

III.14 Design of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

Ken I. Johnson (Primary Contact),
Kyle J. Alvine, Stan G. Pitman, Michael E. Dahl
Pacific Northwest National Laboratory (PNNL)
902 Battelle Blvd.
Richland, WA 99352
Phone: (509) 372-6816; Fax: (509) 375-2379
E-mail: ki.johnson@pnl.gov

DOE Technology Development Manager:
Monterey R. Gardiner
Phone: (202) 586-1758; Fax: (202) 586-9811
E-mail: Monterey.Gardiner@ee.doe.gov

Working Partners:

- Quantum Technologies, Inc. (Quantum)
- Boeing Phantom Works (Boeing)
- Lawrence Livermore National Laboratory (LLNL)

Project Start Date: October 1, 2008
Project End Date: September 30, 2011

Objectives

The project objectives are to develop new manufacturing methods for lower cost Type IV hydrogen storage vessels and to quantify the durability of tank liner materials under high hydrogen pressure cycling. PNNL is collaborating with Quantum, Boeing, and LLNL to optimize composite tank manufacturing methods. PNNL's task objectives are to:

- Analyze the manufacturing costs of advanced manufacturing methods for lower cost hydrogen storage vessels.
- Quantify hydrogen induced blistering of polymer liner materials as a function of material parameters (viscosity, solubility, crystallinity) and operating conditions (pressure, temperature, and decompression rate).

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (D) Durability/Operability

- (G) Materials of Construction
- (M) Lack of Tank Performance Data and Understanding of Failure Mechanisms

2010 Technical Targets

- A. System Weight and Volume = 2 kWh/kg (6 wt%), 1.5 kWh/L
- B. System Cost = \$4/kWh
- D. Durability/Operability = 1,000 filling cycles.
- G. Materials of Construction = resistant to hydrogen permeation and blistering
- M. Lack of Tank Performance Data and Understanding of Failure Mechanisms = understand the fundamental mechanisms of hydrogen permeation in polymer liner materials.

Analyzing the costs of advanced composite tank manufacturing compared to the baseline filament winding process will quantify how new manufacturing methods could improve the composite efficiency and reduce the weight and volume and cost of carbon fiber composite materials. The total manufacturing cost model will weigh material cost savings against modified processing costs.

This project is also developing a strong fundamental knowledge base on hydrogen/polymer interactions necessary for the materials selection for such vessels. This will help to obtain the DOE targets of increased durability and operability for on-board hydrogen storage.

Accomplishments

- Developed system for testing hydrogen/polymer compatibility under hydrogen pressures up to 5,000 psi and temperatures up to 200°C.
- Demonstrated hydrogen damage (surface blisters) occurs in amorphous polymers and is strongly a function of temperature. Testing of crystalline and semi-crystalline polymers to follow.
- Developed a thermal gradient stage for in situ thermal combinatorial testing of hydrogen degradation under high pressure hydrogen atmospheres.
- Identified and prioritized the significant manufacturing costs (considering process steps, materials, equipment, factory space, labor) for compressed hydrogen storage tank.
- The baseline filament winding (FW) process flow is defined. Material processing speeds and hardware

needs are being evaluated to best integrate the automated fiber placement (AFP) method into a hybrid FW + AFP manufacturing process.



Introduction

PNNL is collaborating with Quantum, Boeing, and LLNL to develop new manufacturing methods for lower cost Type IV hydrogen storage vessels and to quantify the durability of tank liner materials under hydrogen pressure cycling. The work began in October 2008 and it directly targets minimizing the weight, volume and cost of tanks plus the durability of tank materials. The durability and lifetime of hydrogen composite tanks is necessarily strongly influenced by the hydrogen degradation of the polymer liner material in direct contact with the high pressure hydrogen. While hydrogen degradation mechanisms are well known for metallic systems including blistering and embrittlement, relatively little is known about the effects of hydrogen on polymer systems. To answer this knowledge gap PNNL has carried out experimental investigations of the degradation of polymer materials in a high pressure hydrogen environment as a function of temperature. An analysis of our preliminary findings indicates that hydrogen blistering is the predominant degradation mechanism in polymer systems and is a strong function of temperature (viscosity) and crystallinity. PNNL hopes to use this and future data to build a predictive model of polymer behavior in high pressure hydrogen to address durability and lifetime issues. PNNL is also developing detailed manufacturing cost models for Quantum's baseline FW process and a hybrid process that will use the Boeing AFP method to improve the fiber placement efficiency in the FW process.

Approach

PNNL investigated the effects of high pressure hydrogen as a function of temperature on the degradation of polymer films with the goal of developing a model to understand hydrogen degradation of the polymer liner in high pressure composite tanks. Most polymer liner candidates are semicrystalline material, consisting of amorphous and crystalline regions. In order to separate the effects of hydrogen in the two different regions PNNL has decided to investigate amorphous, crystalline, and semi-crystalline materials separately in order to better develop a model for degradation. At this stage PNNL has extensively explored the simplest case – amorphous polymers – and has done some preliminary studies on crystalline polymers. Additional studies on all three systems are planned.

Polymer films with ultra-low roughness surfaces are exposed to high pressure hydrogen while mounted on a thermal gradient stage developed at PNNL for this project for in situ combinatorial studies of hydrogen degradation over a large temperature range (see Figure 1 a, b). Samples are typically exposed to high pressure hydrogen for 1 day and undergo controlled decompression under the elevated temperature gradient. Since these are thin films, 1 day is sufficient for hydrogen concentration saturation. Samples are then evaluated with optical microscopy for possible surface degradation. The low roughness aids in observing blistering.

The current FW process will be used as the baseline manufacturing cost for comparison with the advanced processing method. The goal of the advanced processing method is to increase the efficient use of the fibers in

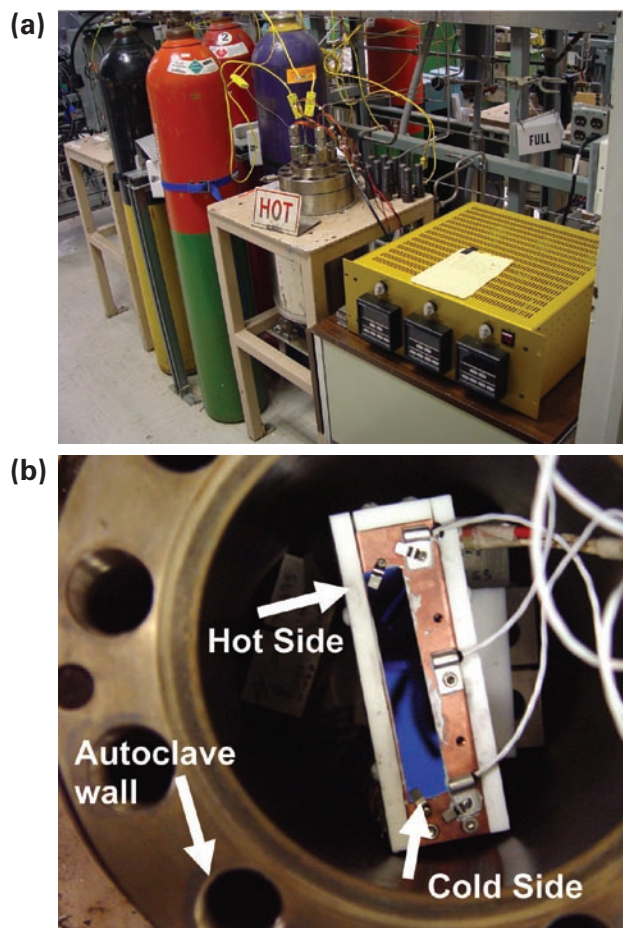


FIGURE 1. (a) Photograph of the high pressure autoclave (center) and thermal gradient control box (right). The high pressure autoclave is capable of hydrogen atmospheres up to 5,000 psi and temperatures of up to 300°C. (b) The thermal gradient stage consists of a heater at one end and a large heat sink tied to the autoclave at the opposite end. The sample sits on top of the bar and is subjected to a linear thermal gradient of up to 50°C over 3 inches. Resistance temperature detection devices allow in situ measurement of the temperature at several locations. The maximum temperature of the hot end is approximately 200°C.

the composite and thus reduce the amount of composite material needed for a given burst pressure. The challenge is to accurately place the fibers in the optimum directions while doing it quickly and with limited additional machinery such that the alternate manufacturing costs do not exceed the material savings cost.

Results and Discussion

PNNL has observed extensive micron-scale surface blistering (see Figure 2) in amorphous (polystyrene) where blister size and density varies strongly with temperature. For the amorphous samples blistering only occurred at temperatures above the glass transition temperature (transition from glassy solid to viscoelastic liquid). Note that most semi-crystalline polymer liner candidates have glass transition temperatures below room temperature which allows them to have superior mechanical properties, including ductility. This temperature dependence is likely due to two main effects. The first effect is that of hydrogen solubility. Hydrogen solubility in polymers has been shown to be strongly a function of free volume which increases as the polymer is heated. Thus the solubility should increase with increasing temperature. The second effect is that of viscosity. The polymer viscosity changes over many orders of magnitude with heating past the glass transition as the polymer goes from a glassy solid to a viscoelastic liquid. Thus mass flow is markedly enhanced at temperatures above the glass transition and more damage is expected to occur. Figure 3 shows that both the blister size and density of blisters increases with increasing temperature (decreasing viscosity).

Preliminary tests of crystalline films with a nearly identical polymer (isotactic vs atactic polystyrene of identical molecular weight) over the same temperature range shows no observable blistering. This is thought to be due to the comparatively decreased free volume of

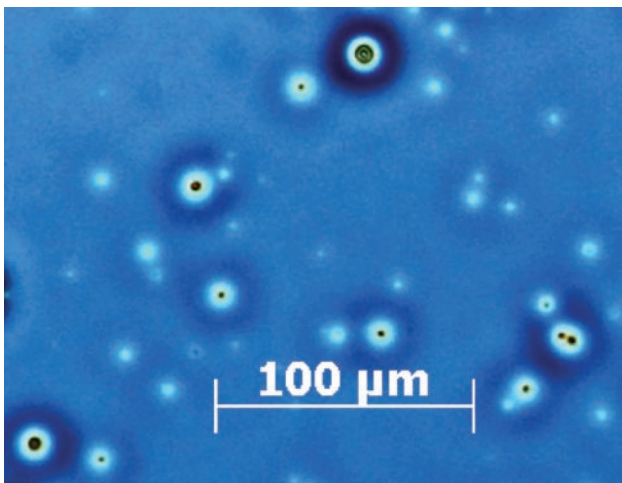


FIGURE 2. Micron-Scale Blisters in an Amorphous Polystyrene Film

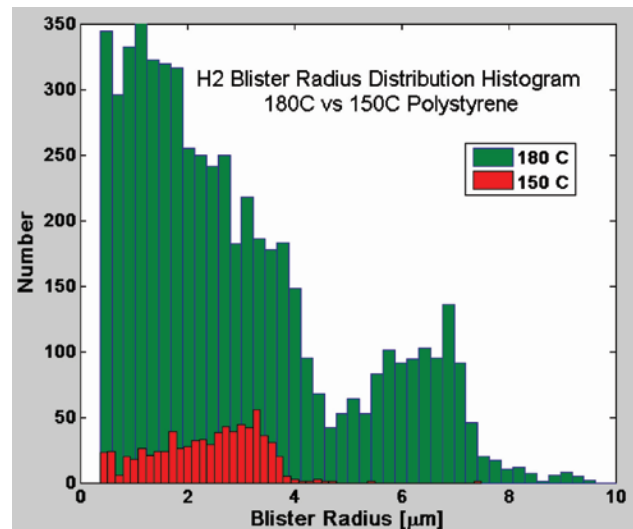


FIGURE 3. Histogram data of blister radius from image analysis of optical micrographs for 150°C and 180°C. Note the data indicates larger blisters for the higher temperature. The second peak at smaller size for 180°C is likely due to subsurface blisters, though further investigation is warranted.

the crystalline polymer as compared with the amorphous case. The hydrogen solubility should be lower and the material stiffer and more resistant to damage from hydrogen. The information from these preliminary examinations and from future work will help to build a model to predict the durability and lifetime of polymer liner materials in high pressure hydrogen.

PNNL's cost modeling efforts to date have focused on identifying the significant cost factors for inclusion in the models. This includes the materials, equipment, factory space, and labor costs for each processing step. The material and labor costs for Quantum's baseline FW process have been defined as the baseline. Material processing speeds and hardware needs are being evaluated to determine how to best integrate the AFP method into a hybrid FW + AFP manufacturing process. During the first year, much progress has been made by Quantum and Boeing to identify compatible materials and processing scenarios for the combined FW + AFP process. An initial cost model comparison of the FW and the hybrid FW + AFP method will be completed by the end of Fiscal Year 2009.

Conclusions and Future Directions

- Hydrogen degradation of amorphous polymers does occur in the form of surface blistering.
- This blistering damage increases with increasing temperature above the glass transition temperature of the polymer.
- Blistering appears not to occur for purely crystalline materials.

- The cost models are progressing and a comparison of the baseline and advanced manufacturing methods will be completed.

PNNL hopes to continue this work to develop a model for polymer durability in a high pressure hydrogen environment by addressing the following issues:

- What is the specific temperature/viscosity dependence on blistering?
- Develop an analytical model to describe this.
- How can this be incorporated into a semi-crystalline system composed of amorphous and crystalline regions?
- What is the role of impurities on hydrogen damage?

References

1. C. S. Marchi *et al*, Sandia National Lab Technical Report (SAND2008-1163), 2008.
2. W.E. Wallace *et al* Nuc. Inst. & Methods in Phys. Res. B 103, 435 (1995).
3. Ren *et al*, Mater. Chem. Phys. 107, 231, (2008).