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 8, 2016

Project ID # ST110

Overview

Timeline

- Project Start Date:
  - Phase I: Feb 2013
  - Phase II: May 15, 2014
- Project End Date: May 2016
- Percent Complete: 94% (Phase I, 90% 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

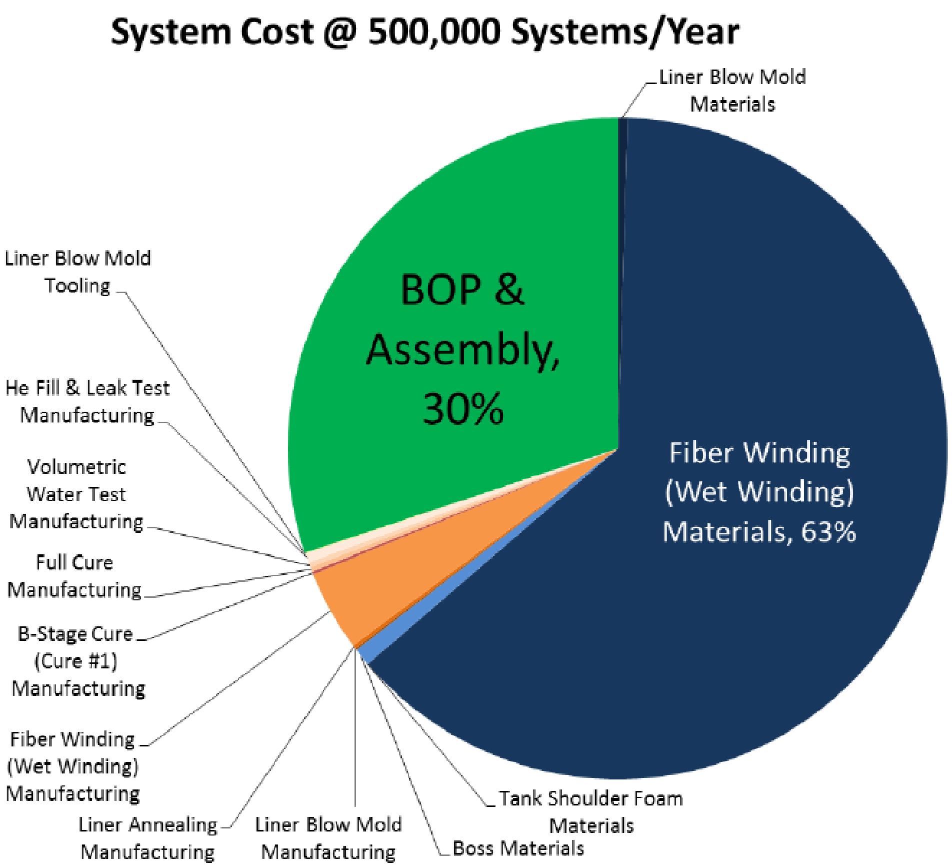
Relevance

- **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

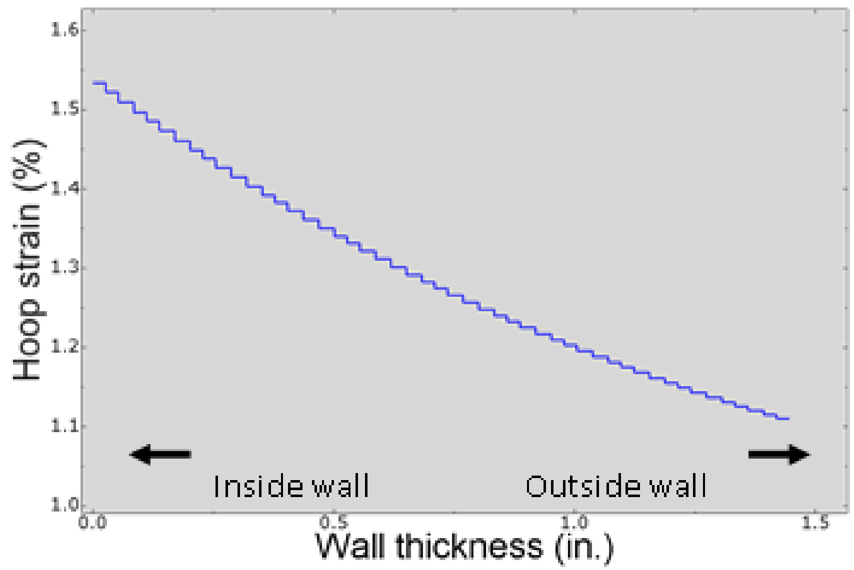


Reducing quantity and cost of carbon fiber represents an excellent opportunity to reduce Type IV tank cost while maintaining performance properties

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**

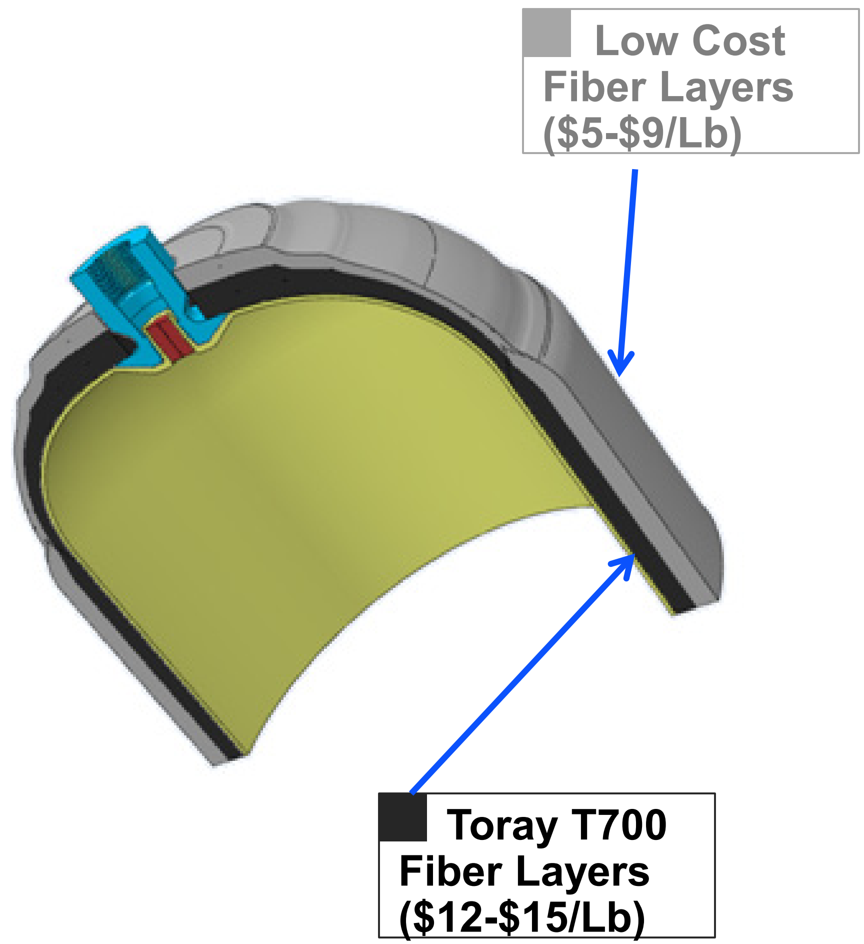


- **Thick composite performance also depends on**
  - **Damage due to microcracking and delamination during pressurization as well as fatigue cycling**
  - **Understanding and incorporation of progressive failure mechanisms is essential to optimize design**

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**

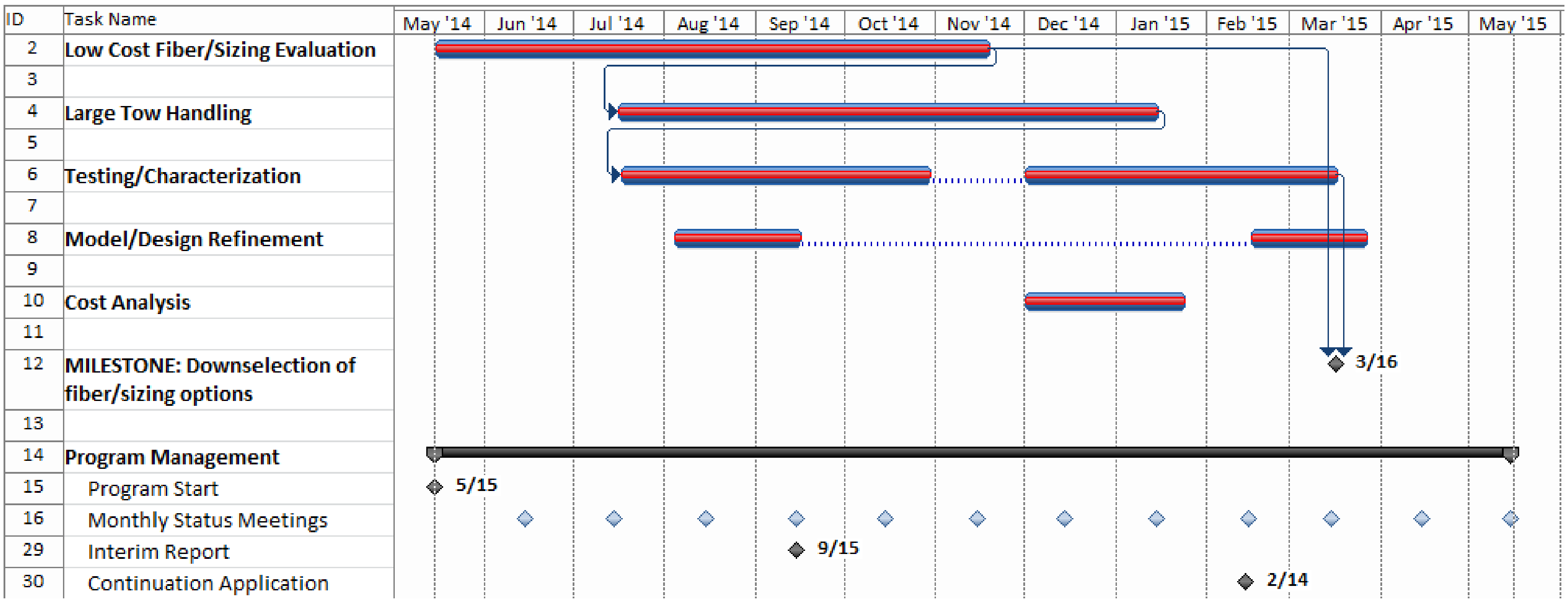
Provide highly efficient composite with excellent fiber translation at a minimal cost due to grading with low cost fibers through tank thickness

Approach – Phase II Goals (cont'd)

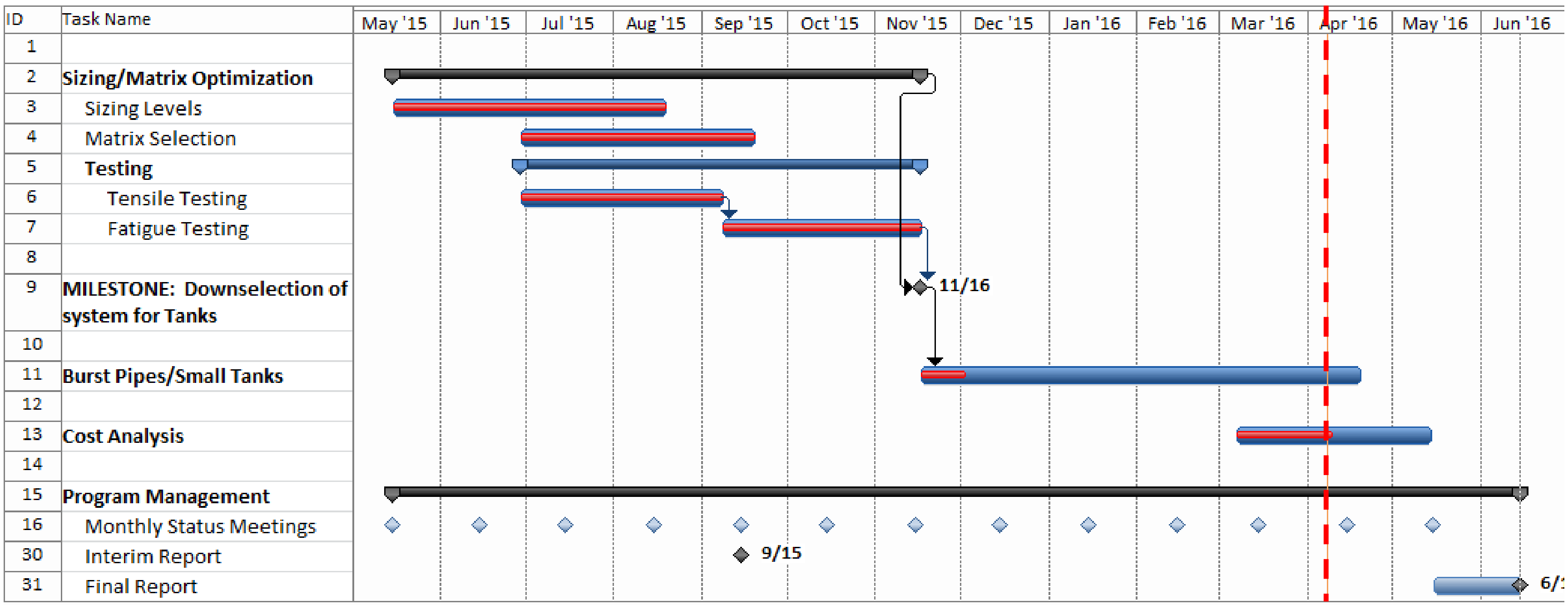
- Optimize structure for highest content of low cost fiber
  - Based on experimental data obtained from unidirectional composites
- Comprehensive cost analysis
  - Material components
    - Primarily carbon fiber cost
    - Wet winding will be standard
    - Towpreg might still be considered as an option 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



Approach – Phase II Schedule, Year 2



- **Currently slightly behind schedule – see Slide 21**
- **No-cost extension (8 weeks) has been requested**

Collaborations

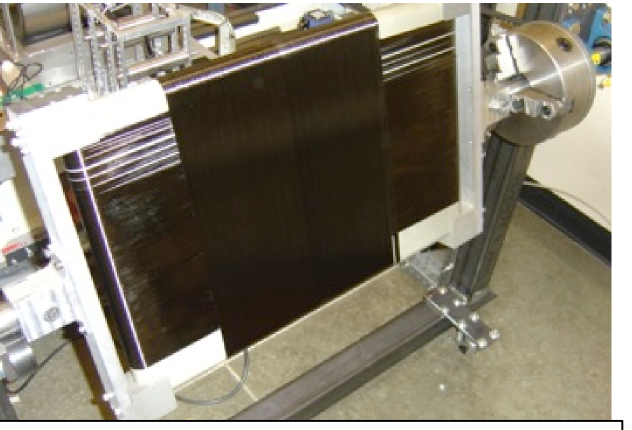
- **CTD**
  - **Material trials – includes sizing, tow handling, etc.**
  - **Product design**
  - **Commercialization**
- **Oak Ridge National Laboratory (ORNL)**
  - **Provide non-commercial low-cost carbon fiber for evaluation**
- **Adherent Technologies, Inc.**
  - **Specialty fiber sizing**

Approach – Phase II Baseline Materials

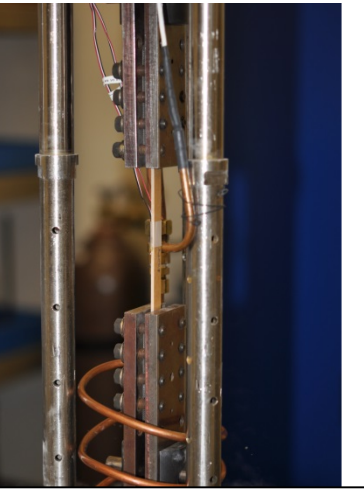
Material	Description	Comments
Toray T700	Commercial carbon fiber	• Currently used in Type IV tank construction • \$12-15/lb
ORNL Low Cost Carbon Fiber	Non-commercial carbon fiber	• Alternate feedstocks for low cost carbon fiber production • Target price point \$5-\$9/lb
Panex® 35	Commercial lower cost 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**
  - Data to verify/refine design models
  - 0°, 90° Tensile (ASTM D3039)
  - In-plane shear (± 45°) ASTM D3518
- **Fatigue**
  - Simulate fill and drain cycles

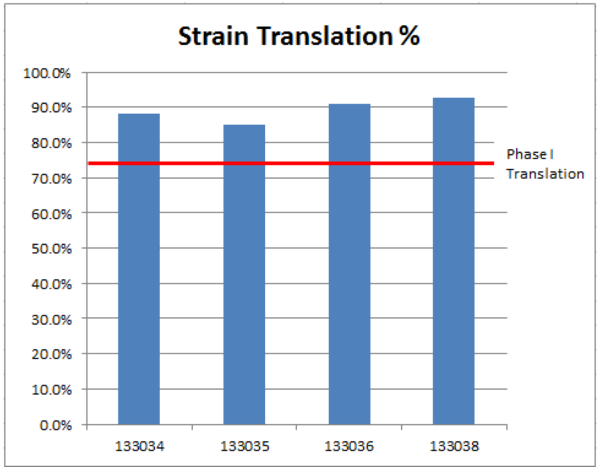


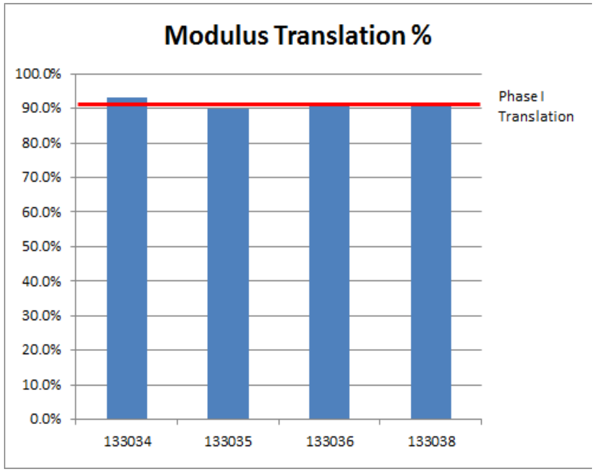
Uni and Cross Ply Panel Winding

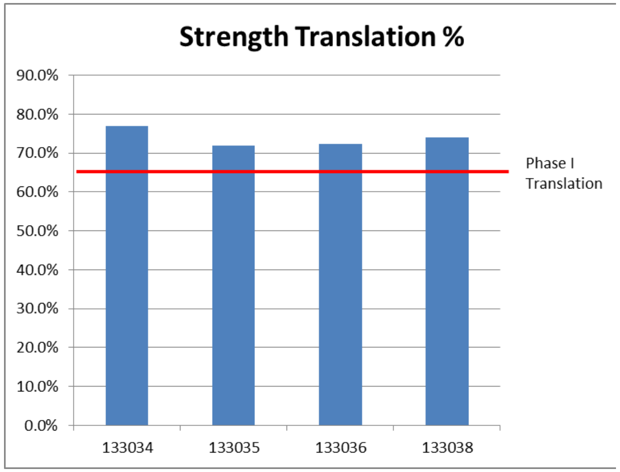


D3039 Tensile

Accomplishments – Fiber Property Translation – Panex® 35





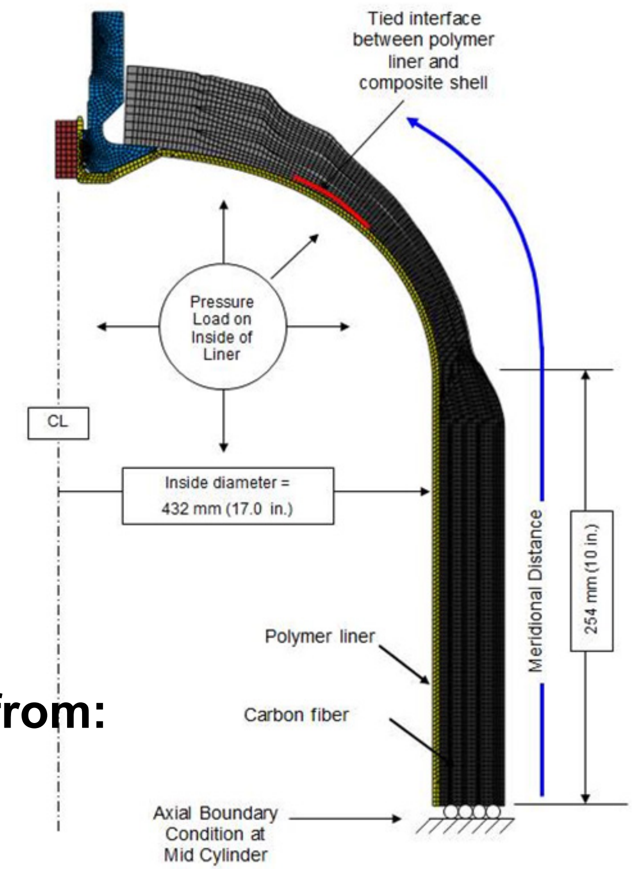


	Phase I	Phase II
Strain	78%	89.2%
Strength	65%	73.8%
Modulus	91%	91.5%

- **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 & 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

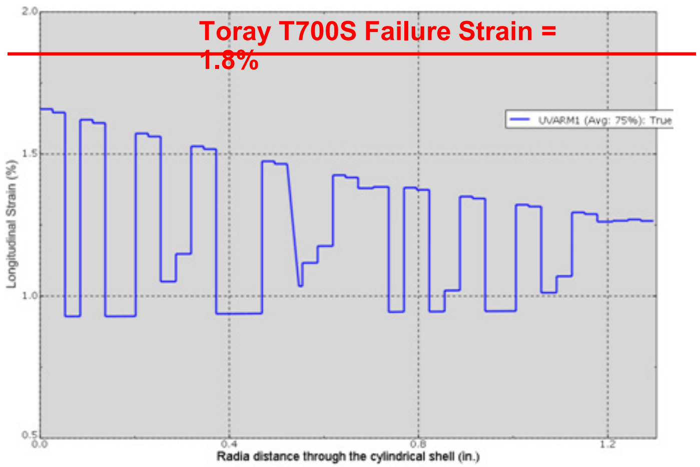


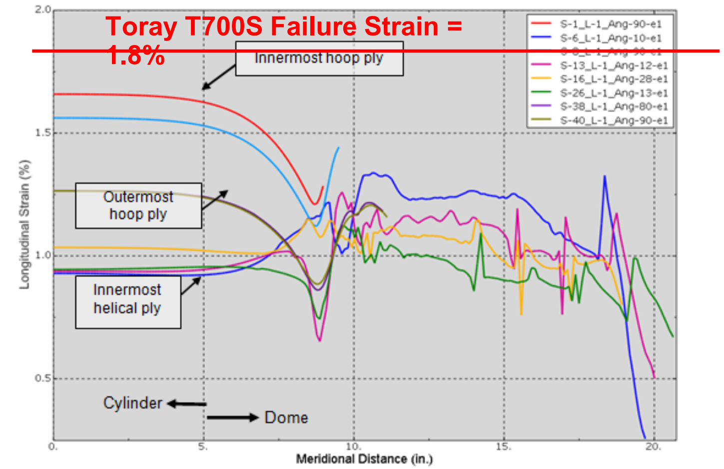
Accomplishments & Progress – Solution for Toray T700 Case

- **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

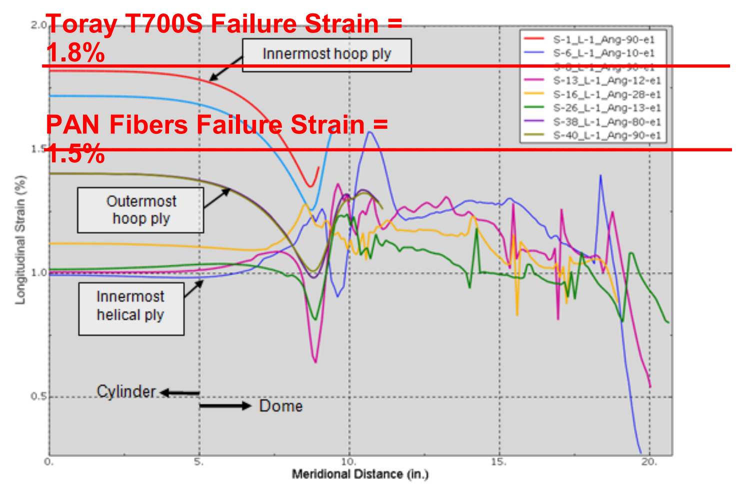
Design Input		
Burst Pressure	bar (psi)	**1645 (23,852)**
Ultimate Fiber Stress	GPa (ksi)	**4.9 (711)**
Average Helical Angle		**10º**
Helical : Hoop Stress Ratio		**0.6**
Computed Parameters		
Number of Hoop Layers		**59**
Number of Helical Layers		**27**
Total Hoop Thickness	mm (in.)	**19.0 (0.75)**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



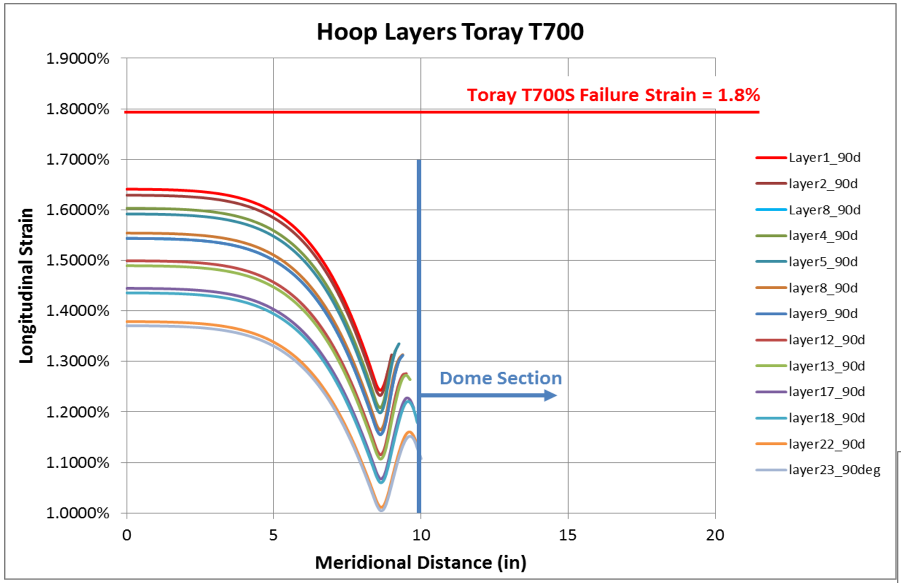
Property	Textile PAN fiber composite
Fiber volume fraction %	60
Longitudinal Elastic Modulus, E_1 GPa (Msi)	103.45 (15.0)
Transverse Elastic Modulus, E_2 GPa (Msi)	8.96 (1.3)
Poisson Ratio, ν_{12}	0.28
Shear Modulus, G_{12} GPa (Msi)	3.45 (0.5)
Longitudinal Failure Strain	1.5%

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**

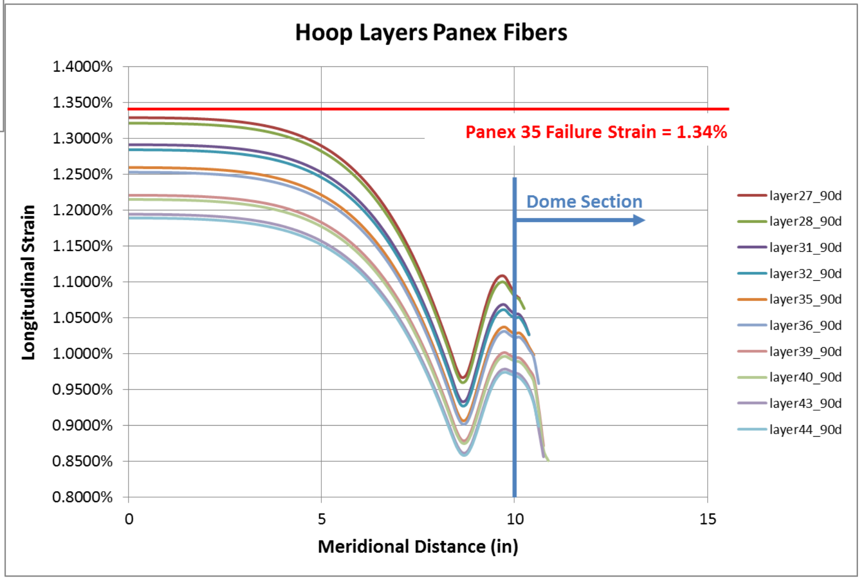
Property	T700S Composite	Panex® 35 Composite
Bandwidth (in)	1.69	1.69
Hoop thickness (in)	0.027	0.027
Helical thickness (in)	0.0164	0.0164
Longitudinal Elastic Modulus, E_1 (Msi)	18.5	19.05
Transverse Elastic Modulus, E_2 (Msi)	1.3	1.01
Poisson Ratio, ν_{12}	.28	.28
Shear Modulus, G_{12} (Msi)	0.5	0.5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

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%**



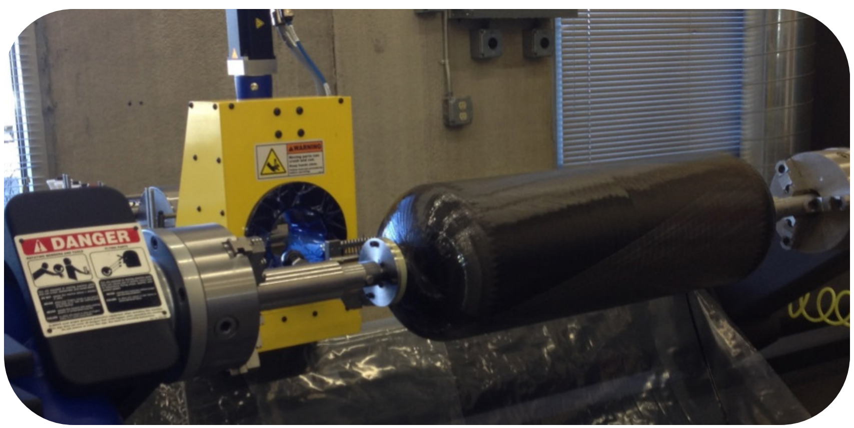
Fatigue Testing

- **Fatigue stresses exceeded expected operating pressure**
- **Most specimens survived 30,000 cycles**
  - **~5000 cycles would resemble weekly refueling for 10 years**
- **Tensile after fatigue showed excellent retention of properties**

Specimen #	Cycles Completed	Material	Max Stress after Fatigue (ksi)	% of Avg Tensile Strength	% Over OP
133142-7	30000	Panex 35	137.60	101.6%	30.0%
133142-8	30000	Panex 35	137.60	101.9%	30.0%
133142-9	30000	Panex 35	172.60	84.3%	63.0%
133142-10	30000	Panex 35	172.60	92.2%	63.0%
133144-7	30000	T700 & Panex 35	108.9	91.3%	2.0%
133144-8	30000	T700 & Panex 35	98.9	99.4%	-7.0%
133144-9	30000	T700 & Panex 35	133.4	83.0%	28.0%
133144-14	30000	T700 & Panex 35	99.5	101.0%	18.0%
133144-15	30000	T700 & Panex 35	116.0	88.5%	12.0%
133144-16	30000	T700 & Panex 35	118.3	100.8%	11.0%
133144-17	30000	T700 & Panex 35	97.8	95.2%	-8.0%
133146-7	30001	T700 & Panex 35	127.7	88.3%	23.0%
133146-10	30000	T700 & Panex 35	147.3	91.3%	15.0%
133149-1	30000	Panex 35 (0/90)	134.1	109.8%	63.0%
133149-2	30000	Panex 35 (0/90)	126.0	103.2%	63.0%
133150-1	30000	T700 (0/90)	209.7	99.9%	63.0%
133150-2	30000	T700 (0/90)	177.1	84.3%	63.0%

Subscale Tank Development

- **HDPE liners being fabricated**
  - **Some delays in fabrication**
  - **Expect delivery mid to late April**
- **Winding pattern development underway**
  - **T700 baseline**
  - **T700 and Panex® 35 fiber graded structure**

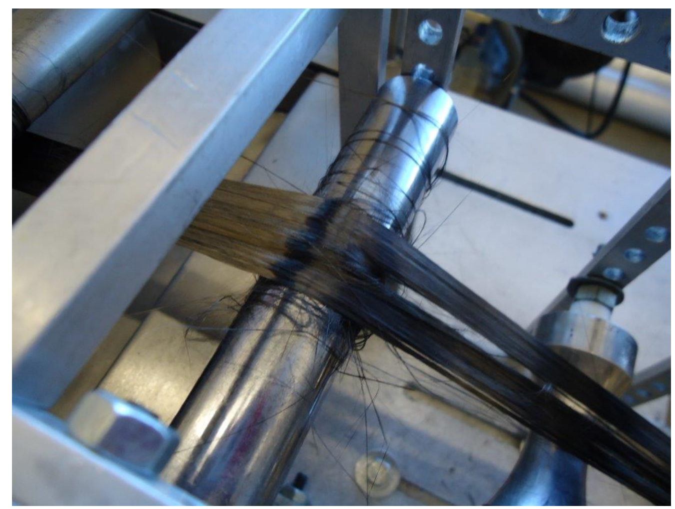


Accomplishments – Low Cost Fiber

From 2015 AMR

- **Received low cost fiber from ORNL**
  - **Textile precursor received as 200k tow, split during processing to yield ~50k tow size**
- **Significant fuzzing of fiber during sizing**
- **Significant tow breakage**
  - **Could not apply tension for filament winding**

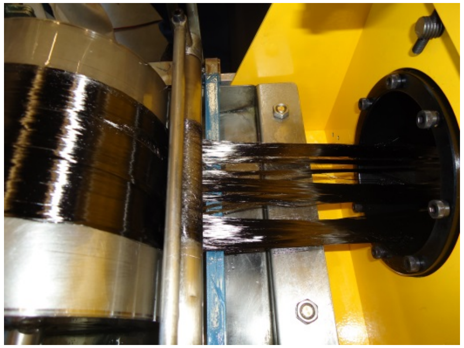
Not suitable for winding



Accomplishments – Low Cost Fiber

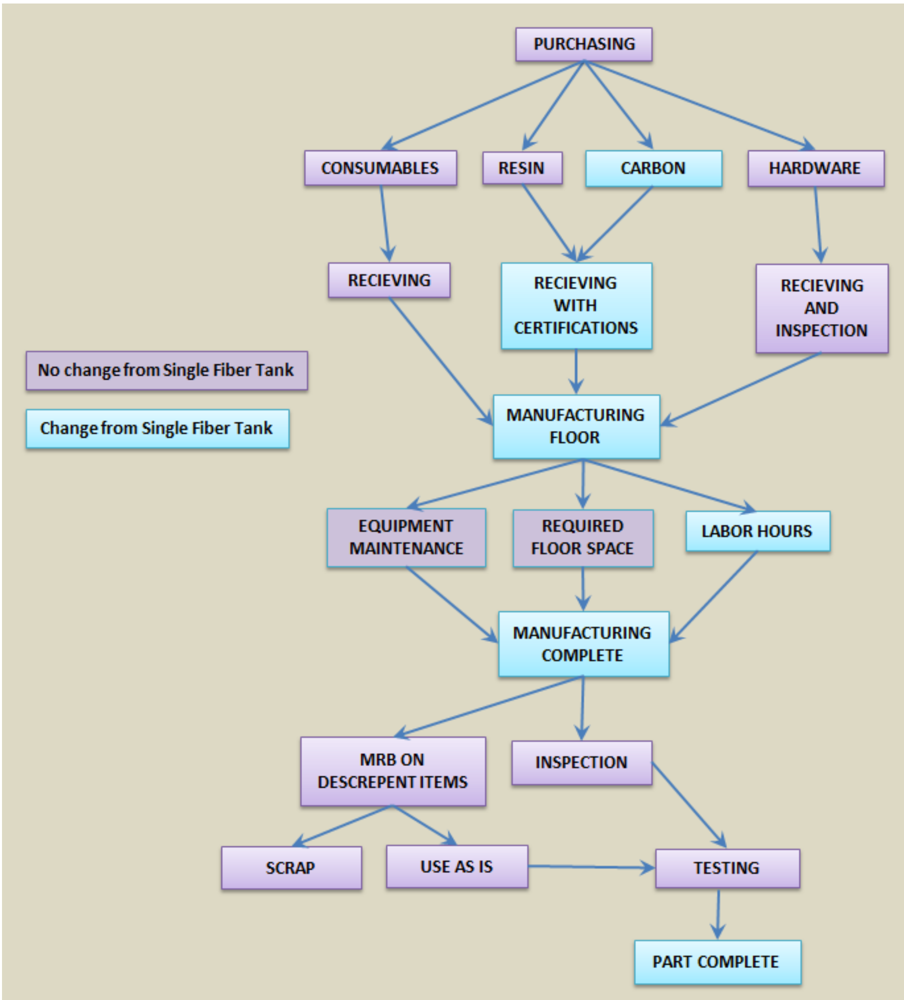
- Kaltex 450K tow supplied by ORNL
  - Significantly better handling
  - 475 ksi strength, 33Msi modulus, and 1.44% strain
- Successfully produced panels for evaluation
  - Still significant fuzzing
  - Difficult to process
  - Fiber volume fraction 54-62%

Avg Tensile Strength (ksi)	Avg Modulus (Msi)	Strain (%)
125.7	17.0	0.76



Composite properties not good enough for tank application
Wide format not suitable for tanks

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 – Updated Cost Analysis

T700 Price Range = $13 - $20
Low Cost Fiber Price Range = $6 - $10

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

50% T700 Toray/50% Low Cost Fiber				
		Low Cost Fiber ($/lb)		
		$6.00	$ 8.00	$10.00
T700 Toray ($/lb)	$13.00	24.2%	16.6%	9.1%
	$15.00	27.5%	21.0%	14.5%
	$20.00	33.1%	28.2%	23.2%

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)		
		$ 6.00	$ 8.00	$10.00
T700 Toray ($/lb)	$13.00	18.9%	12.9%	6.9%
	$15.00	21.7%	16.5%	11.2%
	$20.00	26.2%	22.3%	18.3%

- Models are based on fiber purchase price
- Cost model revised to narrow in on purchase price of Panex® 35 fiber ($8.75/lb at the scale we purchased)
- Cost savings of a graded tank are between 6.9% to 33.1% depending upon composition and fiber cost

Remaining Challenges and Barriers

- Suitable low cost (textile-based) carbon fiber remains an issue
  - Processability
  - Minimum required properties – especially strain to failure
  - Property translation

Commercial low cost fibers such as Panex® 35 are a reasonable alternative, offer some cost benefit

- Fabrication and demonstration of graded structure tank
  - Liner delivery expected mid to late April 2016
  - Winding pattern development in process
  - Tank fabrication & burst testing to be complete by mid July 2016

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	• Tested coupons in fatigue at stresses exceeding expected operating pressures – achieved over 30,000 cycles with little property degradation. • Evaluated large format low cost tow from ORNL – processability remains problematic and properties not sufficient for tank applications. • Liner fabrication and winding pattern development underway for subscale prototype production.
Technology Transfer/ Collaborations	• Active collaboration with ORNL (low cost carbon fiber)
Remaining Work	• Fabrication & burst testing of subscale graded structure prototypes • Refinement of cost models using projected costs for textile-based fiber supplied by ORNL