COMPOSITE TECHNOLOGY DEVELOPMENT, INC.

ENGINEERED MATERIAL SOLUTIONS

# *Optimizing the Cost and Performance of Composite Cylinders for $H_2$ Storage using a Graded Construction*

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**Project ID # ST110**

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# Overview

## Timeline

- Project Start Date:
  - Phase I: Feb 2013
  - Phase II: May 15, 2014
- Project End Date: May 2016
- Percent Complete: 30% (Phase I)

## Barriers

- Type IV Pressure Vessel Cost
- Price and availability of low cost carbon fiber
- Composite properties of lower cost carbon fibers

## Budget

- FY13 DOE Funding: $155K
- Planned FY14 DOE Funding: $208K
- Total Project Value: $ 1.15M

## Partners

- Oak Ridge National Laboratory
  - Low cost carbon fiber
- Adherent Technologies, Inc.
  - Specialty sizing
- Heyliger Consulting
  - Model optimization
- Luxfer Gas Cylinders
  - Cost analysis
  - High rate manufacturing

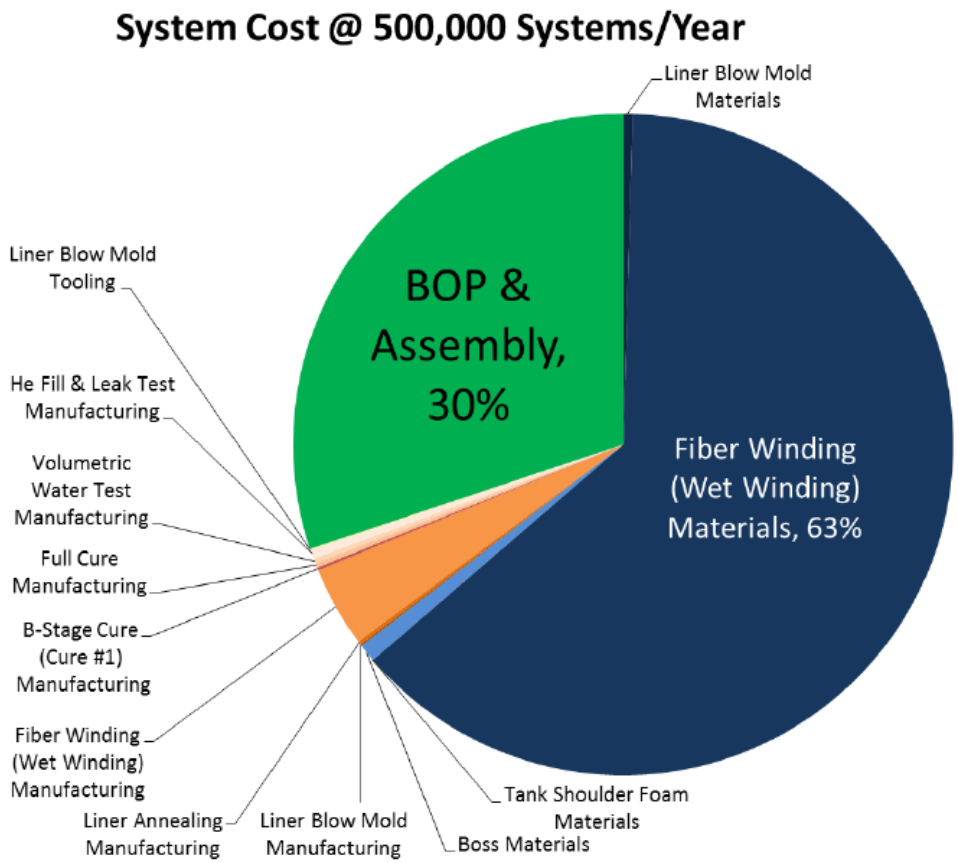
# Relevance

- **Hydrogen fuel cell vehicles require on-board $H_2$ storage systems to support driving distance of >300 miles**
  - **5 kg $H_2$ storage required**
  - **Requires 700 bar (10,000 psi) storage capability**
  - **Current Type III and Type IV COPV will not meet long term cost/performance targets***
    - **Storage system cost significantly higher than 2017 targets**
  - **Carbon fiber identified as primary driver of storage system cost**

**Phase II Goal: Demonstrate technology to reduce cost of Type IV H2 Storage vessel by 10 – 25 %**

* "Technical Assessment of Compressed Hydrogen Storage Tank Systems for Automotive Applications", September 2010, published on the DOE/FCT website: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/compressedtank_storage.pdf

# Relevance – Cost Breakout for Type IV $H_2$ Storage Systems

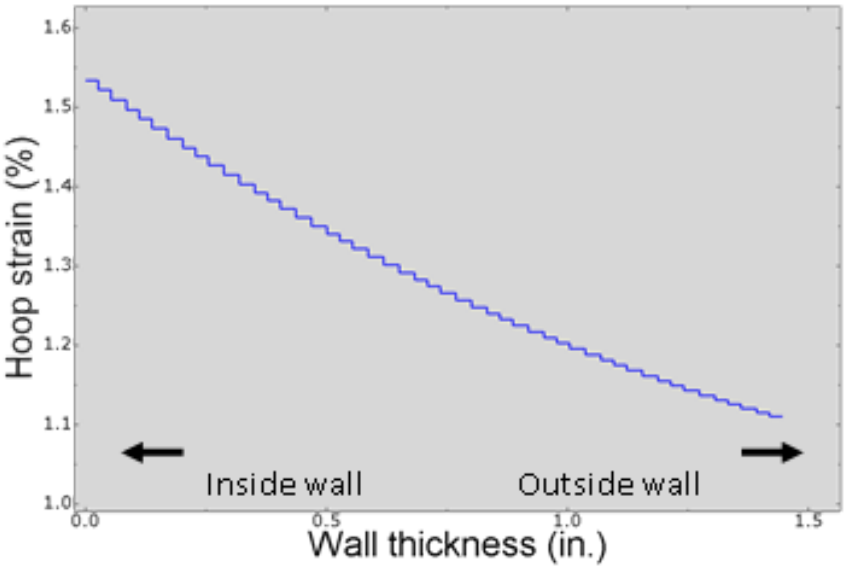



**Reducing quantity and cost of carbon fiber represents an excellent opportunity to reduce Type IV tank cost while maintaining performance properties**

Graphic from "Hydrogen Storage Cost Analysis", U.S. Department of Energy's (DOE's) 2013 Annual Merit Review and Peer Evaluation Meeting (AMR) for the Hydrogen and Fuel Cell Technologies (FCT) Program, http://www.hydrogen.energy.gov/pdfs/review13/st100_james_2013_o.pdf

# Approach – Pressure Vessel Mechanics

- **Efficient composite maximizes fiber strain**
- **700 Bar tank analyzed as thick walled shell**
  - **Thickness/radius > 0.1 invalidates uniform hoop stress distribution through wall**
  - **In thick shell there is a gradation of strain from inner to outer wall**
  - **The outer fibers are strained 20-30% less than the inner fibers at incipient burst failure**

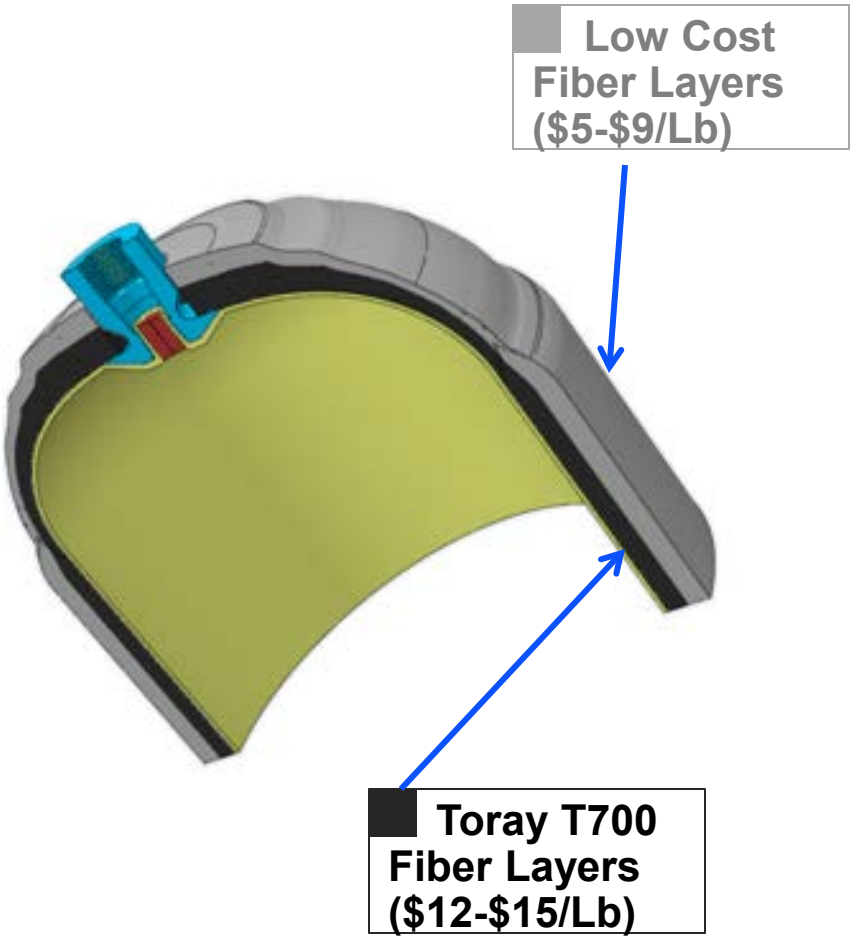



- **Thick composite performance also depends on**
  - **Damage due to microcracking and delamination during hydrostatic pressurization as well as fatigue cycling**
  - **Understanding and incorporation of progressive failure mechanisms is essential to optimize design**

# CTD Approach – Graded Composite

- Carbon fiber is the highest cost component in 700 Bar composite tanks
  - Reducing the cost or quantity of carbon fiber in a tank can yield the biggest savings
- Lower cost carbon fibers tend to have lower strain capabilities than high priced fibers
  - In thick walled shell – outer most fibers are stained to lower levels
  - By using a graded composite where high strain fibers are used in the inner portion and lower strain fibers on the outside can reduce tank cost

**Graded Composite Structure**



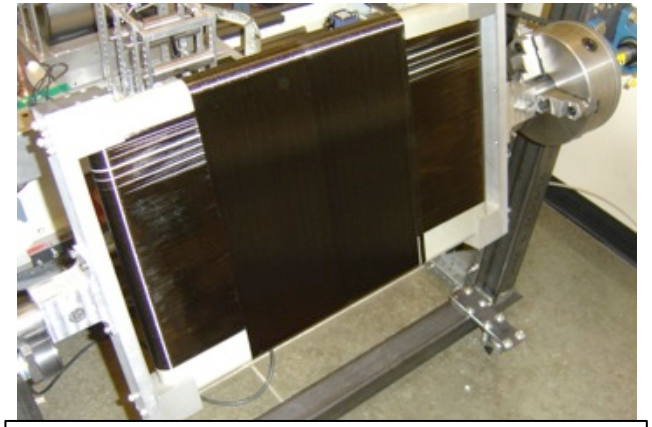
# Approach – Project Goals

- ORNL's textile-PAN based fibers are making significant progress in strength and modulus
  - Material properties have only been explored at the fiber level
- Composite properties under investigation in this program
  - Fiber translation in epoxy matrix composites
  - Compatibility with the filament winding process
  - How composite design rules apply
- Optimize fiber sizing and epoxy matrices to → maximum properties of these carbon fibers
  - Prevent fiber damage during handling and filament winding
  - Damage can reduce burst, fatigue, and stress rupture performance
  - Promotes chemical compatibility and adhesion between the fiber and matrix

**Provide highly efficient composite with excellent fiber translation at a minimal cost due to grading with low cost fibers through tank thickness**

# Approach – Composite Manufacturing and Test Coupons

- Evaluate performance of T700 and low cost carbon fiber options
- Processing of materials for program
  - Unidirectional panels for coupon testing
  - Wet winding
- Coupon Testing
  - Tensile (ASTM D3039)
    - Data for design model
  - Short Beam Shear (ASTM D2344)
    - Some information regarding sizing effects
  - Data to verify/refine design models

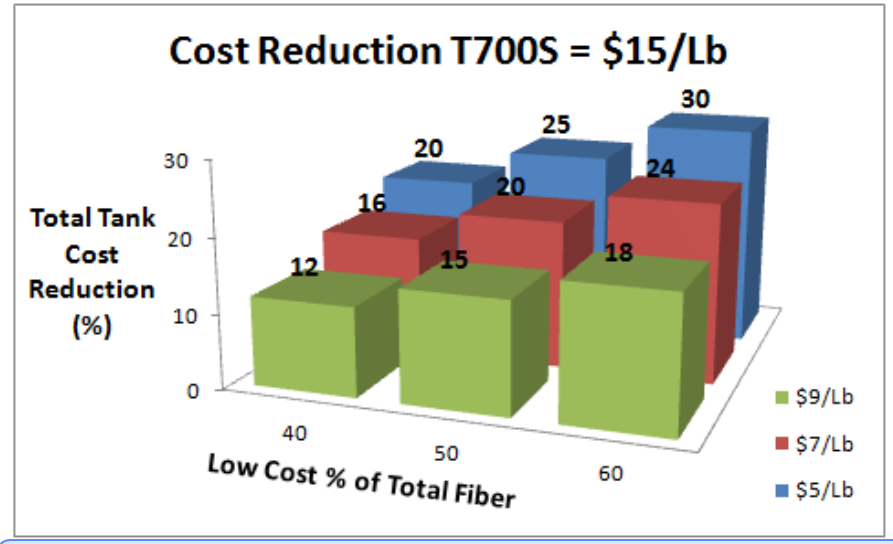


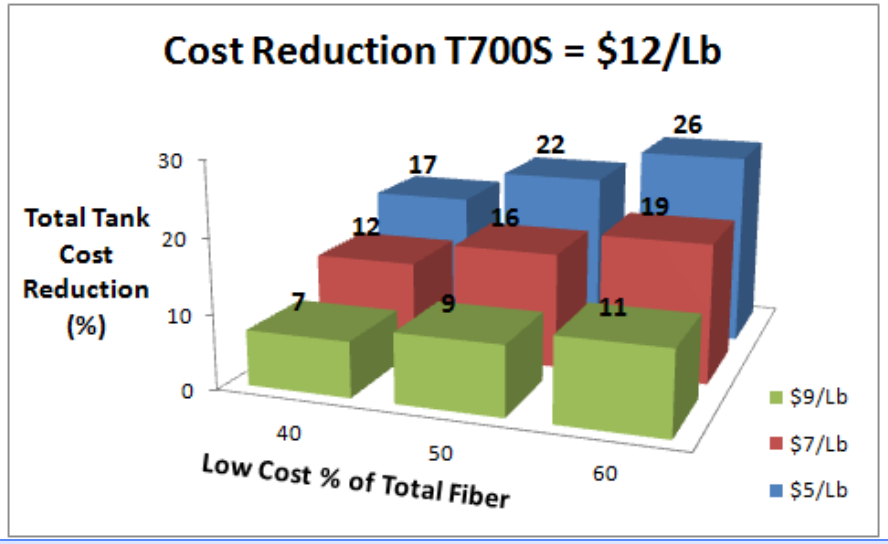
Uni and Cross Ply Panel Winding

Short Beam Shear Test

# Accomplishments & Progress – Phase I Cost Analysis

- Cost reduction potential based on
  - T700S over cost range of $12-15/Lb
  - ORNL low cost carbon fiber range of $5-9/Lb
  - Percentage of low cost fibers used in tank wall between 40%-60%
  - Assumed zero mass change relative to current design




**Lower Cost Fibers and Graded Composite Can Enable 25% Cost Reduction**

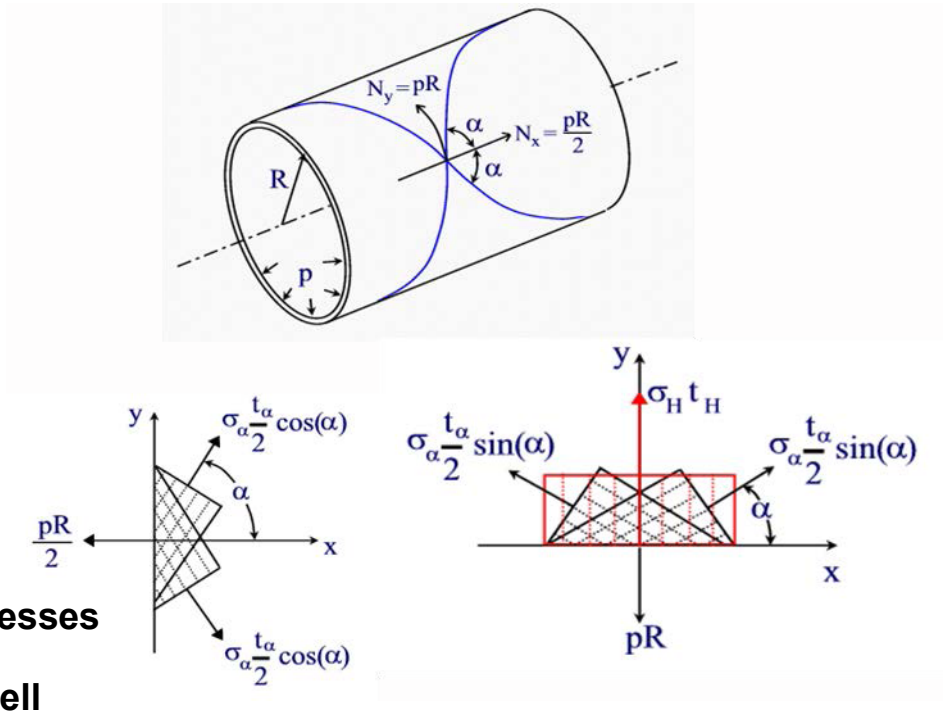
Values Calculated using cost breakout from "Technical Assessment of Compressed Hydrogen Storage Tank Systems for Automotive Applications", September 2010, published on the DOE/FCT website: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/compressedtank_storage.pdf

# Accomplishments & Progress – Phase I Analytical Model

- **Basic shell design determined using netting analysis**

$$\sigma_\alpha = \frac{pR}{2\left(\cos^2\alpha\right).t_\alpha}$$

$$\sigma_H = \frac{pR}{t_H}\left(1 - \frac{\tan^2\alpha}{2}\right)$$




- $\alpha$ is the helical wind angle
- $\sigma_a$ and $\sigma_H$ are the stresses in the helical and hoop plies
- $t_a$ and $t_H$ are the helical and hoop ply thicknesses
- p is the internal pressure
- R is the average radius of the cylindrical shell

- **The equations are solved for $t_a$ and $t_H$ by assuming that the cylinder bursts when the stresses reach the ultimate fiber failure stress.**

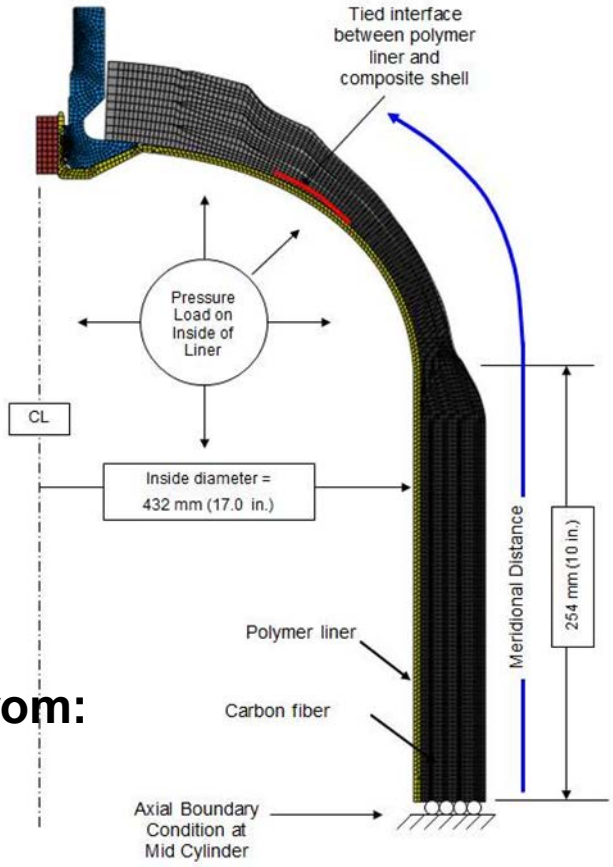
# Accomplishments & Progress – Solution for Toray T700 Case

- **Assumptions**
  - **Liner ID = 437 mm (17.2 in.)**
  - **Cylindrical length = 698.5 mm (27.5 in.)**
  - **Total length of tank = 1041.2 mm (41 in.)**
  - **Water volume of unpressurized tank = 127.75 Liters**
  - **Volume of pressurized tank = 131 Liters**
- **p = 164.5 MPa → thickness of the composite shell**

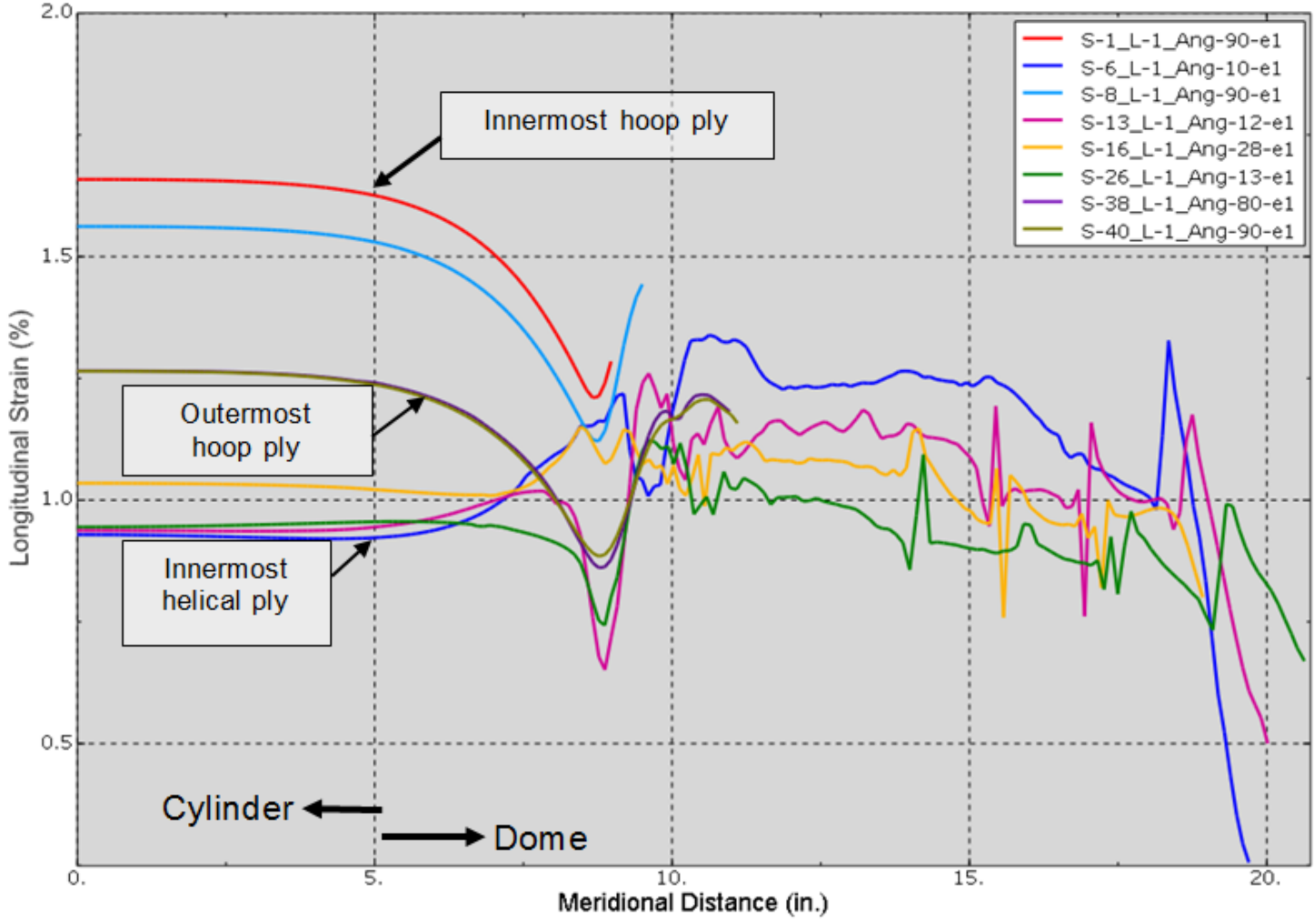
| Design Input | | |
|---|---|---|
| **Burst Pressure** | bar (psi) | **1645 (23,852)** |
| **Ultimate Fiber Stress** | GPa (ksi) | **4.9 (711)** |
| **Average Helical Angle** | | **10°** |
| **Helical : Hoop Stress Ratio** | | **0.6** |
| **Computed Parameters** | | |
| **Number of Hoop Layers** | | **59** |
| **Number of Helical Layers** | | **27** |
| **Total Hoop Thickness** | mm (in.) | **19.0 (0.75)** |
| **Total Helical Thickness** | mm (in.) | **16.5 (0.65)** |
| **Total Thickness of Composite Shell** | **mm (in.)** | **35.6 (1.4)** |

# Accomplishments & Progress – Finite Element Analysis

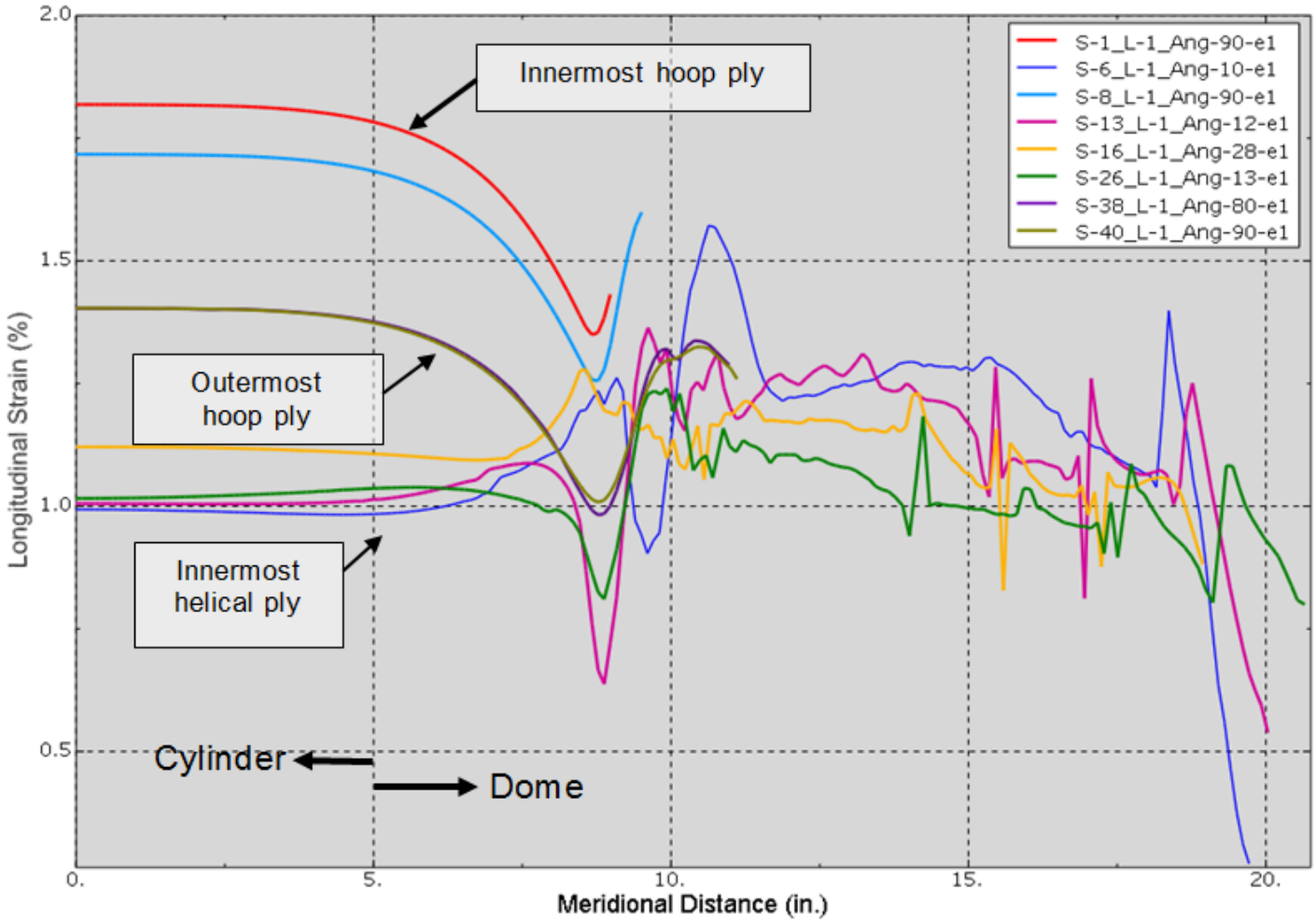
- **FEA accounts for:**
  - Orthotropic properties of the composite layers, properties and thickness of each element
  - Polar buildups during filament winding
  - Hoop stagger at the cylinder-to-dome transition region
- **Geodesic isotensoid dome**
  - Uniform tension in helical plies
  - Minimizes slippage of fibers during helical winding
- **Frictional interface**
- **Material properties for each element generated from:**
  - Unidirectional composite properties
  - COPV geometry
  - Initial wind angle



# Accomplishments & Progress – FEA Results – T700 Case



# Accomplishments & Progress – FEA Results – Graded Case

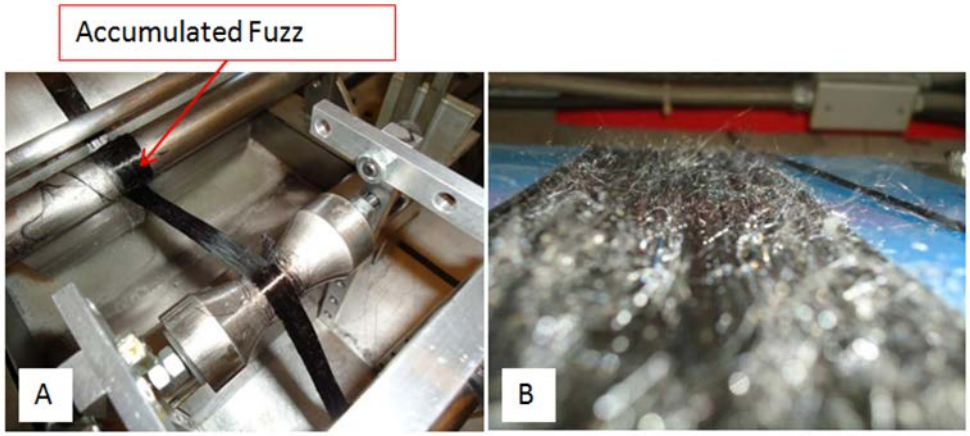


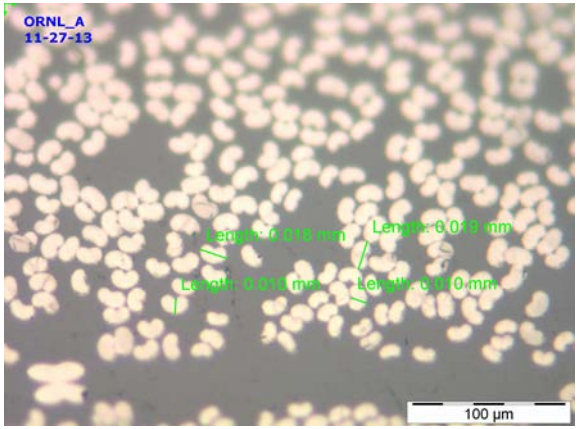
# Approach – Phase I Baseline Materials

| Material | Description | Comments |
|---|---|---|
| Toray T700 | Commercial carbon fiber | • Currently used in Type IV tank construction<br>• $12-15/lb |
| ORNL Low Cost Carbon Fiber | Non-commercial carbon fiber | • Textile PAN feedstocks<br>• Target price point $5-$9/lb<br>• ORNL-A: specialty sizing applied by Adherent Technologies<br>• ORNL-B: conventional sizing applied at ORNL<br>• ORNL-C: conventionally sized, different variant |
| Zoltek Panex 35 | Commercial low cost carbon fiber | • Targeted for automotive applications<br>• $10/lb |
| Standard Epoxy Sizing | Commercially available, applied during manufacture | • Primarily handling function<br>• Some improvement in wetting/adhesion |
| Adherent Technologies AT-9307E finish | Reactive finish | • Dramatic improvements in composite strength and environmental durability |
| CTD-7.1 | Toughened epoxy | • Wet winding<br>• Used in KIBOKO® linerless composite tanks |

# Accomplishments & Progress – Phase I Test Coupons

- Target 60% fiber volume fraction
- Limited quantities of ORNL fiber available
- Significant fuzzing noted for ORNL-A and ORNL-B variant fibers
  - Kidney-shaped cross-section → fiber breakage
- ORNL-C fiber showed significantly less fuzzing
  - Round cross-section



# Accomplishments & Progress – Unidirectional Laminate Data

| | Experimental - Normalized to 60% VF | | | Expected @ 60% VF | | | |
|---|---|---|---|---|---|---|---|
| | **Strength (ksi)** | **Modulus (Msi)** | **Ult Strain (%)** | **Strength (ksi)** | **Modulus (Msi)** | **Ult Strain (%)** | **Strength Translation (%)** |
| **Toray T700** | 343.2 | 18.4 | 1.86 | 425 | 20 | 1.7 | 81 |
| **Zoltek Panex** | 232.8 | 19.1 | 1.18 | 355 | 20 | 1.2 | 66 |
| **ORNL A** | 179.3 | 17.6 | 0.97 | 315 | 20 | 1 | 57 |
| **ORNL B** | 165.3 | 16.5 | 0.96 | 315 | 20 | 1 | 52 |
| **ORNL C** | 190 | 16.8 | 1.1 | | 17.4 | | |

**ORNL A = PAN-VA with custom sizing applied by Adherent Technologies (Albuquerque, NM)**
**ORNL B = PAN-VA with 0.5% sizing applied by ORNL**
**ORNL C = PAN-VA with 2% sizing applied by ORNL – NOTE: different precursor than ORNL A or B**

# Accomplishments & Progress – Phase I Summary & Keys to Success

- **Finite element models generated required failure strains for T700 segments and low cost composite segments**
  - **1.8% strain requirement for T700 close to being met in Phase I**
    - **80% translation vs 85% translation**
  - **1.5% strain requirement for low cost variants not close**
    - **Options under consideration for Phase II are closer to this target**
- **High translation of fiber properties ( ≥ 85%) required**
  - **Challenging for large tows (~50K) characteristic of low cost carbon fibers**

# Approach – Phase II Goals

- **Identify best low cost carbon fiber candidates**
  - **Combination of strength, modulus and strain to failure**
  - **Strength and modulus on target for current variants, strain to failure remains an issue**
- **Maximize fiber property translation**
  - **Large tow handling**
  - **Sizing/matrix interactions**
    - **specialty sizing has been shown to improve fiber property translation**
    - **Comparison with commercially applied sizing**
- **Generate experimental data to validate graded structure models**

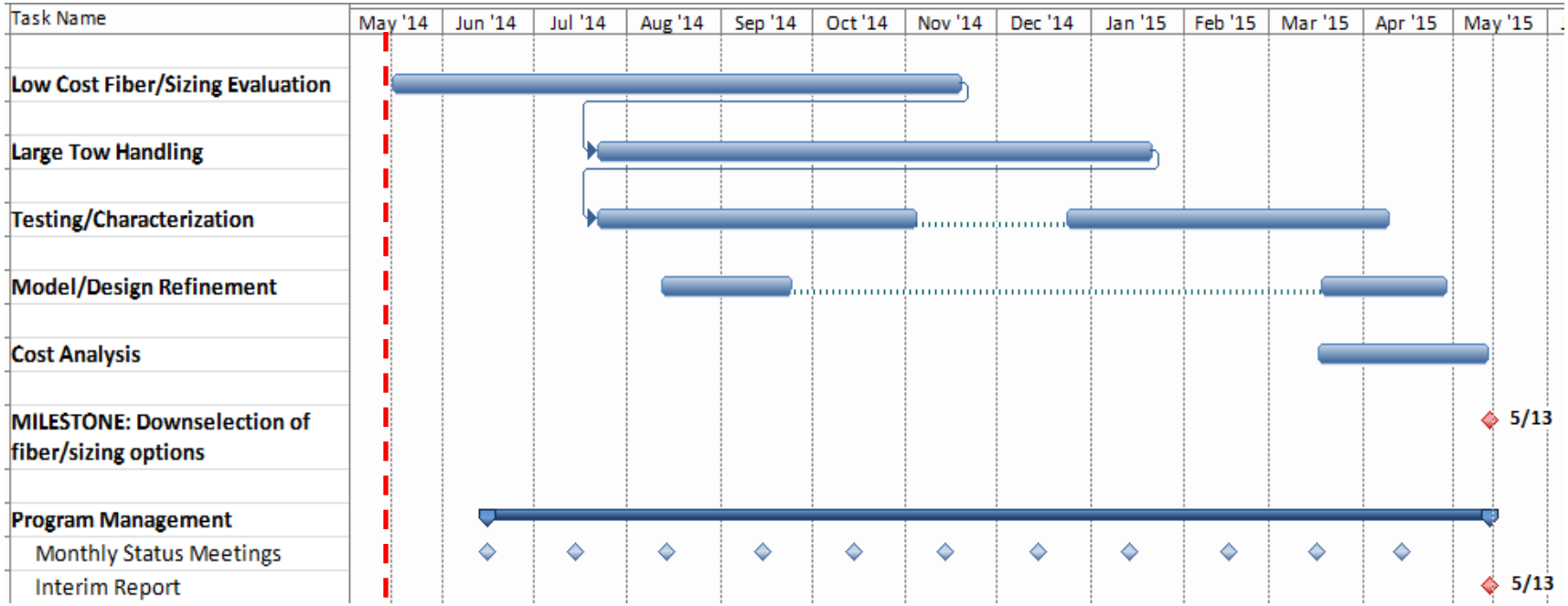
# Approach – Phase II Goals (cont'd)

- Optimize structure for highest content of low cost fiber
  - Based on experimental data obtained from unidirectional composites
- Comprehensive cost analysis
  - Material components
    - Primarily carbon fiber cost
    - Wet winding will be standard
    - Towpreg might still be considered as an option in cost analysis
  - Process-related costs
    - Use of multiple fibers in tank winding
      - Multiple winding stations
      - robotic tow handling

# Approach – Phase II Baseline Materials

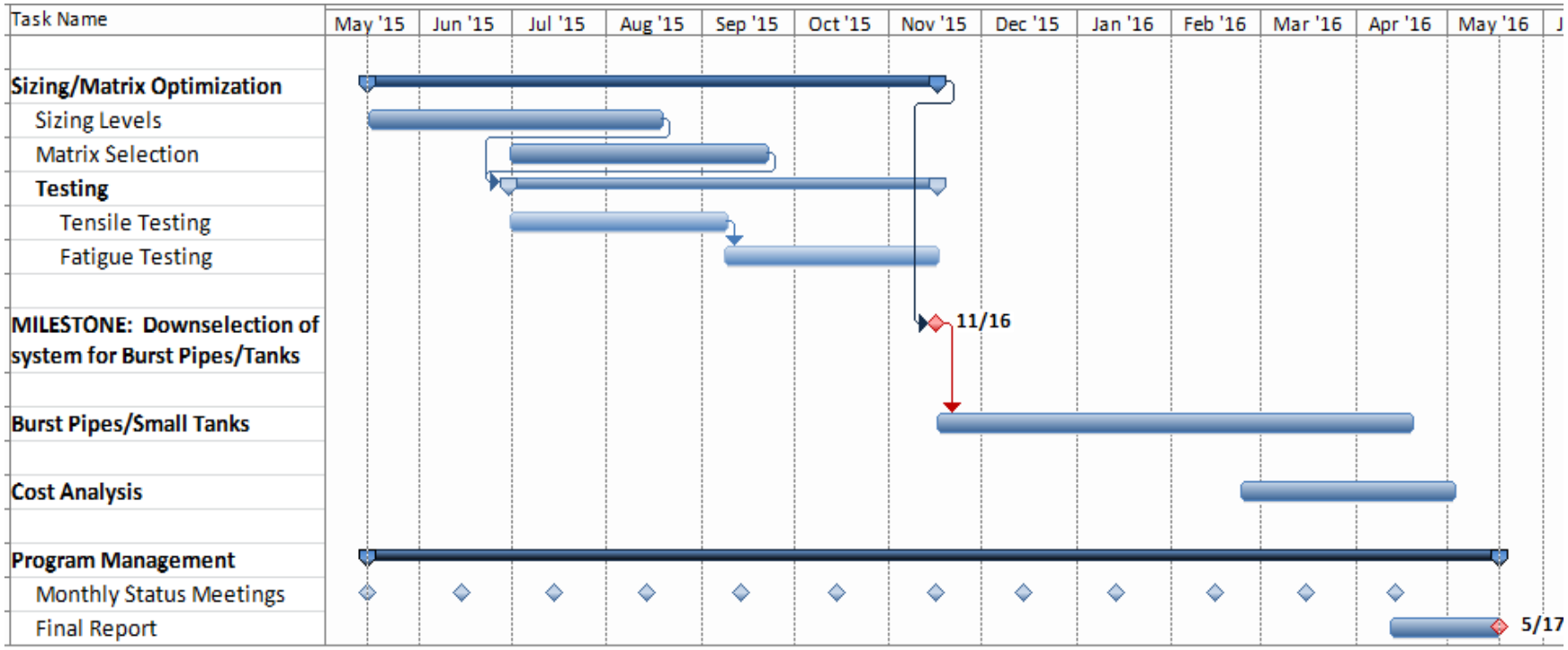
| Material | Description | Comments |
|---|---|---|
| Toray T700 | Commercial carbon fiber | • Currently used in Type IV tank construction<br>• $12-15/lb |
| ORNL Low Cost Carbon Fiber | Non-commercial carbon fiber | • Alternate feedstocks for low cost carbon fiber production<br>• Target price point $5-$9/lb |
| SGL Sigrafil® C30 | Commercial lower cost carbon fiber | • $11/lb |
| Standard Epoxy Sizing | Commercially available, applied during manufacture | • Primarily handling function<br>• Some improvement in wetting/adhesion |
| CTD Sizing | Reactive sizing | • Improved interlaminar shear properties |
| Adherent Technologies AT-9307E finish | Reactive finish | • Dramatic improvements in composite strength and environmental durability |
| CTD-9.1PX | Toughened epoxy | • Prepreg resins<br>• Will be modified for wet winding |

# Approach – Phase II Schedule, Year 1




- **Downselection criteria**
  - **Improved handling – i.e., reduced fuzzing of low cost fiber options**
  - **Improvement of fiber translation for large tows from 55% to at least 70%**
  - **Composite strain to failure approaching 1.5%**

# Approach – Phase II Schedule, Year 2



# Collaborations

- **CTD**
  - **Material trials – includes sizing, tow handling, etc.**
  - **Product design**
  - **Commercialization**
- **Oak Ridge National Laboratory (ORNL)**
  - **Provide non-commercial low-cost carbon fiber for evaluation**
- **Adherent Technologies, Inc.**
  - **Specialty fiber sizing**
- **Heyliger Consulting**
  - **Analytical model optimization**
  - **Laminate optimization**
- **Luxfer Gas Cylinders**
  - **Aid with cost analysis – primarily process-related components**
  - **Test cylinder fabrication**

# Project Summary

| | |
|---|---|
| **Relevance** | Decrease overall cost of on-board hydrogen storage for fuel cell powered vehicles |
| **Approach** | Type IV hydrogen storage tank based on graded composite structure incorporating low cost carbon fibers |
| **Technical Accomplishments & Progress** | Preliminary parametric cost analysis performed; preliminary design trade studies completed; coupon testing has identified target areas for improvement (composite strain to failure, fiber property translation, handling of large fiber tows) |
| **Technology Transfer/ Collaborations** | Active collaborations with ORNL (low cost carbon fiber), Adherent Technologies (specialty sizing), and Luxfer Gas Cylinders (cost analysis, high rate manufacturing) |
| **Proposed Future Research** | Optimization of graded composite tank construction; demonstrate a lower cost Type IV pressure vessel using graded composite construction; work with Luxfer to build and test Type IV tanks |