

2009 DOE Hydrogen Program

Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

Carter Liu, PhD Quantum Fuel Systems Technologies Worldwide Inc.

Brice A. Johnson The Boeing Company

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Overview

Timeline

- Project start date 09/2008
- Project end date: 09/2011
- Percent complete: 9%

Budget

- Total Budget: \$5,486,848
- DOE Share: \$2,566,451
- QT/Boeing Share: \$1,920,397
- FFRDC Share: \$1,000,000
- FY08 Funding: \$475,845
- Funding for FY09: \$350,000





Barriers

- Material system costs
- Manufacturing processes

Partners

- Quantum Technologies, Inc.
- The Boeing Company (Boeing)
- Pacific Northwest National Laboratory (PNNL)
- Lawrence Livermore National Laboratory (LLNL)





Project Objectives- Relevance

To manufacture Type IV H₂ storage pressure vessels, utilizing a new hybrid process with the following features:

- Optimal elements of flexible fiber placement & commercial filament winding
- Reduced production cycle times by adaptations of highspeed "dry winding" methodology

With the aim of achieving:

A manufacturing process with lower composite material usage, cost & higher efficiency









Milestones

Time	Milestone	
09/08-04/09	Program Kick-off Material development investigation; 35% complete Composite design literature review & optimum liner dome profile; 100% complete Fiber placement delivery head modification; 25% complete Initial cost model; input/output & approach; 100% complete	
05/09	Merit Review	
05/09-10/09	Manufacture & test best effort tank using hybrid process Baseline cost model Go/NoGo decision→ provide data that shows AFP & FW processes can manufacture a tank	
11/09-04/10	Dry tape technology evaluation	
05/10	Merit Review	
06/10-10/10	Manufacturing process development; manufacture & test best effort tank Revised cost model Go/NoGo decision→ demonstrate process can reduce material usage and cost	
11/10-04/11	Hybrid manufacturing technology refinement	
05/11	Merit Review	
06/11-10/11	Produce hybrid manufacturing technology tanks; test per EIHP Final cost model	









Approach: AFP Material Study

- Different material requirements: AFP vs. FW
- Approach
 - Cure profile compatibility: DSC (differential scanning calorimetry); Rheological measurement
 - Interface communication for efficient translation¹
 - Compatibility for delamination resistance: interlaminar shear strength, mode I and II interlaminar fracture toughness & tensile fatigue

¹ translation= reinforcing efficiency of carbon fibers









Accomplishment: Liner Dome Profile Investigation

• Reasons:

- The stress distribution along fiber tow path is strongly affected by the 2 principal radii of curvature
- Appropriate dome profile is desired for AFP process and filament winding process
- Weight, volume and cost efficiency
- 4.5 inch 4 Axial Distance, 3.5 3 - Optimum Dome Shape 2.5 2 FWD 1.5 ▲ AFD 1 0.5 0 0.000 1.000 2.000 3.000 4.000 5.000 6.000 7.000 Polar Radius, inch

Deviations due to plastic

 Iso-tensoid dome is designed according to material properties and compared to measurements after molding







molding process

shrinkage

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Improvement in dome design and

Accomplishment: Filament Winding -Quantum



 Conventional technique: Resin impregnated tow / roving wound over the mandrel / liner

- High repeatability
- High automation & low labor cost
- High accuracy
- Relatively fast process









Accomplishment: Filament Winding -Quantum



Quantum's Analytical and FEA study:

- Optimal design = balance between low angle helicals (closer to boss edge, 0~10°) for axial stress + high angle helicals (11~90°) for radial stress
- The balance depends on the surface principal radii of curvature: Cylinder vs. Dome

Limitations on fiber path and orientation & continuous process nature fibers are placed in the cylinder region in order to reinforce the dome









Accomplishment: Fiber Placement is Scalable for High Pressure Storage Needs - Boeing

- Fiber placement, a CNC process adds or cuts multiple strips of composite material on demand.
 - Allows maximum weight efficiency
 - Only places material where it is needed
 - Steering of fiber allows greater design flexibility



- Existing machines don't meet the DOE's objectives
- Process is scalable to smaller parts
- Software available for smaller machines











Overall Concept- Boeing

- Use fiber placement for optimization:
 - Build up plies on the dome sections with minimal limitation on fiber angle
 - Reinforcement of dome without adding weight to cylinder
- Develop method for integration between filament winding and fiber placement
 - Options include:
 - In the same cell
 - In parallel cells
 - Off line fiber placement of reinforcement details









Automatic Fiber Placement Status

- Investigating compatible low temp cure materials between filament winding and fiber placement
- Identified equipment and delivery head to be set up for testing
- Establishing lab capabilities to adapt fiber placement heads to low cost automation systems
- Integrating Boeing designed delivery heads onto these systems
- Preparing for initial layup tests on the dome structure









Fiber Placement Processing Cell Flow



Future Work: Strategies for Program Goals

- Investigate fiber placement on dome structures using new, right sized, equipment
- Investigate material forms compatibility between filament winding and fiber placement
- Optimize tank structure taking advantage of fiber placement capabilities
- Hybridize with filament winding to leverage process productivity
- Fabricate delivery heads optimized for tank design and adapt to low cost automation platforms











Future Work: Head Design Issues

- The fiber placement process usefulness increases the closer the head can reach the center of the dome
- Heads must be designed to minimize clearance with the boss
- Programming focused on geodesic paths for minimal shear loading of composite











Cost Model Development- PNNL

- <u>Purpose</u>: Assess the cost sensitivities of advanced processing methods for manufacturing high pressure composite tanks.
- Significant Composite Tank Manufacturing Costs
 - Alternate Processes Filament winding (baseline), Automatic fiber placement, dry tape techniques, etc
 - Manufacturing time and cost factors: labor + equipment
 - Increased fiber translation = reduced composite weight
 - Material requirements for specific processes
 - Raw Material Cost: Resins, carbon fiber types, ties to alternate fiber placement methods
 - Related Hardware Cost: liner, fittings, bosses, etc
 - Labor rates: domestic or foreign
- Model Outputs = Alternate process tradeoffs for tank cost, weight, and manufacturing time









Cost Model Considerations

- Independent Variables
 - Production Rate [up to 500,000 units/year with 5% rejection rate]
 - Labor rate: domestic or foreign built
 - Winding and placement speeds
 - Raw Material Costs: resins, carbon fiber types, future fiber prices, alternative materials, game changers?
- Related hardware cost: liner, fittings, bosses, etc.
- Alternate Processes
 - Filament winding (baseline)
 - Direct fiber placement
 - Dry fiber placement + resin infusion
- Up-front costs
- Model Output
 - Cost for weight benefit (material trades)
 - Cost of production
 - Return on investment
 - Trade on alternative processes
 - Threshold for profitability
 - Material cost targets
 - Machine speed targets
- Risk Analysis
- Market Analysis
- Departure from existing baseline: choose an existing product and produce deltas for our proposed product









Hydrogen Compatibility Studies- PNNL

Motivation: Polymers are used as hydrogen permeation barriers in high pressure pipelines and vessels; hydrogen is well known to embrittle and blister metals. However, the effects on polymer materials is largely unknown. We are currently investigating these effects to determine the relevant parameters for degradation.

Stage 1: Amorphous polymers

- Variables: viscosity, depth, solubility, diffusion, pressure, temperature, decompression time; polystyrene is a model polymer that is extremely well characterized in the literature
- Preliminary results indicate that blistering does occur and is strongly dependent on viscosity/temperature
- Building thermal gradient stage to do combinatorial measurements of blistering with varying viscosity

Stage 2: Semi-crystalline polymers

- Majority of vessel/pipeline materials are semi-crystalline
- Build on results from amorphous polymers: amorphous vs. crystalline regions
- Variables now include degree of crystallinity & density
- Additionally, some specific materials selected by Quantum will be evaluated









Thermal Gradient Stage for *In-situ* Annealing in High-Pressure H₂: Combinatorial Measurements

Blistering in Polystyrene (amorphous) Preliminary measurements indicate strong viscosity dependence for micron sized blisters Size and density of blisters affected Thermal gradient allows continuous • 80 80 μm μm variation in viscosity (η) by varying T-T_a= 50 C temperature T-T_a= 80 C Allows combinatorial measurements cold Sample η Cold hot Cooling Heater T-7_g 18 Lawrence Livermore National Laboratory

Future Work: Iterations between Composite Optimization & AFP process improvement

- The relationship between fiber tow quantity and angle distribution in the cylinder region to balance the axial and radial stresses
- Fiber tow path in the dome region to homogenize the stress along fiber length
- Interlaminar stress consideration near free-edges
- Non-linear stress distribution across the composite shell thickness
- Limitations from automatic fiber placement process









Future Work: Tape Fabrication Process Proof of Feasibility- LLNL

- Novel and unproven process, with many similarities to wet winding, fiber placement, and thermoplastic matrix composite fabrication processes
 - File patent, pursue trade secret protection and licensing agreements
- Potential for process to be 100 times faster than conventional processes & economical even if 5 times faster
- Proof of Concept experiments are being executed
- Learn enough about far-term process invented at LLNL to determine if it will be worthwhile for team members to adopt











Project Future Work

- A best effort storage vessel will be manufactured using the hybrid process (combination of filament winding & fiber placement)
- Burst test and pressure cycle fatigue test will be performed on this tank
- Further iterations on composite design and AFP process improvements (manufacturing process development)
- Evaluate game-changing LLNL dry tape technology
- Cost model revisions to reflect latest manufacturing processes & large scale volume production









Project Summary

Relevance	Investigate hydrogen storage manufacturing processes to approach the DOE cost targets and high-volume production targets
Approach	AFP process material study; fiber needs to work in AFP & FW
	Composite design & optimization
	AFP process improvement
	Test whether LLNL process is worthwhile to
	incorporate
Proposed Work	Initial filament winding/fiber placement process to produce best effort tank
	LLNL process trials
	Prepare cost model







