Composite Characterization via Analytical Laboratory Techniques

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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
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…)

\[
\begin{align*}
\text{CH}_2\text{N} & \quad \text{CH}_2\text{OH} \\
\text{HC} & \quad \text{H}_2\text{C} \\
\text{R} & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_2 \\
\text{H}_2\text{C} & \quad \text{CH} \\
& \quad \text{CH} \\
& \quad \text{HC} \\
& \quad \text{H}_2\text{C} \\
\text{OH} & \quad \text{OH} \\
\text{OH} & \quad \text{OH} \\
\end{align*}
\]
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

Inset below contains over 500 carbon nanotubes!!!
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 provide 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 565°C until all carbonaceous material has been degraded
- Calculate resin content:

\[
\text{Resin Weight} = 100 - \left[ \frac{(W_1 - W_2)}{W_1} \right] \times 100
\]

Where:  
\( W_1 \) = Weight of Original Specimen  
\( W_2 \) = Weight of Filler Residue
Standard TGA: Inorganic Filler

57.66% inorganic filler
42.34% resin

NOTE: Sample size is 5.18 milligrams
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.

• **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

ASTM D7028

Universal V4.5A TA Instruments
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

**ASTM D7028**
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)

Temperature (°C)

Storage Modulus (MPa)

Loss Modulus (MPa)

Universal V4.5A TA Instruments
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
Moral of the Story:
- Best data fit achieved with \((Q_{10} - \text{relaxation}) = 15.4\)
- Results show that 12-18 hours at 50°C produces equivalent relaxation as 2 years at 23°C
- Simulations developed to predict long-term behavior become rather plausible
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
DSC: Composite Cure
Creep Testing

- **Objective**
  - Determine the long term behavior of composite repair systems under load and at temperature.

- **Why it matters**
  - Long-term predictive analysis of mechanical behavior.
  - Can be used to guide design stress selection for long life.

- **How it’s tested**
  - ASTM D2992
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
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
Questionable Methods

• Hardness Testing
  ▪ Excellent technique for examining whether full cure has been achieved.
  ▪ Surface technique ONLY!
  ▪ High modulus fibers can provide false readings!

• Fourier Transform Infrared Spectroscopy (FTIR)
  ▪ 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 in 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.