IV.D.4 Next Generation Hydrogen Storage Vessels Enabled by Carbon Fiber Infusion with a Low Viscosity, High Toughness System

Brian Edgecombe
Materia, Inc.
60 N. San Gabriel Blvd.
Pasadena, CA 91107
Phone: (626) 584-8400, Ext. 210
Email: bedgecombe@materia-inc.com

DOE Manager
Grace Ordaz
Phone: (202) 586-8350
Email: Grace.Ordaz@ee.doe.gov

Contract Number: DE-EE0006625

Subcontractors
- Montana State University (MSU), Bozeman, MT
- Spencer Composites Corporation, Sacramento, CA

Project Start Date: August 5, 2014
Project End Date: August 30, 2016

Overall Objectives

The project is focused on supporting the key DOE metrics for a 700-bar, Type IV tank by meeting the following objectives:

- Reduce the carbon fiber (CF) composite content by 35%
- Demonstrate cost of composite materials of \$6.5/kWh; this component cost is an important element of the DOE 2020 system cost target of \$10/kWh
- Demonstrate industry standard performance (burst strength of 1,575 bar and 90,000 cycle life)

Fiscal Year (FY) 2015 Objectives

- Select resin formulation compatible with process
- Demonstrate infusion on triaxial wound CF plates
- Evaluate static properties and void content on test plates
- Prepare and burst small tanks via infusion process
- Quantify effect of resin toughness and voids on mechanical performance of composites

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(D) Durability/Operability

(G) Materials of Construction

Technical Targets

The project is focused on the technical targets highlighted in Table 1 related to the gravimetric and cost metrics of onboard automotive hydrogen storage systems. Since a significant portion of the cost is directly from the CF composite overwrap, the project aims to reduce the amount of composite necessary to meet the tank specifications. During FY 2015 the project has met important milestones. However, we are not yet able to estimate the gravimetric and cost values.

TABLE 1. Progress towards Technical Targets for Onboard Automotive Hydrogen Storage System

Characteristic	Units	2020 Target	FY 2015 Status
Gravimetric	kWh/kg system	1.8	TBD
System Cost	\$/kWh at 500,000 units per year	10	TBD

TBD – to be determined

FY 2015 Accomplishments

- Demonstrated the ability to make composite-overwrap pressure vessels (COPVs) and lab-scale prototypes with the less conventional vacuum infusion process
- Achieved burst strength above design pressure (>1,575 bar) for a vacuum-infused COPV (small-scale prototype)
- Prepared thick plate infusion (32 mm) with low void content (<0.5 vol%)
- Completed evaluation of static properties and void content on test plates
- Optimized the processing of COPVs via novel vacuum infusion to obtain low-void composites (<0.1 vol%)
- Started fatigue/cycle testing on composite specimens with high and low void content to elucidate the relationship between void content and composite performance

✧ ✧ ✧ ✧ ✧

INTRODUCTION

The Office of Energy Efficiency & Renewable Energy has established aggressive performance targets for Type IV hydrogen storage vessels for Year 2020. Current designs and materials of construction for COPVs within the industry do not reach the performance targets as shown by the base case published by Ahluwalia from Argonne National Laboratory. The specialty chemical producer, Materia, has developed a novel composite resin system, Proxima®, with ultra-low viscosity (<15 cP) which enables vacuum infusion processing for thick CF composite components. The use of this process with Proxima circumvents some challenges inherent with traditional wet filament winding such as the presence of voids and dry spots. Although the concept of infusing dry filament wound structures has been mentioned in the open literature, the small inter fiber gaps associated with high performance CF composites results in considerable significant processing difficulties. Therefore, the commercial application of this approach appears to be limited which may be related to traditional resins possessing viscosities >200 cP.

In addition to reducing void content, Proxima-based composites have significantly improved fracture toughness and fatigue performance over currently employed composites for hydrogen storage tanks. The project seeks to leverage this new combination of tough resin and new process to produce composite overwrap with better performance, especially in fatigue and damage tolerance testing. These high performing composites will enable the reduction of the quantity of CF composite overwrap which alone can account for over 75% of the storage tank system cost. The tank manufacturing costs for this new process is expected to similar to current manufacturing costs with wet-winding. By reducing the CF composite content in COPVs by 35%, the project aims to reduce the cost and weight of COPVs and contribute to meeting the DOE 2020 cost target of $10/kWh.

APPROACH

Since the project requires expertise in a variety of fields, the project team includes Spencer Composites Corporation to lead the specialized filament winding effort and MSU to evaluate composite materials and also use finite element analysis (FEA) models to anticipate problem areas in tanks designs. Materia is leveraging its experience in infusion process optimization with low viscosity resin (<15 cP) to demonstrate a series of prototype parts including tanks and model flat plates of filament wound composites. In order to manage the risks associated with a new resin and a new process for COPVs, the project activities were divided into the following stages and associated objectives.

- Process optimization: demonstrate infusion feasibility with CF (high-thickness plates)
- COPV design: develop preliminary designs for COPVs using FEA models and materials data (static and fatigue)
- Processing optimization with COPVs: extend processing technique to small COPV prototypes
- Design optimization: quantify relationship between void defects and composite performance
- Scale-up of process: demonstrate and refine process and design with full-scale COPVs to maximum cost effectiveness of performance

In particular, the project team wanted to deploy sufficient resources during FY 2015 on the significant challenge of conducting vacuum infusion to produce high-quality COPVs.

RESULTS

The start of FY 2015 coincided with the ramp-up of this new project with its initial focus on the qualification of a resin formulation for the challenging processing conditions. In vacuum infusion, the rate of resin infusion is dominated by viscosity. Therefore, a modification was made to an existing a resin formulation to allow for the minimum in viscosity (<15 cP) for >4 h. Using traditional viscosity measurement techniques, the work time and viscosity was demonstrated to meet the preliminary targets. To ensure that the modifications of resin formulation did not adversely affect the mechanical performance of the resin, unreinforced resin castings were prepared and tested with success.

With a resin formulation appropriate for the application, processing studies were conducted using high-thickness, flat-plate CF laminates from unidirectional CF fabrics based on Toray T700 fiber. These fabrics are notorious for their low permeability during vacuum infusion processing. Therefore, these experiments provided a fast, low cost manner to provide feedback on the processing during vacuum infusion. The project team demonstrated the ability to produce low-void laminates (<0.5 vol%) with 32-mm thickness with infusion processing times under 2 h. This result was considered an important part of de-risking the key step of infusion of small scale COPVs.

Given the achievement of high quality flat CF composite plates, the processing efforts of the project team moved the focus to small scale COPVs. The infusion studies were conducted on Type III tanks with aluminum liners, 6-in. diameter by 18-in. length in order to speed development. By working with filament winding experts, a winding strategy was selected to achieve >1,575 bar burst strength and the design was validated by the production and testing of wet-wound epoxy tanks. As expected the dry-wound COPVs presented a series of challenges for the team. By optimizing the infusion ports, port placement, process aids and bagging techniques, steady progress was made in improvements until

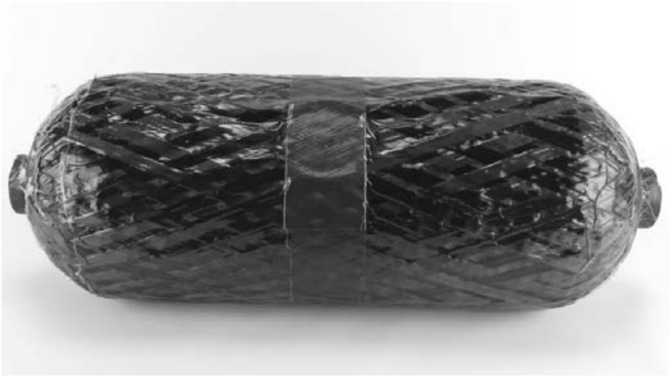
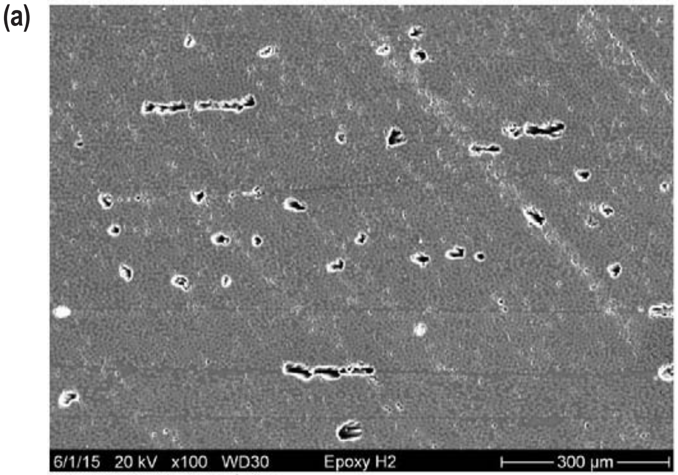
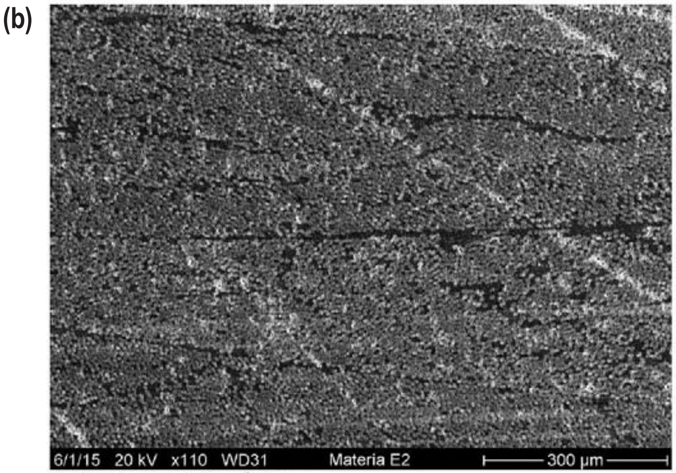


FIGURE 1. Fully infused small-scale (7.5 liter) COPV



Epoxy coupon H at 100X magnification.



Proxima coupon E at 110X magnification.

FIGURE 2. (a) Cross-section of wet-wound epoxy tank with voids (3% to 9% voids across seven regions); (b) Cross-section of infused Proxima tank with no voids

low-void tanks were obtained and repeated. A fully infused Proxima-based tank is shown in Figure 1. Some Proxima tanks were cut and compared for void content to analogous wet-wound epoxy tanks (as a reference). In Figure 2, representative images are shown of the void-containing epoxy tank wall and the low-void Proxima wall.

Although the void content was on target, some visible fiber buckling was observed from the process which had a negative effect on burst strength. In Table 1, burst strength values are compared of three infused Proxima tanks and wet wound epoxy tanks. Since burst strength is known to be sensitive to fiber bending, the first set of Proxima tanks did not reach the target of >1,575 bar and failures appeared to be starting from areas of wrinkles. However, the team is optimistic that significant improvements can be attained by reduction of fiber buckling. Several causes are under investigation, including the winding tension (lower than the epoxy control) and the crimping effect of the current design of infusion ports. Recently, working with a supplier, we were able to confirm that dry-winding can be conducted at the higher levels of tension shown in Table 1 without significant damage of fiber.

TABLE 1. Comparison of Epoxy COPVs with Proxima COPVs

COPV type	Winding Tension (lb)	Burst Strength (bar)	Comment
Epoxy controls (wet-wound)	8–11	1,822 (avg)	Failed near cylinder
Proxima (infused N3)	3–5	853	Failed near wrinkles
Proxima (infused, N5)	3–5	744	Failed near wrinkles
Proxima (infused, N4)	5–8	1,408	Failed near wrinkles
Proxima (infused)	8–10	TBD	In progress
Proxima (infused)	10–12	TBD	In progress
Proxima (infused)	12–14	1,688	Failed near dome transition

In order to support the experimental work at Materia, MSU has developed an infusion model which can be used to predict the flow front of the resin during the infusion process. Refinements of the model will be conducted based on development of permeability data of the dry-fiber. For the full scale prototypes, a preliminary design has been evaluated by Spencer and MSU, and planning has started to validate the assumptions in the model.

CONCLUSIONS AND FUTURE DIRECTIONS

From the current results of the project, the team has derived the following conclusions.

- Preparation of COPVs with <1% void content using vacuum infusion of dry filament wound form is viable, but requires further process optimization.
- Process configurations which eliminate fiber buckling upon application of vacuum appear to be an important consideration.

- Current FEA modeling approaches are useful for estimated static performance, but fatigue results will require extensive testing.

The following activities will be the area of focus in the future.

- Refine full-scale tank design and verify compatibility of vacuum infusion with Type IV polymer liners.
- Develop further fatigue data on plates and small-scale tanks in order to validate the ability to reduce the amount of carbon fiber.
- Develop cost estimates of tanks based on new designs and processes.