Next Generation Hydrogen Storage Vessels Enabled by Carbon Fiber Infusion with a Low Viscosity, High Toughness Resin System

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DOE AMR

Project ID: ST114

Overview

Timeline

Project Start Date: 08/05/2014
Project End Date: 08/30/2016

Barriers

A. System Weight and volume
B. System Cost

Budget

Total Project Budget: $3.0 M

- Total Recipient Share: $1.0 M
- Total Federal Share: $2.0 M
- DOE Funds Spent*: $350 k
  (*as of 3/31/15)

Key Partners

- Montana State Univ.- Bozeman Composite Technologies Research Group (Doug Cairns)
- Spencer Composites Corp.

Relevance / Impact

Overall Objective for 2-Year Project:
The demonstration of a 700-bar, Type IV tank with :
(1) Reduction in Carbon-Fiber(CF) composite volume by 35%

(2) Cost of composite materials of $6.5/kW-hr. This component cost is an important element of the DOE 2017 system cost target of $12/kW-hr

(3) Performance maintained (burst strength of 1575 bar and 90,000 cycle life)

Current Objectives, FY 2	**Completion Date**
Select resin formulation compatible with process	**Done**
Demonstrate infusion on triaxial wound CF plates	**Done**
Evaluate static properties and void content on test plates	**04/31/2015**
Prepare and burst small tanks via infusion process	**07/31/2015**

Impact on FCTO Technical Barriers: A. System weight and volume
B. System Cost

Approach: Technical Premise

By demonstrating Type IV tanks with thinner carbon-fiber composite walls, cost savings can be realized since CF is a major cost contributor.

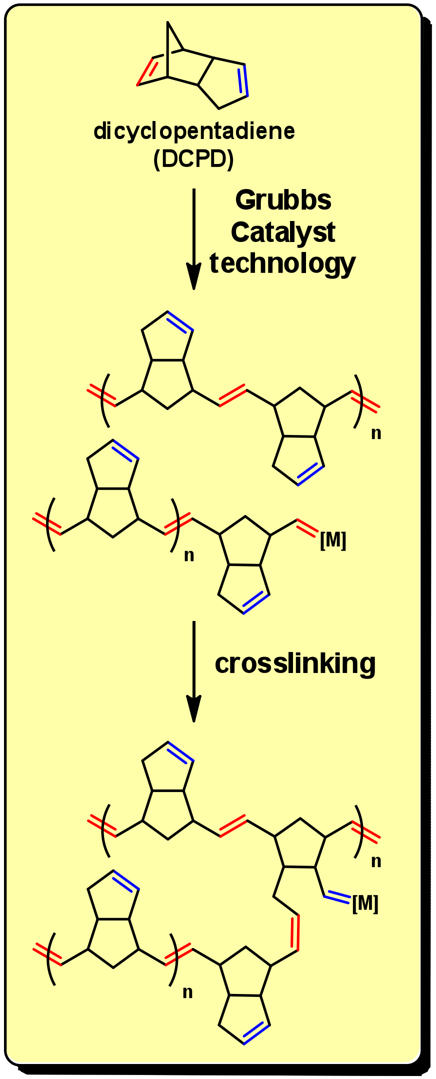
The project will use composite processes and thermoset resins that are "new to the COPV industry" and answer how the following can contribute to CF reduction:

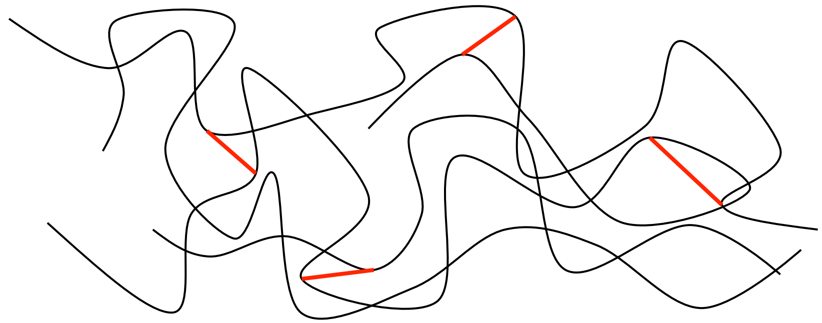
1) Reduction in void defects in the composite wall by using vacuum infusion processing of dry-wound forms enabled by a very low viscosity resin
2) Use of high fracture-toughness resin with better fatigue performance and crack resistance
3) New winding patterns supported by the dry-winding which may not be achievable with wet-winding

Factors 1/2 focus on the start of cracks (voids as stress-concentrators) and crack growth in tanks under static and cyclic loading

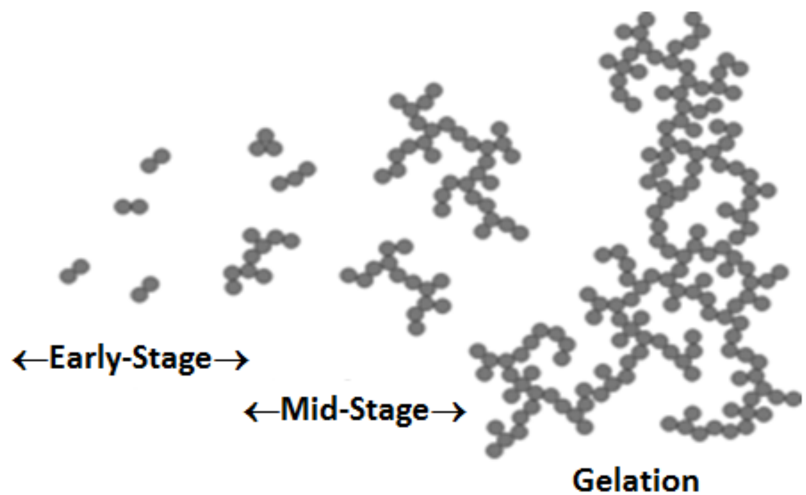
Go / No Go: Feasibility to meet target tank performance with 35% CF reduction based on models and small prototypes (08/15/15)

Approach: Inherent Differences in Resins





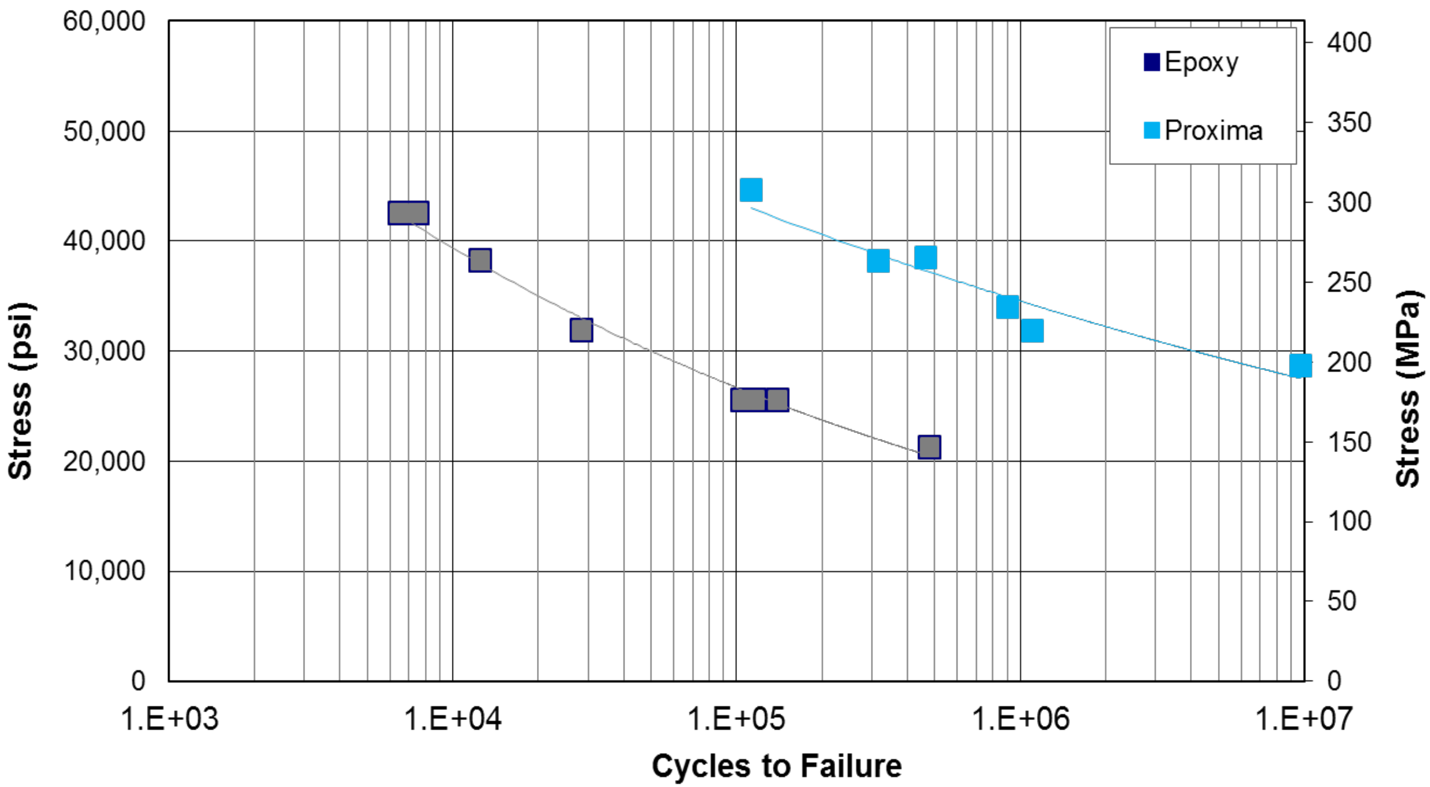
DCPD-based Proxima thermosets cure through early formation of high MW, entangled polymer followed by cross-linking similar to traditional vulcanization of rubber



… unlike epoxy condensation which cures via random branching until the gelation point

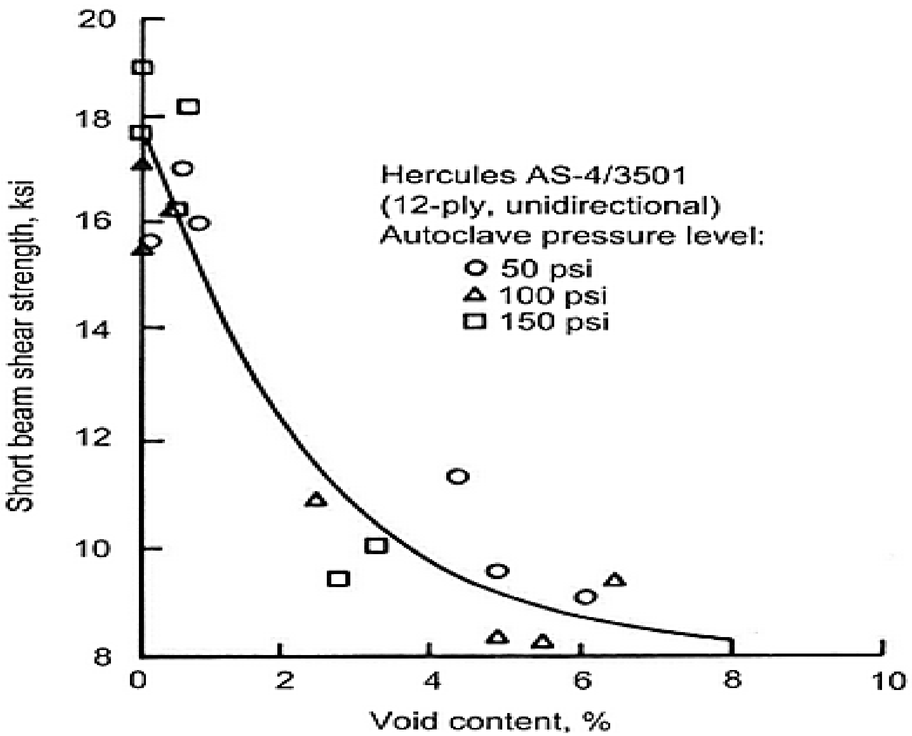
Approach: High Fracture-Toughness

- **High fracture-toughness resin supports better fatigue and off-axis properties**
- **Project will explore the effect of tough resin on design via FEA and sub-scale parts**



Approach: Effects of Void Reduction

- Thorough impregnation of tensioned CF tow is a challenge during wet-winding processes , especially at production rates
- Voids (>2 vol.%) cause large knock-downs in some properties
- To compensate for knock-downs, more CF thickness is needed in vessel wall
- Vacuum infusion can bring void content <1 vol.%



[1] Binetruy, C., Hilaire, B. and Pabiot, J., *Journal of Composite Materials*, Vol. 32 (1998) 223-245.

Approach: Project Phases and Key Milestones

Demonstrate infusion process feasibility (Thin and thick plates)

FY2015

- ☑ **Project start-up**
- ☑ **Achieve thickness > 30 mm (M1.1)**
- ☑ **Show low void content (<1 %)**

Design tank using FEA models and materials data (static and fatigue)

FY2015 / 16

- ☐ **Predict effect of toughness, voids, fiber on tank performance (M6.1, 6.2, 6.3)**
- ☐ **Design tank with lower CF content (M9.2**

Extend process to small tank prototypes

FY2015

- ☐ **Supporting FEA work (M6.1, 6.3)**

Demonstrate and refine process / performance in full-scale design

FY2016

- ☐ **Produce a series of tanks during optimization**
- ☐ **Test tanks for performance**

Approach: Project Team

- Materia's ultra-low viscosity resins (< 20 cP) enable vacuum infusion (VARTM) of thick carbon fiber laminates with low void content (<1%).
- Project partners contribute critical expertise in composite testing, characterization and predictive modeling (Montana State Univ) and non-traditional filament winding and manufacturability (SCC)

Composite Materials (Materia)

- Resin qualification / selection
- Subscale part manufacture
- Infusion optimization (small tanks)
- Full-scale infusions

Filament Winding (SCC)

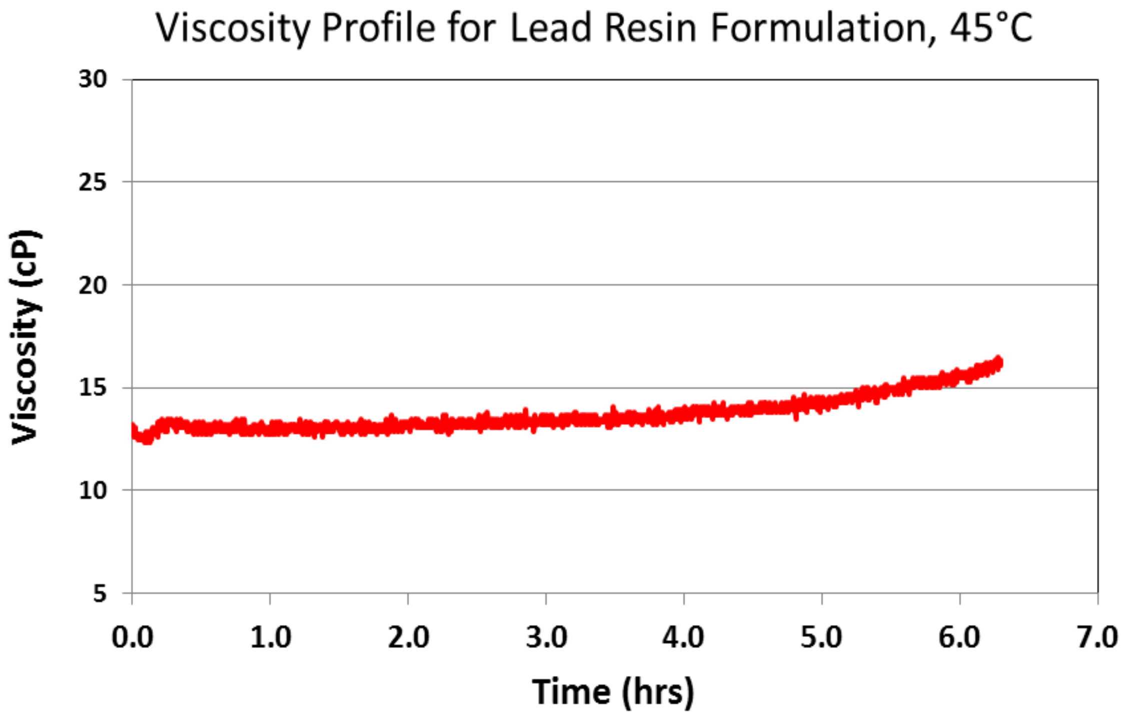
- Dry winding (small-scale)
- Fiber path optimization
- Prototype testing
- Liner Molding
- Full-scale tanks

Testing and Modeling (MSU / Cairns)

- FEA & design studies
- Static / Fatigue testing
- Void analysis
- Infusion process modelling

Accomplishments: Selection of Resin Formulation

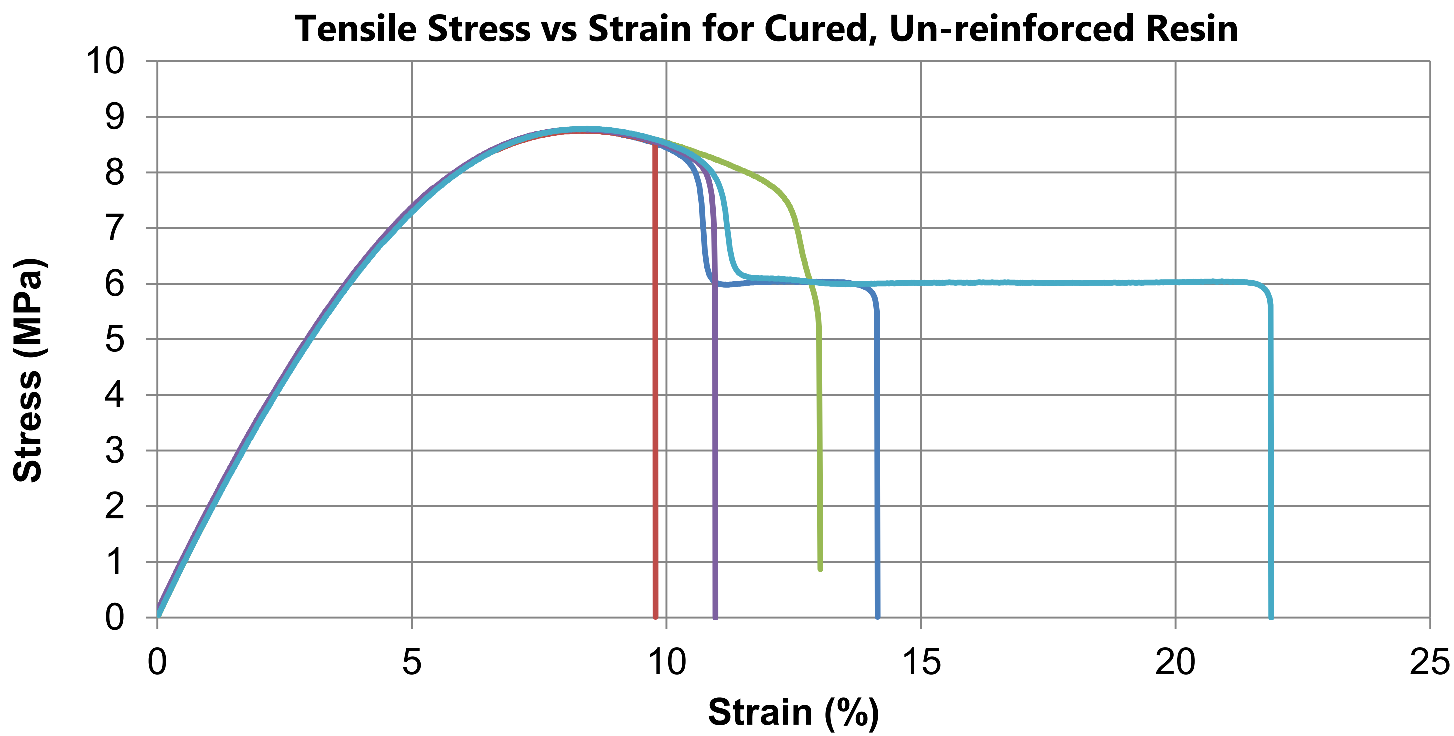
- Flow rate during vacuum infusion is dominated by resin viscosity and permeability of the fiber stack.
- Typical Proxima® resins based on dicyclopentadiene and other cyclic olefin monomers have extremely low viscosity



Take Home: Resin with very low-viscosity (< 15 cP) was demonstrated which is critical for processing. Authors are not aware of other resins with this behavior

Accomplishment: Confirmation of Toughness

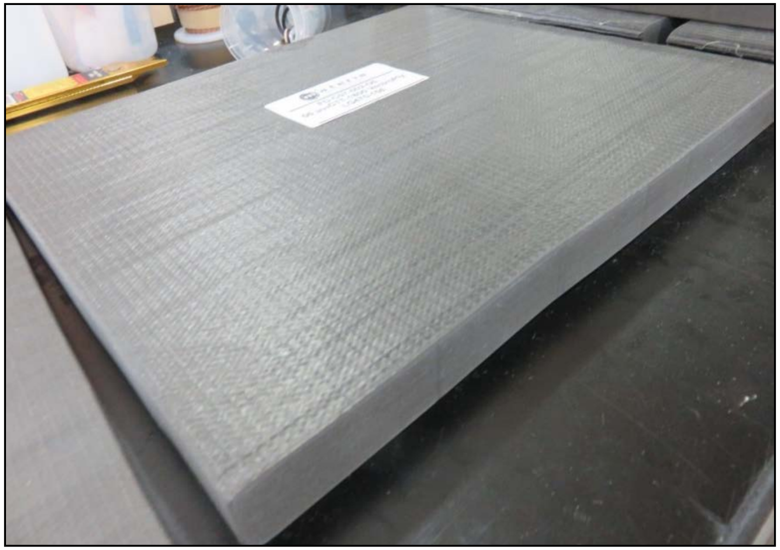
- Static tensile tests confirmed high toughness behavior is maintained in this "low-viscosity, long pot-life" formulation
- Further static and dynamic testing of composites are underway



Take Home: The ductility of the unreinforced resin shows the potential for resistance to crack growth during tank cycling based on Materia's experience

Accomplishment: Success with Thick Panel

- A series of panels based on CF triaxial fabric (Torayca® T700) were prepared in increasing thickness to optimize the infusion processing
- High quality panel with thickness = 32 mm was achieved (an early milestone in the project plan)
- Void analysis via cross-sectional SEM verified <1 vol.%



<u>Take Home:</u> Early success with a thick panel is a "proof of concept" and builds confidence for achieving future challenges with wound tanks

Accomplishment: Small Dry-wound Tank

Progress is under way in the preparation of small COPV tanks which allow for preliminary process optimization for dry-winding and vacuum infusion

Small tank (6” diameter x 18” length x 0.167” wound-CF thickness) is ready for infusion

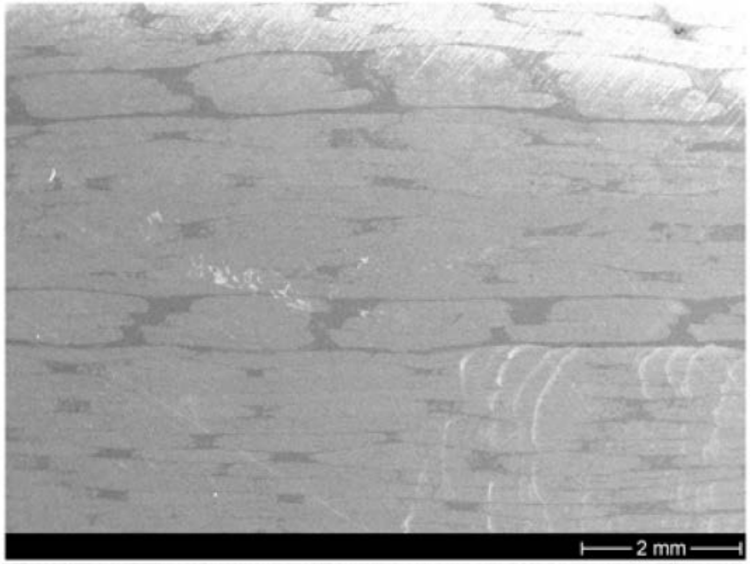
Take Home: A small, dry-wound tank was produced and shipped for infusion without any red flags thereby showing the potential of this non-conventional approach

Accomplishment: Low Void Content

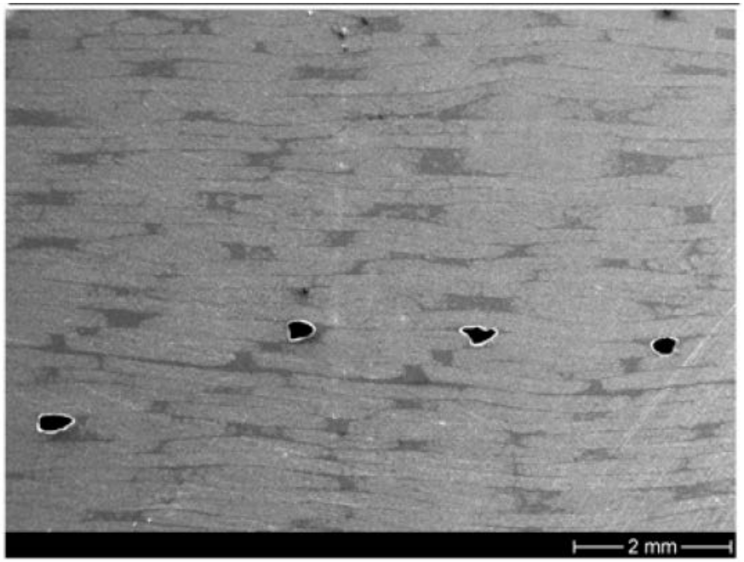
Void characterization conducted on thick CF laminate indicate:

- All areas possess < 1 vol.% of voids (on target)
- Average void content = 0.4 vol.% (based on 6 areas, each 300 mm^2)
- Voids appear to be related to polyester stitching (an artefact of using fabric-based laminates). Future filament-wound composites will not have this feature.

Cross-section with No Voids



Cross-section with Voids



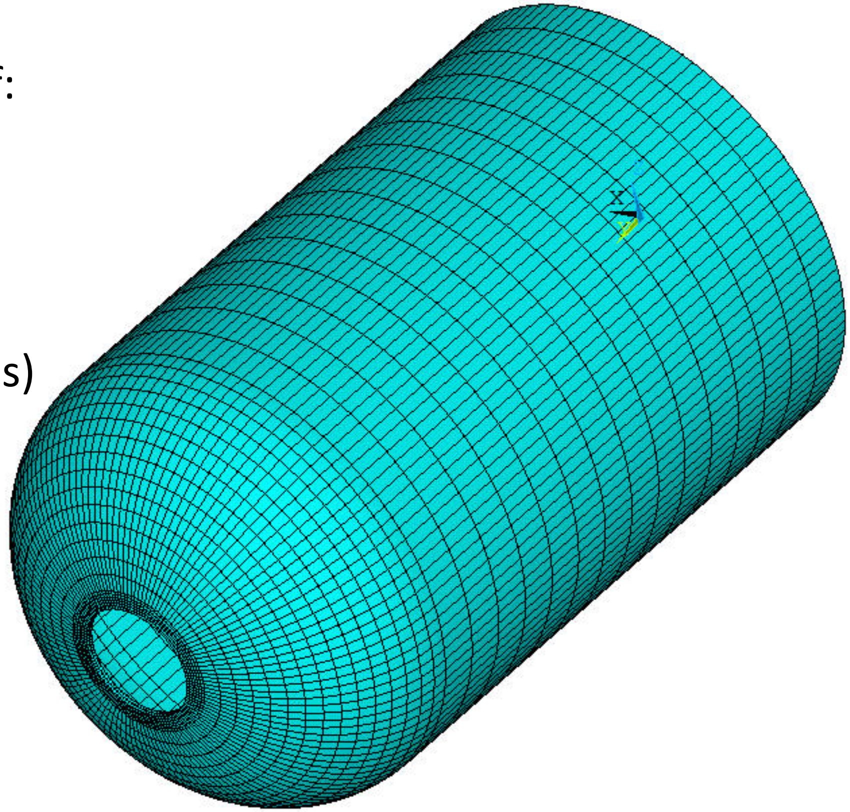
Take Home: Thick CF composites with low void content is achievable with infusion

Accomplishment: Set-up of FEA Models

The MSU team has completed their “in house” model of the ANL/DOE base case (465 mm in diameter by 1401 mm in length)

The model will be used to explore effects of:

(1) Voids on mechanical performance
(2) New resin vs. traditional epoxy
(3) Different winding patterns
 (in conjunction with Spencer Composites)
(4) Attributes unique to dry-winding
 (tow-spreading characteristics)



Analogous models of smaller prototypes will be developed as needed

Take Home: Model is ready for complete data set of mechanicals properties (near completion)

Accomplishment and Progress: Summary

Task	Status
Optimize processing / Formulation for infusion of plates	Completed
Develop data set of key mechanical properties (static)	In progress (April-15)
Design Fiber Placement Patterns for Dry-Winding/Infusion	In progress (May-15)
Optimize vessel design / Fiber placement using models	In progress (Jul-15)
Conduct dynamic testing on composite plates	Just started (May-15)
Prepare small tanks for infusion study and testing	Jun-2015
Develop resin infusion process models	Dec-2015
Optimize infusion on full-scale dry-wound tanks	Jan-2016
Manufacture full-size tanks with CF Reduction and test	Mar-2016

Time	Key Milestones & Deliverables
Year 1	Demonstrate 35% reduction in CF laminate and a composite cost of 6.5 $/kW-hr in subscale parts
Year 2	Produce prototype tanks with reduced CF overwrap that reach DOE 2017 Gravimetric target (1.8 kW-hr / kg)

Response to Previous Year Reviewers' Comments

This new project was not reviewed during the last AMR

Collaborations

Organization	Category	Role
Materia Inc	Industry (Chemicals)	Resin selection and infusion process optimization
Spencer Composites Corp. (SCC)	Industry (Fila. Winding)	Filament winding, fiber winding modelling, burst testing
Montana State University – Bozeman (MSU)	University (Composites Lab)	FEA modelling, mechanical testing,
Hypercomp Engineering	Industry (Fila. Winding)	Supplier / Test Lab only
Powertech Labs	Industry	Test Lab only

Remaining Challenges and Barriers

- Vacuum infusion of filament-wound parts is not well-studied / well-documented and quality is not known.
  Mitigation: Project will leverage low viscosity resin with long worktime by optimizing on small-scale tanks and using guidance from resin flow models

- Void content and void type in current commercial tanks based on wet filament winding is not available in a public database
  Mitigation: Wet-wound controls (epoxy) will be developed to understand the role of voids in causing property knock-downs

- The relationship between resin toughness and fatigue performance is not straightforward to predict via models
  Mitigation: Experimental data on plates then tanks will be developed to augment modelling work

Proposed Future Work

(1) Completion of Static / fatigue data sets for use in FEA models

(2) Completion of small-scale tank infusions and testing

(3) Demonstrate a relationship between defects and performance (Static and fatigue) and validate that infusion-based composites can meet the 90,000 cycles target similar to NGV2-2007

(4) Finalize design for full-scale tanks

(5) Develop resin flow models for guidance processing full-scale parts (FY16)

(6) Optimize winding and infusion processes (FY 16)

(7) Verify properties via burst tests and cyclic loading (FY16)

Summary Table

Objective	Project Target	FY15 Status
Select resin formulation compatible with process and properties	(1) Sufficient pot-life (2) Epoxy-like properties	Done In progress
Thickness of successfully infused CF plates	>= 30 mm	32 mm
Void content in thick plate	<1 vol.%	0.6 vol. %
Mechanical properties	Complete by 3/31/15	Late Target: 4/31/15
Prepare small tanks via infusion process and test	Complete by 7/31/15	In progress

- Progress has been steady, but important milestones are still to come
- The project is on-target to make a Go / No Go recommendation in August 2015

Back-Up Technical Slides

Progress toward DOE Targets

Project goals were created to respond to DOE Year 2017 targets

Comparative Summary of Key DOE Metrics for Hydrogen Storage Systems

				Key DOE Metrics for Hydrogen Storage Projects			
Hydrogen Storage Systems	**System Wt. (kg)**	**System Vol (L)**	**System Cost ($ / unit)**	**Gravimetric (kW-h/kg sys)**	**Volumetric (kW-h/L sys)**	**System Cost ($/kW-h, at 500k units/yr)**	**Comment**
Year 2017 DOE Target	104	224	2238	**1.8**	**1.3**	**12**	**Ref. 1**
Yr 2013 700-bar Type IV, Base Case	128	224	3171	1.5	0.8	17	**Ref. 1**
Proposed 700-bar Type IV	106	215	2313	1.8	0.9	12	Proposed

		Year 2013	Proposed
Composite Material cost	$/kWh	$10.4	$6.5
Composite Processing Costs	$/kWh	$1.0	$0.5
Other System costs (Non-composite)	$/kWh	$5.4	$5.4
Total System Cost	$/kWh	17	12

Ref. 1: McWhorter, S., Ordaz, G., "Onboard Type IV Compressed Hydrogen Storage Systems – Current Performance and Cost," *DOE Fuel Cell Technologies Office Record Number 13010*, June 11, 2013.