

2009 DOE Hydrogen Program



Design of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels



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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**
- ▶ Industry – Quantum / Boeing
 - DOE Share: \$2,566,451
 - QT/Boeing Share: \$1,920,397
 - FY08 Funding: \$475,845
 - Funding for FY09: \$350,000
- ▶ PNNL: \$100K / \$200K / \$200K
- ▶ LLNL: \$200K / 150K / \$50K

Barriers

- ▶ Material system costs
- ▶ Manufacturing processes

Partners

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

Relevance - Project Objectives

Manufacture Type IV H₂ storage pressure vessels, using a new hybrid process with:

- Optimal elements of flexible fiber placement & commercial filament winding
- Reduced production cycle times by adaptations of high-speed “dry winding” methodology

To achieve:

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

Milestones

Time	Milestone
09/08-04/09	<ul style="list-style-type: none"> ▶ 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 ▶ Develop pressurized H₂ exposure testing and evaluation methods; 75% complete
05/09	Merit Review
05/09-10/09	<ul style="list-style-type: none"> ▶ 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



Milestones (continued)

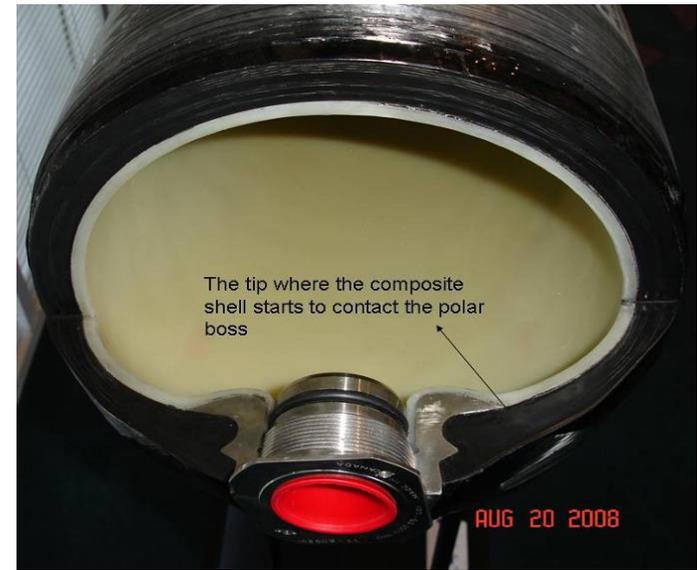
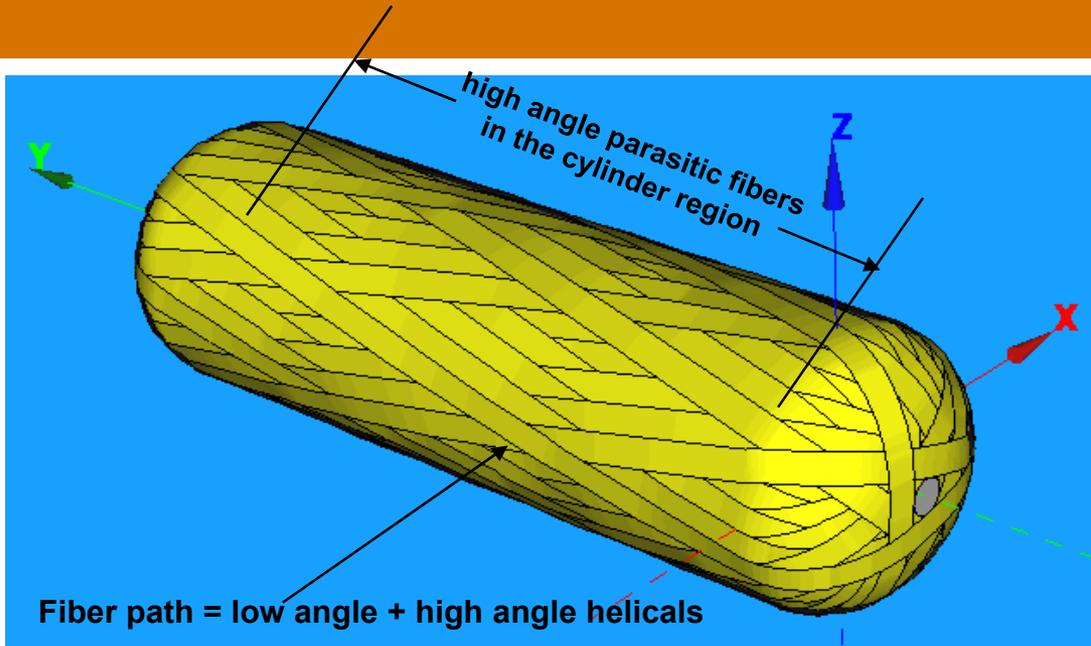
Time	Milestone
06/10-10/10	<ul style="list-style-type: none"> ▶ Manufacturing process development; manufacture & test best effort tank ▶ Revised cost model ▶ Revised H₂ exposure material test results ▶ Go/NoGo decision → demonstrate process can reduce material usage and cost
11/10-04/11	Hybrid manufacturing technology refinement
05/11	Merit Review
06/11-10/11	<ul style="list-style-type: none"> ▶ Produce hybrid manufacturing technology tanks; test per EIHP ▶ Final cost model ▶ Final H₂ exposure material test results

Approach: Develop Fiber Placement Methods to Reduce Cost and Weight of Filament Wound Tanks

- ▶ Develop a fabrication process to increase fiber translation¹, reduce fabrication cost, weight and time
- ▶ Assess hybrid / alternate fabrication methods:
 - Combine filament winding with Boeing automatic fiber placement method
 - LLNL concept for a high speed dry tape fabrication process
- ▶ Baseline: Current 70 MPa, 5 kg H₂, filament wound carbon fiber vessels (~80% fiber translation, hoop stress variation of thick walled pressure vessel)
- ▶ **PNNL Tasks:**
 1. Develop a manufacturing cost model including materials + labor + equipment costs, weight savings, and fabrication time estimates
 2. Pressurized hydrogen exposure testing of composite tank materials

¹ translation= reinforcing efficiency of carbon fibers

Approach: Filament Wound Tanks - Quantum



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

Advantages: High repeatability, High automation & low labor cost, High accuracy, relatively fast process.

Limitations: The achievable fiber path and orientation of this continuous process results in many parasitic fibers placed in the cylinder region to achieve sufficient dome reinforcement.

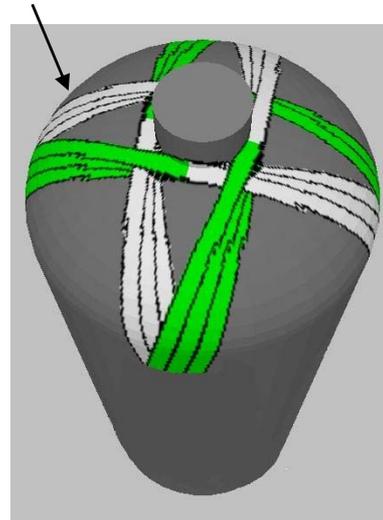
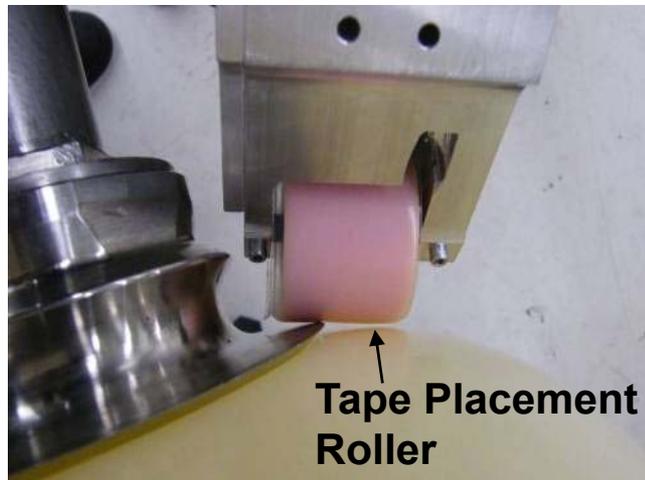
Approach: Automatic Fiber Placement - Boeing

▶ **Automatic Fiber Placement:** A CNC process that adds multiple strips of composite material on demand.

- Maximum weight efficiency - places material where needed
- Fiber steering allows greater design flexibility
- Process is scalable to hydrogen storage tanks
- Optimize plies on the dome sections with minimal limitation on fiber angle
- Reinforce dome without adding weight to cylinder

▶ Integration of filament winding and automatic fiber placement

- In the same cell
- In parallel cells
- Off line fiber placement of reinforcement details



Technical Progress: Cost Factors Identified

- ▶ 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: engineering, factory, capital equipment, product certification/qualification

Technical Progress: Cost Factors Identified

- ▶ 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

Technical Progress: Cost Model Development

- ▶ Purpose: 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, specific materials for 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

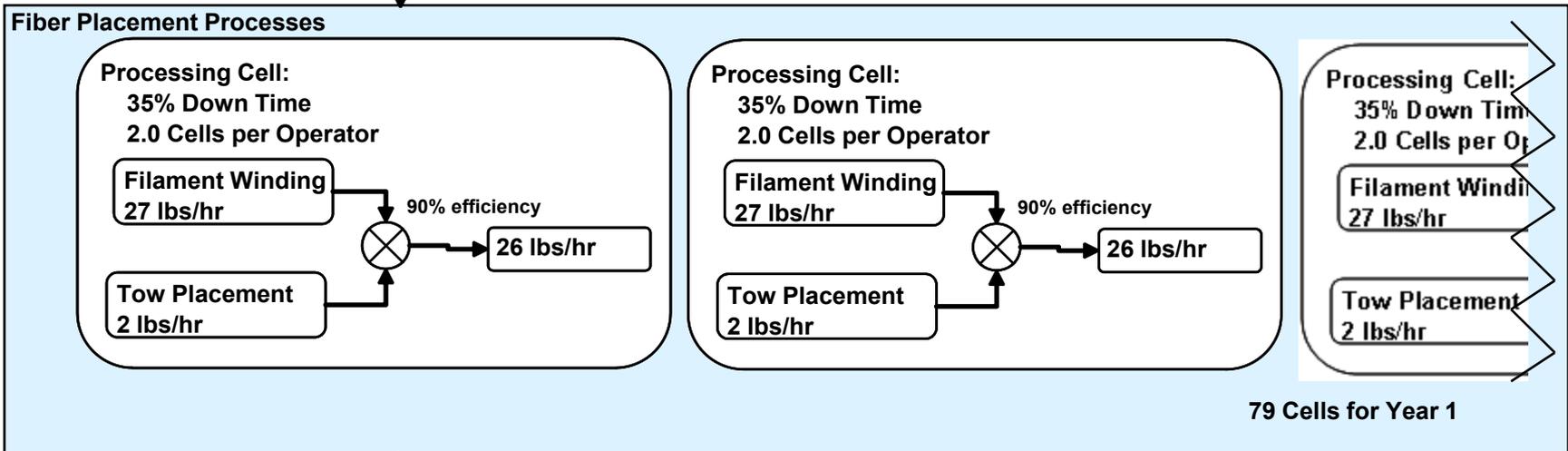
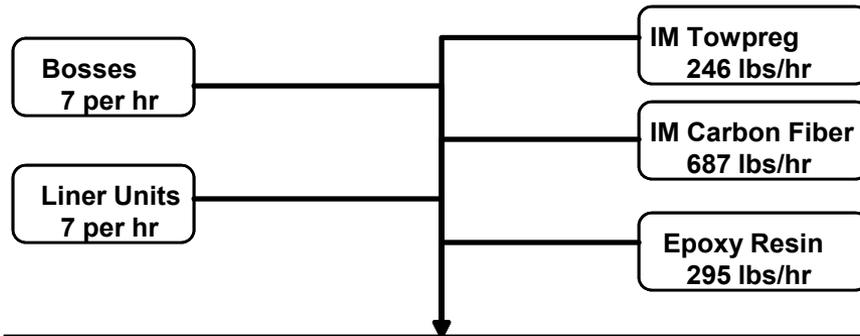
Technical Progress: Baseline Material and Fabrication Cost - Filament Wound Tank

Assumptions				
Production volume	500,000	DOE requirement		
Direct Labor rate	\$25	US Department of Labor Statistics		
Labor Overhead	110%			
Material Overhead	20%			
G&A	10%			
Labor hours per tank	9	hours		
Carbon fiber mass	155	lbs		
Carbon fiber cost	\$15	per pound		
Baseline cost				
Metal fitting cost	\$476	Estimate @ 500K parts	\$3,595	Total material cost
Carbon fiber cost	\$2,325			
Resin cost	\$180			
Bulk material	\$10			
Misc soft goods	\$5			
Indirect material cost	\$599			
Direct labor cost	\$225	9 x \$25	\$473	Total labor cost
Indirect labor cost	\$248	1.1 x \$225		
G&A cost	\$407	0.1 x (\$3,595+ \$473)		
Total cost=	\$4,474			

Technical Progress: Conceptual Fiber Placement Process Cell

Assumptions

- 500,000 units per year production rate
- Escalating ramp to full production in 10-years
- 13,000 year one production rate
- 186 lb composite weight per unit
- Includes a 6% scrap factor
- Hybrid Fiber Placement Cell
- Automatic Fiber Placement – 20% by Weight
- Filament Winding – 80% by Weight



Hydrogen Materials Compatibility Studies

Motivation: Polymers are used as permeation barriers for high pressure hydrogen. It is well known that Hydrogen degrades and embrittles metals. Relatively little is known about the effects of Hydrogen on Polymers.

Preliminary work

- Hydrogen exposure & decompression on amorphous polymers
- Preliminary results indicate that blistering does occur and is strongly dependent on viscosity/temperature
- Goal is to link blistering to: viscosity, depth, solubility, diffusion, pressure, temperature, decompression time

Current & Future work

- Combinatorial approach to viscosity effect with thermal gradient stage
- Crystalline polymers

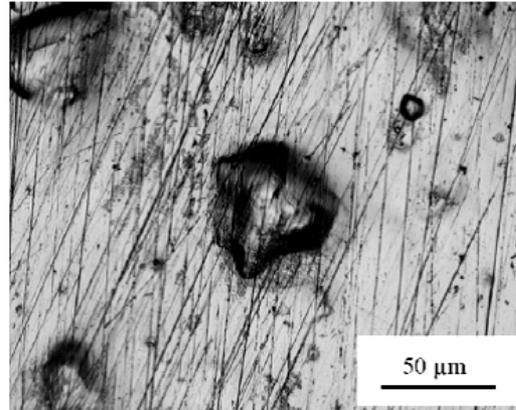
High-Pressure Hydrogen Charging

- ▶ High Pressure Autoclave to simulate H-ICE environment.
- ▶ 100 % Hydrogen
- ▶ Up to 5,000 psi max Hydrogen pressure
- ▶ Up to 200 C temperature
- ▶ *In-situ* thermal gradient stage (under development)

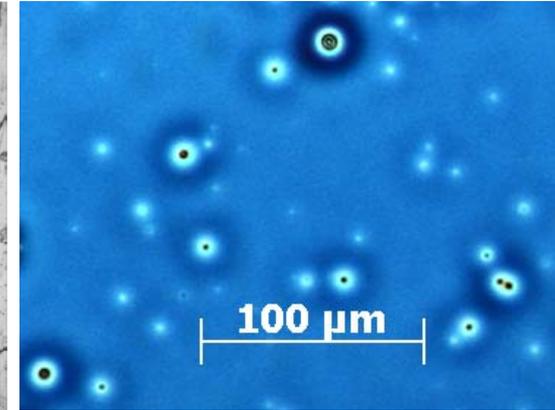


Hydrogen Induced Polymer Blistering

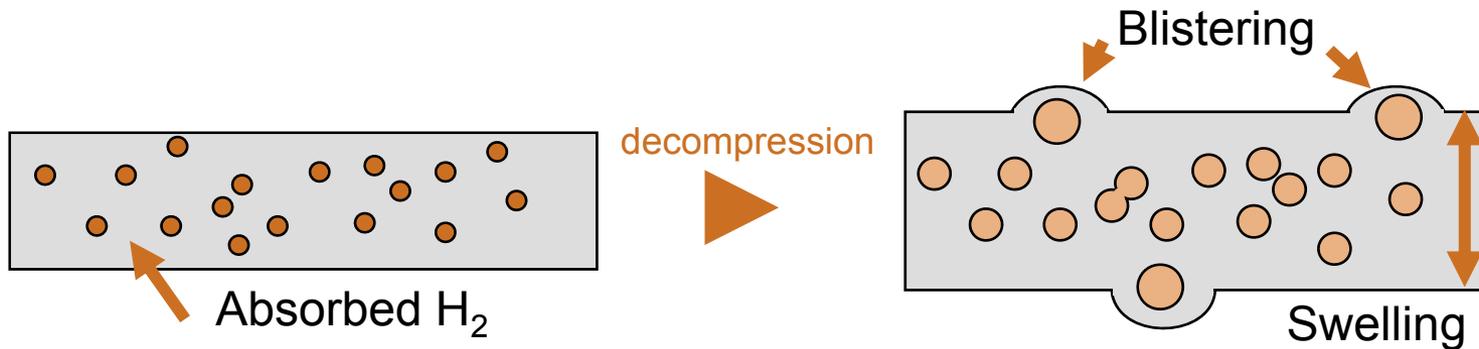
- ▶ Relatively high solubility of H_2 in polymers may lead to mechanical degradation or failure upon decompression.¹
- ▶ Hydrogen swelling and blistering common in metals.
- ▶ Blistering has been evidenced in polyamide films under ion irradiation.²



H_2 Blistering in a Fe surface³



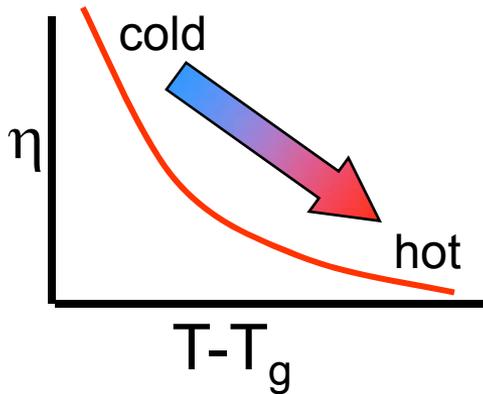
H_2 Blistering in Polystyrene



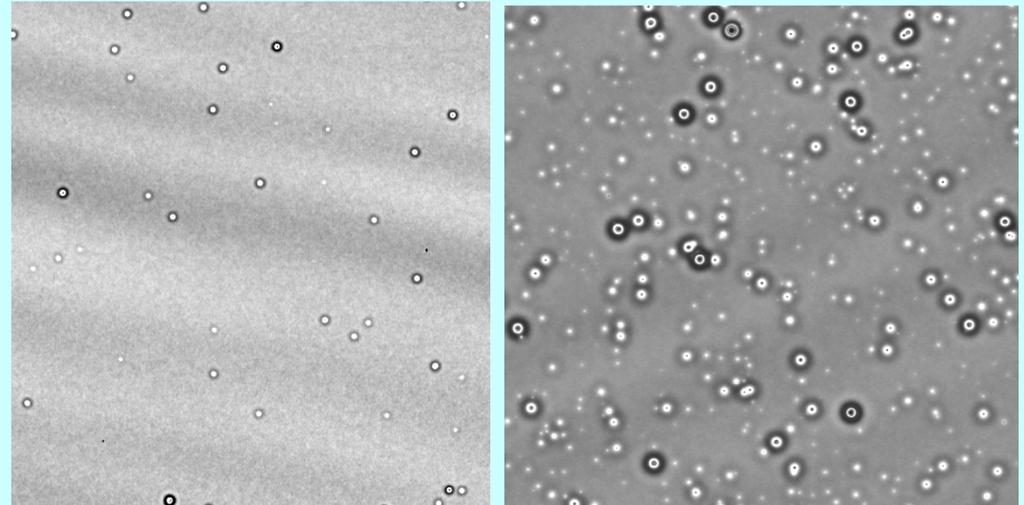
- C. S. Marchi *et al*, Sandia National Lab Technical Report (SAND2008-1163), 2008
- W. E. Wallace *et al* Nuc. Inst. & Methods in Phys. Res. B **103**, 435 (1995)
- Ren *et al*, Mater. Chem. Phys. **107**, 231, (2008)

Temperature Effects on Blistering in High-Pressure H₂

- Strong Viscosity Dependence
 - Blister Size & Density
- *In-Situ* thermal gradient stage allows combinatorial measurements of viscosity(η)

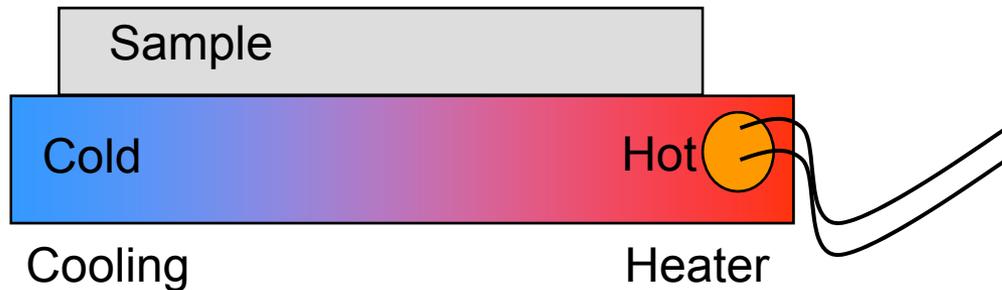


Viscosity/Temperature Dependence

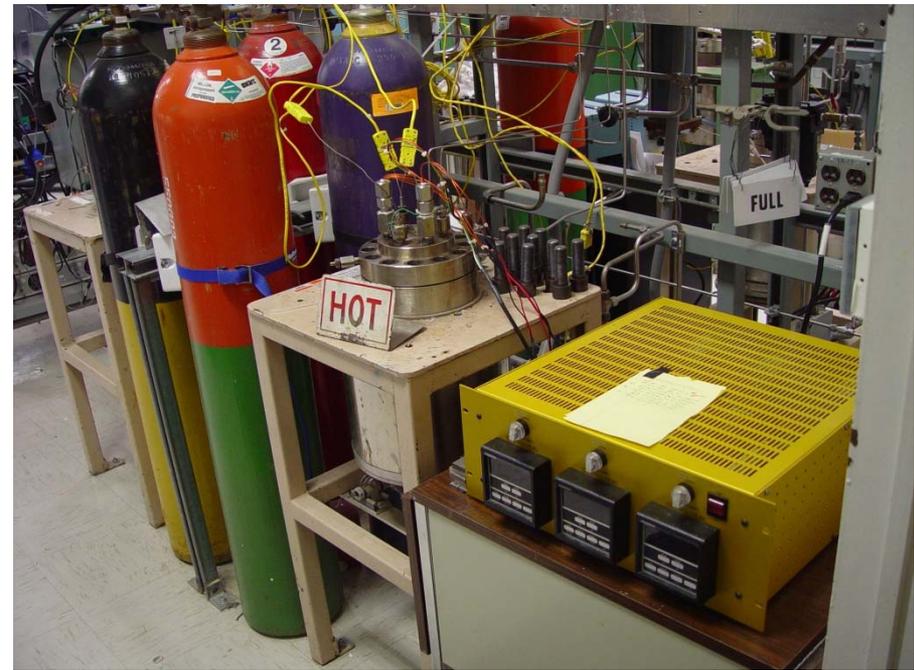
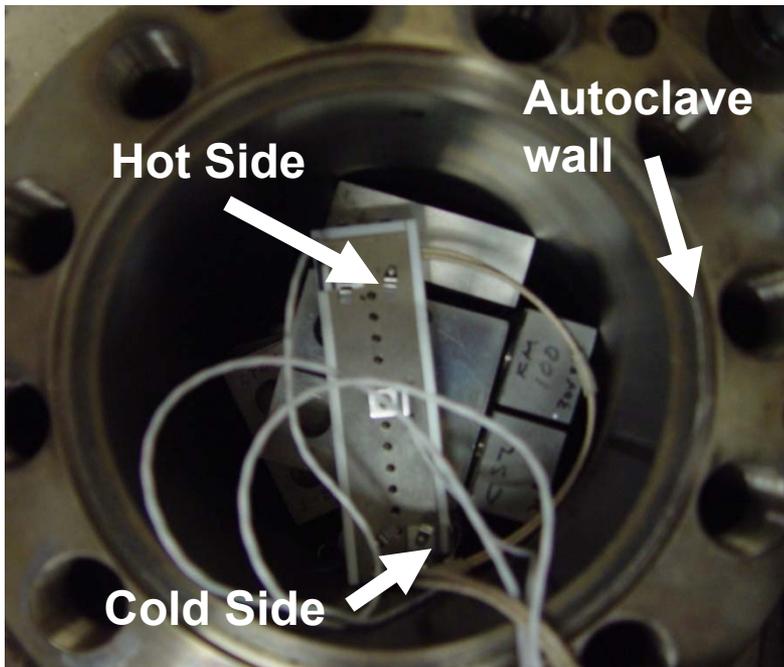


$T-T_g = 50$ C

$T-T_g = 80$ C



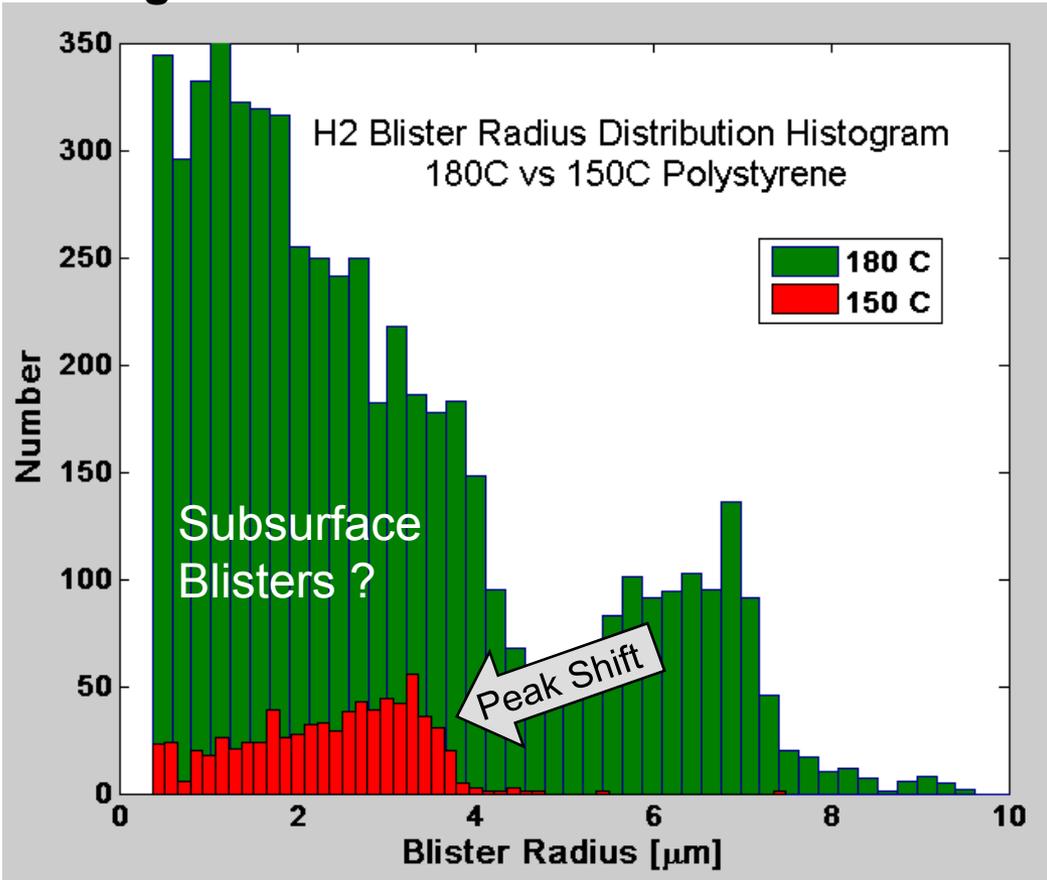
In-situ Thermal Gradient Stage for High-Pressure Hydrogen Charging



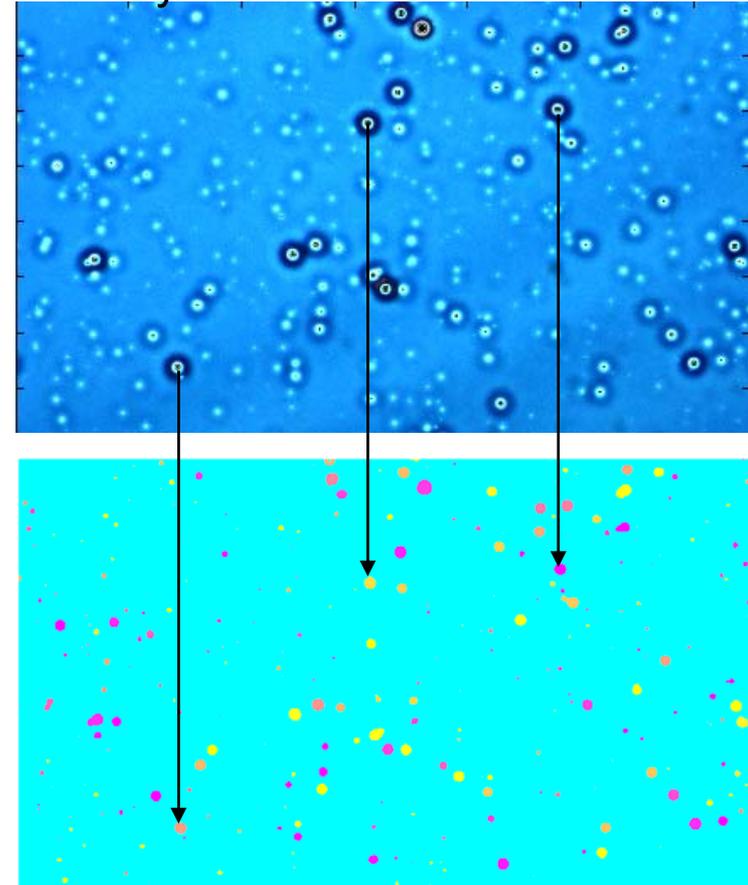
- ▶ In-situ thermal gradient stage allows combinatorial measurements of blistering as function of viscosity.
- ▶ Capable of 100 degree gradient
- ▶ PID control of hot end up to 200C yields large measurement range.
- ▶ Multiple temperature readouts.
- ▶ Under development.

Image Analysis & Blister Size for Different Temperatures

Histograms for 150C & 180C



Identify & Measure Blisters



Hydrogen Materials Compatibility Studies: Summary & Future Work

Summary of preliminary work:

- ▶ Hydrogen induced damage does occur in polymers!
- ▶ Hydrogen induced blisters are clearly observed.
- ▶ Temperature/Viscosity is an important parameter to both blister size & density.
- ▶ Current goal to understand the effects of the different materials properties on the blistering.

Future work:

- ▶ In-situ combinatorial measurements of viscosity/temperature effect on blistering
- ▶ Extend work to crystalline/other polymer systems

Project Future Work

- A best effort storage vessel will be manufactured using the hybrid filament winding & fiber placement method
- Pressure cycle fatigue and burst tests will be performed on this tank
- Further iterations on composite design and AFP process improvements (manufacturing process development)
- Dry tape process proof of concept trials & determine feasibility & utility to combine with AFP and FW processes
- Cost model revisions to reflect latest manufacturing processes & large scale volume production
- High pressure hydrogen exposure tests of tank materials

Collaborators

- ▶ **Quantum Fuel Systems Technologies Worldwide Inc.**
 - Prime contractor, within the DOE H₂ program
 - Industrial manufacturer of carbon fiber composite H₂ storage vessels
 - Manufacturing lead for advanced hydrogen storage vessel development
- ▶ **The Boeing Company**
 - Subcontractor, outside the DOE H₂ program
 - Industrial aerospace manufacturer of carbon fiber composite materials
 - Automated fiber placement method and equipment development lead
- ▶ **Pacific Northwest National Laboratory**
 - Subcontractor, within the DOE H₂ program
 - Federal laboratory
 - Lead for manufacturing cost analysis and hydrogen exposure testing
- ▶ **Lawrence Livermore National Laboratory**
 - Subcontractor, within the DOE H₂ program
 - Federal laboratory
 - Lead for high speed dry tape fabrication process development

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 for both AFP & FW Composite design & optimization AFP process improvement Test whether LLNL process is worthwhile to incorporate Cost model development High pressure hydrogen exposure tests of tank materials
Proposed Work	Initial filament winding/fiber placement process to produce best effort tank LLNL process trials Refine cost model Report on hydrogen degradation of tank materials