MICROCRACK RESISTANT POLYMERS ENABLING LIGHTWEIGHT COMPOSITE HYDROGEN STORAGE VESSELS

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ABSTRACT

Robust, lightweight, storage vessels are needed for on-board storage of hydrogen. Challenges with currently used composite overwrapped vessels include weight due to the non-load bearing liner, performance reliability resulting from separation of the liner, and costs of extra manufacturing steps to fabricate the liner. Linerless composite vessels, where the composite shell serves both as a permeation barrier and a structure, can provide for the lightest weight vessels for a given set of requirements. Preliminary designs show up to 25% weight savings allowing reduced storage system mass and more internal volume. These tanks are targeted to attain hydrogen mass storage efficiency of 15-18% as compared to 3-4% from lined vessels. Manufacturing cost, operational risks and maintenance costs can be reduced due to inherently simple construction. Engineering methods that define material performance requirements, such as polymer strain requirements in a lamina have been used to guide the development of microcrack resistant polymers. Performance of linerless composite tanks has been demonstrated and qualification is on-going.

INTRODUCTION

Hydrogen is an ideal energy carrier that can help increase our energy diversity and security by reducing our dependence on hydrocarbon-based fuels. Hydrogen can be produced from domestic resources that are clean, diverse, and abundant; fuel cells provide a technology to use this energy in a highly efficient way, in numerous applications, with only water and heat as byproducts. The US Department of Energy's initiative and push has already put fuel cell buses on the road, and may soon put new fuel-cell powered vehicles on the nation's rails and waterways.

Figure 1. Hydrogen fuel cell cars

Among the obstacles to commercializing hydrogen-powered vehicles—besides production and infrastructure—is the need for storage systems that can contain sufficient hydrogen onboard a car to compete with the range and performance of gasoline-powered autos. Robust, lightweight, high-strength pressure vessels that can store gaseous hydrogen under high pressure still provide the most commercially viable approach to driving fuel cell cars (Figure 1). The driving range of fuel cell vehicles with compressed hydrogen tanks depends, of course, on vehicle type, design, and the amount and pressure of stored hydrogen. By increasing the amount and pressure of hydrogen, a greater driving range can be achieved but at the expense of cost and valuable space within the vehicle.[1] Volumetric capacity, high pressure, and cost are thus key challenges for compressed hydrogen tanks. Currently, pressure vessels for ambient high-pressure storage are fabricated with metal lined (Type III) or polymer lined (Type IV) composite overwrapped pressure vessels. Tanks and pressure vessels used to store hydrogen at cryogenic temperatures are fabricated from metals (aluminum or titanium). Challenges associated with the use of Type III and Type IV vessels for storage of ambient high pressure gases include additional weight due to the liner (which is generally not load bearing), performance reliability resulting from separation of the liner from the composite, additional cost associated with extra manufacturing steps for liner fabrication (of particular concern with Type IV vessels), and the high cost of tooling modification for tank geometry changes in Type III and IV vessels for different applications.

## OVERVIEW OF KIBOKO® TECHNOLOGY

To address the above-mentioned issues, CTD has developed KIBOKO® lightweight all-composite pressure vessels (Figure 1), which have been designated as Type V pressure vessels. Due to the lack of a metallic or polymeric liner, Type V vessels can provide the lightest possible weight vessels for a given set of requirements. Preliminary designs have shown an approximate 50% weight savings over all metal (Type I), 25% over Type III, and a 10% weight savings over Type IV vessels, allowing reduced total storage system mass. In addition, by eliminating the liner, KIBOKO® Type V vessels can provide more internal volume, which is critical for storage of low energy density gaseous fuel like hydrogen. Due to the combined effect of reduced vessel mass and increased internal volume, KIBOKO® vessels are expected to attain gaseous hydrogen mass storage efficiency of 10-15%. This is a significant performance jump over the current state of the art of 3-4% in commercially available pressure vessels. If properly designed, KIBOKO® vessels can also reduce the manufacturing cost, operational risks, and maintenance costs over their lifetime due to their inherently simple construction.

Figure 2. CTD has fabricated many KIBOKO® all-composite pressure vessels in various sizes and configurations

The improved storage efficiency of a KIBOKO® Type V vessel is easily appreciated by comparing different classes of composite pressure vessels in terms of a common metric. One such industry-accepted yardstick is *Pressure Vessel Efficiency*, commonly defined as $\eta = pV/W$, where $p$ is the design burst pressure, $V$ is tank volume, and $W$ is tank mass. To improve efficiency, it is imperative that the composite structure be optimized to provide the highest burst strength, while reducing tank weight and maximizing storage volume. The bar chart in Figure 1 shows the efficiency advantage of linerless designs, compared to other types of composite pressure vessels commonly used in the aerospace industry.[2]

Previous attempts at linerless composite vessels, by others, showed that these vessels prematurely leaked and structurally degraded. CTD has overcome these inadequacies by developing engineering methods that define specific material performance requirements to prevent this premature leakage and structural failure. Furthermore, CTD has developed and demonstrated materials that provide the performance dictated by these engineering models. Key to the successful performance of these materials is that they do not microcrack within the operating range of the tanks. Understanding the strains at which microcracking initiates in a composite material, and how this inhibits permeation and leakage of fluids is a primary criterion for optimizing the design of these lightweight pressure vessels. The substantial advancements to the technology of all-composite pressure vessels made by CTD can be attributable to an integrated systematic approach that looks concurrently at the totality of critical issues, including material capabilities and tailoring, fabrication process optimization, and structural design optimization (Figure 4).[3]

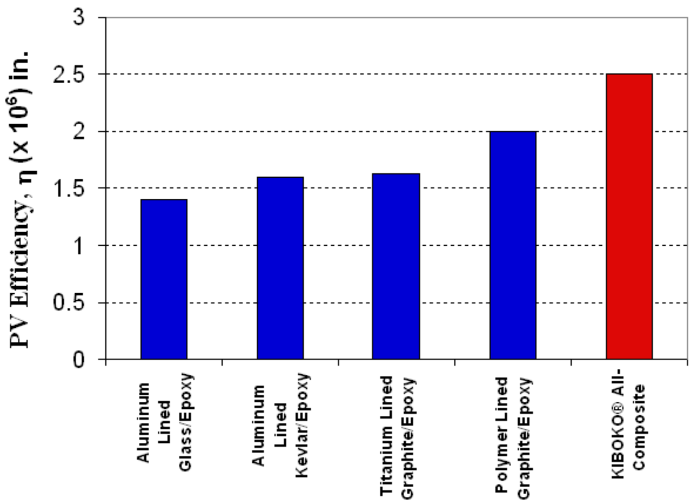


Figure 3. Pressure vessel efficiencies compared for different types of pressure vessels

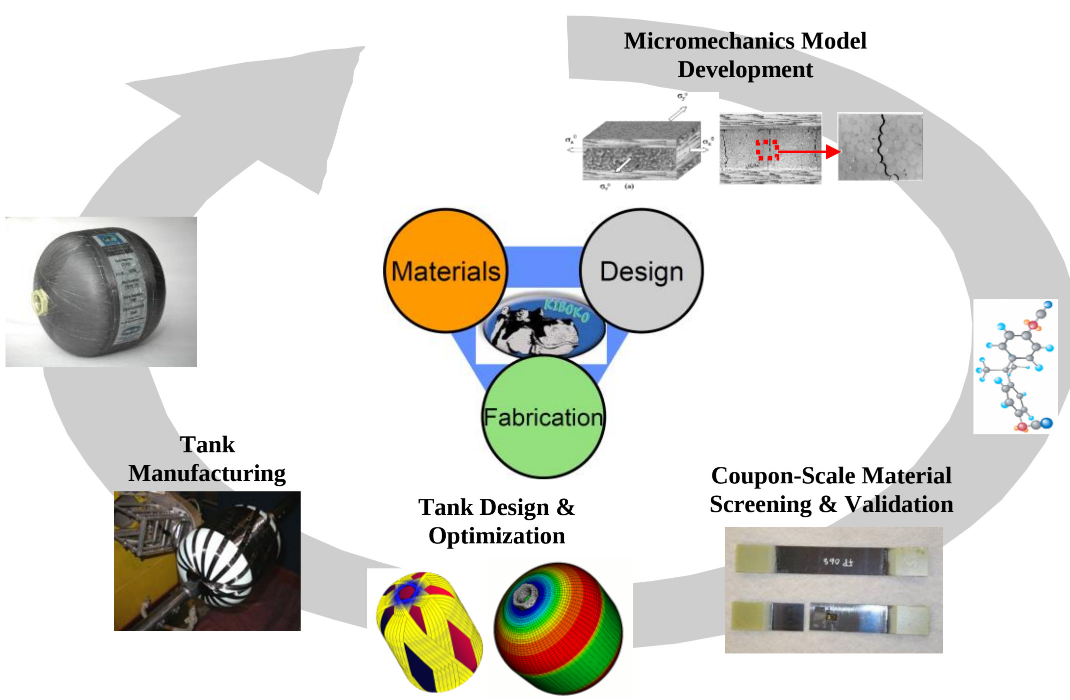


Figure 4. CTD's integrated systematic approach to developing KIBOKO® all-composite pressure vessels.

DEVELOPMENT OF MICROCRACK RESISTANT MATERIALS FOR KIBOKO® PRESSURE VESSELS

KIBOKO® vessels, which do not utilize a polymer or metallic liner use the composite shell to serve both as a permeation barrier as well as to provide the structure necessary to carrying all pressure and environmental loads. CTD has developed engineering models and methods that define specific material performance requirements, such as polymer matrix strain requirements for a particular lamina layer within the composite, that prevent microcracking of the resin and thus premature leakage and structural failure. Key to the successful performance of these materials is that they do not microcrack within the operating range of the vessels. From the structural perspective, the reinforcing fiber of the composite material defines the stress and strain limits of the composite material. To eliminate the potential for leakage and permeation, the matrix, or resin, material used to bind the fibers together into the structural composite, must not microcrack under the tank's operating conditions (Figure 2). Furthermore, the composite structure is constructed of multiple layers of fibers and resins, called lamina. It is also important that the matrix be strong enough to prevent lamina from delaminating until the fiber performance limits are reached.

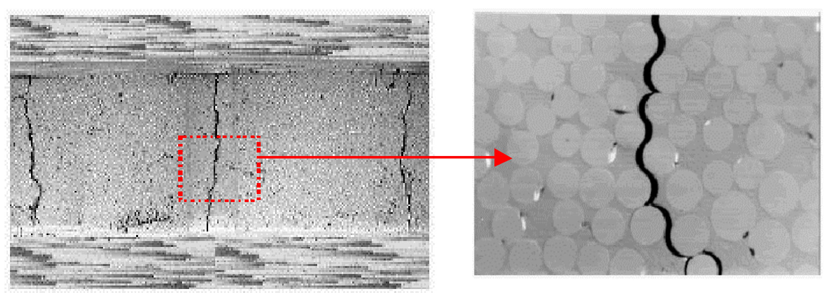

Figure 5. Microcrack in a composite laminate

Key to this effort is the development and validation of new matrix materials that meet these requirements. CTD has developed novel toughened epoxy systems such as CTD-7.1 and CTD-9HX that meet the requirements defined above. Furthermore, to complement the design of composite materials suitable for pressure vessels, CTD has developed micromechanics based material test methods based on microcrack fracture toughness to evaluate and rank their performance.[5] These test methods enable the determination of the strain level at which the matrix starts to degrade. CTD has found that the inclusion of nano-reinforcements in the matrix improves resin modulus and significantly increases the inter-laminar shear strength at the ply interfaces, thus enabling the composite material to fail only when the limits of the fiber performance have been reached. CTD has also found that the addition of suitable nano-reinforcements within composite plies can significantly reduce the permeability of the structure to low-molecular gaseous contents like hydrogen.

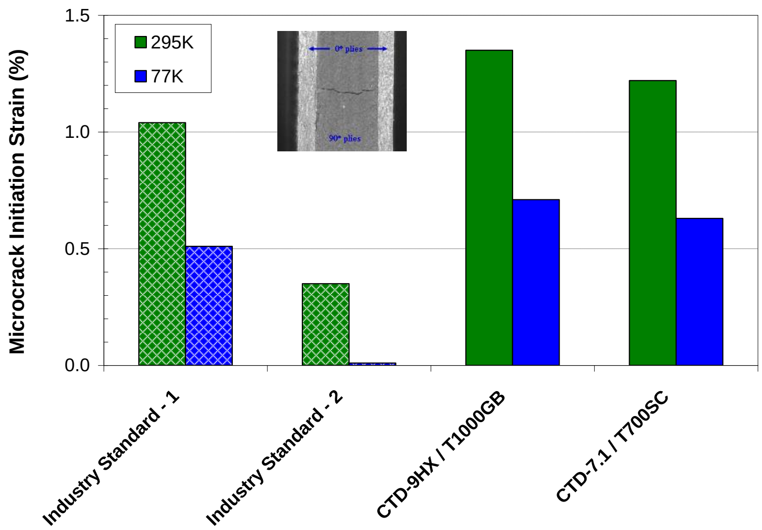


Figure 6. CTD's toughened polymers enable improved microcrack resistance over industry standard materials.

## DEMONSTRATION OF KIBOKO® TECHNOLOGY

### KIBOKO® Pressure Vessels for Satellites

CTD designed, built, qualified, and supplied two Space flight qualified Argon gas storage vessels and two spares to the University of Texas FASTRAC (the Formation Autonomy Spacecraft with Thrust, Relay, Attitude and Crosslink) nanosatellite program (see Figure 7). These vessels were 6" dia. x 6.875" long to fit within the available envelope of the satellite, a size and design not previously built by CTD. A total of 21 pressure vessels were fabricated by CTD, at the Composite Laboratory of AFRL, Kirtland AFB, under a Cooperative Research and Development Agreement (CRADA) between CTD and AFRL, to ensure a sufficient number of pressure vessels to test and deliver. The vessel's 1.8 liter capacity was 15% greater and its 0.35 kg mass was 25% lighter than the previously baselined aluminum pressure vessels that did not pass the qualification tests (Figure 3). However, the KIBOKO® pressure vessels for FASTRAC were far from optimized for minimal weight. With only six weeks to deliver, these pressure vessels were

Figure 7. KIBOKO® linerless composite tanks for Air Force sponsored nanosatellite

designed for a burst pressure of 3,000 psi, pressure tested to 2,000 psi prior to leak and proof tested to 500 psi to ensure a safe operating pressure of 100 psi with negligible permeation of gaseous content.

Permeation Testing of 14-liter KIBOKO® Pressure Vessel

As part of the US Air Forces' Fully Reusable Access to Space Technology (FAST) program, CTD fabricated two 10 in. diameter x 18 in. long, 14L KIBOKO® pressure vessels and tested them at ambient conditions (295 K). The test procedure consisted of three acceptance tests: pre-hydrostatic helium leak test (Figure 3), hydrostatic pressure test, and post-hydrostatic helium leak test. Both pressure vessels exhibited maximum leak rates of 1.4 x $10^{-5}$ scc/sec, which compare favorably with the FE-model-predicted leak rate of 3.4 x $10^{-5}$ scc/sec. This result indicates that there was no significant microcrack or void damage in the pressure vessels after fabrication.

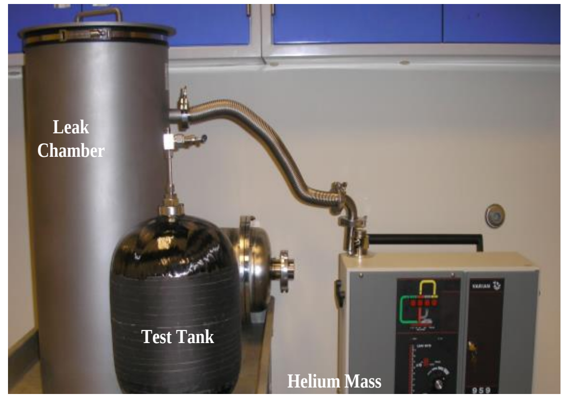


Figure 8: CTD's test bench to measure permeation rate in KIBOKO® tanks using a leak chamber and Helium mass spectrometer.

Following the permeation testing, the pressure vessels were subjected to hydrostatic pressure test. The limiting pressure that the vessel can experience without causing any leakage was determined to be 2,800 psi, which results in a Maximum hoop strain of 1.2%. To test this design values, the vessels were first pressurized with water to 1,900 psi and subsequently to 2,800 psi. Both pressure vessels successfully completed the test with no leakage reported during holds of ten minute at 1,900 psi and 2,800 psi.

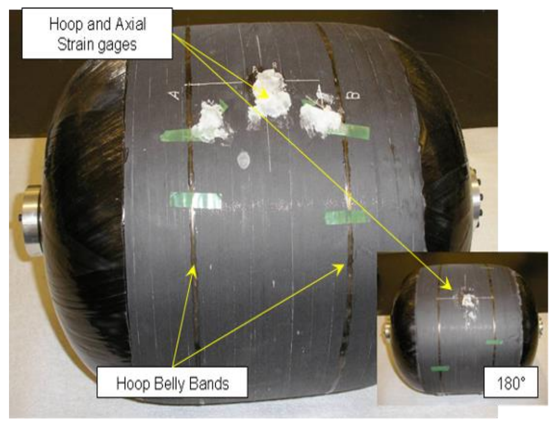


Figure 9. KIBOKO® 14L vessel with strain gages prior to hydrostatic pressure test.

One of the pressure vessels was instrumented with multiple strain gages to measure the strain on the external surface of the cylindrical section of the vessel during the pressure test (Figure 3). This included 2 strain gages aligned along the circumferential (hoop) direction and 2 bellyband gages to measure the hoop strain located about 2" away from the hoop strain gages. Figure 9 shows a photo of the strain gages and bellybands. Figure 10 shows the plots of pressure vs. strain, comparing the finite element model predictions and experimental results. The agreement between the FE analysis and test results is very good.

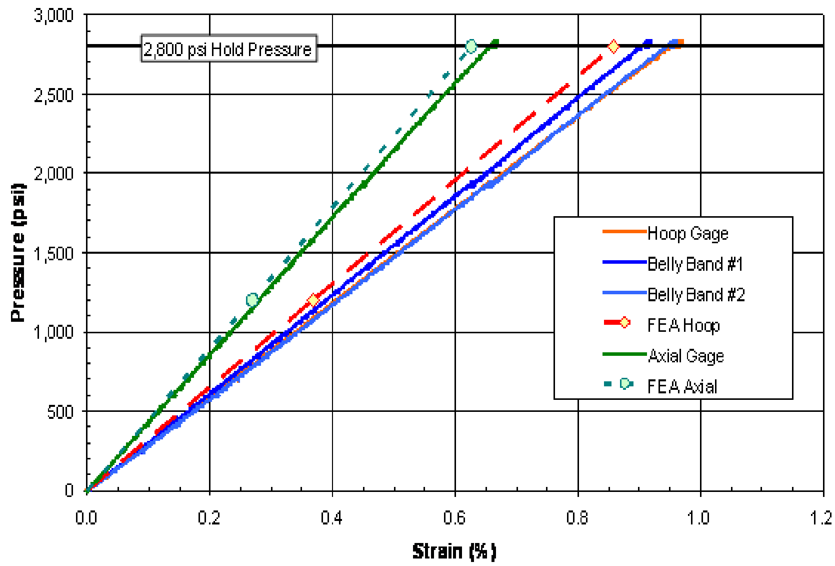


Figure 10. Measured and predicted strain in 14L KIBOKO® pressure vessel.

Following the hydrostatic pressurization test up to 2,800 psi, the pressure vessels were tested again for leaks using the helium-leak test. The first pressure vessel exhibited a maximum leak rate of $2.0 \times 10^{-4}$ scc/sec and the second pressure vessel's maximum leak rate was recorded at $1.0 \times 10^{-5}$ scc/sec. Prior studies of Helium leakage through highly microcracked pressure vessels typically yielded leak rates on the order of $10^{-3}$ scc/sec. Therefore, the lower measured leak rate in the pressure vessels seems to be indicative of molecular permeation, rather than viscous flow (i.e., true "leakage"). The changes in measured permeation rates of both pressure vessels after hydrostatic testing were within the experimental error of measuring the Helium permeation rate.

Cyclic and Permeation Testing

One of the challenges of the pressure vessels intended for H2 storage is to limit the permeation rate of gaseous hydrogen through the vessel wall at the vessel's operating pressure and throughout its life consisting of numerous fill and drain cycles. Under a program funded by General Motors (GM), CTD performed a preliminary evaluation of the structural performance of the KIBOKO® pressure vessels under hydraulic and pneumatic pressure and measured their permeation rate before and after subjecting them to a moderate number of pressure cycles. Seven pressure vessels were fabricated for the program, some of which were tested to failure and the remainder used for measuring Helium permeation rates. The permeation rate was measured at the vessel's working pressure of 15.0 MPa (2,175 psi) and measured over an extended time period (see Figure 8). Test results show that the Helium permeation rate through the vessel wall has good correlation with the predicted value at the vessel's design operating pressure. Additionally, one pressure vessel was tested for permeation rate both before and after pressure cycles. Results from this test indicate that the permeation rate in these vessels remain unaffected by the hydraulic cycles. The average permeation rate of CTD's KIBOKO® composite pressure vessels was measured as 1.4 scc/liter/hr.

Burst Pressure Testing of 6.8L KIBOKO® Pressure Vessels

As part of technology demonstration efforts, CTD wound three (3) KIBOKO® Type V cylinders in collaboration with Luxfer Gas Cylinders (see Figure 11). The design MEOP for these KIBOKO® Type V cylinders was 3,600 psi and the target first failure pressure for these cylinders was 8,100 psi (2.25 x 3,600 psi MEOP) conforming to NGV-2 specifications. The average weight of the CTD KIBOKO® cylinders was 5.75 lbs.


Figure 11. KIBOKO® 6.8L tank with MEOP of 3,600 psi.

Two cylinders that were used for pattern development achieved a first failure (leak) of 7,200 and 7,500 psi respectively during pressure testing. Failure in the form of leakage was observed in the knuckle (cylinder-to-dome transition) area. It was surmised that the hoop transitions in the wind pattern were not adequate and the hoop patterns were revised. A subsequent cylinder with a refined wind sequence layup achieved a failure (burst) pressure of 9,000 psi and successfully met the design goals for first failure pressure.

SUMMARY

The technical feasibility of KIBOKO® Type V all-composite pressure vessels has been demonstrated through an integrated systematic approach to analytical modeling, material development and testing of prototype vessels of various sizes. These vessels promise to provide excellent mass storage efficiency for gaseous hydrogen fuels compared to traditional metal or polymer lined composite overwrapped pressure vessels. The testing of prototype pressure vessels has illustrated the need for a repeatable manufacturing process. CTD hopes that continued work in this area will lead to a robust product that can provide storage efficiencies not yet achievable with other storage vessels for hydrogen storage.

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