Materials Challenges for Cryogenic Hydrogen Storage Technologies

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Overall Objectives

- Develop a mechanistic understanding of polymer behavior and performance in hydrogen environments under pressure and thermal cycling conditions.
- Develop models and experimental test methodologies that predict material and pressure vessel performance in hydrogen infrastructure environments.
- Use knowledge gained to inform material development and selection for improved resistance to hydrogen-induced degradation, therefore improving reliability and durability, and reduce system weight, volume, and cost.
- Disseminate material characteristics to the community that will assist in improving materials in hydrogen infrastructure components.

Fiscal Year (FY) 2019 Objectives

- Complete installation of a new cryogenic testing capability at Pacific Northwest National Laboratory (PNNL) and validate its performance.
- Evaluate and qualify epoxy resins modified with additives and different curing agents and long- and short-chain molecules to provide flexibility in designing target thermal properties.
- Evaluate unique carbon fiber reinforced composites with tailored interfacial composition based on incorporation of nanomaterials and demonstrate 10% increase in inter-lamellar shear strength (ILSS).
- Establish the relationship between coefficient of thermal expansion (CTE), ILSS, and mechanical properties of carbon fiber reinforced epoxy matrix composites at various temperatures, including cryogenic conditions.
- Evaluate polymeric and metallic liner material options, investigating the combined effects of hydrogen and low temperature.
- Establish protocols for conducting cryogenic, ambient, and elevated temperature mechanical testing to evaluate potential for micro-crack formation, combining thermal cycling with cyclic mechanical fatigue.
- Conduct finite element simulations and analytical models of filament-wound composite tank cylinders, using material parameters generated by the project, to estimate tank pressure retaining and burst performance.
- Formulate damage tolerance models and conduct studies to define acceptability envelopes for defects in liners and 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[1]:

- Weight and Volume
- System Cost
- Durability/Operability

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- Materials of Construction
- Lack of Tank Performance Data and Understanding of Failure Mechanisms.

Technical Targets

This project is conducting studies to understand, predict, and control the performance of materials used for cryogenic storage of hydrogen. Insights gained from these studies will be applied toward the selection of hydrogen storage materials and design of storage systems that meet the following DOE hydrogen storage targets (cryo-compressed storage at 276 bar):

- Gravimetric: 1.9 kWh/kg
- Volumetric: 1.4 kWh/L
- Cost: $12/kWh.

FY 2019 Accomplishments

- PNNL completed installation of its new cryogenic test system, developed test methods and fixturing, and completed mechanical properties testing on unfilled epoxy resin samples at ambient baseline, 200 K, 140 K, and 40 K temperatures.
- Oak Ridge National Laboratory (ORNL) successfully prepared and tested specimens of carbon fiber-epoxy matrix composites modified by incorporating 30 nm titania particles onto the surface of the fibers, which showed up to 14.7% improvement in ILSS.
- PNNL developed a finite element simulation of a filament-wound composite tank cylinder and used it to show that epoxy selection significantly affects the potential for material failure under thermomechanical loading.
- Argonne National Laboratory (ANL) created a verification model of a composite tank case with a stainless steel liner to use in the composite damage model and completed verification of the damage model with inputs from PNNL.
- ANL created a “real” cryo tank model (one without deliberately introduced design flaws) and conducted a buckling analysis.
- PNNL and Sandia National Laboratories (SNL) designed and began to fabricate metal liner material test specimens.

INTRODUCTION

Low-cost physical hydrogen storage vessels will be required to realize DOE’s H2@Scale vision. New high-performance materials will be needed that are inexpensive and lightweight yet strong and resistant to degradation and failure under thermal and pressure cycling in the presence of hydrogen. These materials must resist micro-cracking, avoid loss of volatile constituents, and maintain stiffness and ductility under extreme environmental conditions. While some specialty materials have been proposed, manufacturers typically test the performance of storage vessels using sub-scale and full-scale prototypes, and these tests are expensive and require large amounts of material. The ability to screen materials, composite laminates, and liner materials for use in hydrogen service conditions without such testing would greatly facilitate innovation in alternative materials.

APPROACH

This project investigates cryogenic material systems for use in 350+ bar cryo-compressed and sub-ambient (~77 K) hydrogen pressure vessels. The project includes tests of both resin and carbon fiber composite and aluminum and stainless welded liner systems over this temperature range. Parameters derived from experimental testing will be used in numerical models to predict the relative change in full tank burst properties at different temperatures. These simulations will enable development and deployment of existing and new polymer material systems in high pressure sub-ambient and cryogenic hydrogen pressure vessels.

RESULTS

PNNL: Test Method Development and Cryogenic Temperature Effects

A variety of epoxy compositions were fabricated with several epoxy resins and curatives. Cure schedules for each combination were determined by differential scanning calorimetry to determine cure time and temperature appropriate to achieve fully cured epoxy products. Test methods were developed to study dynamic mechanical properties and linear thermal expansion over the range -150°C to +200°C.

Tensile mechanical properties of two resin systems were evaluated at 25°C, -75°C, and -130°C using a liquid nitrogen cooled servohydraulic mechanical test system. Initial tensile tests using standard geometry for tensile testing of polymers (ASTM D638) demonstrated unexpectedly low tensile strength due to the presence of defects in the tensile specimens. Further inspection of the fracture surfaces revealed that all fractures initiated at the corners of the square cross-section, resulting in an artificially low tensile strength measurement that was deemed not representative of the mechanical properties. To mitigate this issue, a new specimen geometry (Figure 1) with circular cross-section and smaller dimensions overall was designed to reduce the total number of defects present in each specimen. A new molding system and curing strategy was adopted to cast specimens with minimal defects and warping during the cure cycle. Tensile testing fixtures were designed to accommodate the new geometry and allow for ease of use at cryogenic conditions where icing and cryogenic personal protective equipment hinder traditional methods. Tensile tests of these new specimens resulted in a 40% increase in tensile strength at -130°C compared to the ASTM standard geometry.

A cryogenic mechanical testing system was designed and built to enable tensile testing at temperatures as low as -269°C. To accomplish this task, a mechanical load frame was selected and modified to accommodate a servo-electric actuator, liquid helium cryostat, and multiple vacuum and compressed gas systems. Thus far, one epoxy composition has been tested at 25°C and -233°C.

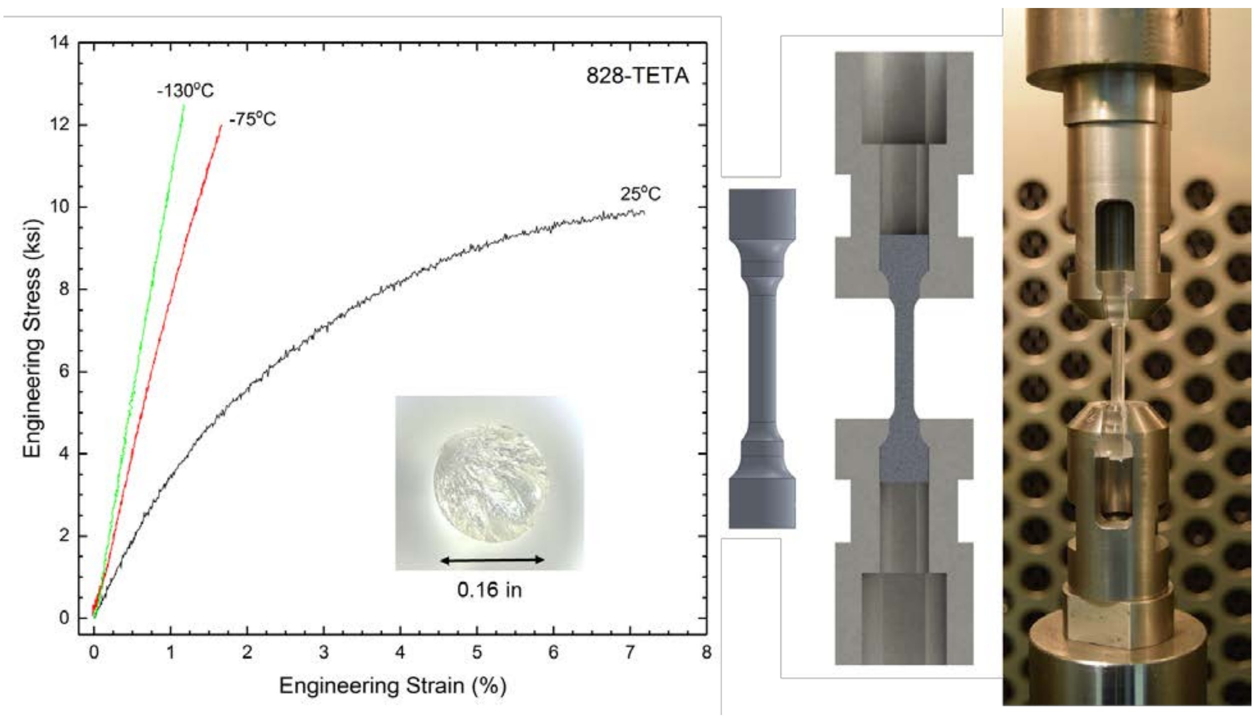


Figure 1. Tensile properties of baseline epoxy at various temperatures (left). Tensile geometry designed to minimize the presence of flaws and facilitate testing at cryogenic temperatures (right).

ORNL: Unique Carbon Fiber Reinforced Composites with Improved ILSS

ORNL worked to establish a technique to control both sizing content and nanoparticle concentration on the carbon fiber surface. Initial experiments dispersed SiC nanoparticles (45–65 nm) homogeneously in the sizing emulsion with homogeneous fiber coating. TiO_2 nanoparticles (30 nm) also dispersed well using this technique and provided even better structural reinforcement than SiC nanoparticles of similar dimensions. Carbon fiber coated with TiO_2 nanoparticles is shown in the scanning electron microscope images in Figure 2a and 2b. These fibers were fabricated into unidirectional composites and tested using a short beam shear test to quantify their ILSS. Figure 2c shows the average ILSS for the composites containing TiO_2 coated carbon fiber with various nanoparticle concentrations. The strength showed increased performance from 0.1 wt % to 2.5 wt %, but after 2.5 wt % the strength decreased. The optimal increase in ILSS was 14.7% as compared to the 0 wt % nanoparticle composite. Further experiments were performed with cellulose nanocrystals and aramid nanofibers. These polymer nanomaterials were successfully coated on the carbon fiber but did not deliver any significant increases in ILSS at ambient temperature. They may, however, show promising results at cryogenic conditions in future testing.

For testing at cryogenic conditions, an environmental chamber was installed on the tensile frame and protocols were developed for low temperature short beam shear testing. The best performing TiO_2 nanoparticle composite at room temperature was selected for testing at -75°C. However, the increase in ILSS at ambient temperature did not translate to the ILSS at -75°C, necessitating further development.

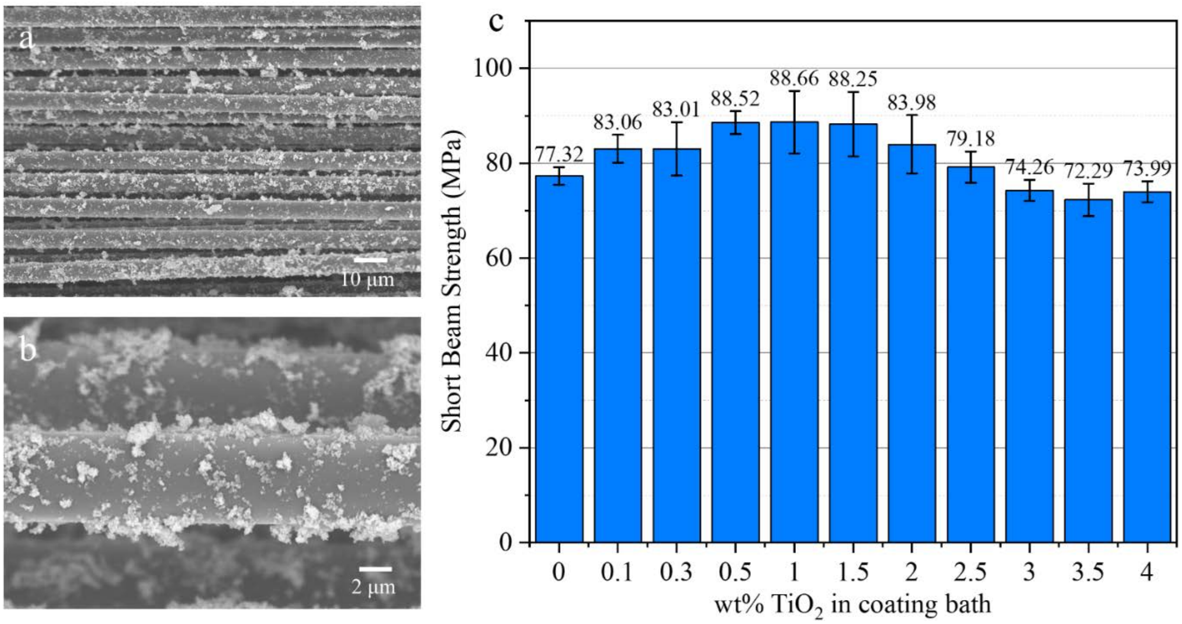


Figure 2. (a-b) Scanning electron microscope images of TiO_2 nanoparticle coated carbon fibers with (c) the corresponding results of the short beam shear tests as a function of the concentration of nanoparticles in the coating bath.

PNNL: Structural Modeling Using Finite Element Methods

Composite cryogenic hydrogen storage vessels are subjected to thermomechanical cycling that can induce high stresses in the carbon fiber/epoxy overwrap, which can in turn cause matrix cracking, fiber/matrix debonding, delamination, and fiber rupture, leading to vessel failure. Predictive finite element modeling capabilities were developed to support a material acceptance process that will provide guidance to evaluate specialty resins, vessel liner options, and carbon fiber composites through thermomechanical testing. Thermo-elastic-plastic analyses of a simplified Type-3 hydrogen vessel model using a multiscale mechanistic approach [1–2] were performed to assess the magnitudes of the *composite* and *constituent stresses* in the vessel overwrap subjected to different thermomechanical loading scenarios. Thermal stresses arising from mismatches of CTEs and elastic properties between the carbon fiber and epoxy matrix and between the vessel composite overwrap and its metallic liner were computed. The analyses show that high-strength epoxies with low CTE for the composite overwrap will be needed for the whole operating temperature range from room temperature to cryogenic temperatures. In addition, under an adequate thermomechanical loading scenario, the risk of vessel failure could be reduced or mitigated. Figure 3a compares the evolutions of failure criterion (0: safe; ≥1: failed) based on the use of Epoxy 1 (from literature) and Epoxy 2 (high-cross-link density epoxy with lower CTE developed at PNNL) for a helical layer of a vessel model subjected to a prescribed loading scenario. Compared to Epoxy 1, the use of Epoxy 2 as the matrix material reduces the failure criterion by about a factor of two at the end of the cooling step. PNNL and ANL applied this multiscale modeling approach to preliminarily analyze Type-3 hydrogen vessel models to predict burst pressure and improve the vessel's layup. Figure 3b shows the failure criterion distribution in a vessel model at final failure (90.8 MPa burst pressure).

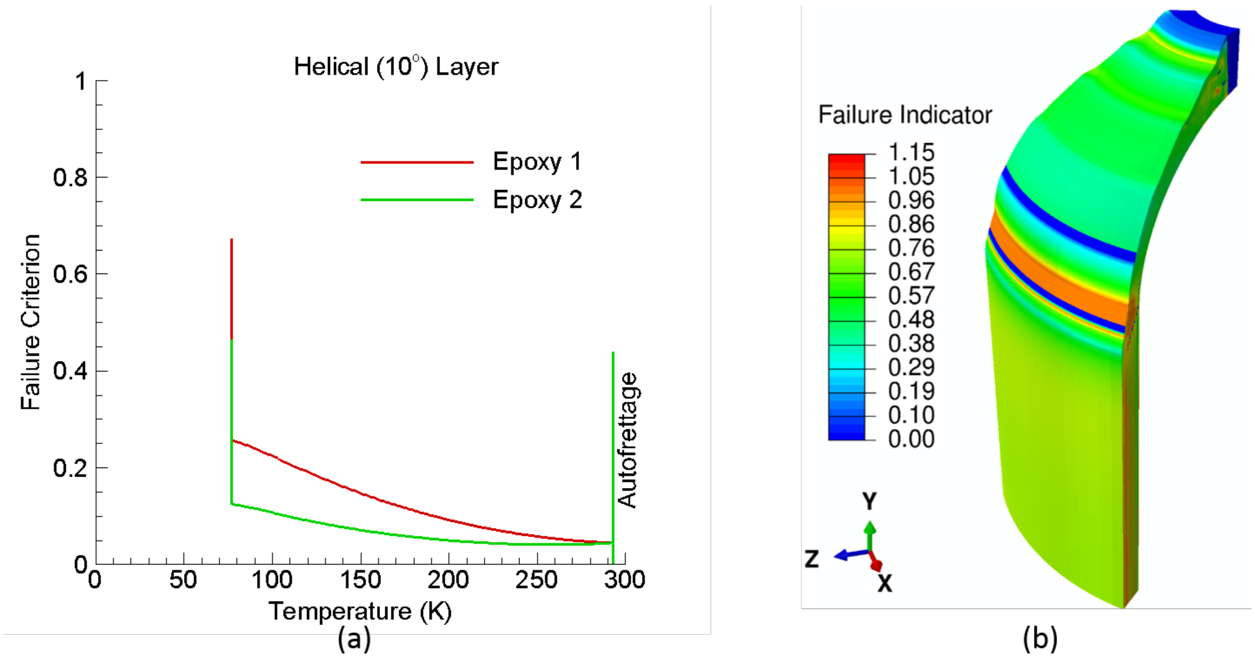
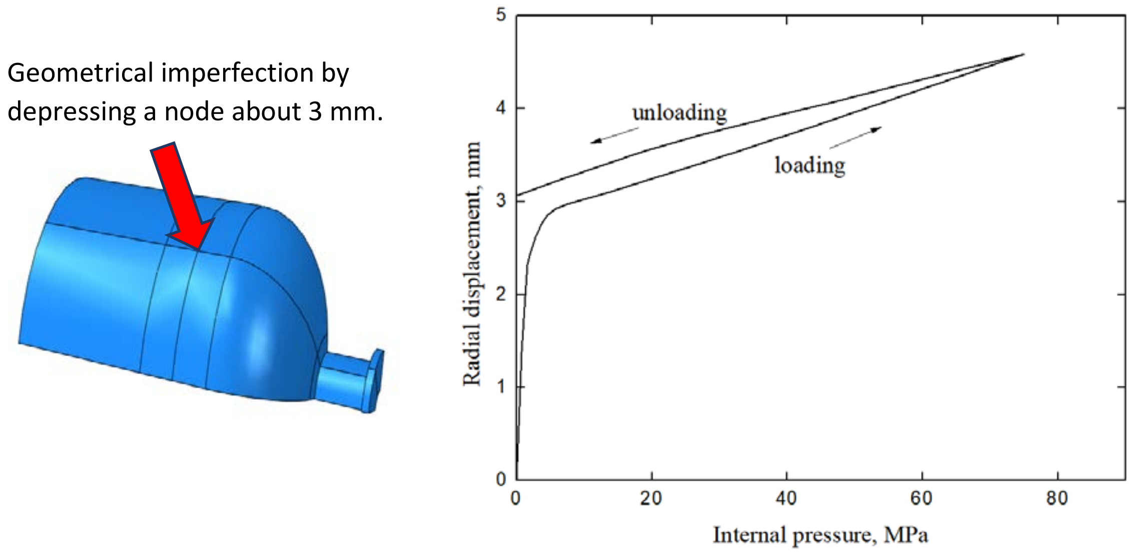


Figure 3. (a) Effect of the matrix CTE on failure criterion, and (b) 3-D finite element analysis of a hydrogen storage vessel using multiscale modeling: vessel complete failure is predicted at 90.8 MPa pressure.

ANL: Structural Modeling Using Finite Element Methods

ANL conducted the damage modeling of Type-3 hydrogen storage tanks with PNNL. A cryo-compressed hydrogen tank was designed to operate at 50 MPa and to fail over 113 MPa of burst pressure. A computational tool, EMTA-NLA developed by PNNL, was implemented into the Abaqus finite element analysis to predict failures of composite materials over whole operation conditions such as autofrettage, cooling down, and burst pressure. Finite element results showed that most composite damages occurred near the junction between cylinder and dome sections during the burst pressure step. By using the damage modeling results, a new tank was created adding more helical layers to reinforce the junction where damages were found.

The Type-3 tank consists of metal liner and overwrapped carbon filaments, which can cause liner buckling during autofrettage. To verify the buckling potential of the liner, a Riks method was applied to the buckling analysis of a designed hydrogen tank because the Riks method is suitable for problems with geometry- and material-nonlinearities. A finite element model included a geometrical imperfection to introduce a continuous response, which is necessary to monitor post-buckling behavior after bifurcation buckling load. As seen in Figure 4a, the geometrical imperfection was located at the cylinder section. Figure 4b presents a displacement of the depressed node as the internal pressure changes. As the internal pressure increased to 5 MPa, the initial depression was returned to its original state. As the internal pressure increased to the autofrettage pressure of 75 MPa, the radial displacement increased. In the unloading, the radial displacement decreased linearly, and no buckling behavior was found.



(a) (b)

Figure 4. Buckling analysis of a Type-3 hydrogen tank. (a) Liner with a geometrical imperfection and (b) displacement and internal pressure curve.

CONCLUSIONS AND UPCOMING ACTIVITIES

Metal liner material with and without welds will begin at PNNL in FY 2020. Additional epoxy systems and composite materials will be tested down to 40 K. PNNL will test ORNL ILSS samples for sub-ambient behavior down to 40 K.

Because the 14.7% increase in ILSS in the ORNL-developed materials at ambient temperature did not translate to the ILSS at -75°C, further development and analysis of the fracture mechanics are needed. Additional fiber surface modifications will be explored during FY 2020 to increase mechanical strength at cryogenic conditions.

ANL and PNNL will continue to work together on the damage mechanics in pressure vessels for burst pressure predictions related to sub-ambient temperatures.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. K.L. Simmons, B.N. Nguyen, D.R. Merkel, K.I. Johnson, D.W. Gotthold, C.W. San Marchi, A.K. Naskar, et al., “Material Challenges for Cryogenic Hydrogen Storage Technologies,” Hydrogen Storage Tech Team, Detroit, Southfield Township, Michigan, January 17, 2019.
2. K.L. Simmons, D.R. Merkel, D.W. Gotthold, K.I. Johnson, H.S. Roh, B.N. Nguyen, et al., “Material Challenges for Cryogenic Hydrogen Storage Technologies,” Poster, DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington D.C, April 30, 2019.

REFERENCES

1. B.N. Nguyen and K.L. Simmons, “A Multiscale Modeling Approach to Analyze Filament-wound Composite Pressure Vessels,” *J. Compos. Mater*. 47, no. 17 (2012): 2113–2123.
2. B.N. Nguyen, D.R. Merkel, K.I. Johnson, D.W. Gotthold, K.L. Simmons, and H.S. Roh, “Modeling the Effects of Loading Scenario and Thermal Expansion Coefficient on Potential Failure of Cryo-compressed Hydrogen Vessels,” *Int. J. Hydro. Energy* (in press).