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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June 10, 2015

Project ID # ST110

Overview

Timeline

- Project Start Date:
  - Phase I: Feb 2013
  - Phase II: May 15, 2014
- Project End Date: May 2016
- Percent Complete: 60% (Phase I, Year 1 of Phase II)

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
- FY14 DOE Funding (May-September): $166K
- FY15 DOE Funding (October-April): $250K
- Total Project Value: $ 1.15M

Partners

- Oak Ridge National Laboratory
  - Low cost carbon fiber
- Adherent Technologies, Inc.
  - Specialty sizing

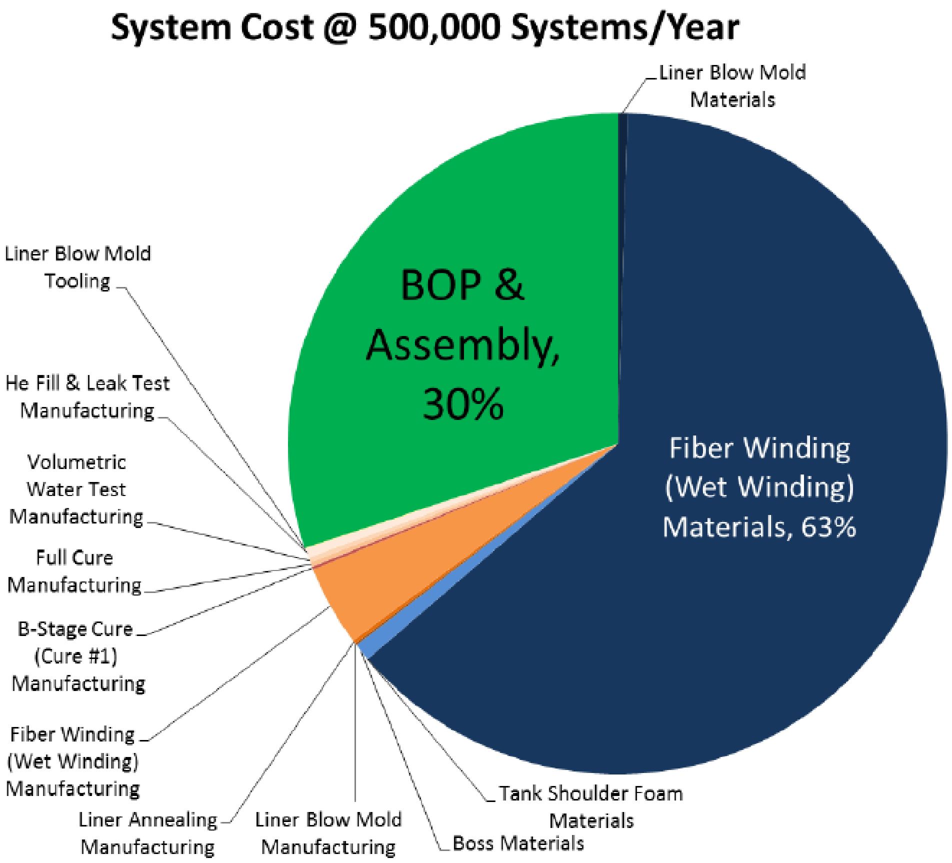
Relevance

- **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 2020 targets**
  - **Carbon fiber identified as primary driver of storage system cost**

Phase II Goal: Demonstrate technology to reduce cost of Type IV H_2 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

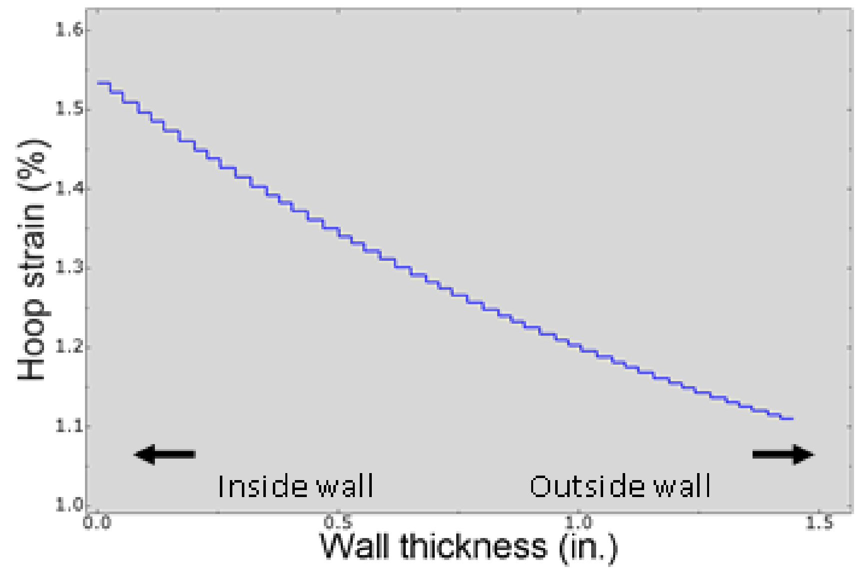


Reducing quantity and cost of carbon fiber represents an excellent opportunity to reduce Type IV tank cost while maintaining performance properties

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**

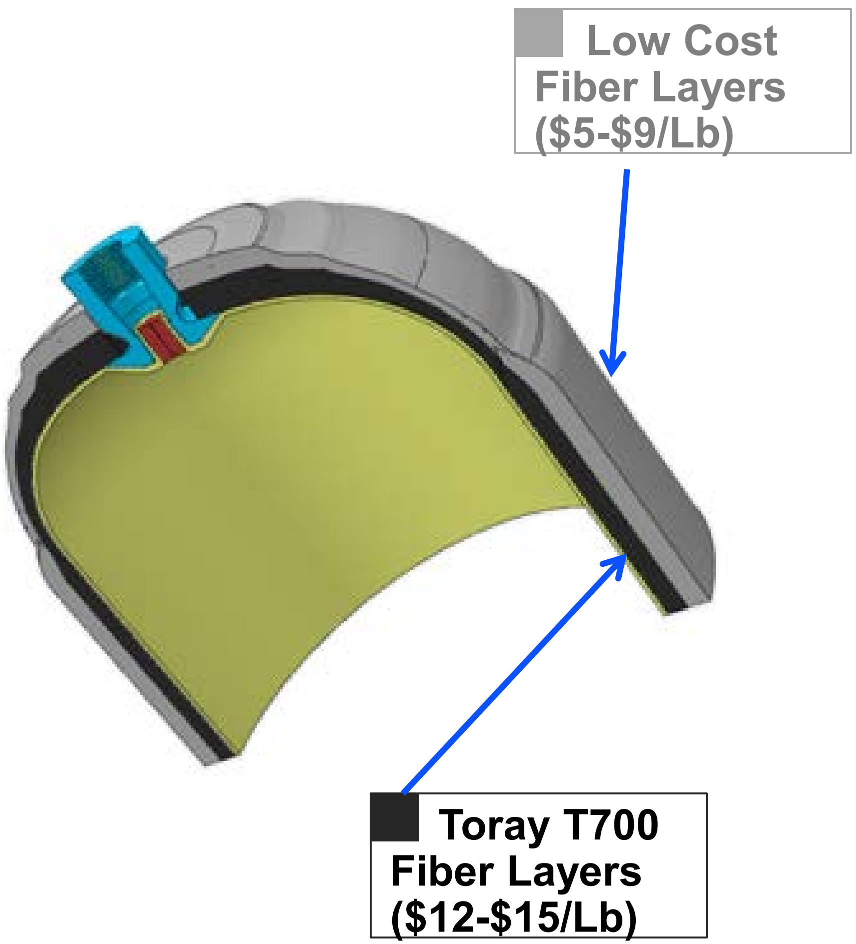


- **Thick composite performance also depends on**
  - **Damage due to microcracking and delamination during hydrostatic pressurization as well as fatigue cycling**
  - **Understanding and incorporation of progressive failure mechanisms is essential to optimize design**

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 – 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

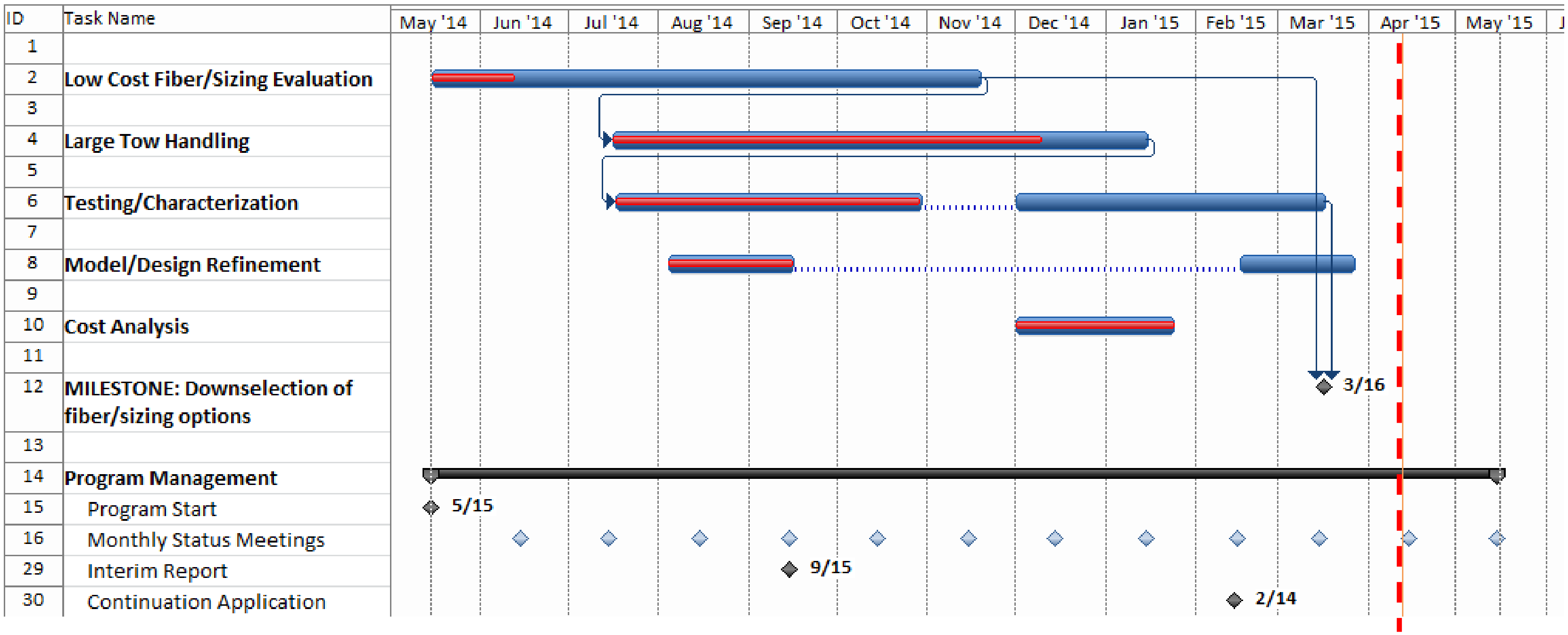
Provide highly efficient composite with excellent fiber translation at a minimal cost due to grading with low cost fibers through tank thickness

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

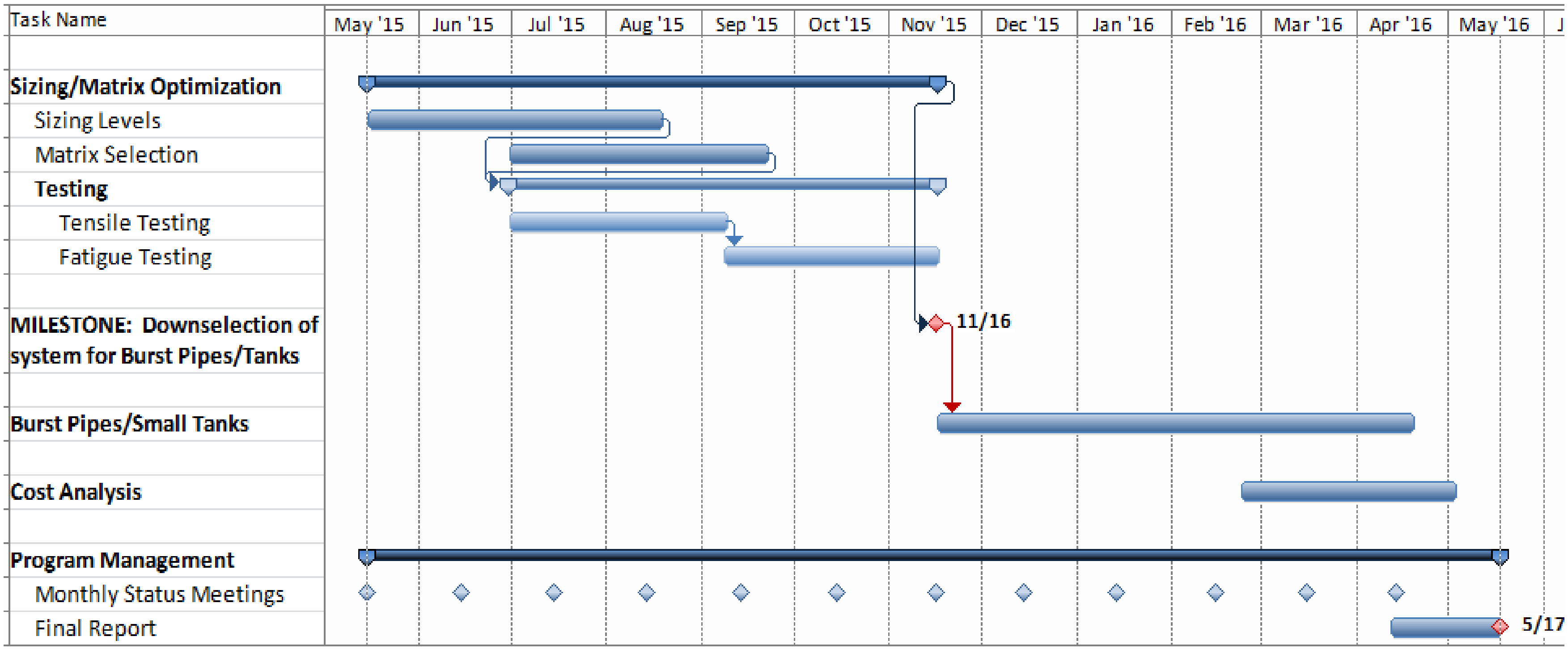
Provide highly efficient composite with excellent fiber translation at a minimal cost due to grading with low cost fibers through tank thickness

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

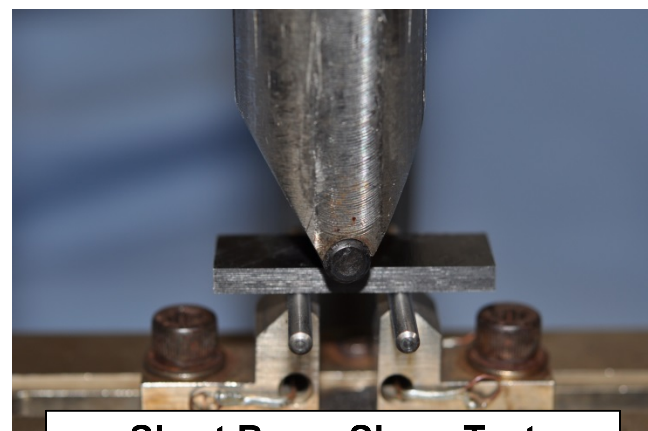
Approach – Phase II Baseline Materials

Material	Description	Comments
Toray T700	Commercial carbon fiber	• Currently used in Type IV tank construction • $12-15/lb
ORNL Low Cost Carbon Fiber	Non-commercial carbon fiber	• Alternate feedstocks for low cost carbon fiber production • Target price point $5-$9/lb
Panex® 35	Commercial lower cost carbon fiber	• $11/lb
SGL Sigrafil® C30	Commercial lower cost carbon fiber	• $11/lb
Standard Epoxy Sizing	Commercially available, applied during manufacture	• Primarily handling function • 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-7.1	Toughened epoxy	• Prepreg resins • Will be modified for wet winding

Approach – Composite Manufacturing and Test Coupons

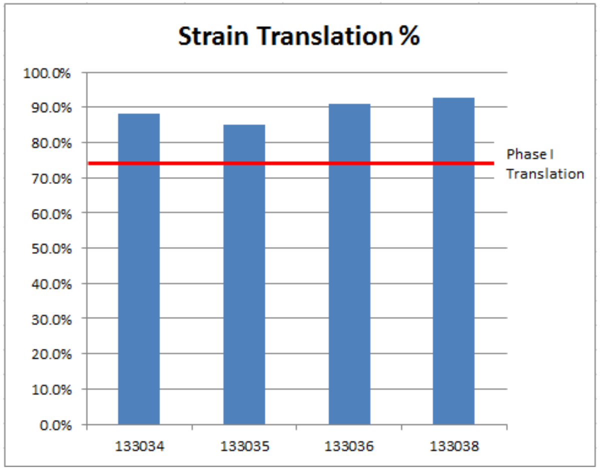
- Evaluate performance of T700 and low cost carbon fiber options
- Processing of materials for program
  - Unidirectional panels for coupon testing
  - Wet winding
- Coupon Testing
  - Tensile (ASTM D3039)
    - Data for design model
  - Short Beam Shear (ASTM D2344)
    - Some information regarding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

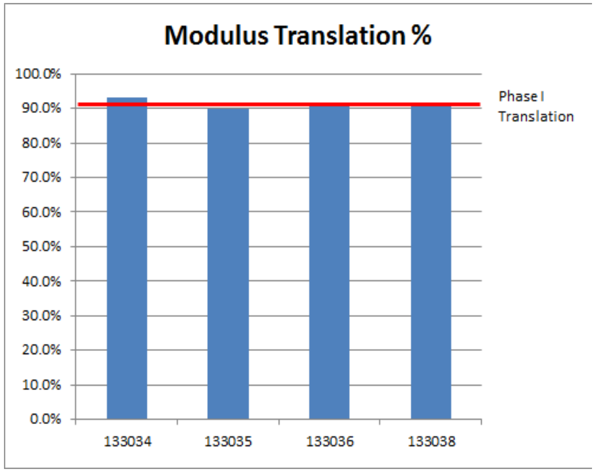
Uni and Cross Ply Panel Winding

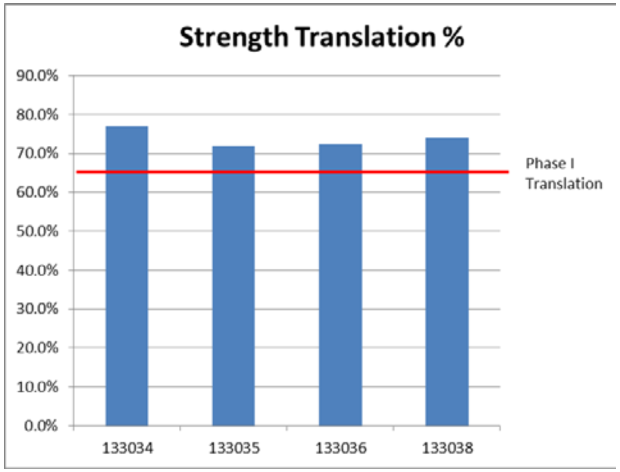


Short Beam Shear Test

Accomplishments – Fiber Property Translation – Panex® 35



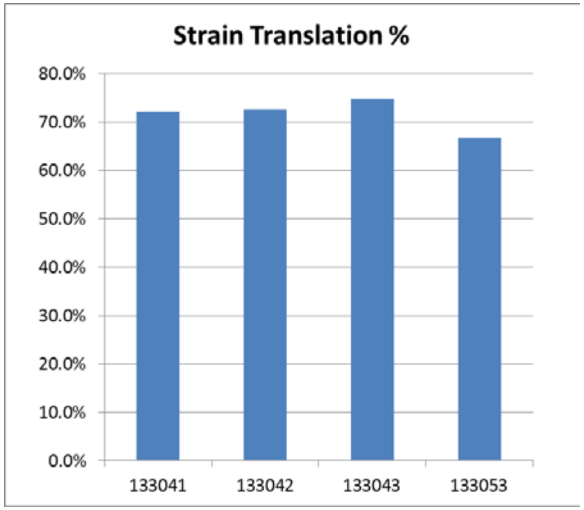


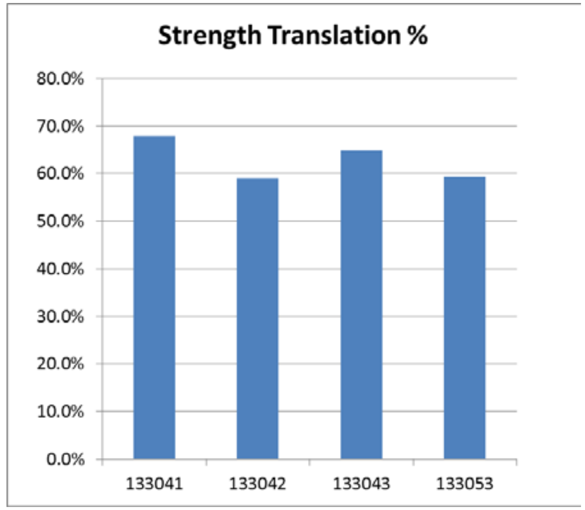


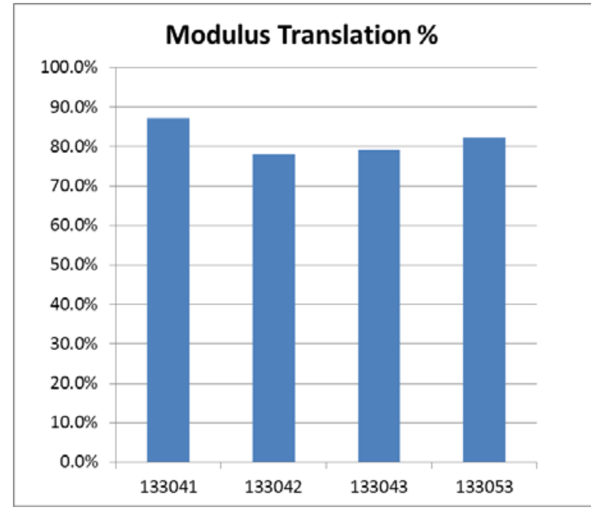
	Phase I	Phase II
Strain	78%	89.2%
Strength	65%	73.8%
Modulus	91%	91.5%

- **Substantial improvement in fiber property translation achieved over Phase I results**
- **Resulted from improved tow spreading and wetting**
- **System shows promise for use in graded construction**

Accomplishments – Fiber Property Translation – Sigrafil® C30



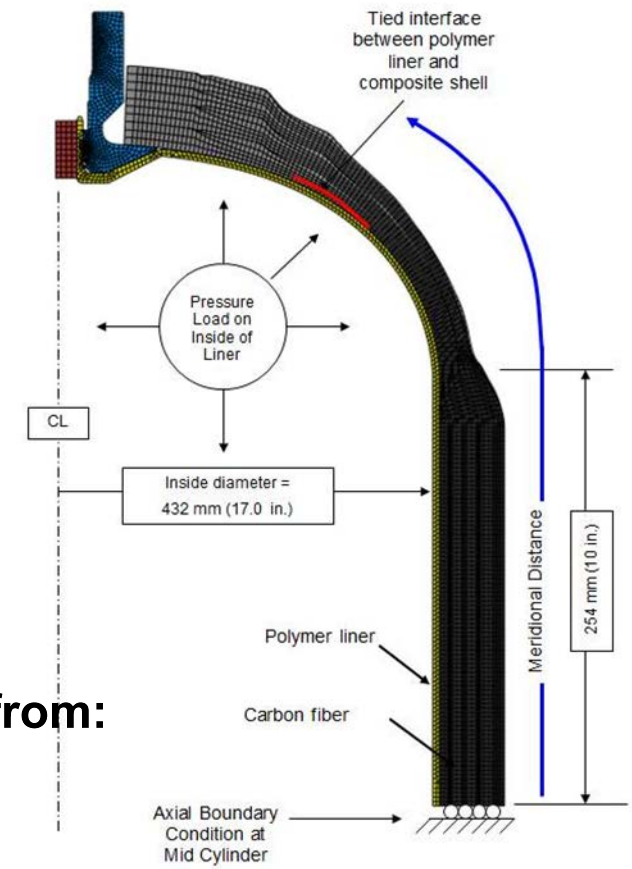




- **Fiber property translation short of 85% target**
- **Qualitatively appears to have higher void content, lower fiber density than Panex® counterpart**
- **Spreading / wetting of fiber was initially a problem**
- **False twists**
- **Working with SGL to address handling issues**

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

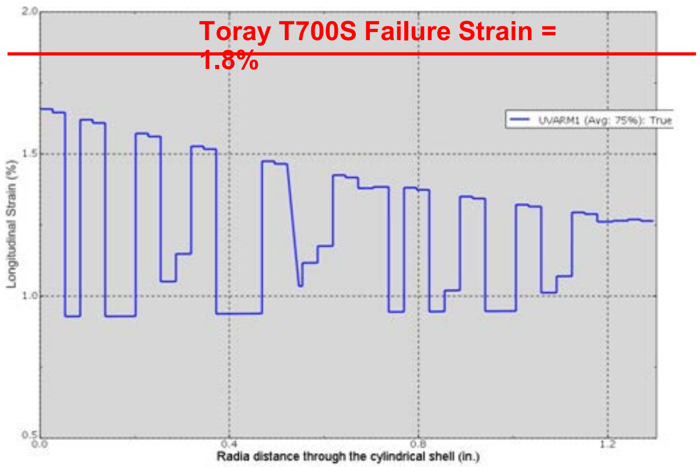


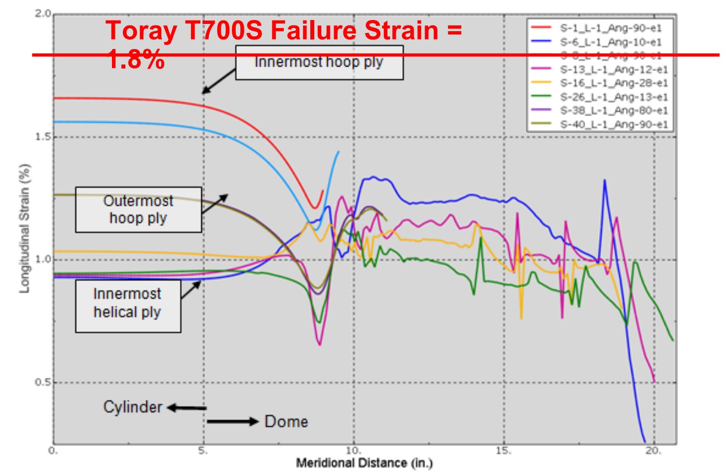
Accomplishments & Progress – Solution for Toray T700 Case

- **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		10º
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)

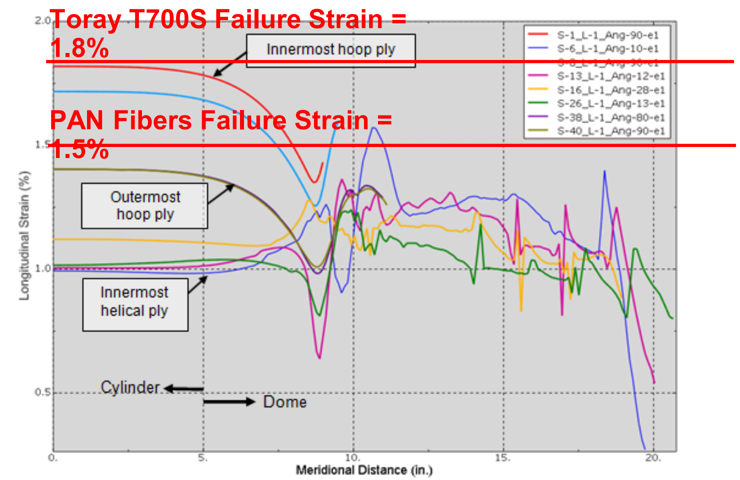
Accomplishments – Viability of the Approach





Outer layers are strained 25% less than the inner layers → underutilization of high strength fiber

Property	Textile PAN fiber composite
Fiber volume fraction %	60
Longitudinal Elastic Modulus, E_1 GPa (Msi)	103.45 (15.0)
Transverse Elastic Modulus, E_2 GPa (Msi)	8.96 (1.3)
Poisson Ratio, ν_{12}	0.28
Shear Modulus, G_{12} GPa (Msi)	3.45 (0.5)
Longitudinal Failure Strain	1.5%

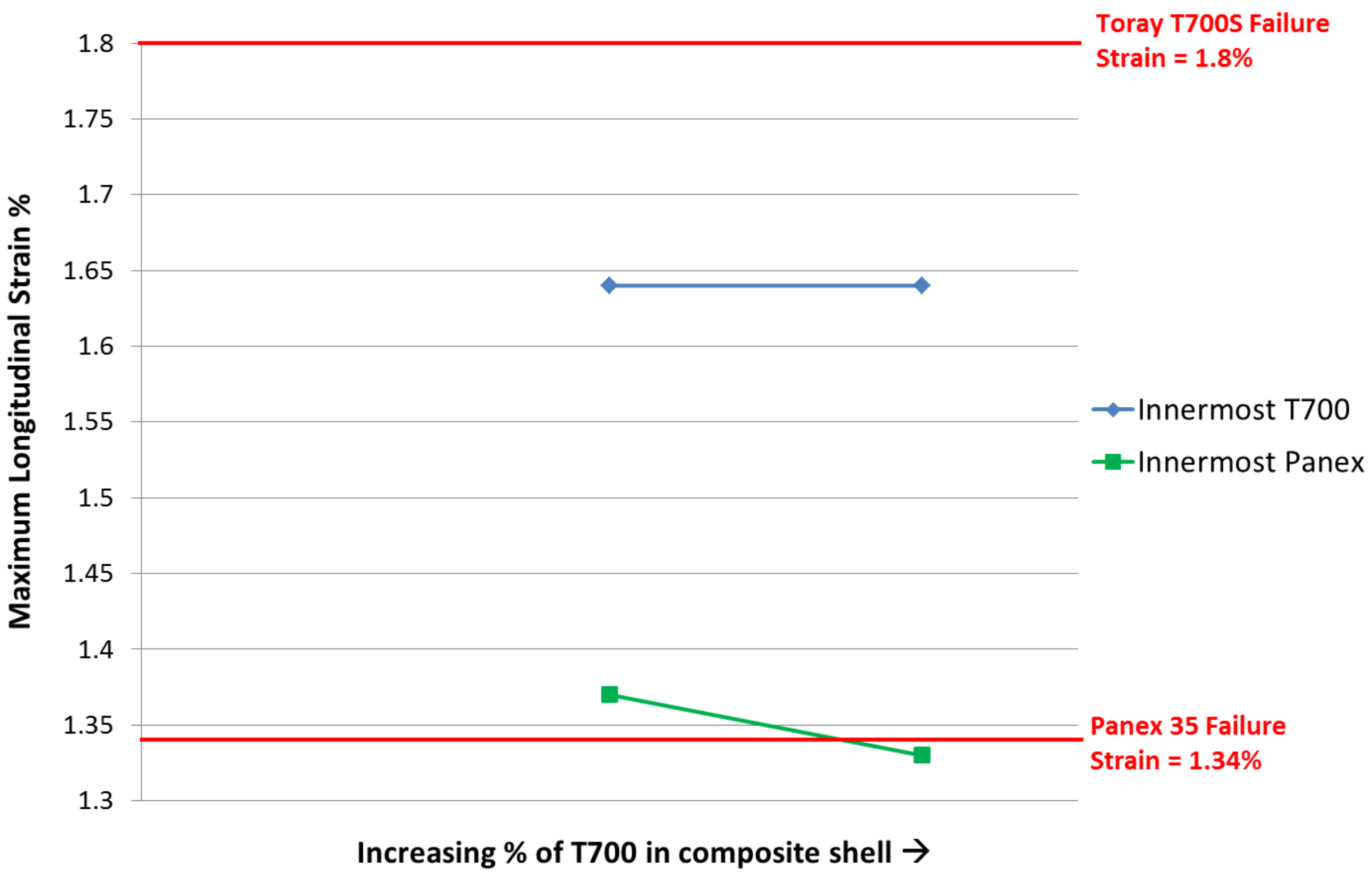


Accomplishments – Commercial Fiber Models

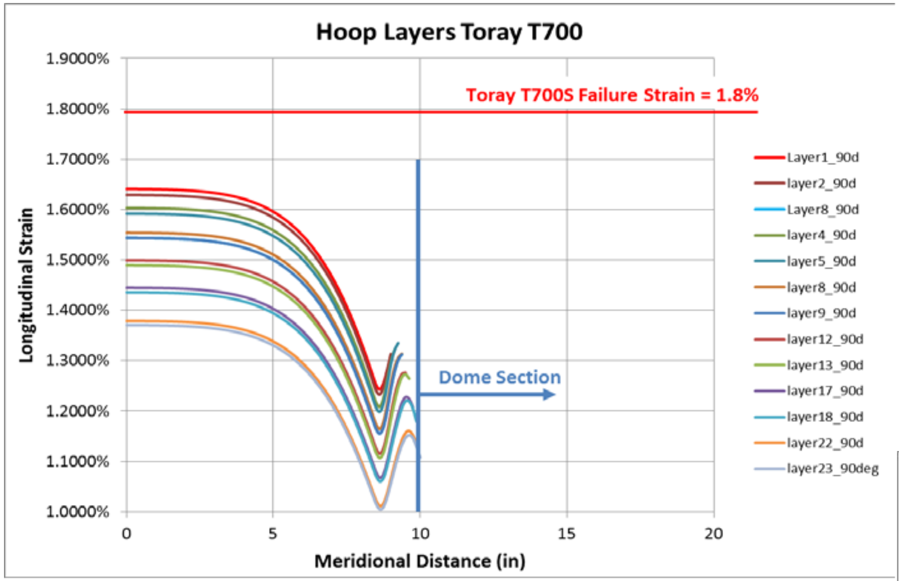
- Same model used to predict performance of commercial lower cost fibers in a graded structure
- Experimental composite data obtained from flat laminates used in basic model used to predict graded structure performance
- Fiber volume fraction of 60% in composite shell assumed

Property	T700S Composite	Panex® 35 Composite	Sigrafil® C30 Composite
Bandwidth (in)	1.69	1.69	1.69
Hoop thickness (in)	0.027	0.027	0.027
Helical thickness (in)	0.0164	0.0164	0.0164
Longitudinal Elastic Modulus, E_1 (Msi)	18.5	19.05	16.9
Transverse Elastic Modulus, E_2 (Msi)	1.3	1.01	1.08
Poisson Ratio, ν_{12}	.28	.28	0.28
Shear Modulus, G_{12} (Msi)	0.5	0.5	0.5
Failure Strain in fiber direction (%)	1.8	1.34	1.145

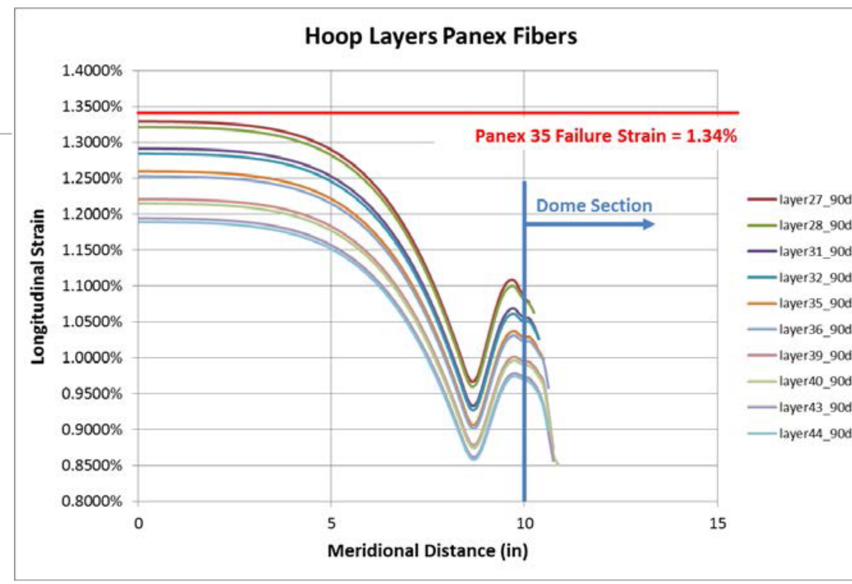
Accomplishments – Panex® Replacement (current properties)



Accomplishments – Hoop Layer Analysis Panex® 35 Case

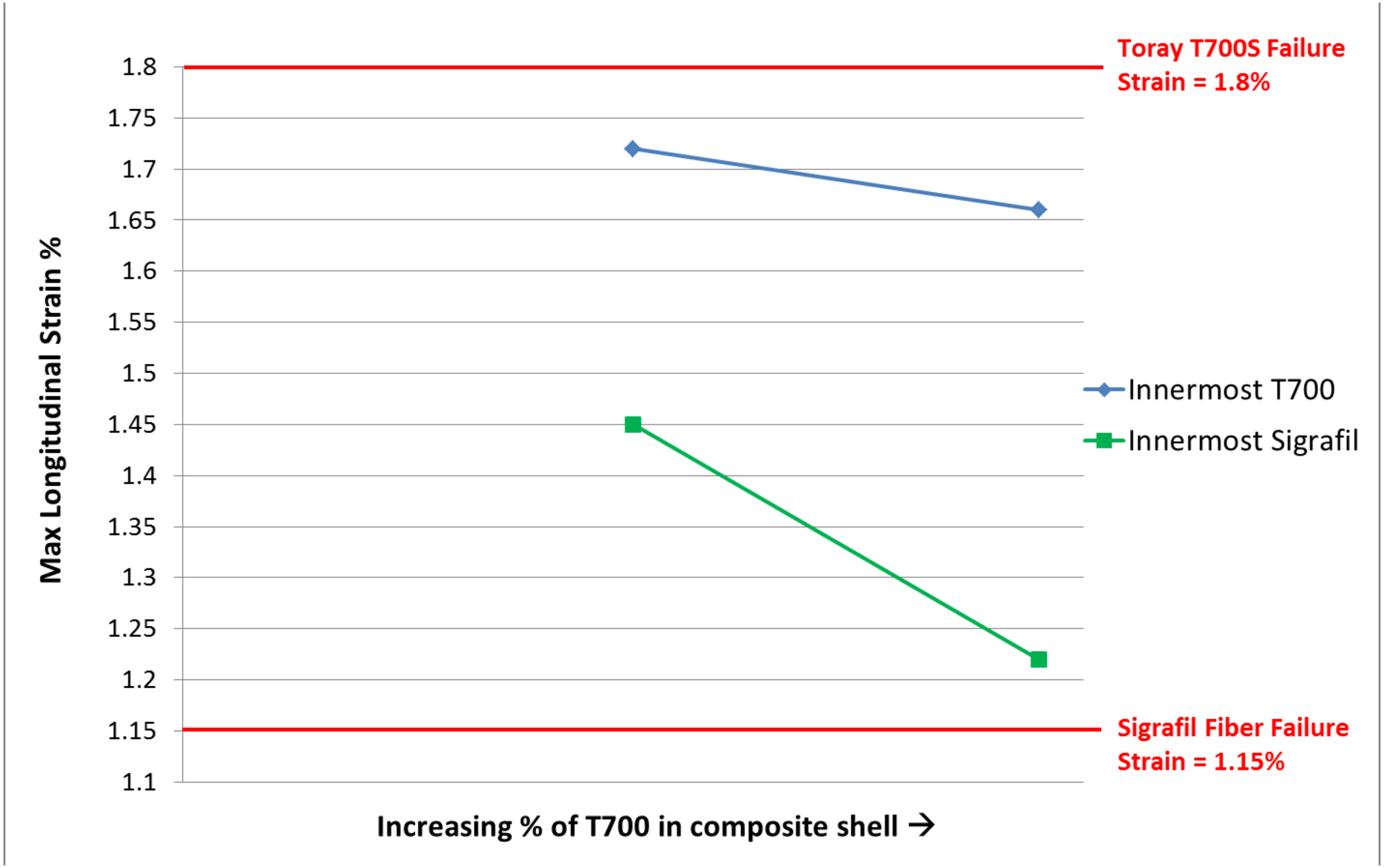


- Prior analysis showed that failure should occur in hoop layers
- A graded structure containing a substantial fraction of Panex® 35 appears feasible



- Innermost layers of T700 strained well below failure strain of 1.8%
- Innermost layers of Panex® 35 strained below current measured failure strain of 1.34%

Accomplishments – Sigrafil® Replacement (current properties)



Accomplishments – Low Cost Fiber Sizing

- **Received low cost fiber from ORNL**
  - **Textile precursor received as 200k tow**
  - **Split during processing to yield ~50k tow size**
- **Shipped to Adherent Technologies, Inc. for sizing**

Low Cost Carbon Fiber Properties
K30-HTC, Lot Number TN651140902

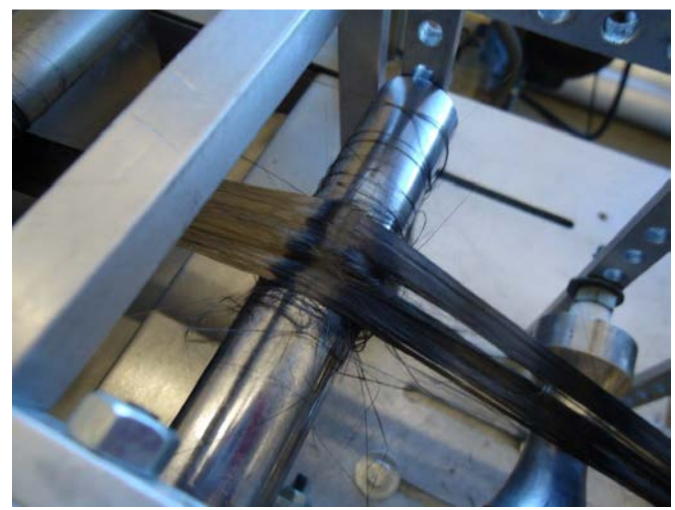
Property	Average (standard deviation)
Tensile Strength (Ksi)	379.8 (± 17.3)
Tensile Modulus (Msi)	30.8 (± 0.4)
Elongation (%)	1.23 (± 0.04)

Summary of Candidate Sizings

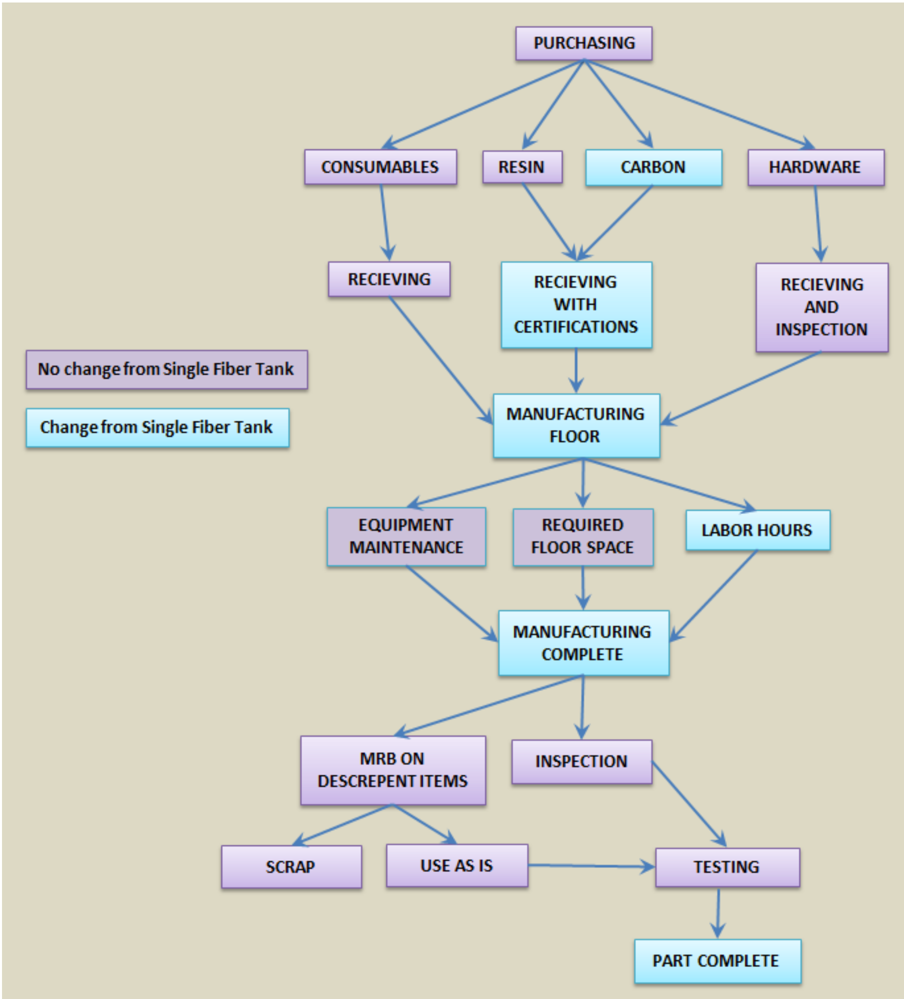
Sizing ID	Description	Loading Level
Michelman U6-01-1	Commercial epoxy compatible sizing	1%
Michelman U6-01-4	Commercial epoxy compatible sizing	4%
AT9307E-1.5	Reactive epoxy compatible finish	1.5%
AT9307E-3	Reactive epoxy compatible finish	3%
AT9307K-1.5	Reactive toughened epoxy finish	1.5%
AT9307K-3	Reactive toughened epoxy finish	3%
CTD-FI-323-2	High shear strength sizing	2%
CTD-FI-323-4	High shear strength sizing	4%

Accomplishments – Fiber Sizing Trials

- **Significant fuzzing of fiber observed during sizing operation**
- **Fuzzing not improved for sized fiber**
- **Likely a result of tow splitting**
- **Currently evaluating other options for tow splitting at ORNL**
- **Activity will resume in May 2015**



Accomplishments – Cost Analysis – Flow Chart



- Minimal impact on purchasing and receiving
- Impacts to Manufacturing
  - Multiple winding stations
  - Multiple fibers at delivery system
- Multiple fibers at the delivery system.
  - Work stations need remains the same
  - Added labor for fiber routing
- Largest change occurs with labor hours

Accomplishments – Cost Analysis – Details

Color Key	Input	Calculation

RAW MATERIAL INPUTS			
"Material A" Price	44	$/kg	20 $/lb
"Material A" Net Quantity	44	kg/part	96.8 lb/part
Yield	90%		

MANUFACTURING INPUTS			
Annual Part Volume	50000	parts	
Average Equipment Downtime	15%		Will increase for 2 fibers system
Number of Laborers	1		
Cycle Time	1200	seconds	3600s/3 tanks per station
Equipment Investment	$ 80,000	/station	$240000/3 tanks per station
Dedicated Equipment Investment?	1	[1=yes,0=no]	
Consumable Cost	$ 10.00	$/unit	
Consumable Rate	1	unit	
Power Consumption/Station	5	kW	
Building Space/Station	37	sq m	400 sq ft

INTERMEDIATE CALCULATIONS		
Effective Cycle Time	1333	sec/part
Machine Utilization	363%	
Number of Parallel Stations	5	
Total Equipment Investment	$ 600,000	

GENERAL INPUTS			
Direct Wages	$ 20	/hr	
Benefits on Wage and Salary	35%		
Overhead and Indirect Labor	$ 100,000	/yr	
Working Days per Year	250	days	
Available Production Hours per Day	24	hrs	
Labor Hours Per Day	24	hrs	
Equipment Recovery Life	10	yrs	
Price of Electricity	$0.10	/kWh	
Price of Building Space	$ 108	/sq m	$ 10.03 /sq ft
Auxiliary Equipment Cost	15%		
Equipment Installation Cost	35%		
Equipment Maintenance Cost	5%		

OUTPUT	$/part	$/yr
Material Cost	$2,162.22	$108,111,111
Direct Labor Cost	$16.20	$810,000
Energy Cost	$0.22	$10,893
Equipment Cost	$1.20	$60,000
Building Cost	$0.08	$4,018
Maintenance Cost	$0.06	$3,201
Overhead and Indirect Labor Cost	$2.00	$100,000
TOTAL COST	$2,181.98	$109,099,223

- **Cost analysis worksheet provided by Jon Sienkowski of Dawnbreaker**
- **Assuming 3 tanks manufactured at a time per workstation**
- **Used 2 of these charts to determine price of graded tank**

Accomplishments Cost Analysis – Savings in Percentage

T700 Price Range = $13 - $20
Low Cost Fiber Price Range = $7 - $12

These calculations come from a composite that has 50% fiber volume

50% T700 Toray/50% Low Cost Fiber				
		Low Cost Fiber ($/lb)		
		$ 7.00	$10.00	$12.00
T700 Toray ($/lb)	$13.00	20.4%	9.1%	1.6%
	$15.00	24.3%	14.5%	7.9%
	$20.00	30.6%	23.2%	18.3%

Weight of Fiber				
Percent	T700 lb	T700 kg	LC Fiber lb	LC Fiber kg
60/40	58.0	26.36	38.8	17.64
50/50	48.4	22.00	48.4	22.00
100	96.8	44.00		

60% T700 Toray/40% Low Cost Fiber				
		Low Cost Fiber ($/lb)		
		$ 7.00	$10.00	$12.00
T700 Toray ($/lb)	$13.00	15.9%	6.9%	0.8%
	$15.00	19.1%	11.2%	6.0%
	$20.00	24.3%	18.3%	14.4%

- Cost savings of a graded tank are between 0.8% to 30.6% depending upon composition and fiber cost
- Largest cost savings occur relative to the production cost of the fiber
- Second largest cost savings occur relative to increasing fiber material properties, i.e., larger volume of low cost fibers can be utilized

Remaining Challenges and Barriers

- **Obtain suitable low cost carbon fiber from ORNL**
  - **Alternative precursors and tow splitting options under consideration**
- **Identification and procurement of suitable liner for fabrication of demonstration tanks**
- **Fabrication and demonstration of graded structure tank**

Proposed Future Work

- **Work with ORNL to evaluate low cost fiber candidates**
- **Optimize sizing with Adherent Technologies, Inc.**
  - **Sizing trials will be reduced to help bring program back on schedule**
  - **Down-select and produce sufficient quantity of sized fiber for remaining mechanical testing and tank fabrication**
- **Continue to evaluate commercial lower cost fiber as needed**
  - **Intended as an alternative to ORNL fiber**
- **Identify and procure liner for Type IV cylinder**
- **Manufacture and burst test control (Toray T700) and graded cylinders**

Technology Transfer Activities

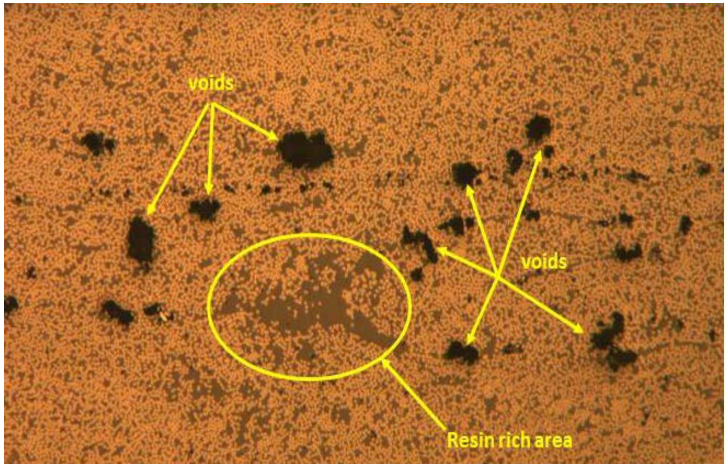
- **Patent application submitted**

Project Summary

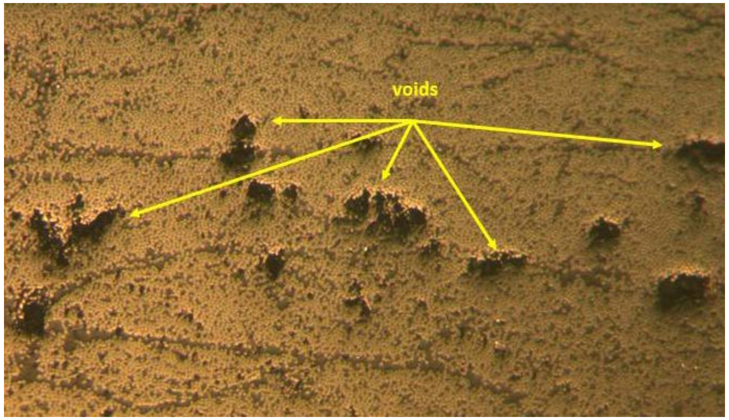
Relevance	Decrease overall cost of on-board hydrogen storage for fuel cell powered vehicles
Approach	Type IV hydrogen storage tank based on graded composite structure incorporating low cost carbon fibers
Technical Accomplishments & Progress	Coupon testing has demonstrated improved fiber property translation for a commercial lower cost fiber, preliminary graded structure using Panex® 35 modeled; initial sizing trials with ORNL low cost fiber identified issues to be addressed; detailed cost analysis started – preliminary results show potential for significant cost savings
Technology Transfer/ Collaborations	Active collaborations with ORNL (low cost carbon fiber) and Adherent Technologies (specialty sizing)
Proposed Future Research	Further evaluation of ORNL low cost fiber; demonstrate a lower cost Type IV pressure vessel using graded composite construction (either ORNL or commercial option); build and test Type IV tanks

Technical Backup Slides

Technical Backup – Fiber Distribution/Void Content with Commercial Fibers



Sigrafil® C30 Composite



Panex® 35 Composite

- **Both composites show some voids**
- **Fiber consolidation appears lower for Sigrafil® case**
- **Larger fraction of resin-rich areas in all Sigrafil® specimens**
- **Differences in handling characteristics**
  - **Panex® 35**
    - **unspools as rope**
    - **easy to spread and wet**
  - **Sigrafil® C30**
    - **unspools as ribbon**
    - **sizing feels smoother, somewhat more difficult to spread**
    - **false twists**