Nanomechanical Property Characterization of Adhesive Bondlines

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FAA Sponsors: Cindy Ashforth, Larry Ilcewicz

Outline

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 Æhygrothermal effects
  - Cyclic loading Æratchet and fatigue effects
  - Oxygen-rich and elevated temperatures Æthermo-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

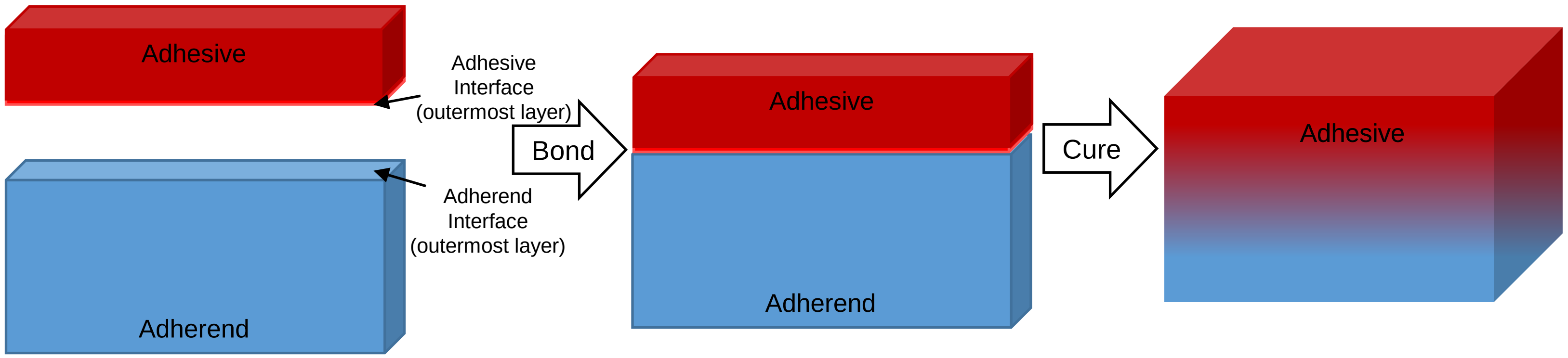
¾ Do regions within the bondline behave differently long-term?

¾ Are bonds changing, and if so, are they changing at different rates?

Composite Bond Architecture Types

Motivation & Key Considerations

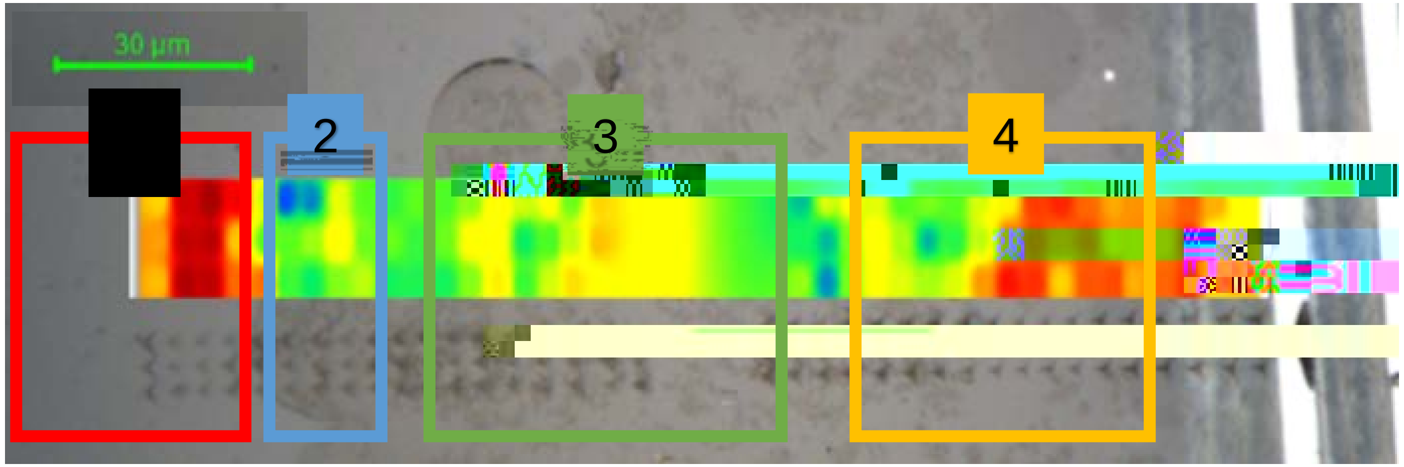
- Bonding creates an interphase between two materials
  - Interphase can affect bond strength and durability
  - factors influencing interphase development need further investigation
- Characterization of the micron-scale regions within bondlines is complex due to their size
  - Complex microstructures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

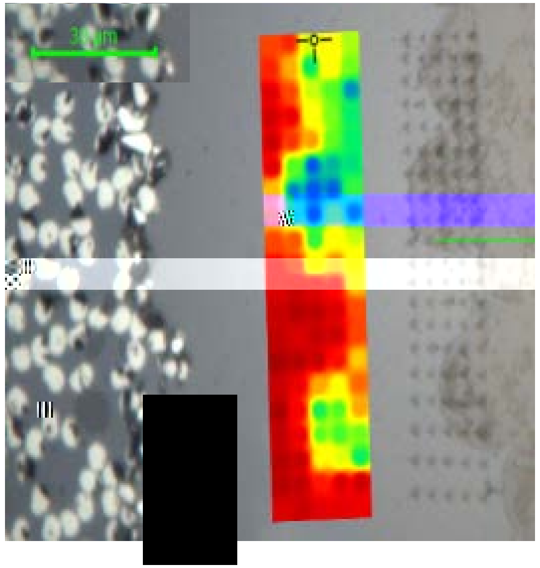


Interface of each layer are distinct

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

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
  - C01 (har)-3 (ac)-1 M (y)-1 ( )93.6f2 (s)-1o (oc)-.6 mel-1 (s)-5 rsPot5acemts

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

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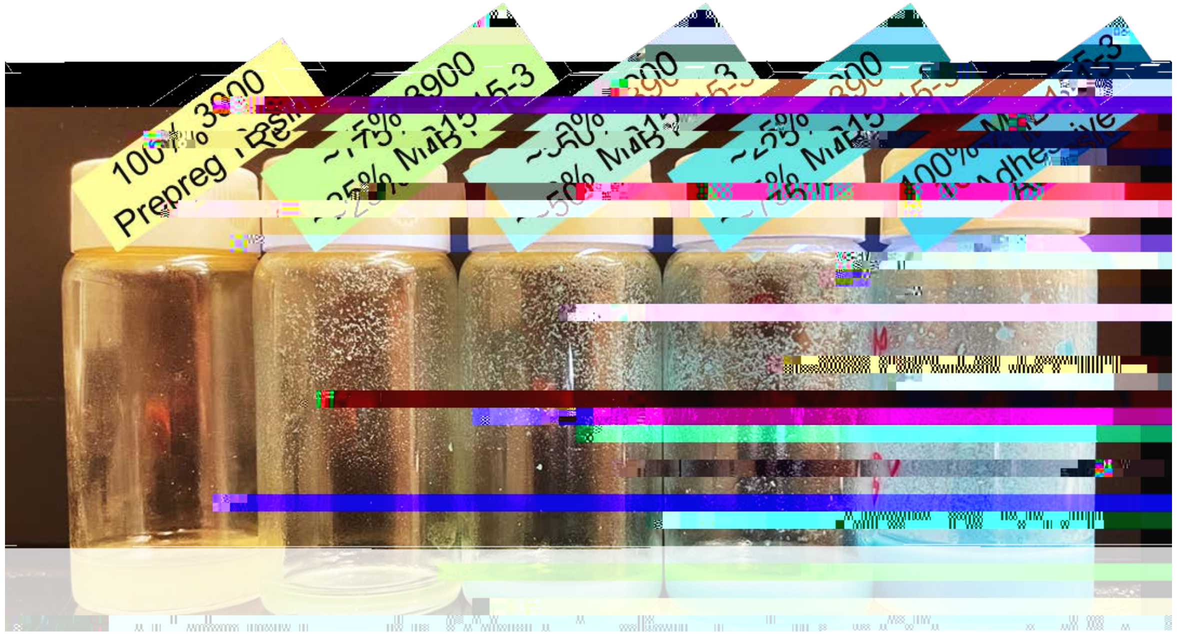
Model #	Fabrication Method	Adherend Resin	Adhesive Resin
1	Acetone Extraction	Toray T800S/3900-2 Prepreg	Solvay Metlbond® 1515-3 modified epoxy supported
2	“Neat” Resin, FlackTek SpeedMixer®	Toray 3900-2 Same Qualified Resin Transfer Molding (SQTRM)	AF 555 unsupported film



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 DCB Sample[F4]	Secondary Bond	Toray T800S/3900 resin	Diatex 1500EV6 woven polyester peel ply	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
2hrs @ 330 qF DCB Sample[F5]	Cobond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
1hr @ 400 qF DCB Sample[F5]	Cobond	Toray T800S/3900 resin	Precision Fabric Group 60001 polyester peel ply	Solvay Metlbond® 1515-3 modified epoxy supported
30days @ 3300 qF DCB Sample[F5]	Cobond	Toray T800S/3900 resin	Precision Fabric Group 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	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
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-ine variation re W n BT 0 scn /TT0 1 Tf 1

Nanomechanical and Nanochemical Anaylsis

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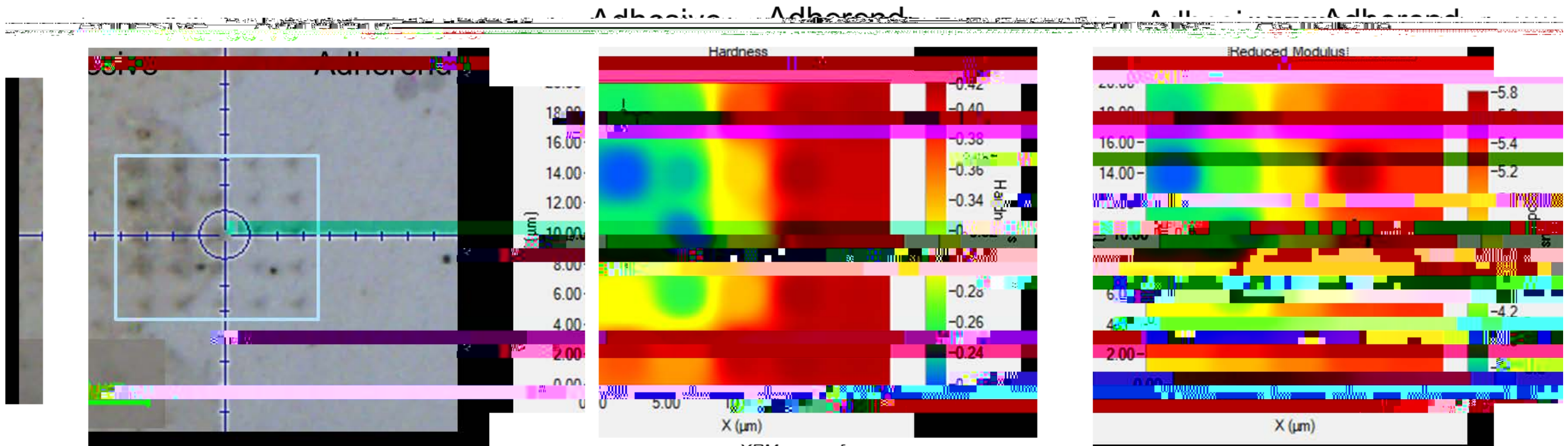
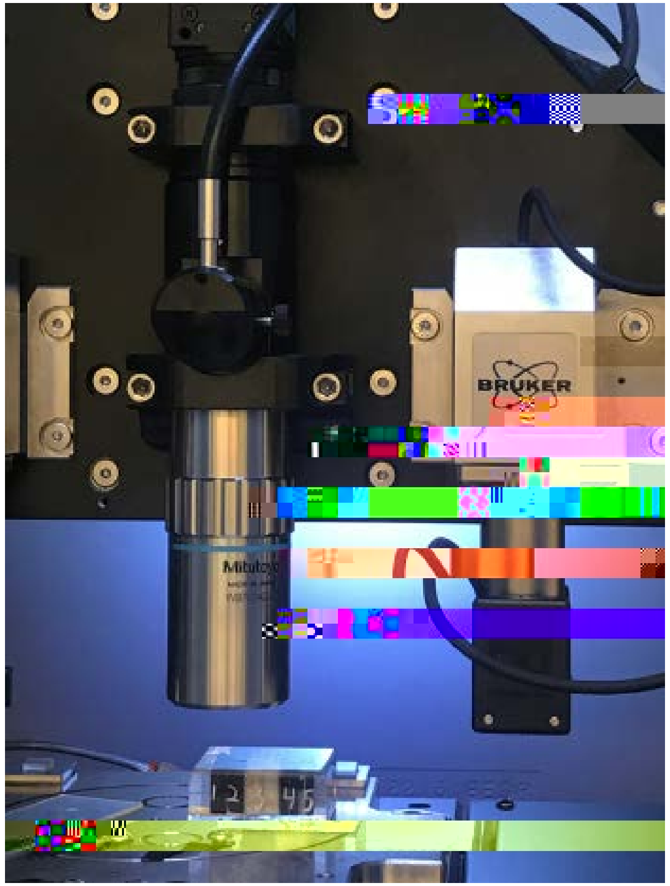
Nanoindentation Methodology

- Hysitron TriboIndenter 980 with Berkovich diamond indenter tip
- Indent surface from tens of nanometers to several micrometers deep
- Extreme Property Mapping (XPM^{TM})
  - 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

- Nanodynamic mechanical analysis on a submicron scale
  - ÆOscillating force applied to nanoindenter tip
  - Æsinusoidal stress is applied
  - Æstrain of the material is measured
  - ÆMeasures viscoelastic properties of the material

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

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 -3 (h scn (x)Qn)]TJ   0.103 Tw-99.0 -0.96 Td   [id iial c
  - nti-1 (f)-3 bycacteri-1 scti oriosycii-3 (h s)]TJ   0.003 Tw 0 -0.9 am(er)-3 (at)-.r]

Preliminary Results

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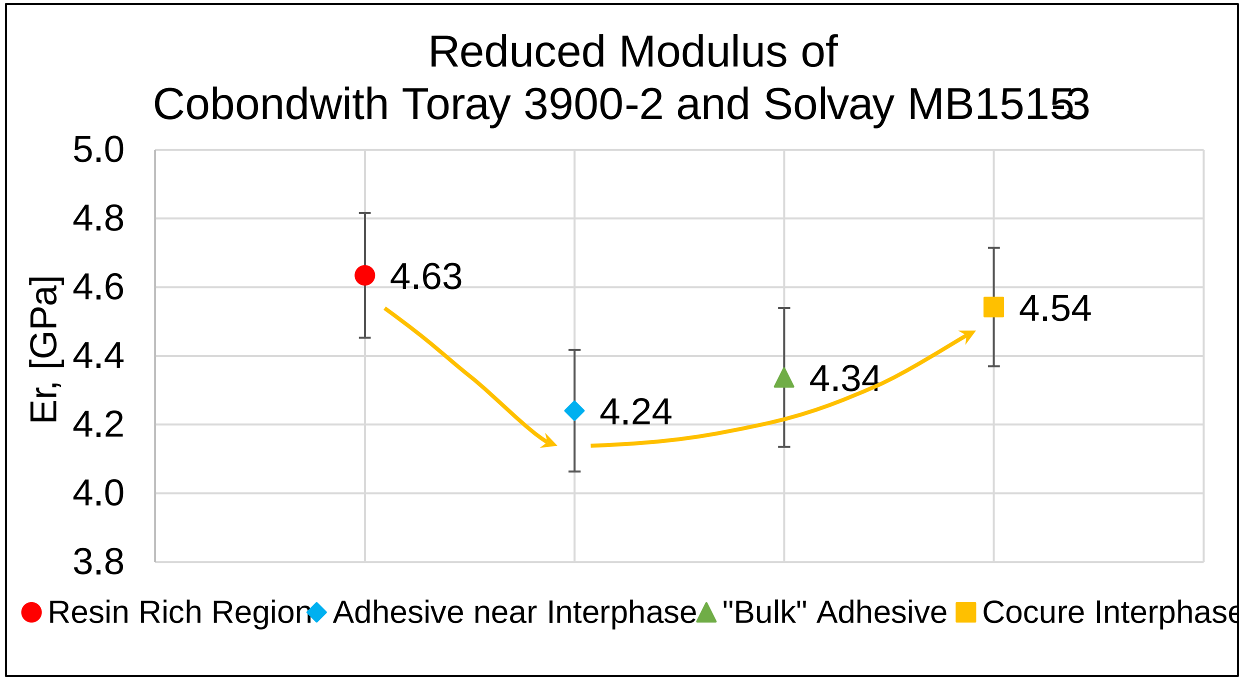
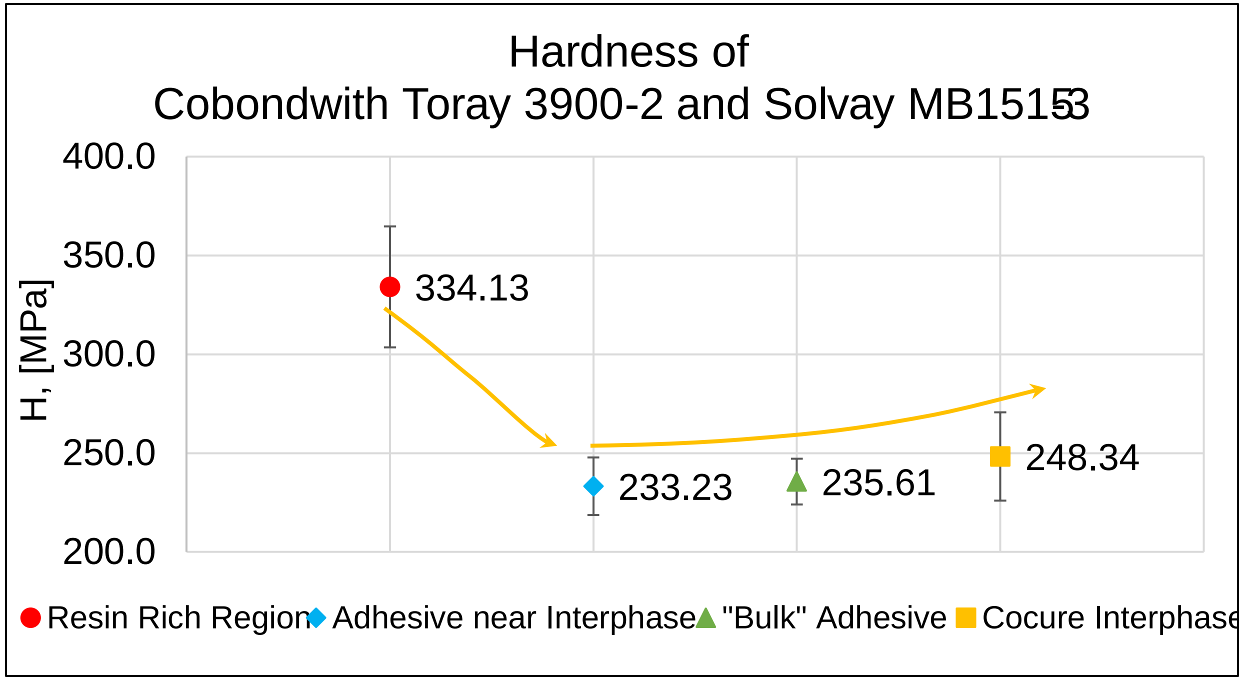
Bondline Property Mapping

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



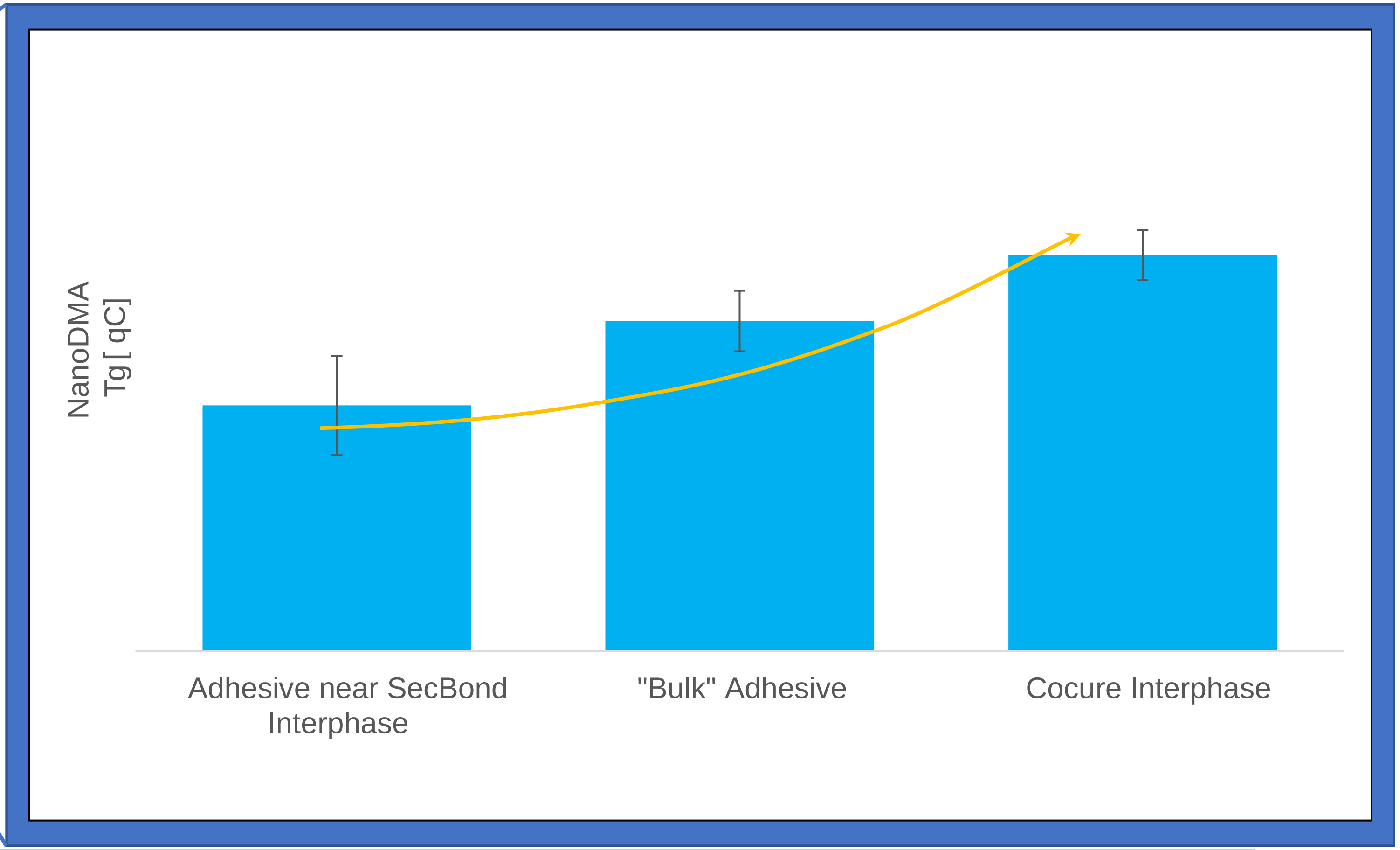


Cobonded systems show distinctive mechanical property trend within bondline:

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

NanoDMA

Cobond Toray 3900-2 and Solvay MB1515-3



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

Preliminary Conclusions

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

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

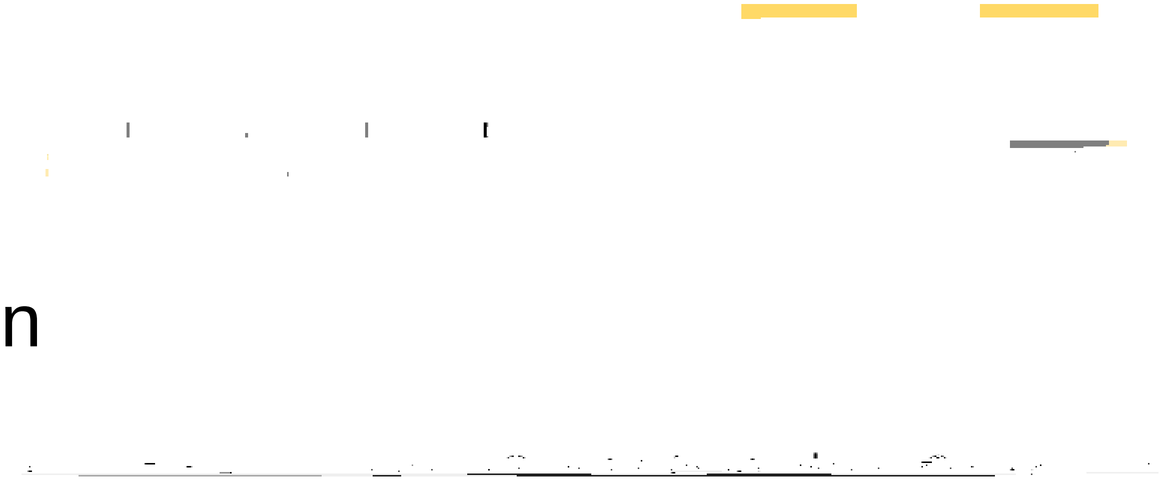
- Nanomechanical properties change with high temperature exposures
  - Increase in modulus and hardness suggest “post cure” effect after high temp exposure <u>below</u> T_g
  - Decrease in modulus potentially indicating change of materials after high temp exposure <u>above</u> T_g
  - NanoDMA may be 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 Æ understand the effect of heat exposures on bondline properties

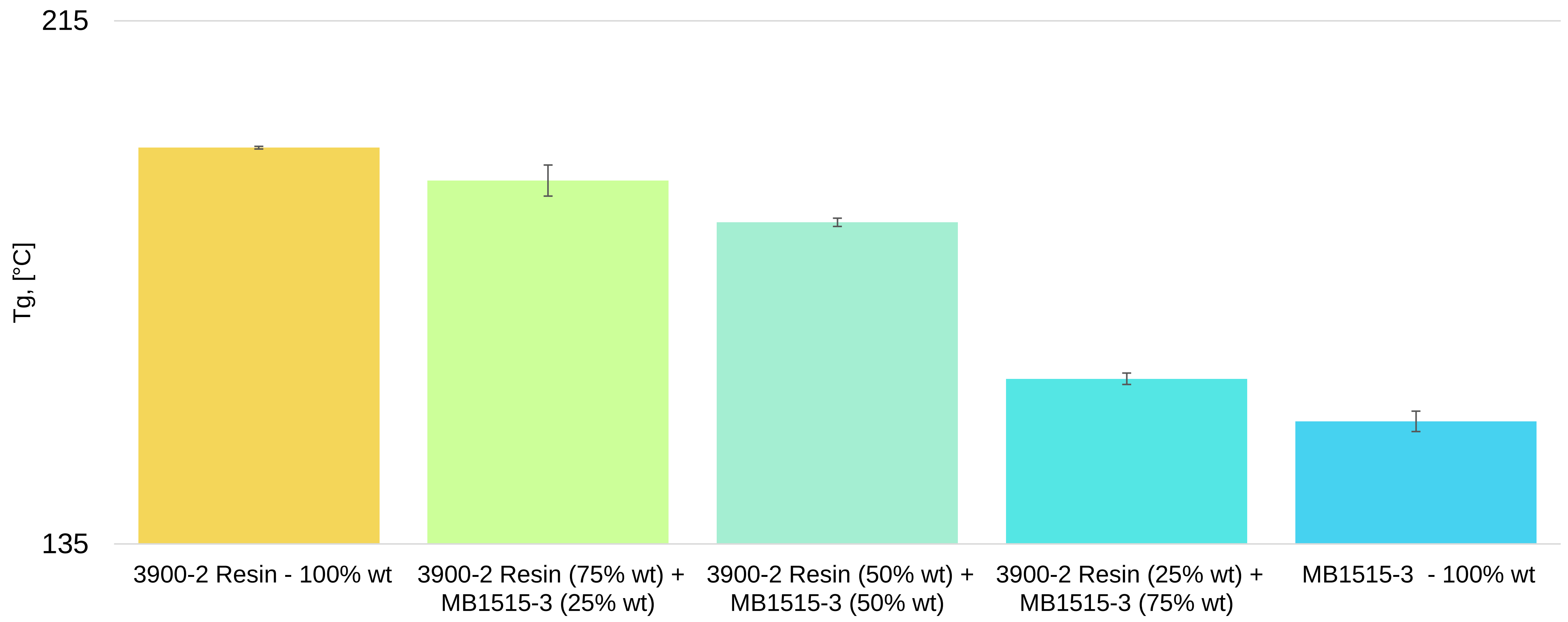
On-going Work

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


215
135
Tg, [°C]
3900-2 Resin - 100% wt
3900-2 Resin (75% wt) + MB1515-3 (25% wt)
3900-2 Resin (50% wt) + MB1515-3 (50% wt)
3900-2 Resin (25% wt) + MB1515-3 (75% wt)
MB1515-3 - 100% wt

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