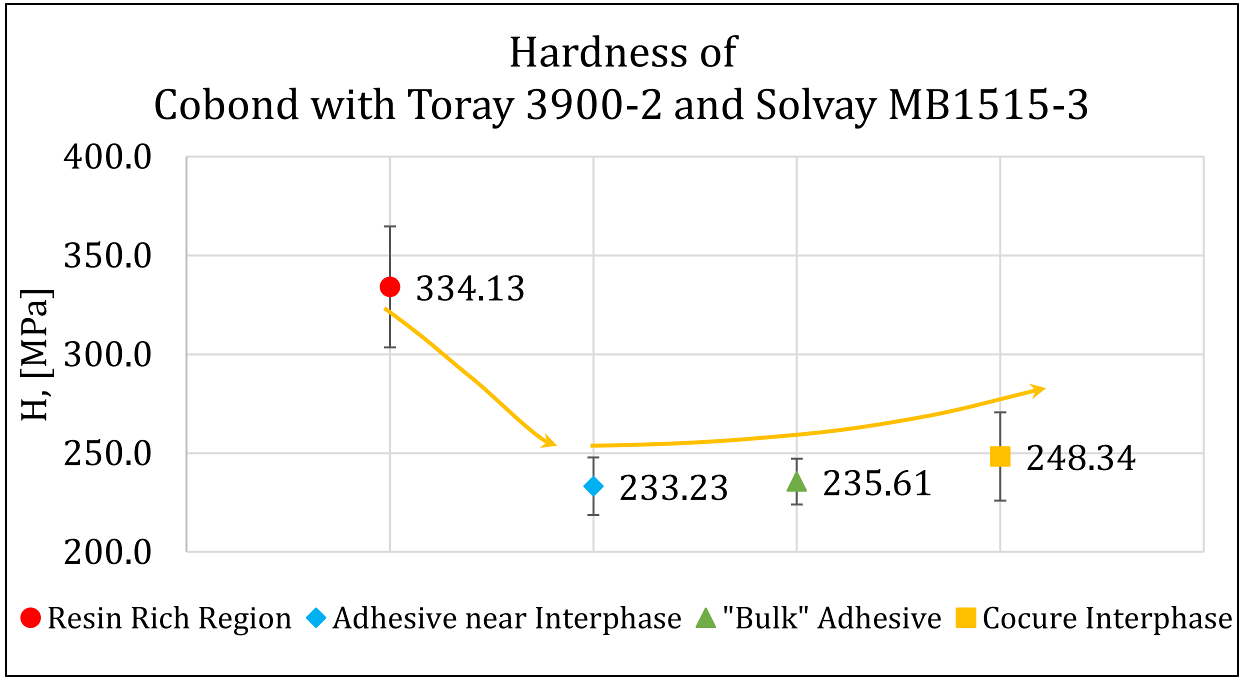
Bondline Property Mapping

XPM – Cobond Toray 3900-2 and Solvay MB1515-3



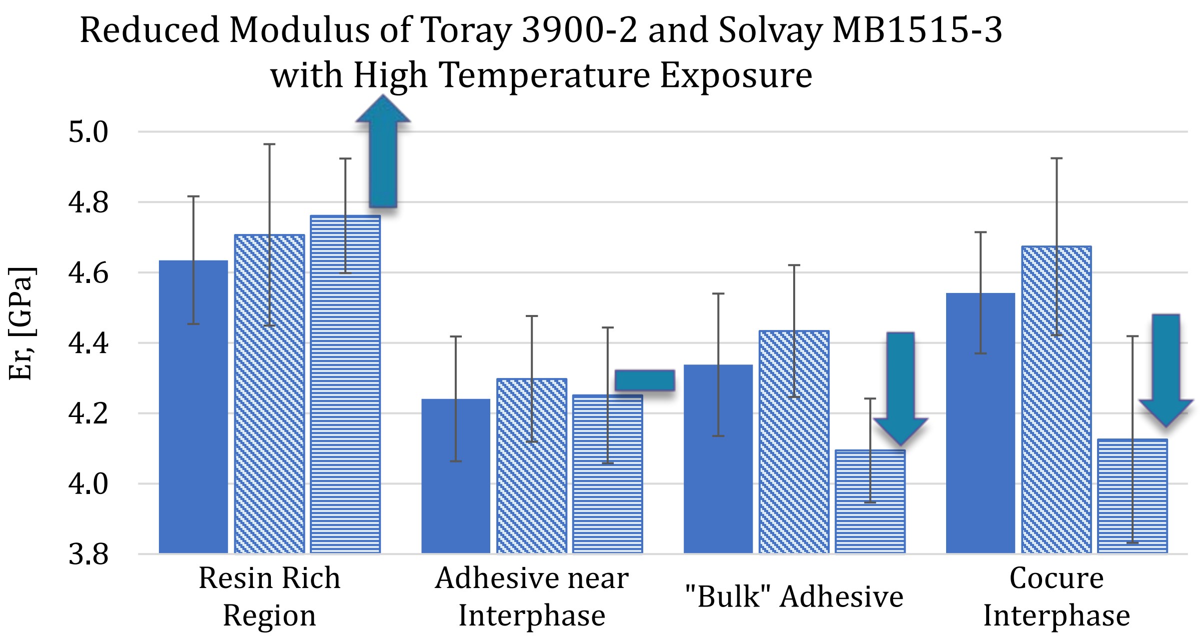


Cobonded systems show distinctive mechanical property trend within bondline:

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

Bondline Property Mapping

XPM – Cobond Toray 3900-2 and Solvay MB1515-3



	Resin Rich Region	Adhesive near Interphase	"Bulk" Adhesive	Cocure Interphase
Control	4.63	4.24	4.34	4.54
2hrs at 330°F	4.71	4.30	4.43	4.67
1hr at 400°F	4.76	4.25	4.09	4.12

<u>Solvay MB1515-3 TDS</u>

Dry T_g is 338°F (170°C) G' knee by dynamic mechanical analysis

Exposure below reported T_g of the adhesive (330°F) → potential "post cure" effect
Exposure above reported T_g of the adhesive (400°F) → potential change in adhesive regions

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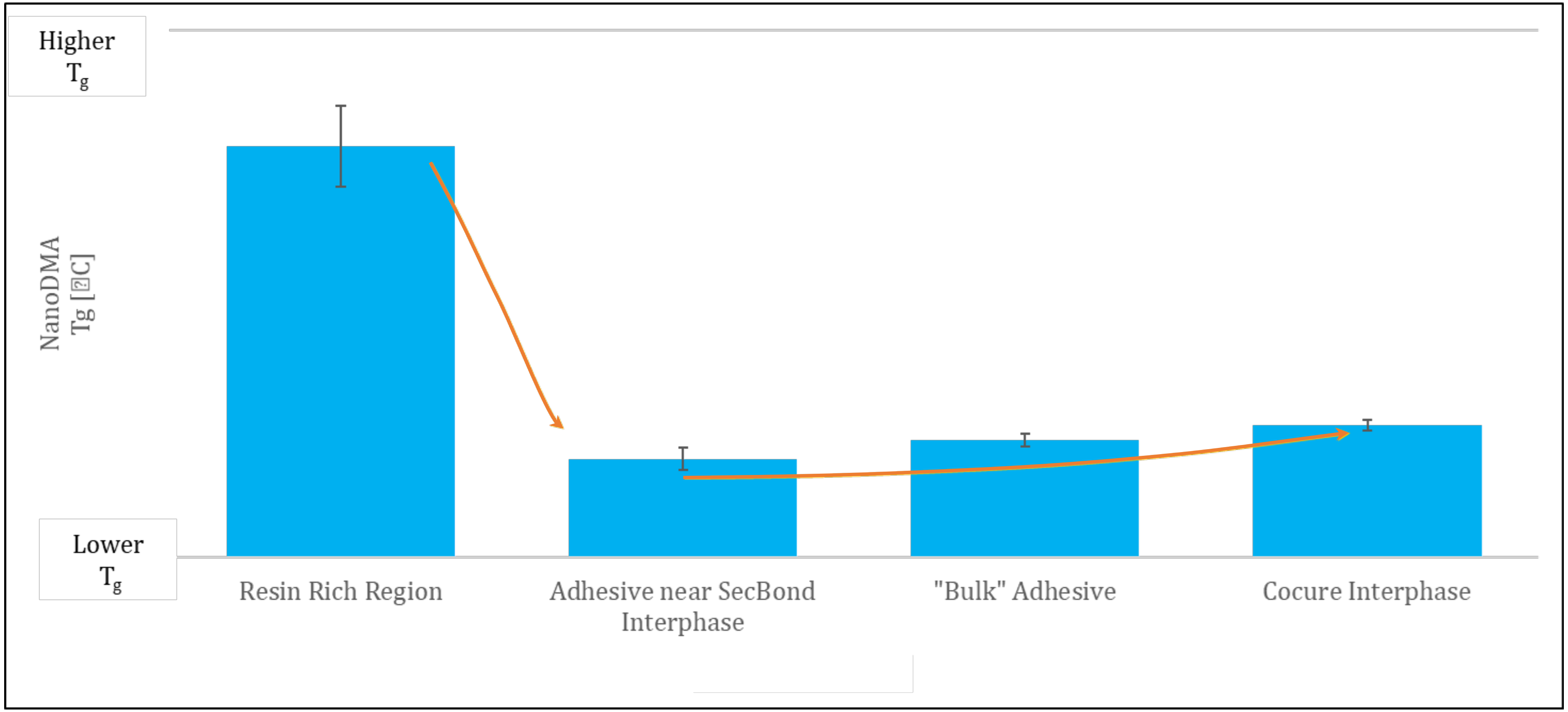
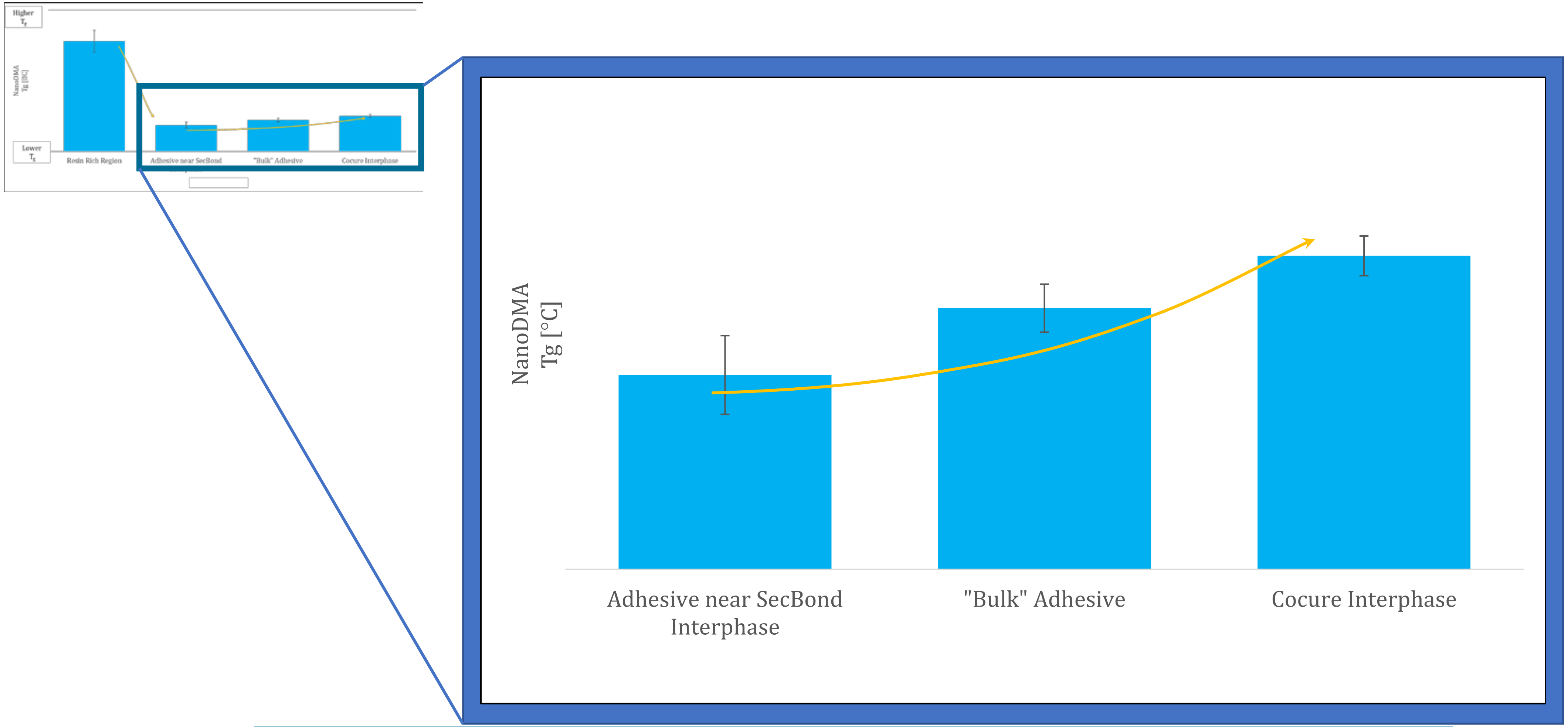
NanoDMA

Cobond Toray 3900-2 and Solvay MB1515-3



NanoDMA

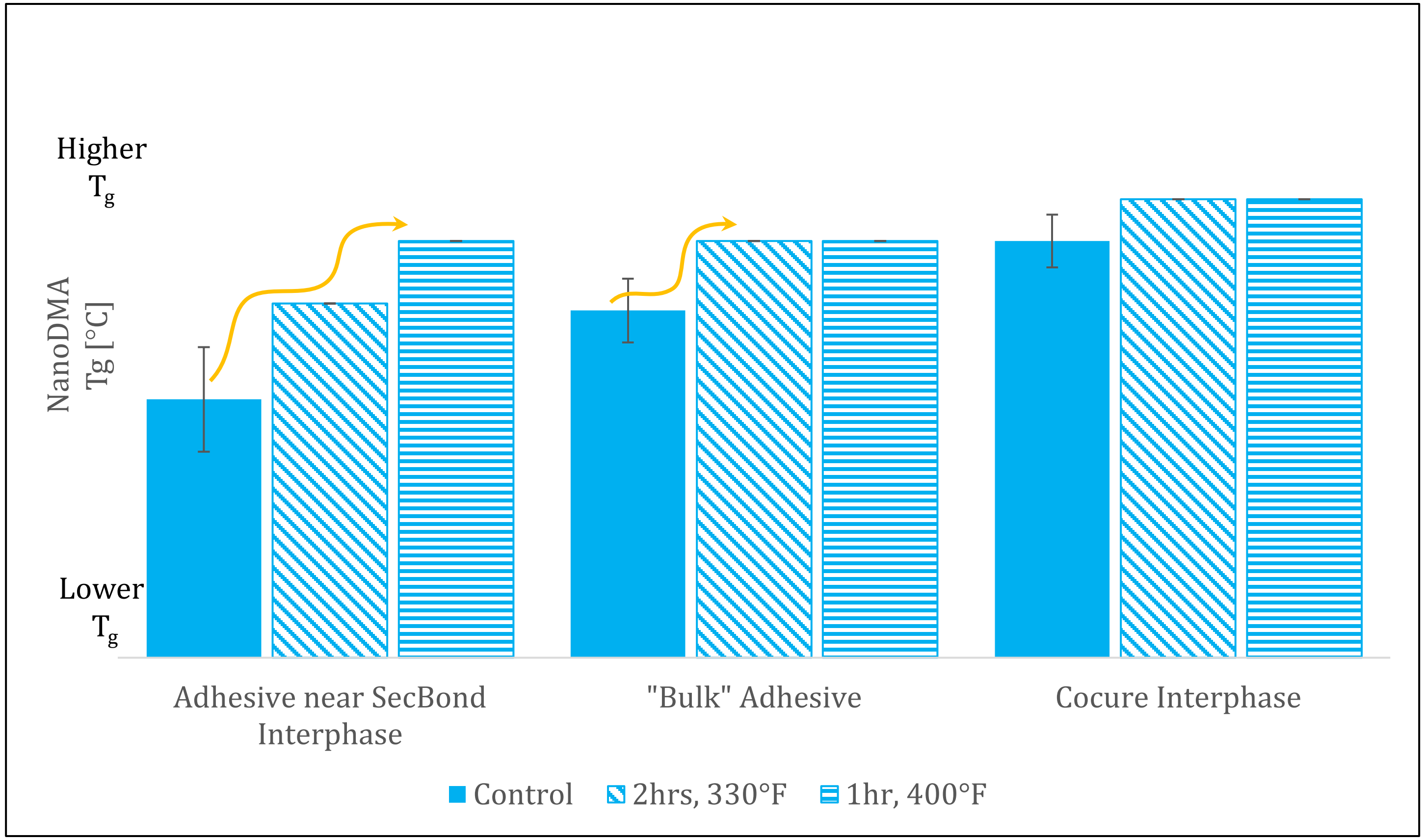
Cobond Toray 3900-2 and Solvay MB1515-3



Subtle increase in average nanoDMA $T_g^{Tan(\delta)}$ as comingling increases

NanoDMA

Cobond Toray 3900-2 and Solvay MB1515-3 with High Temperature Exposures



Only significant change in T_g occurs in Adhesive near Secondary Bond Interphase

Preliminary Conclusions

- Cobonded Systems have distinctive nanomechanical properties
  - Cobonded interphase regions showed intermediate values between the “bulk” properties of the adhesive and resin → significant mixing during cure
  - Nanomechanical property trend within bondline

↑

Resin

Cocure Interphase

“Bulk” Adhesive

Adhesive near Secondary Bond Interphase

- Nanomechanical properties change with high temperature exposures
  - Increase in modulus and hardness suggest “post cure” effect after high temp exposure below T_g
  - Decrease in modulus potentially indicating change of materials after high temp exposure above T_g
  - NanoDMA may be able to detect subtle changes in T_g due to the degree of comingling across bondline regions in cobonded systems

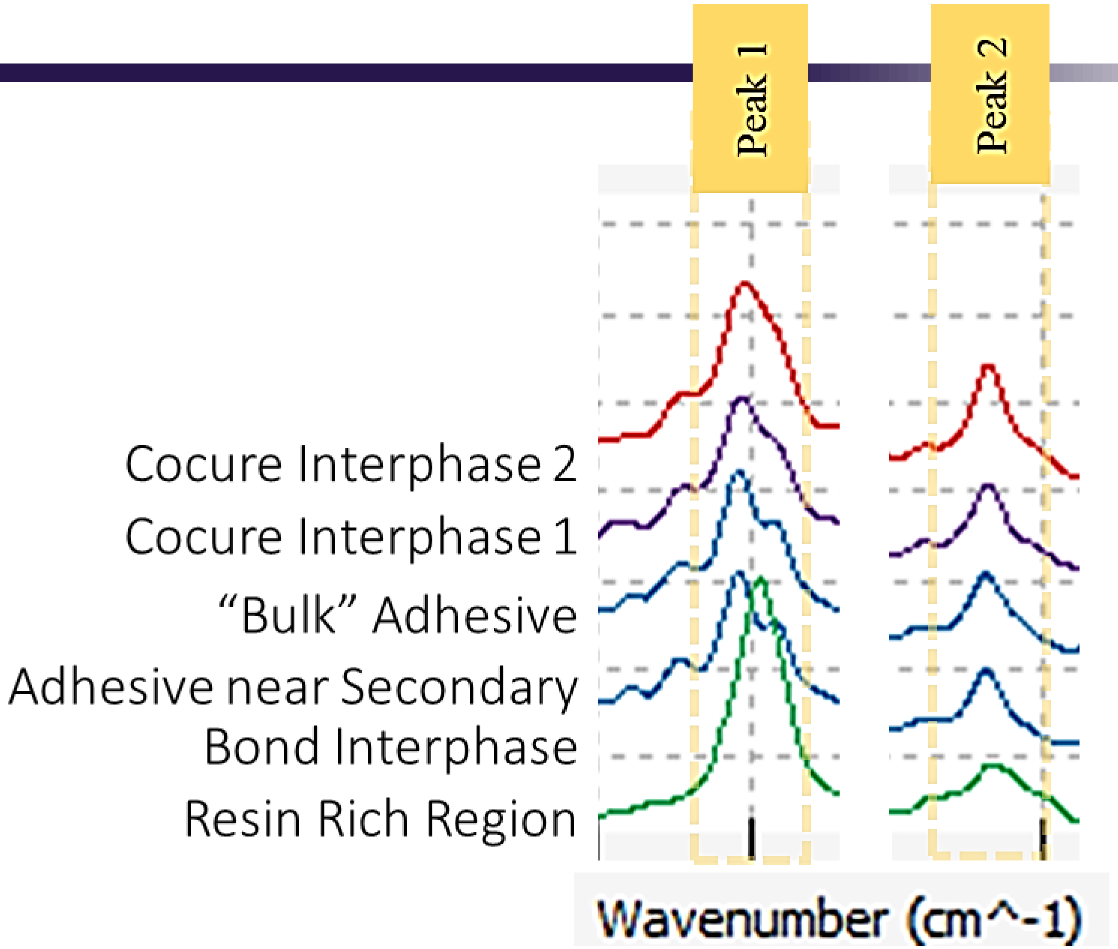
On-going Work

1. Nanochemical Analyis – PiFM on bonded systems
2. “Cocure Interphase Mixtures” Model System
   - Characterization of comingling regions using controlled mixtures
     - T_g
     - Chemical Analysis
3. Characterize adhesive bondlines with various heat exposures
   - Correlate adhesive bondlines with various exposures to controlled mixtures → understand the effect of heat exposures on bondline properties

On-going Work

1. Nanochemical Analyis – PiFM

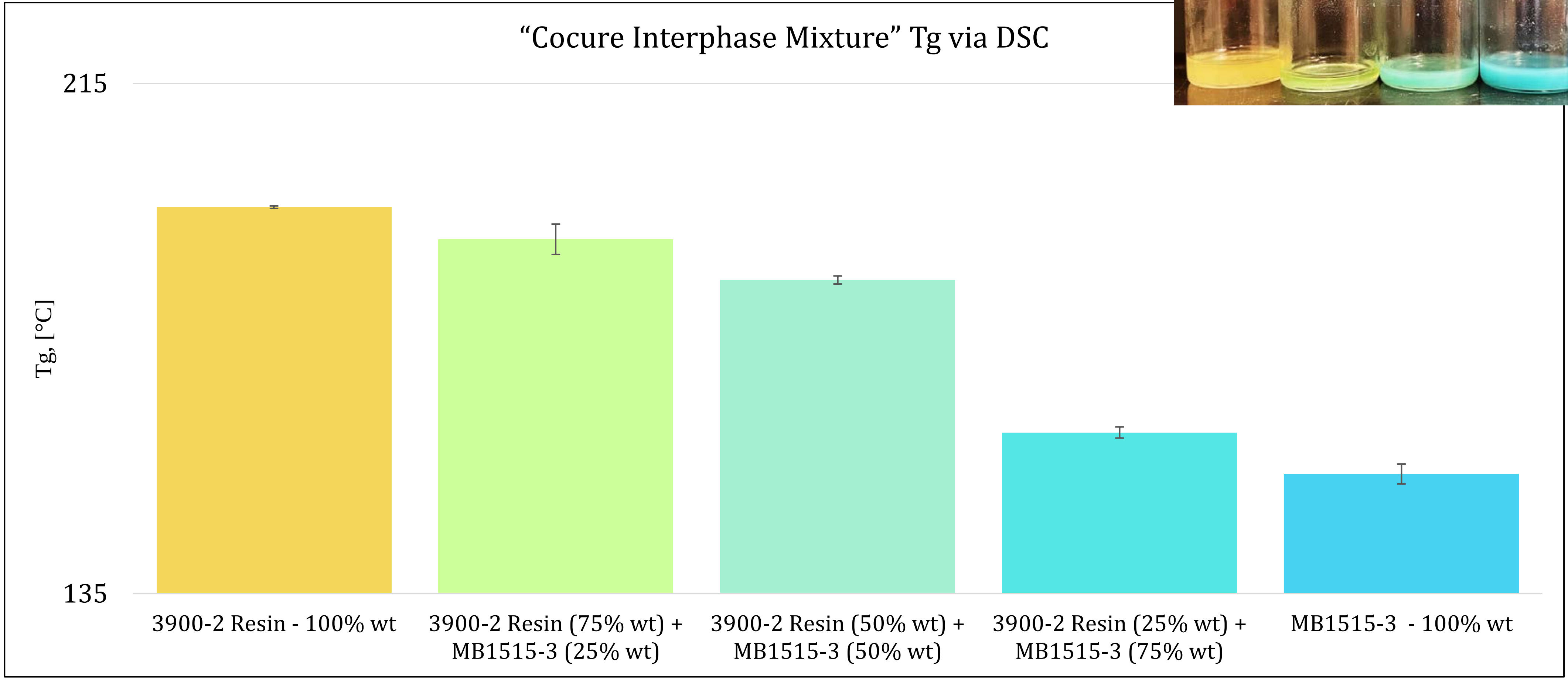
- PiF spectra indicates peak location shifts, broadening/sharpening, absorbance
  - Peak 1 – shift with increased comingling
  - Peak 2 – peak broadening with increased comingling

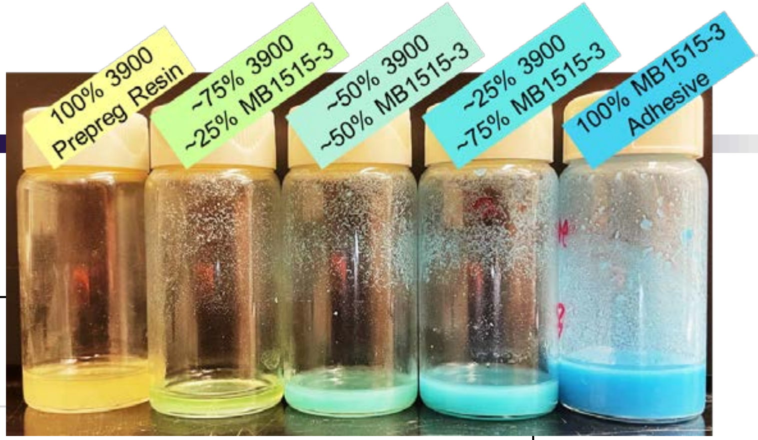


PiFM can be used to estimate the degree of comingling in each bondline region

On-going Work

2. "Cocure Interphase Mixtures" Model System





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    - Flinn Group
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