

---

# Material Challenges for Cryogenic Hydrogen Storage Technologies

Kevin L Simmons (Primary Contact), Ken Johnson, David Gotthold, Ngheip Nguyen  
Pacific Northwest National Laboratory  
PO Box 999  
Richland, WA 99352  
Phone: (509) 375-3651  
Email: [kl.simmons@pnnl.gov](mailto:kl.simmons@pnnl.gov)

DOE Manager: Bahman Habibzadeh  
Phone: (202) 287-1657  
Email: [Bahman.Habibzadeh@ee.doe.gov](mailto:Bahman.Habibzadeh@ee.doe.gov)

Project Start Date: January 1, 2018  
Project End Date: September 30, 2020

## Overall Objectives

- Provide the scientific and technical basis to enable full deployment of hydrogen and fuel cell technologies by filling the critical knowledge gap for polymer performance in hydrogen environments.
- Develop an understanding of material interaction with hydrogen to mitigate impacts on reliability and durability.
- Develop experimental test methodologies that provide material performance under hydrogen infrastructure environments.
- Disseminate material characteristics to the community to begin discussions on how to improve materials in the hydrogen infrastructure environment.
- Develop a material acceptance process that will provide detailed information to evaluate specialty resins and carbon fiber composite materials through thermomechanical testing by combining cryogenic temperature, thermal cycling from cryogenic to elevated temperatures (-253°C + 120°C), off-gassing under vacuum ( $10^{-6}$  torr), and fatigue cycling at non-ambient conditions equivalent to the stress states in the composite at the maximum allowable working pressure and standard test cycles.

## Fiscal Year (FY) 2018 Objectives

- Complete the lab meeting report on the material properties that were identified for the thermal and mechanical models to more accurately predict pressure vessel performance through thermal cycling from cryogenic to ambient temperatures.
- Provide DOE a roadmap for the cryocompressed and cold gas storage pressure vessel materials and containment qualifications.
- Establish cryogenic testing capability requirements and procure equipment.
- Develop material models for predicting pressure vessel material performance at cryogenic temperatures under different pressure fill scenarios.

## 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<sup>1</sup>:

- System Weight and Volume
- System Cost
- Efficiency
- Durability/Operability
- Codes and Standards
- Materials of Construction
- Thermal Management
- Lack of Tank Performance Data and Understanding of Failure Mechanisms.

## FY 2018 Accomplishments

- Held a federal lab meeting at Pacific Northwest National Laboratory (PNNL) and developed a roadmap for materials testing and qualifications.

---

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

- Completed a final report on results of the federal lab meeting at PNNL and submitted the report to DOE.
- Identified and procured a liquid helium cryogenic dewar with mechanical testing capability and thermal control of temperatures from 1.2 K to 300 K.
- Completed thermoelastic stress analysis to assess the magnitude of thermal stresses in the composite overwrap of a Type 4 hydrogen storage vessel model.
- Identified a composite material resin system for sub-ambient and cryogenic testing.

## INTRODUCTION

The H2@Scale vision is to increase U.S. energy security, resiliency, economic growth, and jobs via high-scale hydrogen production. Hydrogen storage is a key part of H2@Scale, but new materials will be required for low-cost, lightweight storage vessels. The objective of this project is to develop a material acceptance process that will provide detailed information to evaluate specialty resins and carbon fiber composite materials through thermomechanical testing by combining cryogenic temperature, thermal cycling from cryogenic to elevated temperatures (-253°C + 120°C), off-gassing under vacuum ( $10^{-6}$  torr), and fatigue cycling at non-ambient conditions equivalent to the stress states in the composite at the maximum allowable working pressure and standard test cycles. The production of full-scale pressure vessels to validate tank materials and designs is expensive and time consuming. The ability to screen new pressure vessel materials (alternative resins, fibers, and liner materials) at the coupon level before transitioning to full-scale tank testing would significantly reduce cost and allow for more innovation through prescreening new concepts and materials. Experimental data will feed tank-level numerical modeling to predict temperature-dependent burst pressures. This process will develop and establish test methods to evaluate resins, fibers, composites, and liner materials prior to full-scale tank construction. This will either verify or disprove the hypothesis that new alternative resin, fiber, and liner systems designed for sub-ambient and cryogenic conditions will perform within acceptable limits at elevated temperatures.

## APPROACH

PNNL's approach to developing the materials qualification strategy for cryogenic materials evaluation was to:

- Develop a comprehensive roadmap with input from federal lab and industrial subject matter experts
- Develop test methodologies for cryogenic materials testing
- Establish a cryogenic material properties database
- Provide material properties to performance models that predict pressure vessel performance
- Provide material testing guidelines for cryogenic materials qualifications.

The material testing data will provide input into pressure vessel models for performance analysis. The analysis will provide technical feedback loops, supporting safety factor performance and long-term pressure vessel performance.

## RESULTS

On April 24, PNNL hosted a meeting of more than 20 subject matter experts from federally funded national laboratories and other government research agencies to discuss methods and technologies to test, evaluate, and rapidly screen materials for use in pressurized cryogenic storage applications and accelerate the pathway to tank qualification.

Based on the presentations, breakout sessions, and general discussions, several barriers were identified that must be addressed for the thermal and mechanical models to more accurately predict pressure vessel performance through thermal cycling from cryogenic to room temperatures. These include needing a better understanding of target operating conditions, improved testing methodology, and general lack of material performance data at low temperatures. The key materials properties that were identified are summarized in Table 1 with critical material-test combinations highlighted.

**Table 1. Material Property Test Data Needed to More Accurately Simulate Hydrogen Pressure Vessel Performance throughout the Pressure and Temperature Range**

Test Method/Properties	Material
<b>Uniaxial tension</b> providing the stress-strain curve to failure at selected temperatures throughout the entire temperature range <b>Resulting properties:</b> Elastic modulus, yield strength, ultimate strength, and ultimate elongation as a function of temperature	Metal liner Polymer liner <b>Composite overwrap: resin, fibers, lamina, and laminate</b>
<b>Short beam shear:</b> Interlaminar shear strength	Composite laminate
<b>Coefficient of thermal expansion (CTE) and thermal conductivity:</b> The CTE and thermal conductivity of composite lamina and laminates changes when matrix cracking occurs	Metal liner Polymer liner <b>Composite overwrap: resin, fibers, lamina, laminate</b>
<b>Glass transition temperature</b>	Polymer liner Composite resin
<b>Fracture toughness</b> <b>Charpy impact test:</b> Nil-ductility transition temperature as a function of combined hydrogen exposure and temperature	Metal liner Metal welds and joints
<b>Fatigue testing:</b> Thermomechanical cyclic loading for laminates; thermal and pressure induced for composite overwrap	<b>Metal liner</b> Polymer liner Composite overwrap: resin, fibers, lamina, laminate <b>Joints (welds, etc.)</b>
<b>Thermal properties:</b> Conductivity, specific heat, and thermal expansion of many solid materials at cryogenic temperatures are available from the NIST Cryogenic Materials website: <a href="https://trc.nist.gov/cryogenics/materials/materialproperties.htm">https://trc.nist.gov/cryogenics/materials/materialproperties.htm</a> The conductivity and specific heat of cryogenic liquids and gases are available at the NIST Chemistry WebBook website: <a href="https://webbook.nist.gov/chemistry/fluid/">https://webbook.nist.gov/chemistry/fluid/</a>	<b>Metal liner</b> <b>Polymer liner</b> Composite overwrap: resin, fibers, lamina, laminate Hydrogen

A comprehensive survey of the literature revealed limited knowledge of mechanical properties at cryogenic temperatures and insufficient data to support modeling efforts. The available data is largely limited to tensile properties at those temperatures that are readily achievable by submersion in liquid cryogenics (i.e., 4 K [liquid helium] and 77 K [liquid nitrogen]). Additionally, information on material strain, which is critical to developing a mechanical model, is largely absent from the literature. To address these shortcomings, PNNL has purchased a cryogenic dewar for use with a mechanical load frame capable of operating throughout the range between 2 K and 300 K. Strain data will be gathered continuously with an MTS extensometer rated to 4 K.

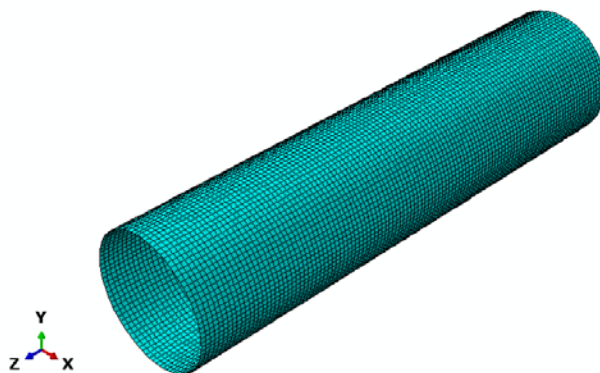
Once validated by experimental testing, a second dewar will be specifically designed to accommodate digital image correlation (DIC) for more in-depth strain analysis, along with fatigue testing capability. This unique experimental setup will allow for comprehensive characterization of mechanical properties of pure epoxies and fiber-epoxy composites along with valuable thermal contraction information.

Previous efforts by the National Institute of Standards and Technology (NIST) demonstrated a strong influence of specimen flaws on mechanical properties at cryogenic temperatures. To mitigate this issue, a mold was specially designed to limit the presence of flaws in epoxy tensile specimens. These unique specimens require custom gripping fixtures, which have been designed and machined at PNNL.

The literature survey also identified two base resins and several curing agents as candidates for development of an epoxy system designed for use in cryogenic composite tanks. Resins diglycidyl ether of bisphenol A

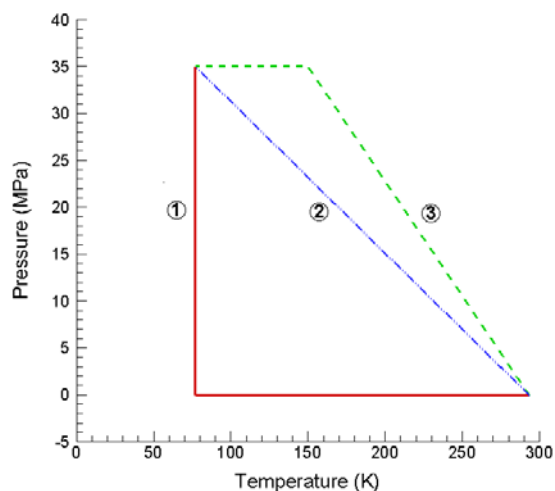
(DGEBA) and diglycidyl ether of bisphenol F (DGEBF) were selected based on frequency of use in research and commercial settings, material availability, and performance at cryogenic conditions. Several common aliphatic amine curing agents, such as diethylene triamine (DETA) and triethylene tetramine (TETA), were used frequently in the literature. However, other curing agents known to increase ductility in the cured products, such as amino ethyl piperazine (AEP) and dodecyl succinic anhydride (DDSA), have not previously been studied at cryogenic temperatures. The influence of additives including reactive diluents and resin modifiers will be studied along with other modifiable factors such as cure procedure. A design of experiments has been developed to account for which factors influence cryogenic material performance.

The modeling effort has applied PNNL's EMTA-NLA (Eshelby-Mori-Tanaka Approach to Nonlinear Analysis) tool for composite materials (e.g., [1-6]) implemented in the ABAQUS finite element (FE) code to analyze an existing Type 4 hydrogen storage vessel model to predict the composite and constituent thermal stresses in the helical and hoop layers (plies) of the composite vessel. This vessel model involves six layers, which have the following stacking sequence:  $90^\circ/+10^\circ/-10^\circ/90^\circ/+15^\circ/-15^\circ$  with respect to the axial direction, and thicknesses (in mm): 5 / 1 / 1 / 2.5 / 1 / 1. The fiber volume fraction of each layer is 0.6. The cylindrical part of the vessel was discretized using the composite layered shell elements of ABAQUS while the vessel's dome contribution was replaced by a distributed load at one end totalizing a force equal to  $P \pi r^2$  (with  $r$ , internal radius, and  $P$ , internal pressure). Figure 1 shows the FE model of the vessel cylindrical part. The length of this part is 1.338 m and its internal radius is 0.167 m.



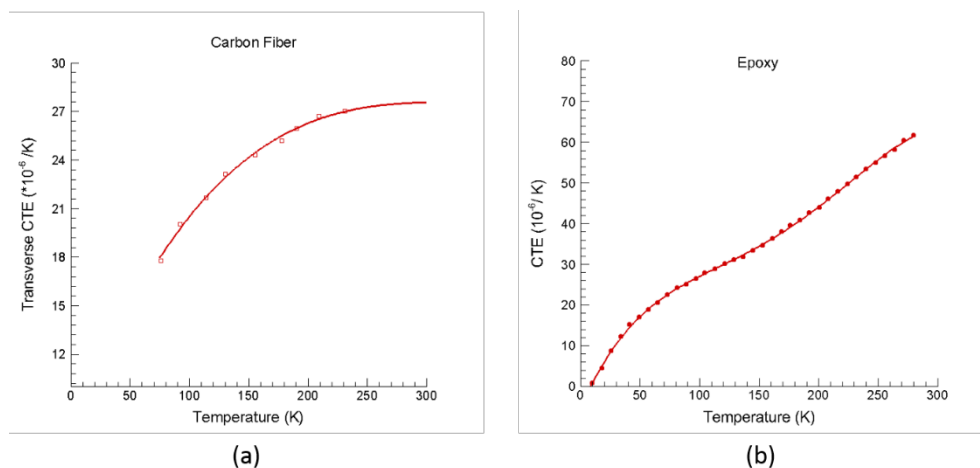
**Figure 1. The simplified FE model of a Type 4 hydrogen storage vessel**

The FE analyses were performed accounting for the variations of constituent thermoelastic properties with temperature according to three thermomechanical loading scenarios shown in Figure 2. In Scenario 1, the vessel is first cooled from room temperature (RT) to 77 K and then an internal pressure is applied incrementally to achieve 35 MPa at 77K. In Scenario 2, the vessel is also cooled from RT to 77 K but the internal pressure is applied concurrently until attaining 35 MPa. In Scenario 3, the vessel is cooled from RT to 150 K and during the same time, the internal pressure is applied incrementally to 35 MPa, and finally it is cooled down to 77 K at 35 MPa.



**Figure 2. The three thermomechanical loading scenarios considered in the FE analysis of the hydrogen storage vessel**

The analyses used existing thermoelastic properties of CF from [6] and TORAYCA’s datasheet for T700S assuming that CF’s elastic properties and longitudinal CTE were constant in the 77 K–293 K range. However, the variations of CF’s transverse CTE with temperature were accounted for in the analyses using the data in [7]. The epoxy elastic modulus was assumed to linearly vary from the value at RT (4,000 MPa) to the one at 77 K (6,000 MPa). The epoxy CTE as a function of temperature was from [8]. Figures 3(a) and 3(b) illustrate the CTEs of CF and of epoxy in the 77 K–293 K range, respectively. The longitudinal and transverse CTEs of the CF/epoxy lamina predicted as a function of temperature by EMTA-NLA during the analyses are given in Figures 4(a) and 4(b), respectively.



**Figure 3. (a) Transverse CTE of CF based on [7] and (b) CTE of epoxy based on [8]**

The analyses predicted not only composite stresses in different plies but also stresses in the fiber and matrix. As elevated thermal stresses in the epoxy matrix can induce cracking if the epoxy does not exhibit sufficient strength at low temperatures, we examine the fiber-direction and transverse-to-fiber-direction *matrix stresses* given in Figures 5 and 6 according to three thermomechanical loading scenarios. In Scenario 1, the cooling from RT to 77 K without the internal pressure application resulted in purely thermal effects that have caused matrix stresses to build up in all the plies. The application of internal pressure has then further increased matrix stresses to the highest levels at the end of loading. The evolutions of matrix stresses with temperature and pressure according to Scenarios 2 and 3 have reached the highest levels at the end of loading lower than the

levels attained in Scenario 1. If the analyses had used constant thermoelastic properties, the levels of matrix stresses at the end of loading would have been identical for all the loading scenarios. Tables 2 and 3 provide the values of matrix stresses at the end of loading according to all the loading scenarios. Compared to the other scenarios, Scenario 3 has led to the lowest matrix stresses in both fiber- and transverse-to-fiber directions.

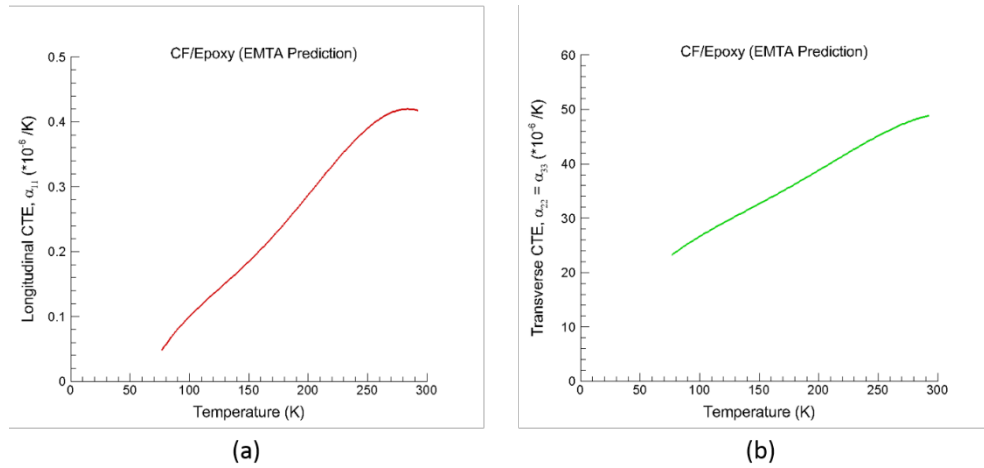


Figure 4. (a) Longitudinal and (b) transverse CTEs predicted for CF/epoxy

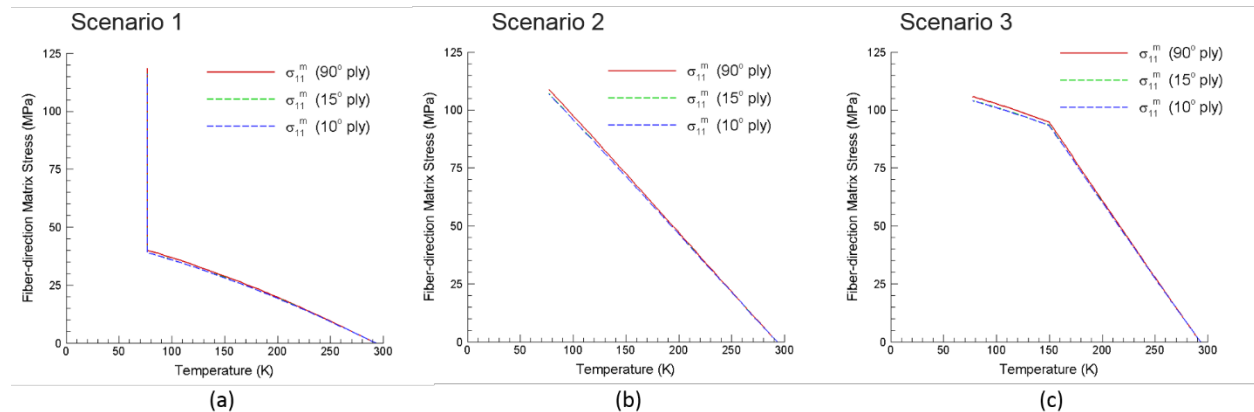


Figure 5. Predicted fiber-direction matrix stress in the helical (10° and 15°) and hoop (90°) plies according to (a) Scenario 1, (b) Scenario 2, and (c) Scenario 3

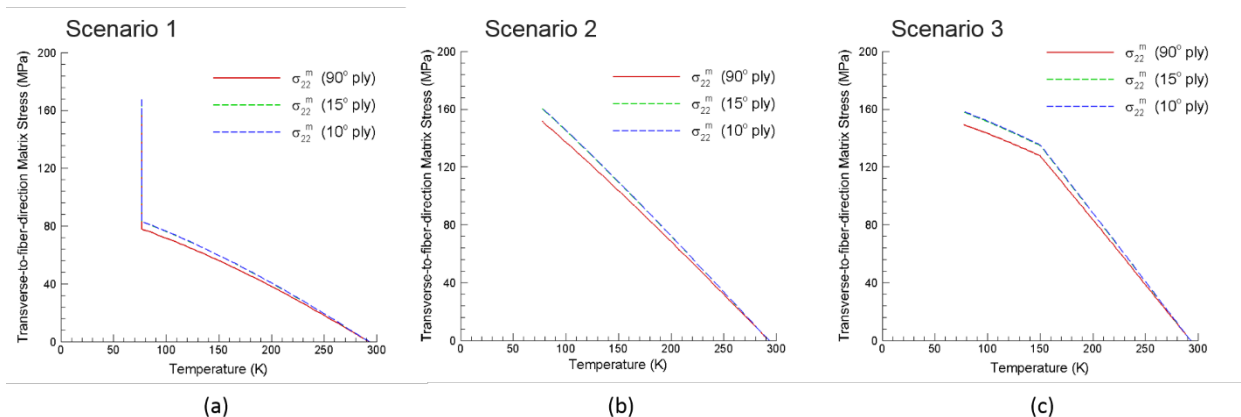


Figure 6. Predicted transverse-to-fiber-direction matrix stress in the helical (10° and 15°) and hoop (90°) plies according to (a) Scenario 1, (b) Scenario 2, and (c) Scenario 3

Table 2. Fiber-Direction Matrix Stress at the End of Loading

	90° Ply	15° Ply	10° Ply
Scenario 1	118.7	116.3	116.2
Scenario 2	109.1	107.2	107.1
Scenario 3	105.8	104.1	104.0

Table 3. Transverse-to-Fiber-Direction Matrix Stress at the End of Loading

	90° Ply	15° Ply	10° Ply
Scenario 1	159.2	168.9	169.4
Scenario 2	152.0	160.9	161.3
Scenario 3	149.3	158.0	158.4

### CONCLUSIONS AND UPCOMING ACTIVITIES

Upon installation of the cryogenic mechanical properties test system, a series of tests will be conducted to identify the most influential constituents of epoxy systems. Epoxies will then be optimized for mechanical performance in fiber composite tanks. With validation of the cryogenic test system, a second system designed for fatigue testing and DIC capabilities will be procured. Data gathered during this process will be incorporated into a finite-element model that is currently in development.

Preliminary analyses of a Type 4 pressure vessel model were performed assuming the thermoelastic behavior of the constituents (i.e., CF and epoxy) and of the as-formed CF/epoxy composite overwrap. The analyses accounting for variations of thermoelastic properties with temperature have provided estimates of constituent and composite stresses resulting from three prescribed thermomechanical loading scenarios. Although these analyses were preliminary and based on simplified vessel geometry and loading conditions, they have indicated significant matrix stress levels at the end of loading that would need to be mitigated through improved material and vessel design in order to avoid failure of the composite overwrap due to transverse matrix cracking when the vessel operates in the cryogenic temperature range. Another important finding from this work is that the thermomechanical loading scenario has a significant impact on thermal stresses in the composite. Optimizing the loading scenario could help reduce the constituent stresses—in particular, matrix stresses—during the cycle, and this would help mitigate thermal stresses.



Future research activities include performing analyses for a Type 3 vessel, assessing thermal conductivity and CTE predictions, and modeling the damage and failure mechanisms observed in testing representative CF/epoxy specimens at selected temperatures from RT to a given cryogenic temperature.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. K. Simmons, N. Menon, D. Smith, A. Naskar, and M. Veenstra, “Hydrogen Compatibility of Polymers,” presented at the 2018 Annual Merit Review, Washington DC, June 14, 2018.
2. K. Simmons, D. Gotthold, and K. Johnson, 2018 Material Challenges for Cryogenic Hydrogen Storage Technologies, Summary Report from the Material Qualification Lab Meeting.
3. Proceedings from the Material Challenges for Cryogenic Hydrogen Storage Technologies: Summary Report from the Material Qualification Lab Meeting, August 2018, PNNL-27830.

## REFERENCES

1. J.D. Eshelby, “The Elastic Field Outside an Ellipsoidal Inclusion.” *Proceeding of the Royal Society London, Series A: Mathematical and Physical Sciences* 252 (1959): 561-569.
2. T. Mori and K. Tanaka, “Average Stress in Matrix and Average Elastic Energy of Materials with Misfitting Inclusions,” *Acta Metallurgica* 21 (1973): 571-574.
3. B.N. Nguyen, *EMTA User's Guide* (Richland, WA: Pacific Northwest National Laboratory, 2010), PNNL-19997.
4. B.N. Nguyen, *EMTA-NLA User's Guide* (Richland, WA: Pacific Northwest National Laboratory, 2010), PNNL-20013.
5. B.N. Nguyen, S.K. Bapanapalli, V. Kunc, J.H. Phelps, and C.L. Tucker III, “Prediction of the Elastic-Plastic Stress/Strain Response for Injection-Molded Long-Fiber Thermoplastics,” *Journal of Composite Materials* 43 (2009): 217-246.
6. B.N. Nguyen and K.L. Simmons, “A Multiscale Modeling Approach to Analyze Filament-Wound Composite Pressure Vessels,” *Journal of Composite Materials* 47 (2013): 2113-2123.
7. M.G. Huson, “High-Performance Pitch-Based Carbon Fiber,” In: *Structure and Properties of High-Performance Fibers*, Woodhead Publishing Series in Textiles (2017): 31-78.
8. U. Escher, “Thermal Expansion of Epoxy Resins with Different Cross-Link Densities at Low Temperatures,” *Cryogenics* 35 (1995): 775-778.