III.4 Failure Analysis, Permeation, and Toughness of Glass Fiber Composite Pressure Vessels for Inexpensive Delivery of Cold Hydrogen

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Project End Date: October, 2012

Fiscal Year (FY) 2012 Objectives

- Optimize hydrogen delivery by tube trailer
- Develop materials and manufacturing for low-temperature hydrogen delivery
- Quantify performance and economics of delivery pressure vessels

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery (3.2) section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Cost

(G) Storage Tank Materials and Costs

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Delivery

Characteristic	2005 value (Table 3.2.2)	DOE Targets FY2012/2017	LLNL + SCC 2012 status
Delivery Capacity (kg H_2)	280	700/1,100	1,100
Operating Pressure (psi)	2,640	<10,000	<10,000
Purchased Capital Cost ($)	$165,000	<$300,000	<$291,000

FY 2012 Accomplishments

Developed a deep understanding of composite pressure vessel (CPV) failure analysis and anomalous toughness degradation in ring-opening metathesis polymerization (ROMP) castings.

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Introduction

This project has developed the key missing component necessary for LLNL's "cold glass" delivery approach: trailer-scale pressure vessels. Other technologies can build low-temperature-capable pressure vessels, but their vessels are either much too costly or too heavy for delivery trailers.

Only CPVs are light enough to carry compressed hydrogen in sufficient quantity to achieve LLNL's optimized delivery costs within the volume and mass limitations of a trailer. LLNL's target (below $1/kg, not including forecourt storage, compression, or dispensing) must pay for energy and capital to refrigerate, plus operating and capital costs of the trailer cab (including labor to drive and load/unload).

Development effort required to produce trailer payloads filled with economical CPVs can be categorized on the manufacturing readiness level (MRL) scale [1]. When first proposed in 2007, this CPV development effort expected to advance from MRL 4 (proven manufacturing feasibility) to MRL 8 (manufacturing processes that operate at target cost, quality, and performance). Across the past two and a half years this MRL characterization encountered setbacks, which caused its MRLs to be revised from MRL 3 (manufacturing process identified) to MRL 7 (proven manufacturing processes). Careful study of these setbacks has produced a new understanding of vessel failure mechanisms. This new understanding is the focus of this report.

Approach

Because the processes that build plastics into composites and liners do not scale from one size to another without posing significant risks to CPV performance and cost, only proof at full scale of a CPV technology will prove that LLNL's trailer design is practical. Due to the severe cost scaling of tooling to build such CPVs, LLNL's system integration and subsequent development efforts have focused on 23" diameter, 18 CPVs per International Organization for Standardization (ISO) container cross section, as full scale. Considerable development risk reduction testing has been performed with 3” diameter subscale vessels, and with strength test coupons.

Results

Hydrogen delivery by trailer cannot meet DOE targets for dollars-per-kilogram without new technology. This project performs research and development on an approach to delivering centrally-produced hydrogen that can achieve DOE targets with high likelihood.

Reaching these objectives demands significant learning because the expertise necessary to determine the safety of our new technology is scarce. In particular, neither regulators nor aerospace experts have valid precedents for large pressure vessels designed to operate economically at near-cryogenic temperatures, on highways, built from unprecedented materials.

In pursuit of a fundamental reduction in the manufacturing cost of pressure vessels, a new category of plastics with properties and manufacturing process advantages was researched. This category will be termed “ROMP” catalyzed, which stands for ring opening metathesis polymerization. Among the features of this plastic are low thermal expansion and full property retention at temperatures as low as 77 K. These plastics are expected to form both liner and matrix of a new generation of inexpensive pressure vessels.

Failure Analysis

Even CPVs built and operated with thousands of person-years of aerospace experience gained over 40 years with ‘proven’ processes using graphite fibers, familiar polymers, and stainless steel connections fail for unknown reasons. A deep understanding of failure modes is necessary for improved vessel safety.

In collaboration with National Aeronautical and Space Administration (NASA) White Sands Test Facility (WSTF), National Institute of Standards and Technology (NIST), and Department of Transportation (DOT), LLNL produced the first expert-consensus methodology in nearly 30 years to plan how to determine the root causes of a CPV failure. This procedure makes selective use of many new techniques, which it triages for affordability in a better adaptation to motor vehicle CPVs. The procedure prunes the branches of an LLNL-supplied fault tree (Figure 1), as thoroughly as data will allow, to determine the root cause of a CPV failure.

The current LLNL effort seeks novel hydrogen CPVs that will not fail in service, and expects to develop interest at DOT

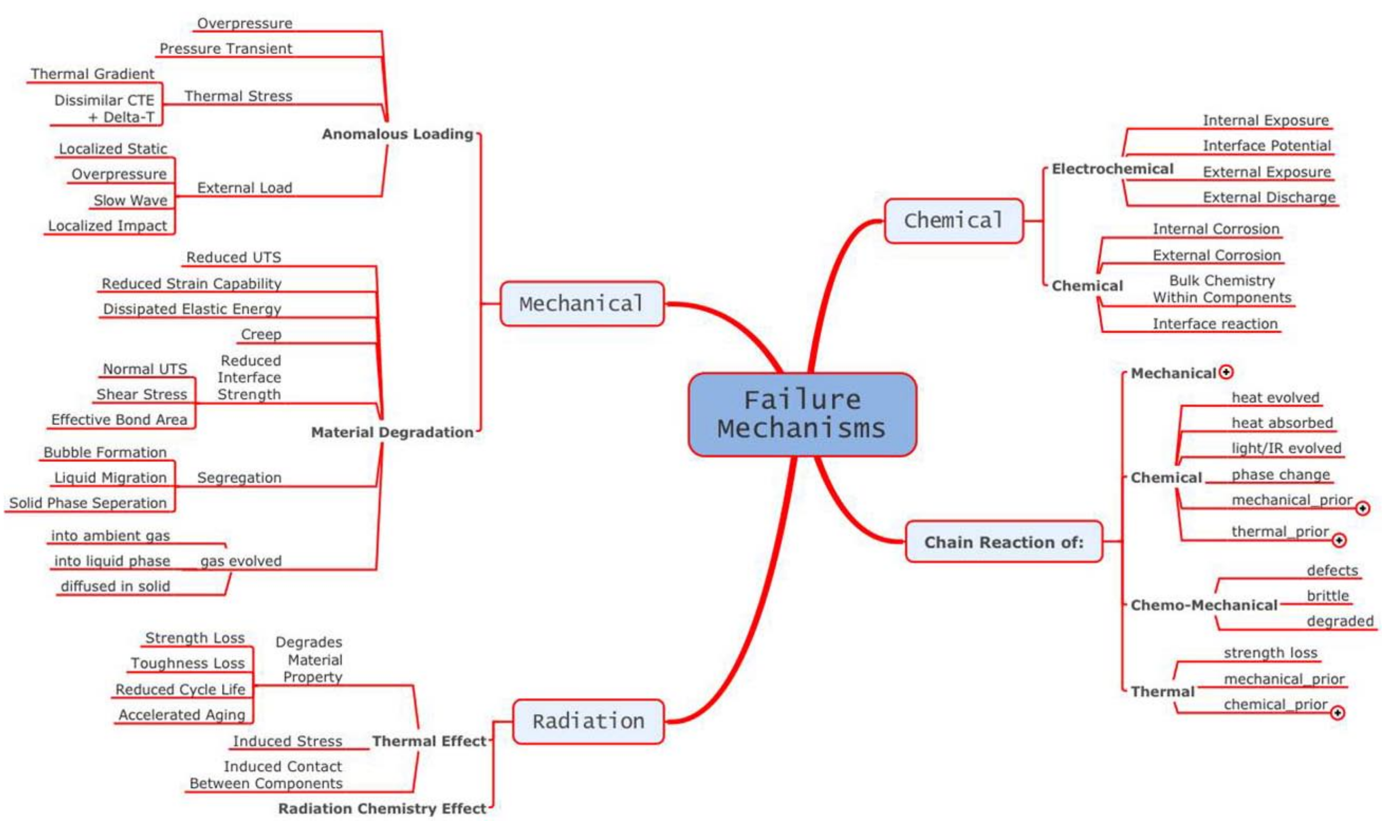

FIGURE 1. Expert-consensus methodology plans how to determine the root causes of a CPV failure, based on using a wide variety of affordable tests to prune branches on the above fault tree, which was prepared by LLNL in support of a multi-agency CPV failure analysis collaboration with NASA WSTF, NIST, and DOT.

for a hydrogen delivery trailer solicitation. This argument depends on quantitative data, including empirical probabilities of failure collected from multiple ‘identical’ CPVs and sorted into failure modes. In particular, the challenges of a probability of disaster limited in the low parts-per-million have focused LLNL on two branches on the CPV fault tree: manufacturing defects and stress rupture. LLNL’s efforts to date have reduced the risk of unpredictable burst strength and should reduce the risk of inadequate cycle life.

Permeation

Permeation of hydrogen through plastics poses a risk to this project. While the only ROMP permeation data (collected at LLNL in 1997 with flat coupons at ambient temperature) indicates extremely low permeation (several orders of magnitude too low to have a negative effect on the proposed delivery approach), it is still important to accurately quantify permeation by conducting full-scale tests.

LLNL has been working with SCC on conducting safe, remotely operated, full-scale CPV permeation tests. A suitable site that contractor personnel can secure for weeks against tampering and intruders was leased by SCC to practice initial ‘coffin’ emplacement and determine manpower costs for long endurance permeation tests. One LLNL coffin is shown emplaced in the trench dug at that site in Figure 2.

Toughness and Toughness Decay

Applications for ROMP chemistry were originally sought in the 1980s. However, their utility as resins for inexpensive polymers failed because their toughness decayed over time. Adding anti-oxidants was a partial solution that maintained higher toughness than toughened epoxies for a month after casting. If their initial toughness persisted, ROMP formulations would be thirty times as tough as toughened epoxies.

In an effort to organize the hypotheses collected to explain anomalous toughness decay in cast ROMP liners, LLNL developed a tree diagram (Figure 3). Hypotheses in Figure 3 are color coded to distinguish their experimental validation over the course of this project. Green font hypotheses were proven to occur and be responsible for faulty ROMP processing. Blue font hypotheses were proven, yellow were disproven except for highly localized defects due to unclean molds and gaps in seals that retained air at mold parting lines. Orange font hypotheses turned out to be both true and untrue in different senses. The purple font hypothesis appears to be caused by the same driving force that appears in the turquoise font, which represents the root cause of anomalous embrittlement: the differential shrinkage between liquid resin and solidified ROMP, by a novel mechanism this project has come to call ‘nanocracking’.

Detective work with scanning electron microscopy (SEM) explained a sequence of events that evolve gases and liquids from catalyzing gel. The key to identifying these events was careful observation of the “smoking gun crater” (Figure 4). Observation revealed that there was material missing between the walls of such crater because a gel had torn itself apart here while shrinking and then a bubble had forced itself out through a smooth wall caused by strength anisotropy and not by imposed stress, and finally the almost conical volcano had further shrunk to form sharp facets. All this must have happened before the liner failed, in the final phases of its solidification inside a mold, where the catalysis wave ran out of liquid to knit and could not make up for the volume loss of solidification. Any gas pressure would attempt to burst out of a gel under tension. Solids with such stress-

FIGURE 2. Photographs show ‘coffin’ emplacement and steel deck plate covering operations at SCC’s leased permeation test site. The coffin provides a clean environment for transportation (over dirt roads) and plumbing and data collection from a CPV under long duration testing with dangerous high-pressure fluids.

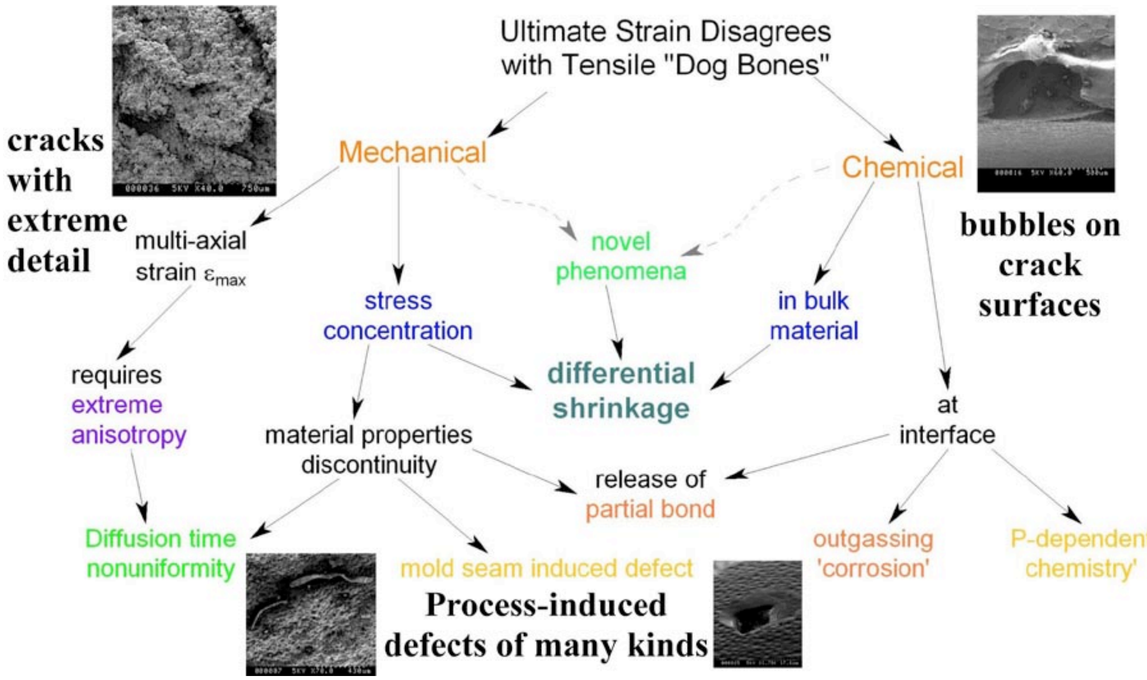

FIGURE 3. A tree diagram organizes the possible hypotheses collected to explain anomalous toughness phenomena in cast ROMP liners. Orange font hypotheses turned out to be both true and false in different contexts. Green hypotheses were proved to occur and be responsible for CPV failures. Yellow hypotheses were not responsible, blue proved to occur, purple responsible, and turquoise the root cause of all responsible hypotheses.

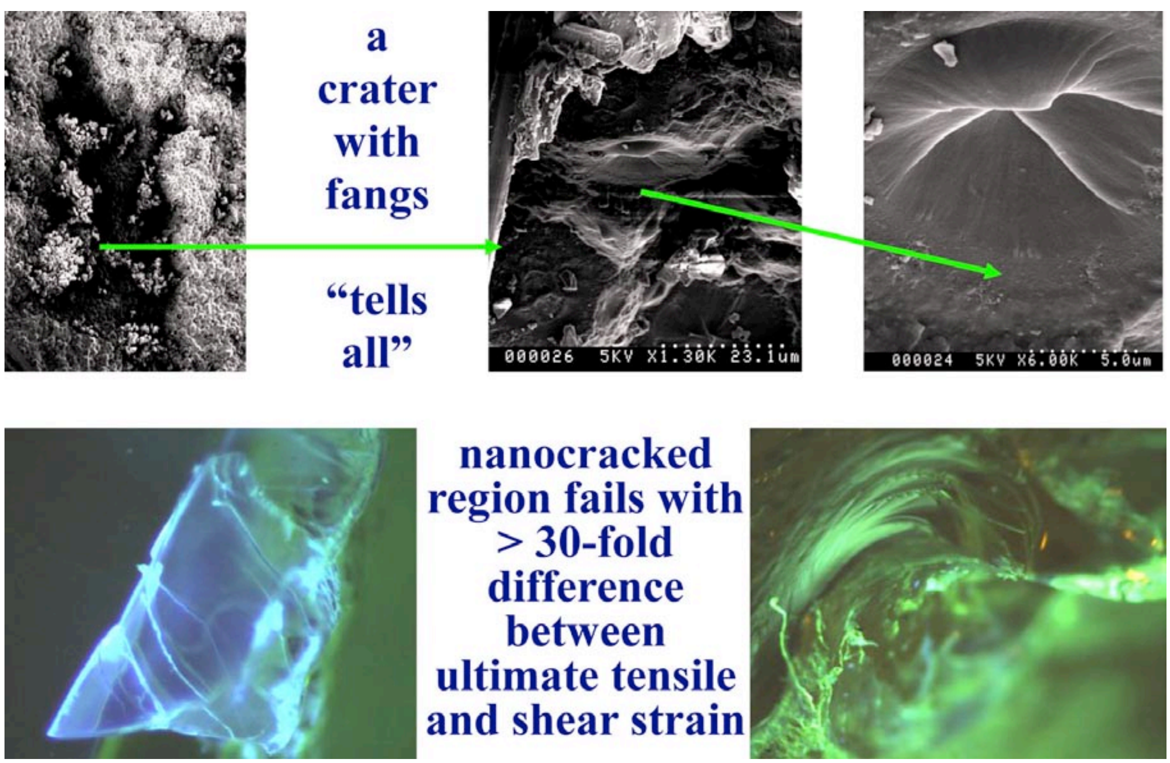

FIGURE 4. Micrographs pivotal to the discovery of new materials science taken in the course of debugging anomalous toughness. Specimens of ROMP liners, their production during deliberate failure, subsequent preparation, and conclusions based on these micrographs are briefly described in the text.

concentrating defective regions built into them were bound to fail if those regions came under subsequent tension even slightly perpendicular to some surface nanocrack.

With toughness loss explained, the remedy was to drive catalysis waves away from solid surfaces and into free surfaces, whereat solidification shrinkage allows the cast surface to recede rather than crack. The team learned to bias catalysis direction by mold design and active thermal control, and to control liner bending during curing. SCC found a technique to detect nanocracked surfaces without breaking liners, sectioning portions of a crack surface, coating specimens with ~50 nanometers of metal to conduct electricity, or even using an SEM. LLNL found some nanocracked regions interior to cast parts where catalysis waves had arrived from different directions at different times. LLNL isolated one of these regions wherein the nanocracked volume appears faintly as a hazy tree under bright light. Successful liner geometries and molding processes were found which did not put nanocracked regions in tension.

This research is continuing with investigation of toughness in ROMP at low temperatures. Countermeasures against toughness loss are under development at SCC, and the likelihood that uncatalyzed molecules must be kept in nanopores to preserve extreme toughness could be tested later this year by correlating Sharpe toughness with weight loss from different cure cycles. Meanwhile a more precise toughness measurement is about to be exercised by LLNL experiments in a 0.5% accurate impact test rig at NASA WSTF. Figure 5 illustrates that rig, its potential for tests that produce shrapnel, and the exercises that LLNL has already conducted at SCC to determine the drop weight and practice cool down operations in preparation for those tests.

Conclusions and Future Directions

- Considerable scientific effort has generated significant understanding of ROMP failure mechanisms, and further effort will be capable of limiting significant hydrogen delivery cost uncertainties. Subscale and full-scale CPV permeation tests are planned without government funding at leased facilities that have already been exercised to plan safe, long-duration-under-pressure experiments.
- Further quantitative understanding of cold strength at various reduced temperatures is anticipated at multiple glass fiber manufacturers from testing subscale glass fiber pressure vessels in expendable Dewars.
- Joint DOE/DOT demonstration program remains a possibility suitable for discussion early in 2013.

References

1. Manufacturing Readiness Level chart (and accompanying 72 page category descriptions) provided by Department of Defense web site www.dtic.mil/whs/directives/corres/pdf/500002p.pdf.

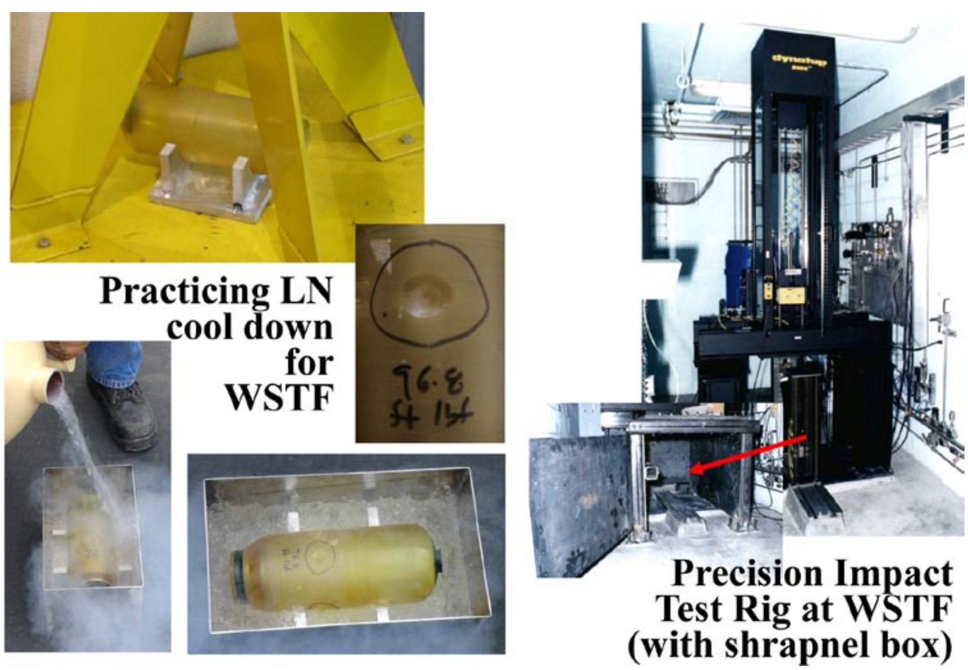

FIGURE 5. Preparations for cold liner toughness measurements yet to be performed at NASA WSTF include a medley (on the left) showing practice for safe cold liner handling, impact fracture, and cooling in liquid nitrogen. Coarse toughness measurements made in the ASTM International drop tower inside SCC facilities at the upper left were performed to specify drop weights for WSTF impact testing.