Composite Characterization via Analytical Laboratory Techniques

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Taking on your toughest technical problems

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Overview

- General Introduction
- Common Fiber/Resin Systems
- Curing Process
- Sample Preparation Considerations
- Analytical Testing Methods
  - Thermogravimetric Analysis (TGA)
  - Dynamic Mechanical Analysis (DMA)
  - Differential Scanning Calorimetry (DSC)
  - Creep Testing
  - Void Content Testing
- Questionable Testing Methods
- Review
- Questions

Introduction

- For more than 20 years, the pipeline industry has been making repairs using composite materials.
- A significant body of research exists addressing a variety of repair types.
- We continue to learn more, which improves our confidence in composite performance.
- Validating long-term performance is a critical effort to ongoing and future efforts.
- The ASME PCC-2 Standard has brought significant uniformity to this industry.

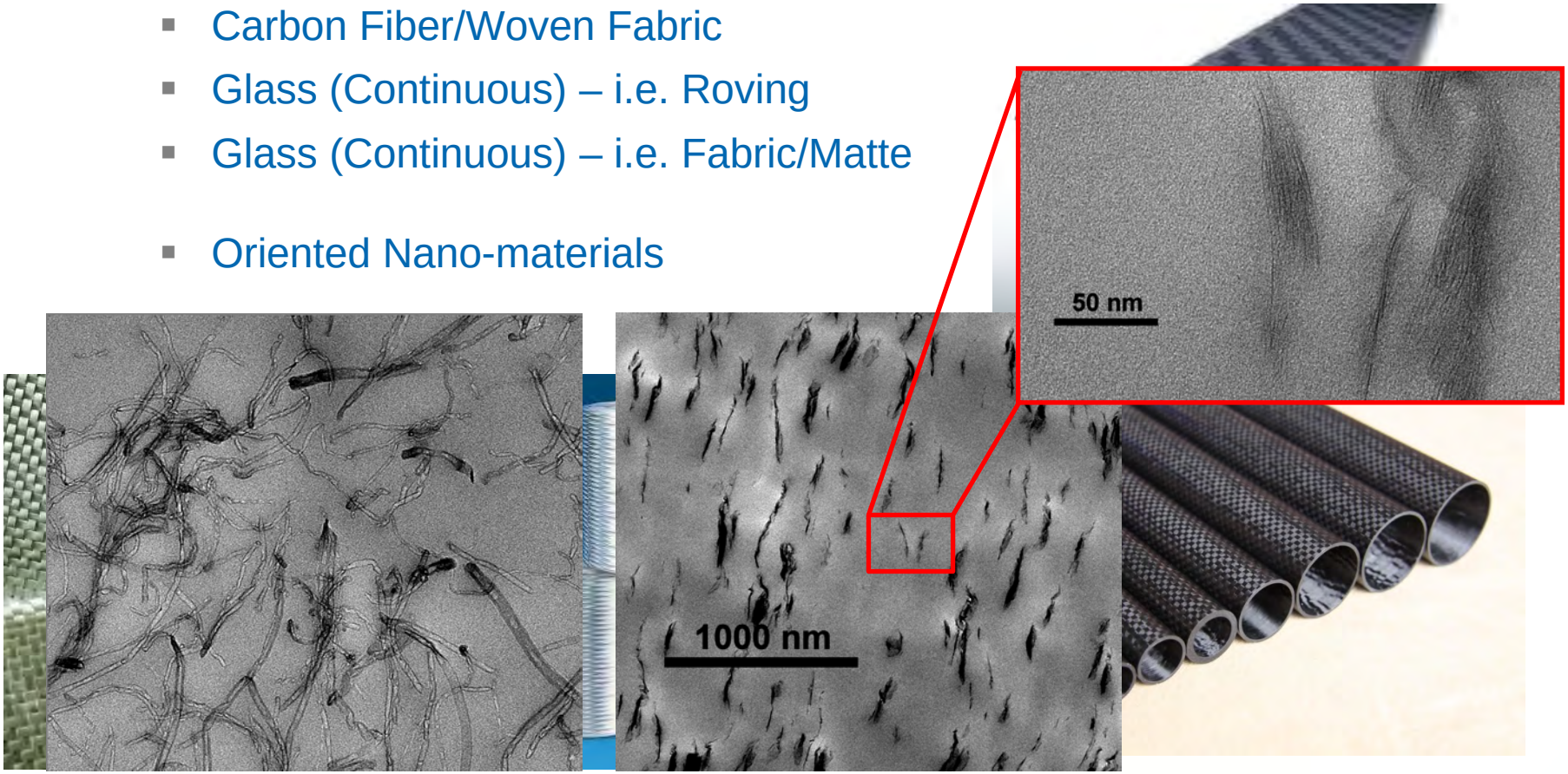
- per Chris Alexander (SES) and Derrick Rogers (SES)

Introduction

- Rehabilitation of existing pipe systems is a cost-effective endeavor as compared to replacement of such systems.
  - Limited system down-time.
  - Allows for localized repair.
  - Potential for reduced inspection requirements.
- Within the composite repair industry, much discussion has been centered on the effectiveness of a given repair.
- Difficulty exists in the determination of the *existing assets anticipated lifetime* – and – the effectiveness of the corresponding repair and its *anticipated lifetime*.
  - What are the mechanical properties of the system?
  - How can you determine whether effective patching occurred?
- Thus, development of analytical techniques that can be used to probe and measure key performance metrics that align with the condition of the installed asset is **mission critical.**

Material Considerations – Fiber

- Advanced and High Performance Composites rely upon fiber technology for the *majority* of their mechanical performance in a given application.
  - Carbon Fiber/Woven Fabric
  - Glass (Continuous) – i.e. Roving
  - Glass (Continuous) – i.e. Fabric/Matte
  - Oriented Nano-materials



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Material Considerations – Resin

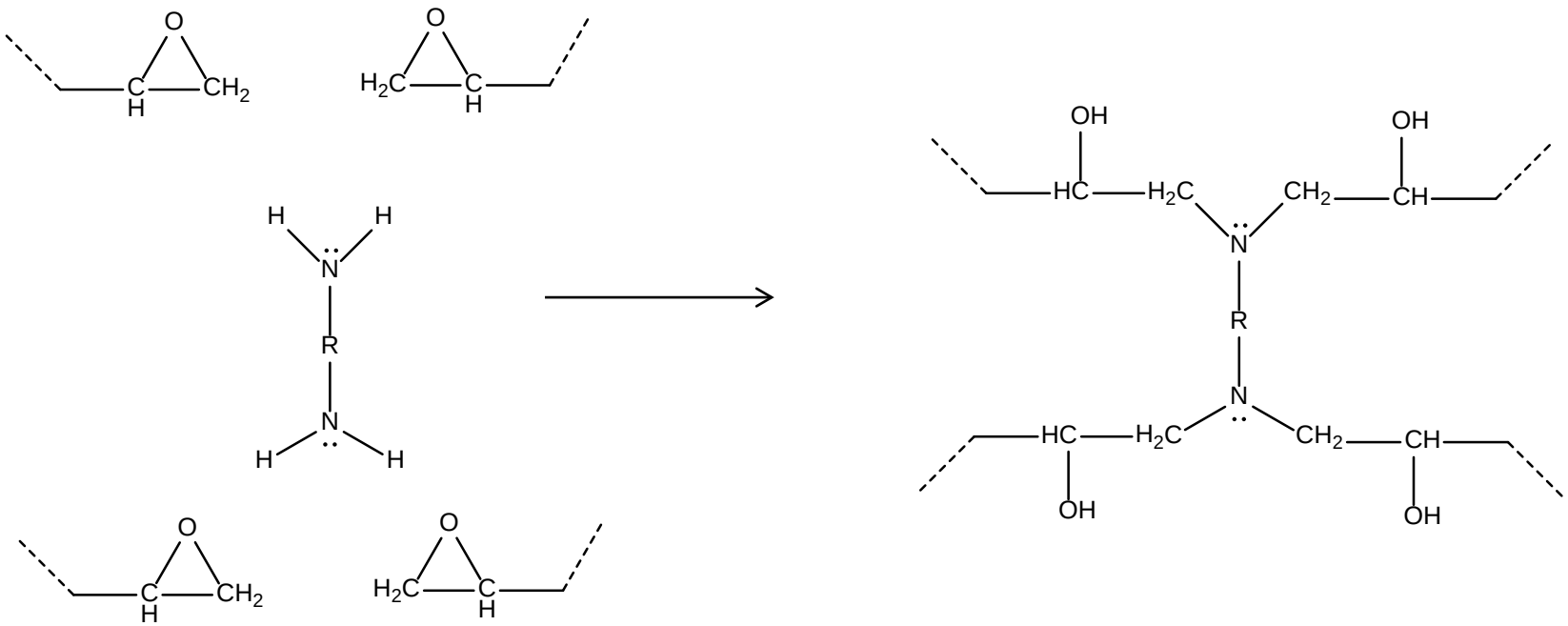
- Resin technology is mainly used as a binder – but – ultimately serves a critical function in imparting chemical and mechanical resistance (load transfer between fibers/shear), as well as developing a bond with the substrate.
- The following resin systems are rather common in composite repair applications:
  - Epoxy matrix based Composites
  - Unsaturated Polyester/Vinyl Ester based Composites
  - Polyurethane based Composites

  - These classes of resins are thermosetting in nature – that is – they require UV Light, heat/catalyst or curing agents to form their **crosslinked** network.
  - Once cross-linked, these resins are incapable of re-melting.
  - Quality control of such systems compared to conventional plastics is difficult as the curing reaction ***can*** be difficult to control.

Curing Process

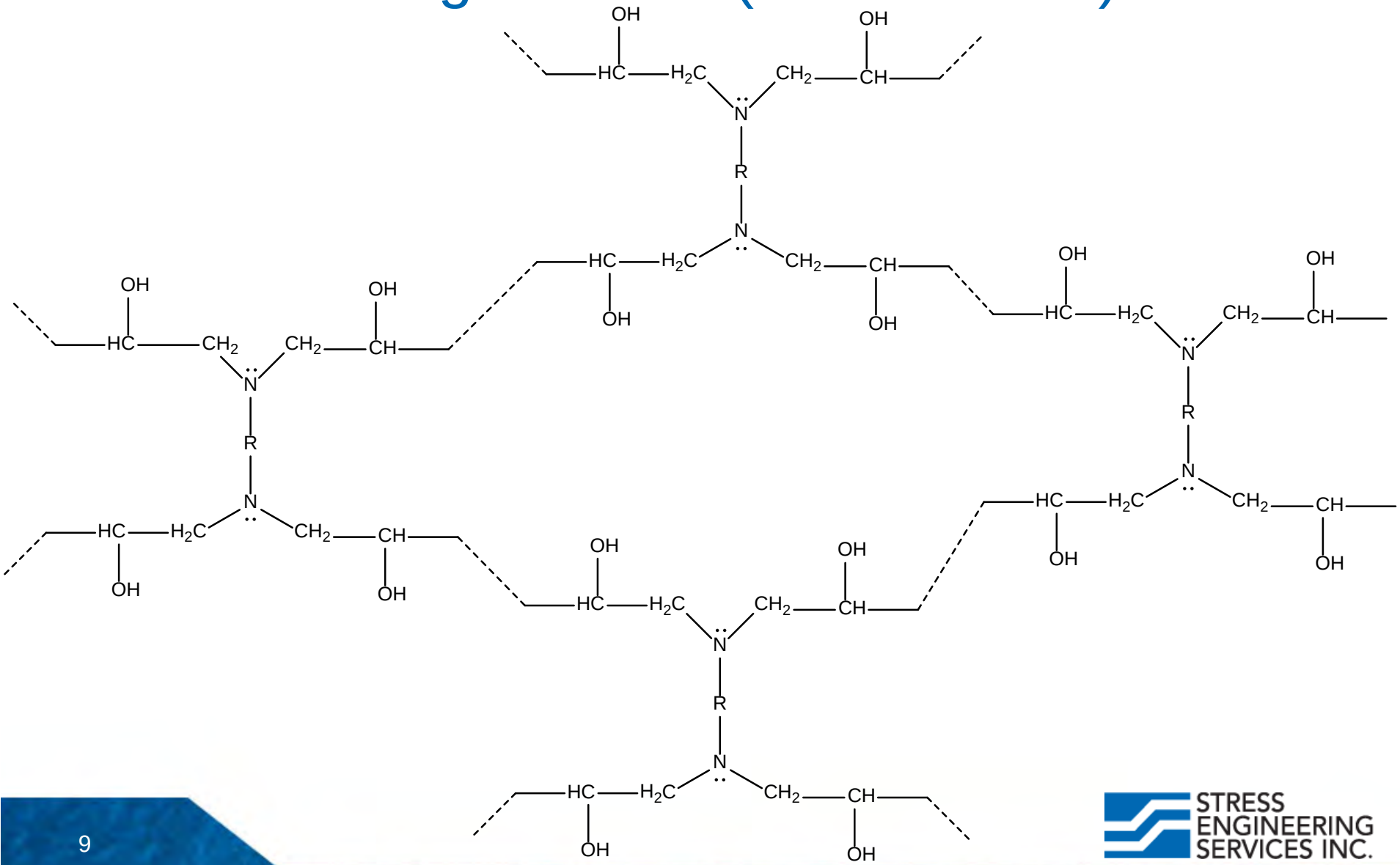
- Resin/fiber mixtures can be in a wide variety of forms.
- Cure in place pipe systems (CIPP) are evolving as the applications – and – working environments become more challenging and aggressive.
- Patches can be applied in the form of paste, pre-preg's, liquids, impregnated fabric, hand-layup, and other methods.
- In most composite pipe repair applications, a crosslinking reaction occurs to harden/cure the resin to provide the *maximum* properties.

Curing Process



- **Start with Epoxide(s) and a Catalyst/Curing Agent**
- **Bi-Functional Amine in this instance**
- **Ring opening of the epoxide occurs (alcohol)**
- **…Reaction Advances!**

Curing Process (Continues…)



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Sample Fabrication Considerations

- General considerations can be broken down into three distinct categories:
  - Thermal
  - Mechanical
  - Sample Formation

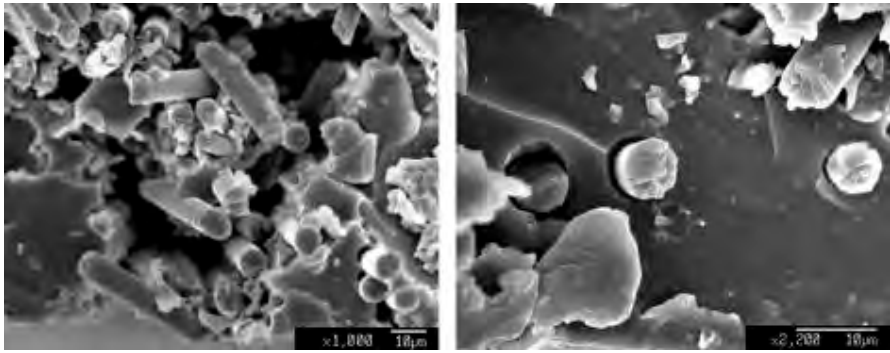
- Furthermore, analytical techniques generally measure small coupons. Analysis of such coupons must be done with extreme caution to ensure acceptable repeatability.
  - Photo documentation of all samples is recommended.
  - Multiple samples are recommended in order to acquire a statistical population.
  - Abnormalities have been observed during testing from time to time, making multiple samples important.
  - Samples should have similar quality as repairs (misalignment due to ply distortion).

Sample Considerations: Thermal

- The curing profile in CIPP applications can be difficult to measure compared to standardized laboratory plaques.
- Instrumented thermocouples can provide remote temperature information during the cure process allowing for accurate curing profiling.
- Post-curing, if conducted, must match the sample coupon fabricated for testing.
- If mechanically cutting samples, heat generation can alter the cure profile and provide misleading analytical test results.

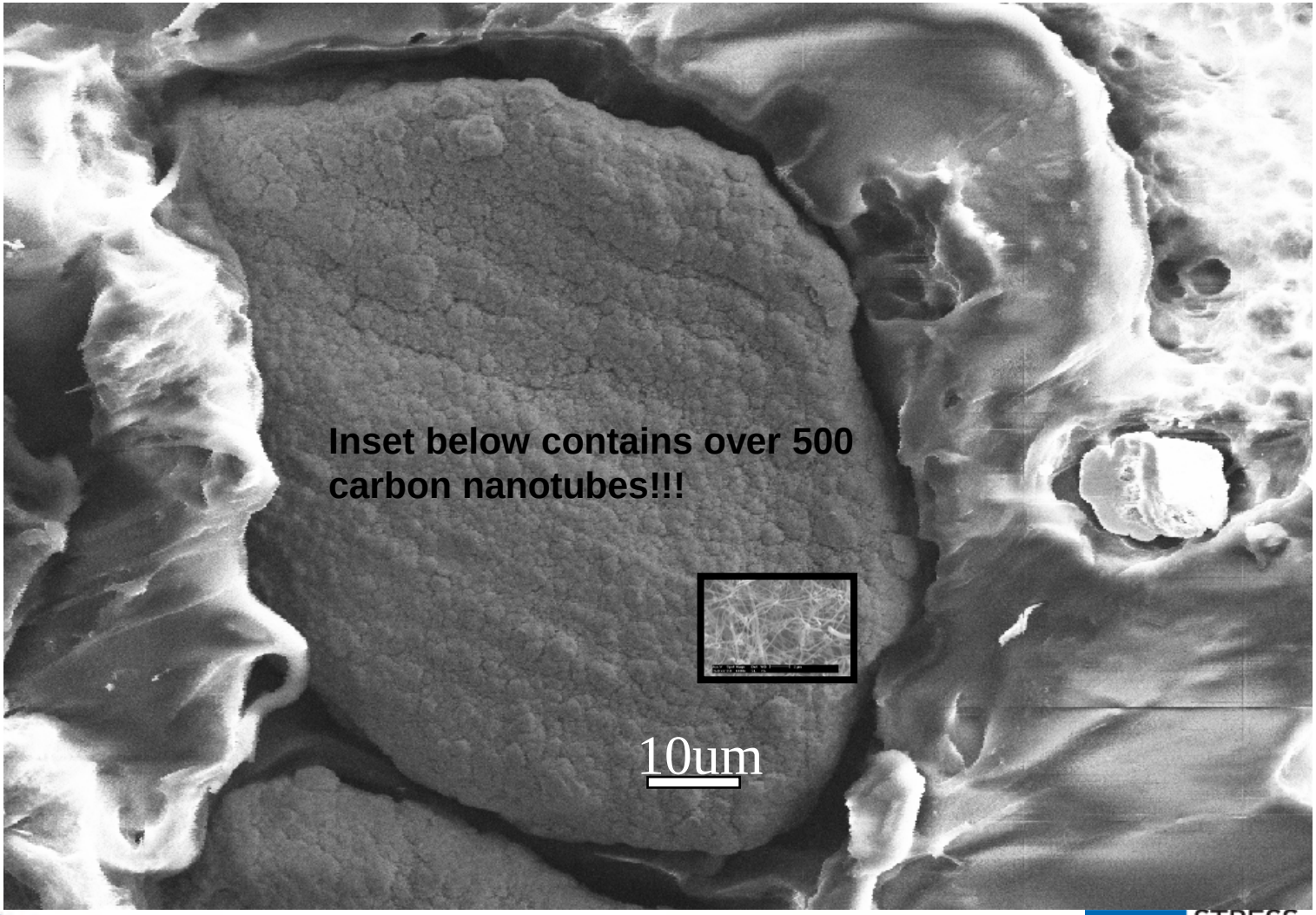
Sample Considerations: Mechanical

- CIPP systems are advantageous because they allow for field repair.
- Thus, creation of standard laboratory based coupons for analytical testing can become difficult, if not impossible.



- When producing test coupons:
  - Matching ply orientation is critical.
  - If machining of coupons is required, fiber structure will be disturbed and may not be representative of the field application.
  - Simulation of loading in the application is critical when evaluating mechanical performance.

Sample Homogeneity



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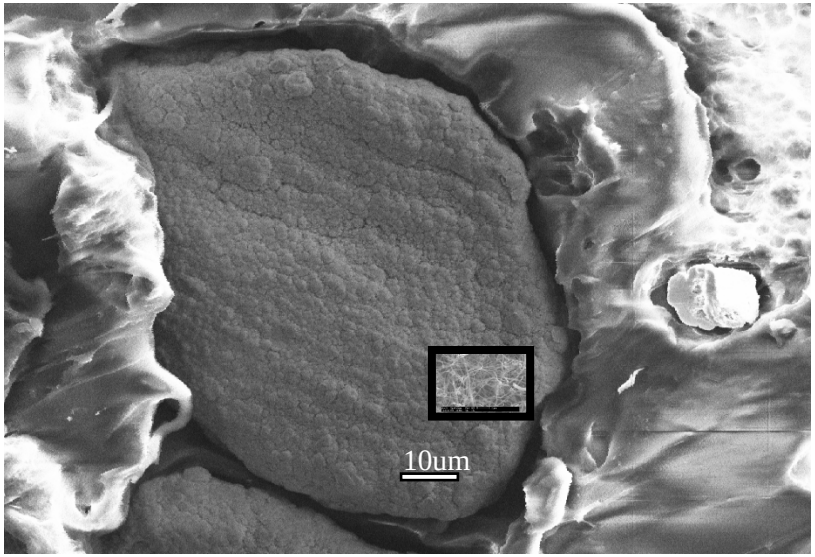
Sample Homogeneity



- Many analytical techniques utilize small (micro-gram) size samples. The above image indicates why – depending on the composite being investigated – multiple sample regions are necessary!
- Standard procedures are important – and – should be developed for all analytical techniques.
- Sample geometry and extraction is just as important, and should be described in full disclosure for ANY analytical testing method.

Analytical Test Methods

- Applicable General Test Methods:
  - Thermogravimetric Analysis (TGA) (or muffle furnace testing)
  - Dynamic Mechanical Analysis (DMA)
  - Differential Scanning Calorimetry (DSC)
  - Creep Testing
  - Void Content Testing (brief)

- Questionable Test Methods:
  - Hardness (Shore D)
  - Fourier Transform Infrared Spectroscopy (FTIR)

TGA/Muffle Furnace Testing

- Objective
  - Determine the ratio of organic resin and fiber content in a composite structure.

- Why it matters
  - The reinforcing agent (fiberglass, carbon fiber, etc.) provides the vast majority of mechanical performance in the composite.
  - Inconsistent ratios provides inconsistent mechanical performance.
  - Many CIPP systems have a relatively low volume fraction of resin that can lead to wet-out issues with the resin. These dry spots can lead to multiple failure mechanisms.

- How it's tested
  - ASTM D2584 – inorganic fillers (Muffle Furnace)
  - ASTM D6370*/E1131* – organic fibers (TGA)

***Limitations exist**

Muffle Furnace: Inorganic Filler

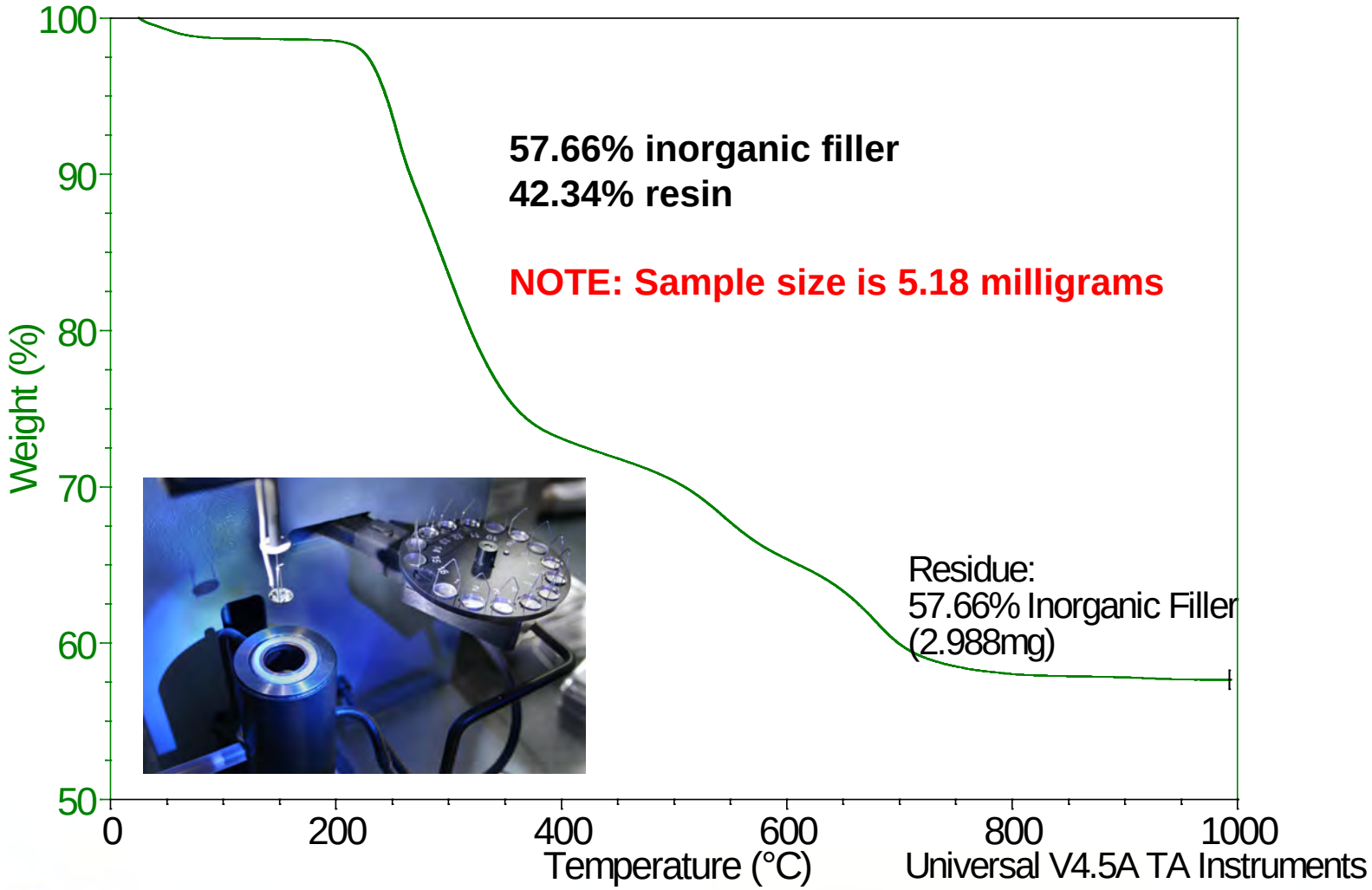
ASTM D2584

- **Heat the crucible to 565C until all carbonaceous material has been degraded**
- **Calculate resin content:**

$$\textbf{Resin Weight} = 100 - [[(W_1 - W_2)/W_1] \times 100]$$

Where: **W_1= Weight of Original Specimen**
W_2= Weight of Filler Residue

Standard TGA: Inorganic Filler



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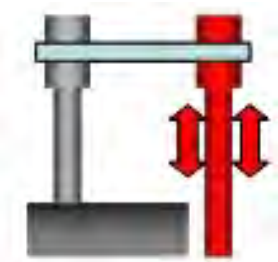
DMA Testing

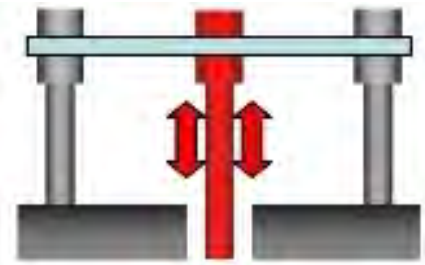
- Objective
  - Determine the mechanical response as a function of temperature and/or frequency.

- Why it matters
  - Long-term predictive analysis of mechanical behavior.
  - Can be used to determine mechanical transition and the glass transition.
  - Can be used to assess the degree of cure in a composite material.

Single Cantilever

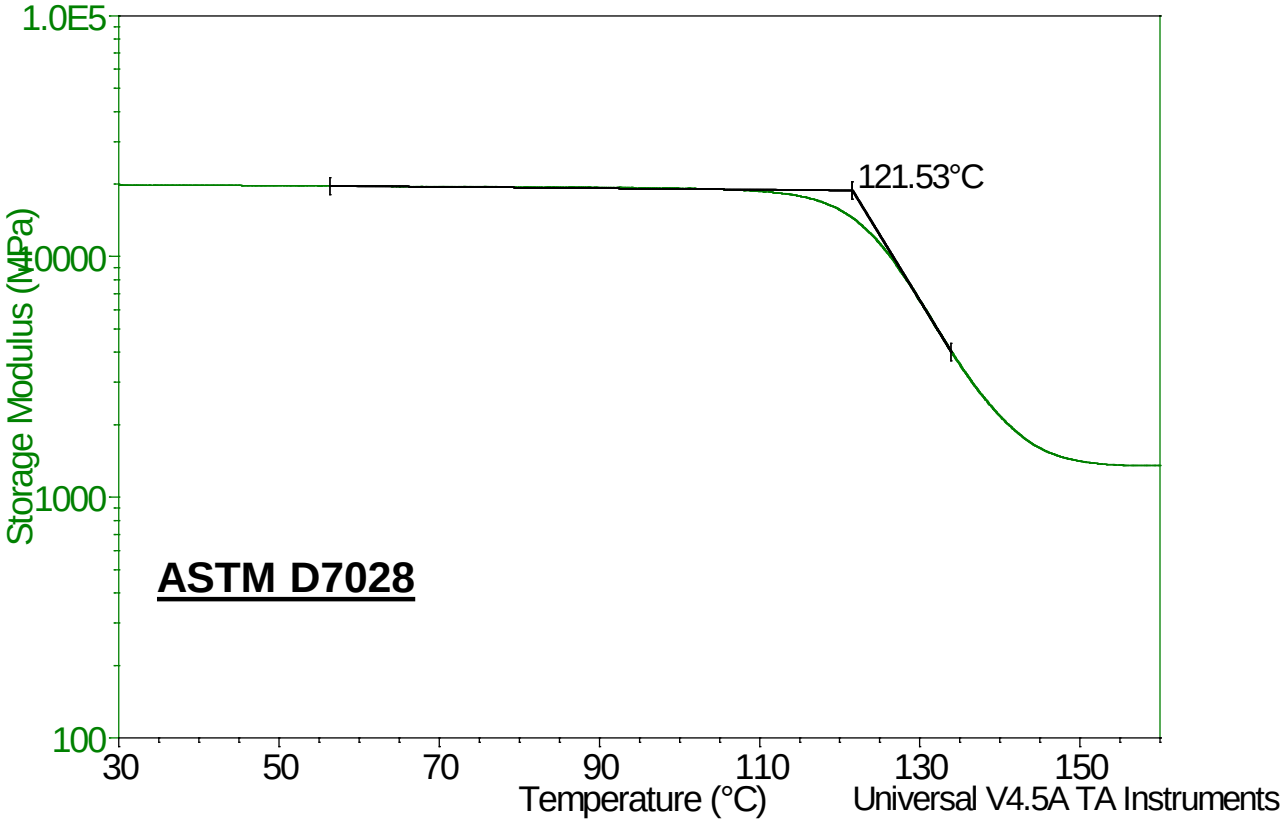


Dual Cantilever



- How it's tested
  - ASTM D7028
  - ASTM E1640

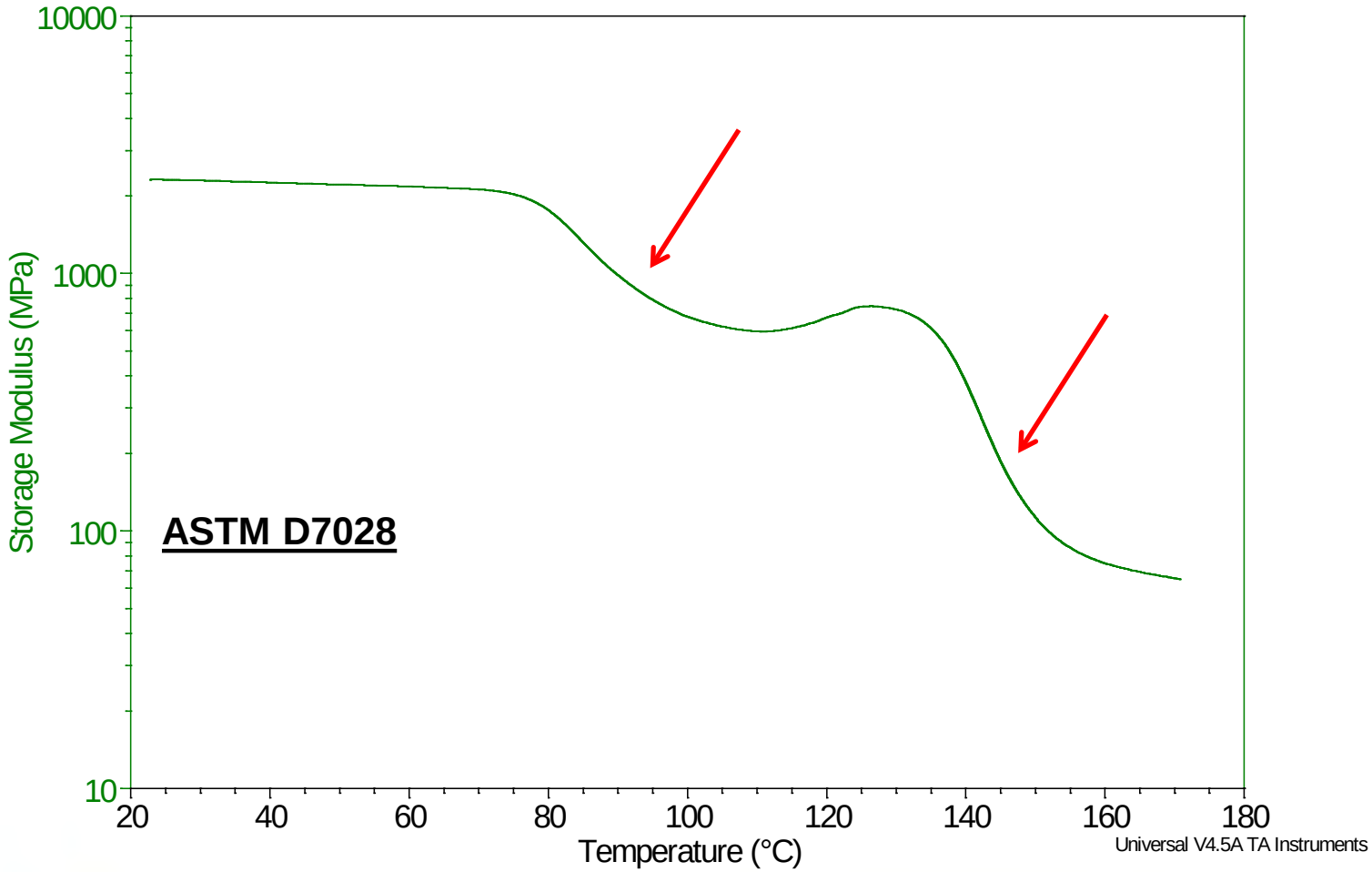
DMA: Glass Transition Temperature (T_g)



- **Heat the sample from Room Temperature to 200°C**
- **Constant Frequency/Strain**
- **Measure Storage Modulus**
- **T_g is the inflection observed in the curve**

Epoxy Composite
Catalyst Cured (MEKP, DMA, Co Nap)
***No Post-cure Cycle**

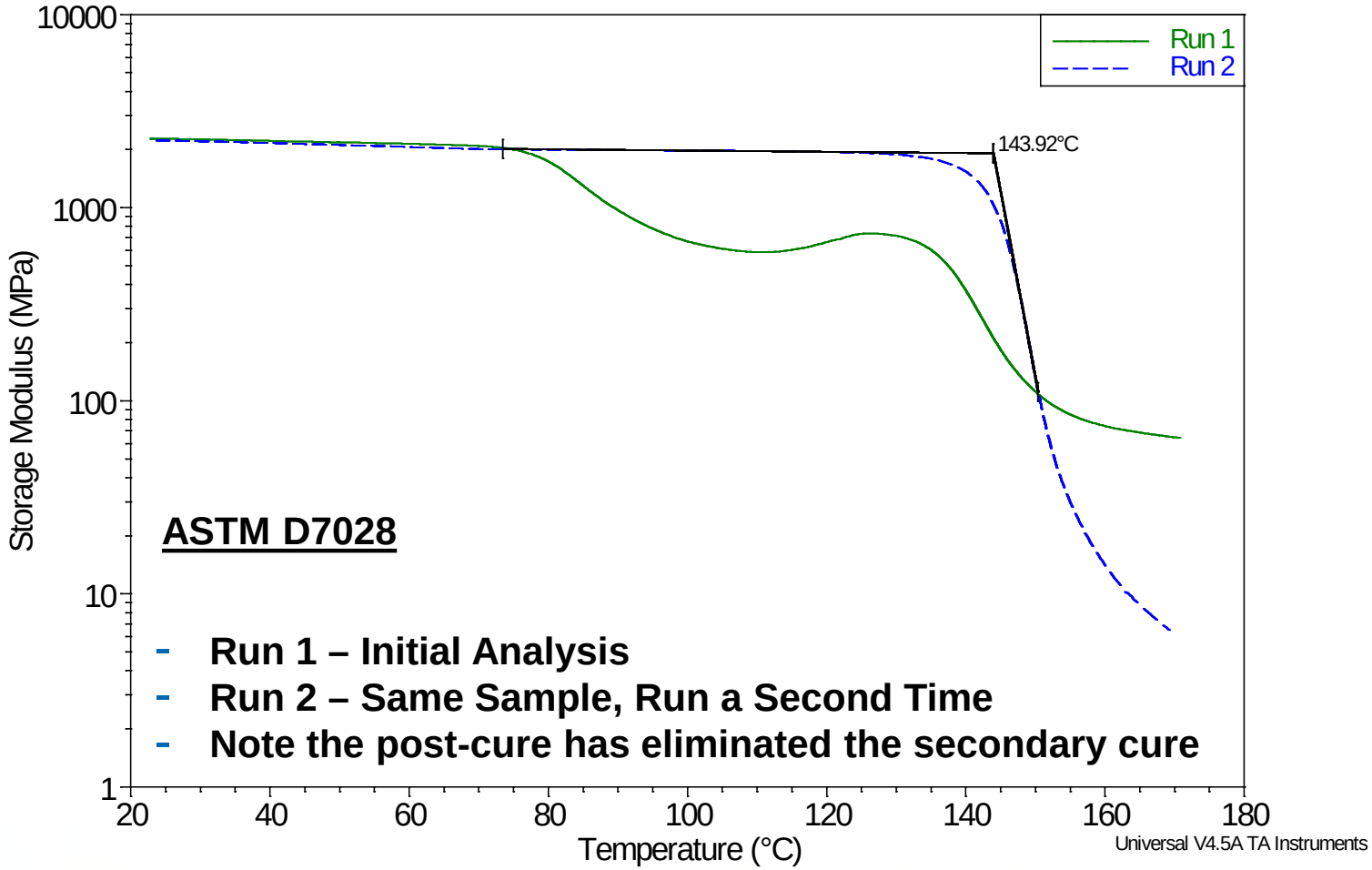
DMA: Curing Analysis



- **Note the initial decline in storage modulus**
- **Note the secondary decline in storage modulus**

Epoxy Composite
Catalyst Cured (MEKP, DMA, Co Nap)
***No Post-cure Cycle**

DMA: Curing Analysis

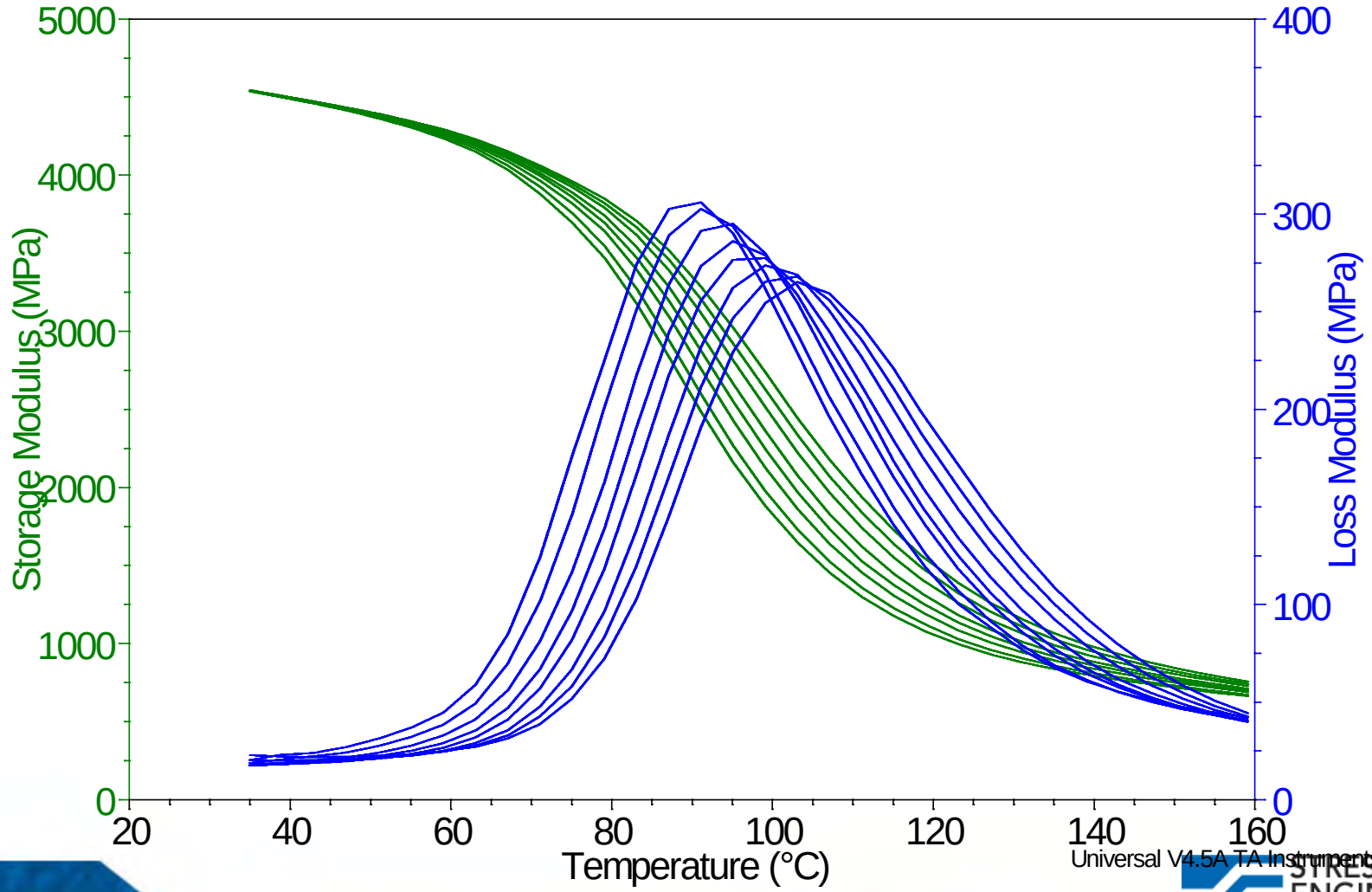


ASTM D7028

- **Run 1 – Initial Analysis**
- **Run 2 – Same Sample, Run a Second Time**
- **Note the post-cure has eliminated the secondary cure**

- **To acquire maximum properties, post-curing is often required.**
- **Analysis of test coupons is critical.**

DMA Advanced Features (TTS)



Universal V4.5A TA Instruments

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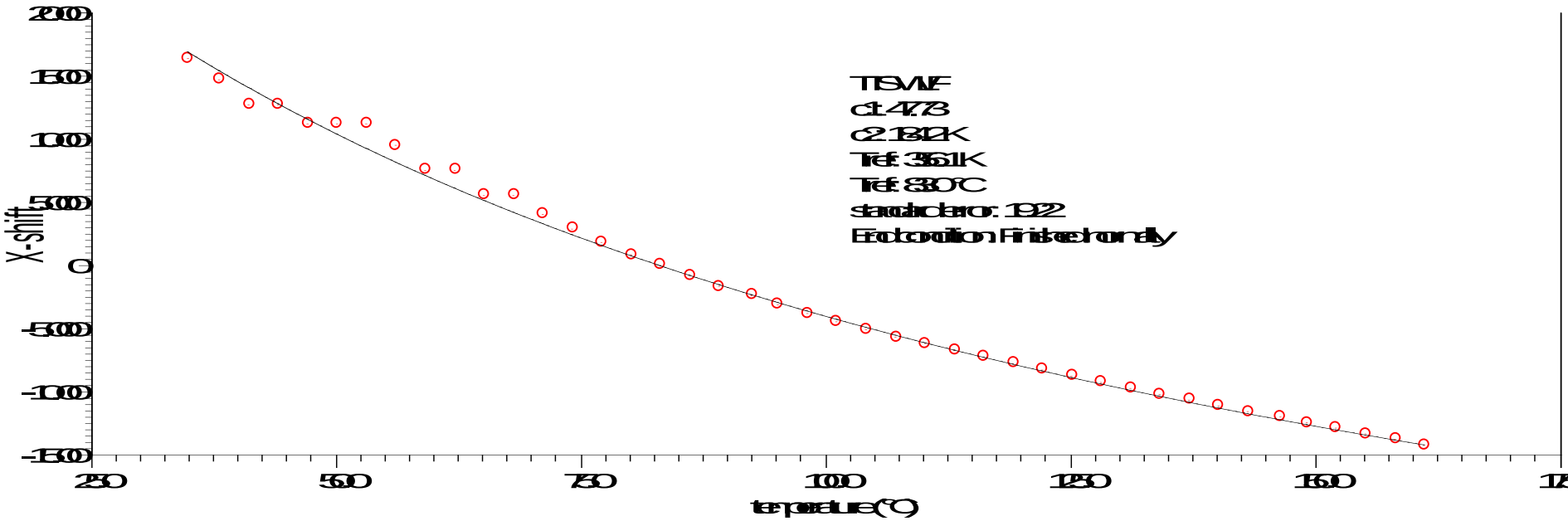
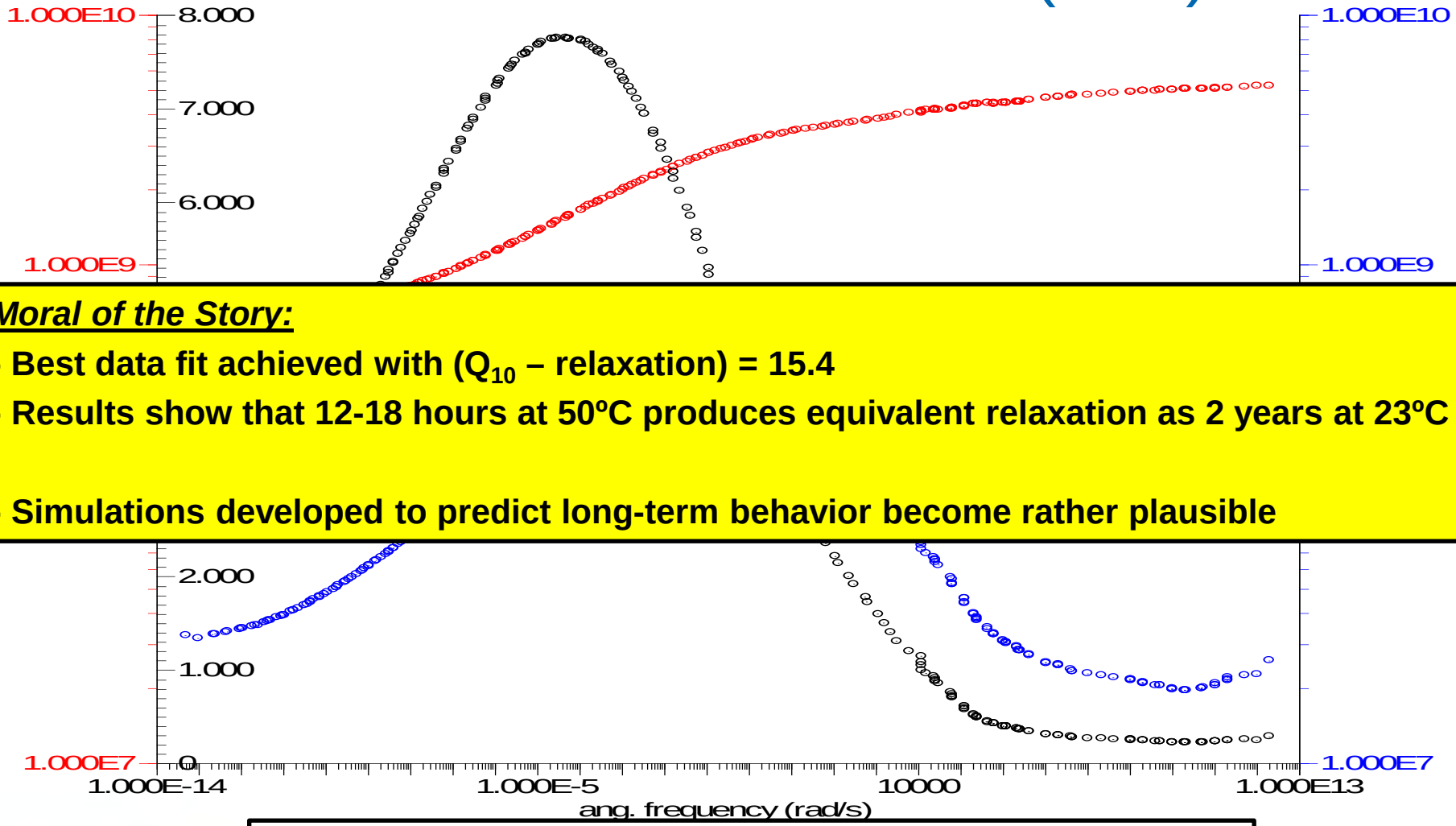
DMA Advanced Features (TTS)



1) **Create Reference Curve based on T_g (~ 80°C for this composite)**
2) **Apply WLF Fit**
3) **Shift Curves/Generate Master Curve**

DMA Advanced Features (TTS)



Moral of the Story:

- Best data fit achieved with (Q_{10} – relaxation) = 15.4

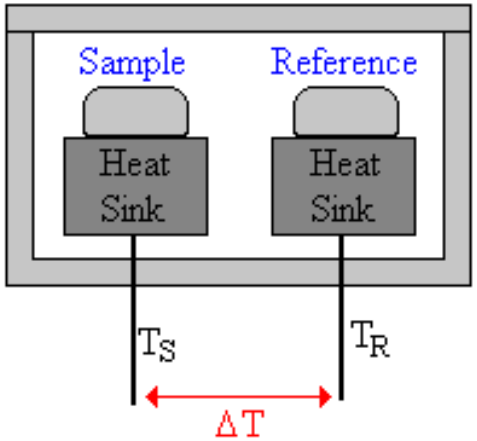
- Results show that 12-18 hours at 50ºC produces equivalent relaxation as 2 years at 23ºC

- Simulations developed to predict long-term behavior become rather plausible

1) Create Reference Curve based on T_g (~ 80°C for this composite)
2) Apply WLF Fit
3) **Shift Curves/Generate Master Curve**

DSC Testing

- Objective
  - Determine the glass transition of a composite.
- Why it matters
  - Similar to DMA testing, determination of the glass transition temperature is critical in understanding whether full curing has occurred in the composite.
- How it's tested
  - ASTM D7028
  - ASTM E1640



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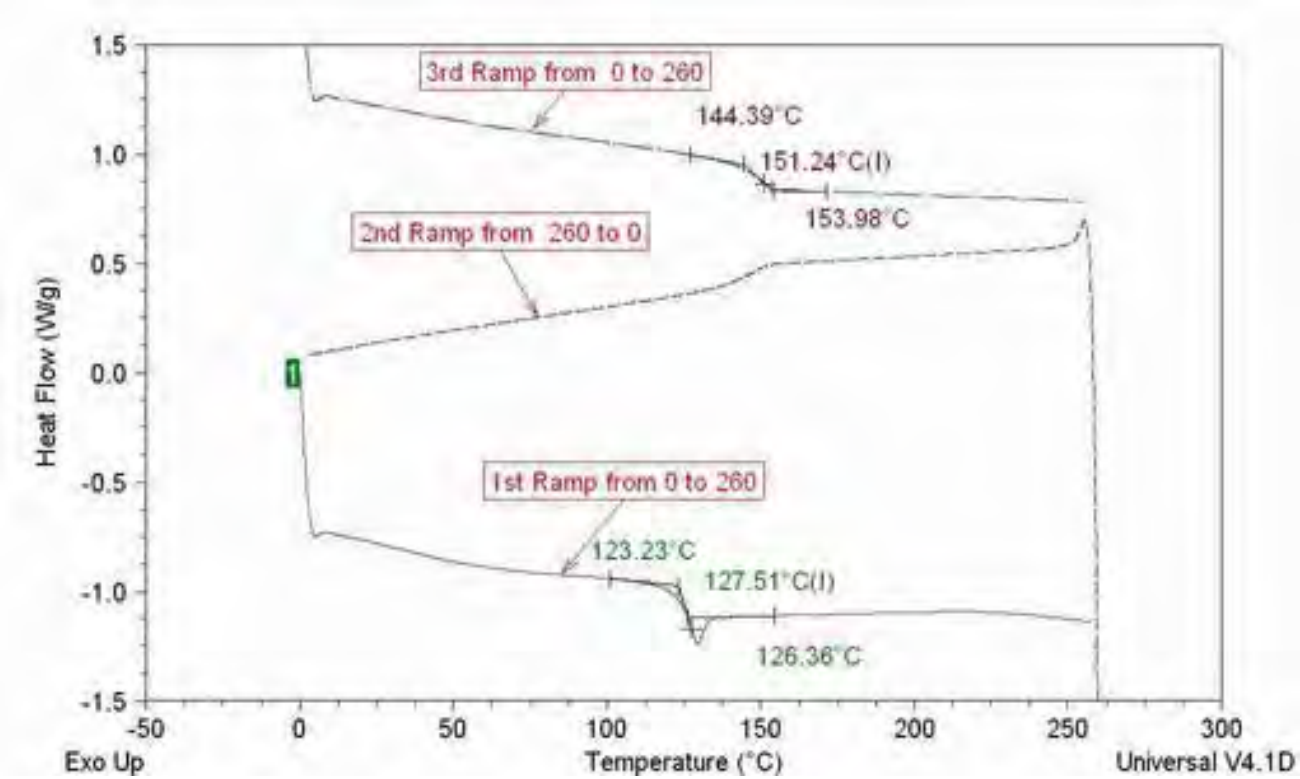
DSC: Composite Cure



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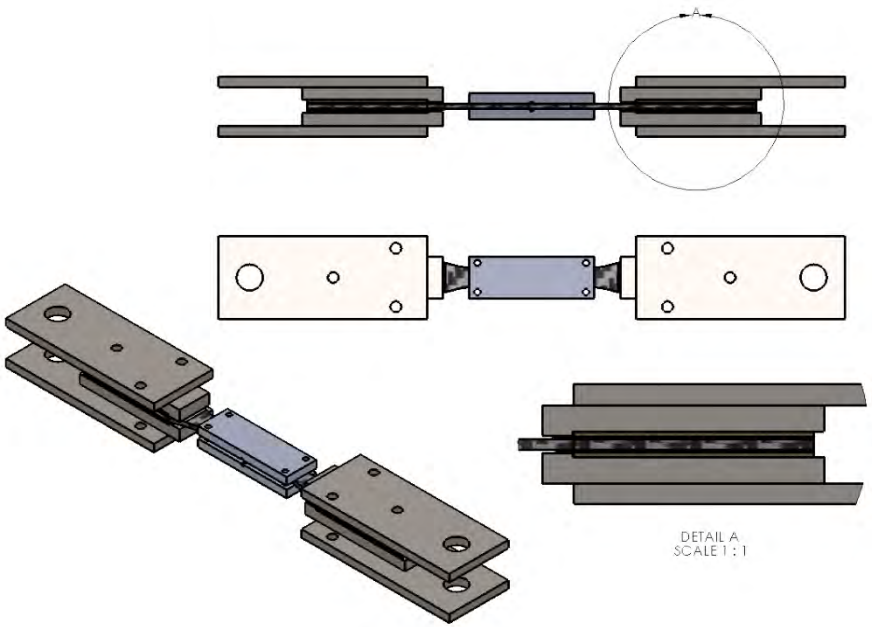
Creep Testing

- <u>Objective</u>
  - Determine the long term behavior of composite repair systems under load and at temperature.
- <u>Why it matters</u>
  - Long-term predictive analysis of mechanical behavior.
  - Can be used to guide design stress selection for long life.
- <u>How it's tested</u>
  - ASTM D2992



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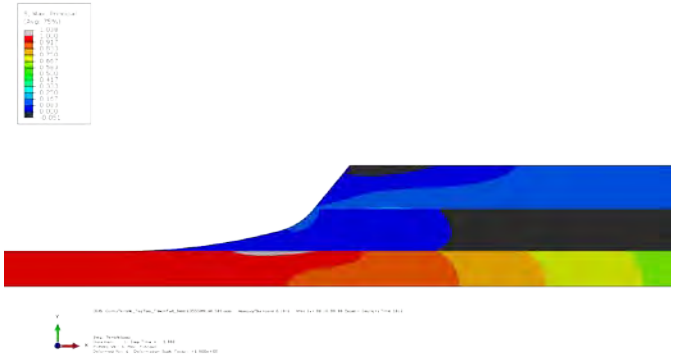
Creep Testing: Sample Preparation

- Sample preparation initially based on DOT/FAA/AR-02/106 *"Tabbing Design Guide for Composite Test Specimens"*

- New tabbing configuration was developed to meet demands of higher strength carbon fiber systems at high temperatures

- Key Points:
  - Sample cut to narrowed gauge length with generous radius
  - Sampled ends tabbed with epoxy and fiberglass
  - Epoxy transition is filleted to reduce stress concentration
  - Local heating of sample gauge length keeps tabbed ends cool



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Creep Rupture Testing

- Loaded on lever-arm type creep frame
- Heated to operating temperature by local resistance heating pads clamped to both sides of gauge length.
- Arm levels as sample creeps.
- Loads set based on tensile test results, ranging tests, and trial-and-error approach

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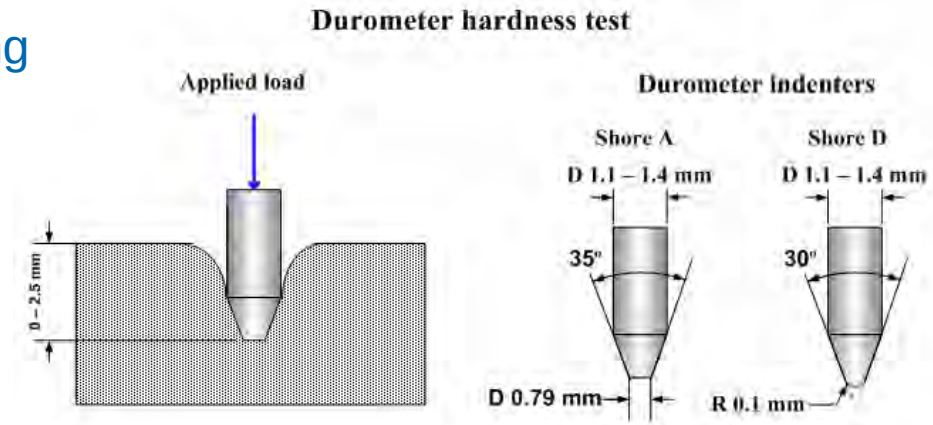
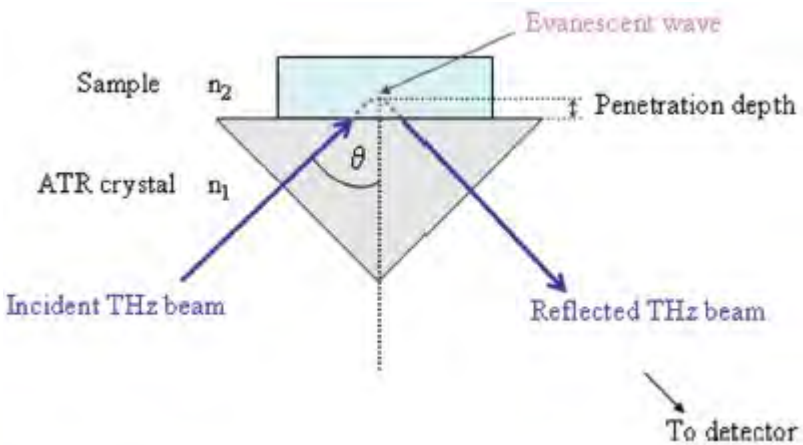
Questionable Methods

- <u>Hardness Testing</u>
  - Excellent technique for examining whether full cure has been achieved.
  - Surface technique ONLY!
  - High modulus fibers can provide false readings!



- <u>Fourier Transform Infrared Spectroscopy (FTIR)</u>
  - Excellent technique for identifying reaction products, degree of cure in adhesives and epoxies!
  - Infrared penetration is LIMITED to 0.5 to 2.0 μm.
  - Surface effects as compared to the bulk will be difficult to reconcile.



Conclusions

- Without appropriate curing of a composite sample, performance in field applications can be compromised.
- Analytical techniques can be effective tools to measure degree of cure.
- Analytical techniques can be effective tools to measure the repair material homogeneity, which is also a significant factor is long-term performance.
- Analytical techniques can be effective tools to measure accelerated aging factors through time-temperature superposition (TTS).
- Analytical techniques are sensitive to sample preparation.
- As CIPP type systems – and – composite pipe repair systems increase in popularity and usage, quality control will continue to increase in importance rendering such analytical techniques as critical test methods.