VIII.9 Compatibility of Polymeric Materials Used in the Hydrogen Infrastructure

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Overall Objectives

- Provide 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.
- Identify applications, conditions, and materials of interest to the hydrogen infrastructure community by interfacing with stakeholders.
- Develop experimental test methodologies for evaluating polymer hydrogen compatibility that are relevant to the stakeholder's needs.
- Evaluate relevant polymeric materials with these test methodologies and disseminate the results through literature, databases, or codes and standards organizations to support the deployment of the hydrogen infrastructure.

Fiscal Year (FY) 2016 Objectives

- Gather and evaluate stakeholder input with regards to challenges, materials, and conditions of interest for hydrogen polymeric compatibility.
- Develop standard test methods for evaluating polymer compatibility with high pressure hydrogen; specifically for: (1) pressure cycling tests, (2) in situ tribology tests, and (3) neutron scattering.
- Develop an approach to disseminate these test methods and compatibility data to stakeholders and support the deployment of hydrogen infrastructure.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Safety Data and Information: Limited Access and Availability

(G) Insufficient Technical Data to Revise Standards

(J) Limited Participation of Business in the Code Development Process

(K) No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achieving the following DOE milestones from Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- Milestone 5.2: Update materials compatibility technical reference. (4Q, 2011 – 2020)

FY 2016 Accomplishments

- Solicited input from over 50 hydrogen infrastructure stakeholders on polymers of interest, test methods currently employed, and challenging operating conditions and applications to identify knowledge gaps for hydrogen compatibility with polymeric materials. Stakeholders included hydrogen system designers, component manufacturers, polymer producers, code committee members, and hydrogen suppliers.
- Based on infrastructure applications such as compressors, valves, hoses, and piping, we have selected an initial set of materials to evaluate with tribology and pressure cycle aging. These include the elastomers Buna-N and Viton®, PTFE as a low temperature appropriate thermoplastic, polyoxymethylene (Delrin®) as a hose material and a HDPE as a piping liner material. These materials offer a good span of the polymers used in infrastructure and will enable sound test methodologies. Further down-select or materials for

consideration will be revisited during the course of the project.

- Developed an in situ hydrogen tribometer at PNNL with the capability of operating under hydrogen pressures up to 345 bar and 99.995% purity. Carried out initial comparative tests on Buna-N material at 345 bar hydrogen and observed increased friction and wear in the hydrogen environment.
- Performed at Sandia National Laboratories a static, isobaric (1,000 bar) soak of target polymer materials: Buna-N, Viton, HDPE, and PTFE. These materials were then evaluated using dynamic mechanical thermal analysis, compression set (elastomers only), polymer volume change, thermal gravimetric analysis/differential scanning calorimetry, tensile strength (thermoplastics only), and micro-computed tomography (micro-CT) analysis before and after high pressure hydrogen exposure.
- Performed small angle neutron scattering, wide angle X-ray diffraction, and small angle X-ray scattering on HDPE samples exposed to a high pressure hydrogen soak.
- Initiated the evaluation of relevant American Society of Mechanical Engineers, ASTM International, and other standards and test methodologies that could be adapted to evaluate hydrogen compatibility with polymers. Also initiated conversations with CSA Group (Canadian Standards Association) on relevant input to "Test Methods for Evaluating Material Compatibility in Compressed Hydrogen Applications—Non-Metals" (CHMC 2) for hydrogen interactions with non-metallics. Ford subcontractor Mike Veenstra was selected as its interim chair.

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INTRODUCTION

Polymers are critical to hydrogen infrastructure applications to reduce cost and mitigate potential design constraints of metallic components. However, unlike metals that have been studied extensively in high pressure hydrogen, there is a significant knowledge gap in the understanding of polymer performance under these conditions. Also, standardized qualification methods and databases of acceptable conditions and polymers are not currently available to the hydrogen design community to guide material selection. The overall goal of this project is to address these knowledge gaps and support stakeholders in the safe selection of polymers for use in the wide range of required applications and conditions for infrastructure needs.

This will be accomplished by developing a technical foundation to understand the effects of high pressure hydrogen environments and pressure cycling on polymers and composites to enable the development of appropriate test protocols for evaluating these materials for hydrogen service. The information generated from tests of target polymeric materials will be disseminated to interested stakeholders and standards and code development organizations.

APPROACH

The project consists of four main tasks: (1) gather information from stakeholders, (2) develop test methodologies, (3) characterize polymers for hydrogen compatibility, and (4) disseminate the information generated. The information gathered from stakeholders will be used to ensure that the materials being evaluated, the range of conditions of study, and the testing protocols being developed as part of this project will benefit stakeholders from polymer, component, and system manufacturers. The aim of the test methodologies being developed is to generate a set of appropriate experimental guidelines to evaluate hydrogen compatibility. As a by-product of this test methodology development, the project will also develop a partial database of the hydrogen effects on certain polymers used to generate these tests. Because properties differ widely for a single polymeric material based on its additives and processing approach, testing results would be meaningless unless key polymer characteristics are understood. The project will fully characterize the baseline properties of the polymers to allow others to compare their materials to those that were tested. The information generated will be disseminated through material databases, standards organizations, and peer-reviewed journals.

RESULTS

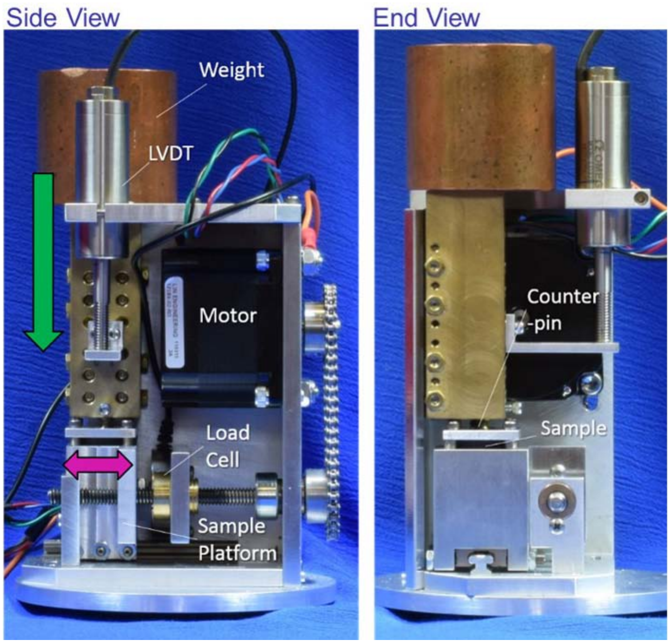
Approximately 20 stakeholders have provided feedback (to date) to the questionnaire requesting information about the knowledge gaps for compatibility of hydrogen with polymers. The challenges with hydrogen compatibility most often cited in the questionnaire results were rapid pressure transients, wear and abrasion of valves, and long-term impacts of pressure cycling. Based on these results, it appears that the pressure cycling tests planned at Sandia National Laboratories and the tribology tests at PNNL do represent concerns of high importance within the hydrogen infrastructure stakeholder community. The questionnaire results suggested a wide range of polymers of interest for testing including thermoplastics, elastomers, and thermosets. These results helped direct the identification of the following polymers for initial test methodology development: (1) Viton and Buna-N as representatives of elastomeric materials; (2) PTFE for its use in low temperature seals; (3) HDPE as a typical pipe liner material; and (4) Delrin as a delivery hose material. Conditions of interest were pressures between atmospheric and 880 bar and temperatures between -40 and

+85°C. This questionnaire result has prompted future plans to expand the range of testing temperatures for the tribology and pressure cycling in future years. We are continuing to reach out to additional stakeholders as they are brought to our attention as the project progresses.

PNNL is developing test methodologies for in situ high pressure hydrogen tribology as tied into application for infrastructure valves and seals. The new PNNL system is a linear reciprocating pin configuration as shown in Figure 1. Frictional load and wear track depth are measured in situ both in air and with 99.995% pure hydrogen up to 345 bar. The current system was developed for room temperature operation but future upgrade plans include sample heating and cooling. Preliminary testing has been performed with Viton and Buna-N in an effort to begin the development of test methodologies, and quantify the impact of the hydrogen environment on the material friction and wear performance. During an initial shake down and debugging phase, researchers have mitigated the lateral wobble of the sample during reciprocation to improve the reproducibility of the system. Preliminary results suggest that for Buna-N, friction and wear may be elevated in hydrogen as compared with identical load conditions in ambient pressure air (Figure 2). Furthermore, a post mortem analysis of the wear tracks with optical profilometry indicates increased damage in the high pressure hydrogen environment as compared to ambient air. Further testing is being carried out to confirm and better understand these preliminary findings.

Sandia National Laboratories performed preliminary experiments to investigate the testing parameters of a high pressure hydrogen system for a select group of two elastomers (Buna-N and Viton) and two thermoplastics (HDPE and PTFE). These polymers were exposed to static conditions of 100 MPa hydrogen at ambient temperature for one week. Both non molded and molded parts made from these polymers were examined to differentiate the effect of residual thermal stresses that can be present in molded specimens and potentially influence performance in a real-life hydrogen application. Characterization of the materials before and after exposure included dynamic mechanical thermal analysis, compression set (elastomers only), polymer volume change, thermal gravimetric analysis/differential scanning calorimetry), tensile strength (thermoplastics only), and micro-CT.

As expected, the elastomeric materials experience significantly more swelling than the thermoplastics as a result of the hydrogen soak. Viton showed a higher change in volume and hydrogen retention than Buna-N. In both materials swelling subsided after the material was removed from the hydrogen, with most of the recovery occurring within the first 48 h. However, some residual swelling remained indefinitely. Viton's higher capacity to hold hydrogen may be due to the greater amount of free volume in the Viton polymer microstructure compared to Buna-N and agrees with the fact that its solubility coefficient is higher than Buna-N. Furthermore, micro-CT demonstrated that hydrogen produced voids that can be seen around the filler particles in the Viton but were not seen with Buna-N. The elastomers also experienced an increase in compression set with hydrogen exposure as seen in Figure 3. Unexposed Buna-N has a higher compression set than Viton, but Viton showed the larger increase with hydrogen exposure. The dynamic mechanical thermal analysis showed a decrease in



LVDT – Linear variable differential transformer

FIGURE 1. Photograph of the tribometer being developed to operate at hydrogen pressures up to 345 bar

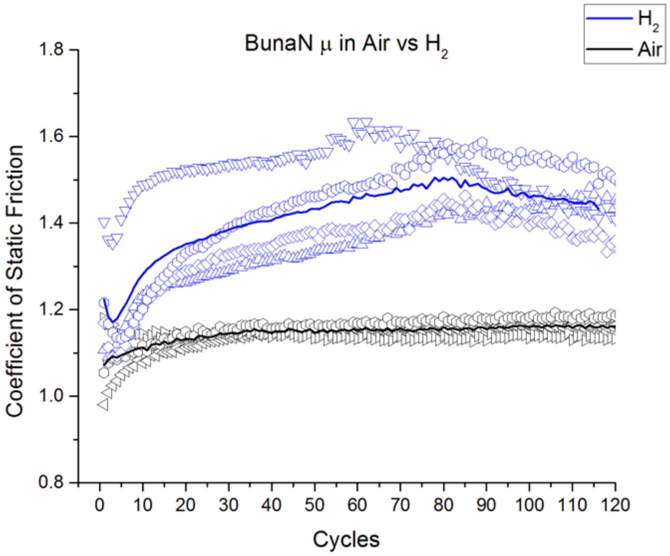


FIGURE 2. Comparison of coefficient of friction for Buna-N in air and 275 bar hydrogen

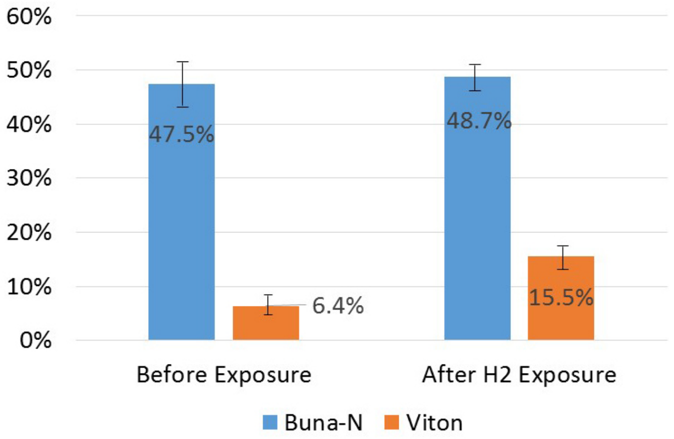


FIGURE 3. Comparison of compression set for Viton and Buna-N both before and after exposure to 1,000 bar hydrogen for 7 days

the storage modulus of the polymers after hydrogen exposure as compared to those before exposure as shown in Table 1. The glass transition temperature was only marginally affected.

In contrast to elastomers, the thermoplastic materials did not exhibit significant changes with hydrogen exposure. There was very little change in density, strength, and glass transition temperature between the samples exposed to hydrogen and those that were not. Unlike the elastomers, these thermoplastics showed a slight increase in the storage modulus with hydrogen exposure rather than a decrease.

Although the stress strain results for the thermoplastics showed a small increase in tensile strength before and after hydrogen exposure, there was a significant increase in the Young's modulus after exposure as shown in Table 2. It was 35% higher for PTFE and 15% higher for HDPE. It is possible that there was a crystalline phase change that results in a stiffening of the material due to the hydrogen exposure.

To address the changes found in the thermoplastic samples from Sandia National Laboratories, the samples exposed to hydrogen were provided to Oak Ridge National Laboratory (ORNL) for X-ray and neutron scattering studies. Both wide angle X-ray diffraction and small angle X-ray scattering were performed with the samples. Of particular interested was the impact of the hydrogen soak on the HDPE which showed a discoloration after hydrogen exposure and rapid decompression. Wide angle X-ray diffraction was performed on the pre- and post-exposure HDPE samples and the change in the patterns demonstrate different intensity ratios of orthorhombic (110) and (200) diffraction peaks. This change suggests that applied high pressure hydrogen induced lamellar rotation along the in-plane direction (see Figure 4). Evaluation with small angle X-ray scattering also showed a change in intensity (q) as a function of hydrogen exposure. The scattering upturn at low-q indicates the formation of micro voids while the peak shift to higher q values indicates that the inter-lamellar distance was compressed from 26.9 to 25.4 nm with hydrogen exposure. These changes in material

TABLE 1. Dynamic Mechanical Thermal Analysis Results Before and After Hydrogen Exposure

	Before Hydrogen Exposure		After Hydrogen Exposure	
Polymer Properties	T_g (°C)	Storage Modulus (MPa)	T_g (°C)	Storage Modulus (MPa)
Buna-N	-32	34.0 ± 2	-31	19.9 ± 3.7
Viton	-2	10.7 ± 0.5	-3	5.4 ± 1.4
HDPE	-110	848 ± 7	-111	913 ± 25
PTFE	34, 137*	431 ± 12	36, 137*	441 ± 14

*PTFE shows two T_g because of possible separation of components

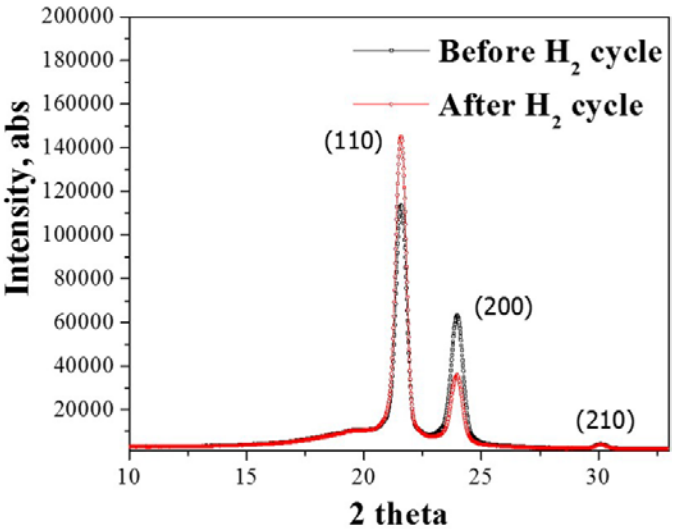


FIGURE 4. Wide angle X-ray diffraction patterns of HDPE both before and after exposure to 1,000 bar hydrogen for 7 days

TABLE 2. Stress–Strain Properties of the Thermoplastic Materials Before and After Hydrogen Exposure

	Before Hydrogen Exposure			After Hydrogen Exposure		
Polymer Properties	Young's Modulus (MPa)	Yield Stress (MPa)	Strength (MPa)	Young's Modulus (MPa)	Yield Stress (MPa)	Strength (MPa)
HDPE	863	20.3	24.0	990	22.3	25.8
PTFE	493	8.8	24.4	667	9.1	25.4

properties will help us better understand the fundamental polymer changes that drive their compatibility with hydrogen.

CONCLUSIONS AND FUTURE DIRECTIONS

Work has begun to address the knowledge gaps that exist in regards to the performance and degradation of polymers in hydrogen environments. Stakeholder feedback has been elicited to assist the project in identifying the applications of concern, polymers to be tested, and temperature and pressure conditions. An in situ tribology system has been developed and tested with elastomers. Preliminary results indicate high pressure hydrogen can impact the frictional properties of the materials. Preliminary high pressure hydrogen soak tests were performed with the initial materials. Significant differences in the response to physical tests were observed for the thermoplastic and elastomeric materials evaluated after hydrogen exposure. Analysis with X-ray scattering identified polymer microstructural changes as well. A high pressure cycling manifold for pressure cycle aging has been designed and is in the initial stages of assembly for further polymer testing.

Future work will continue to develop test procedures and conditions for tribological tests and high pressure cycling tests. Although the initial scoping studies are being performed with non-pedigreed materials, as the test procedure and conditions are refined, characterized materials will be used to ensure statistically meaningful results can be produced and compiled into a database. As the samples are produced during the scoping studies, we will evaluate hydrogen effects on the microstructure of the polymers using neutron scattering and X-ray diffraction to provide a fundamental understanding of the microstructural changes in the polymer upon hydrogen exposure. Work has begun to reach out to codes and standards committees such as the Canadian Standards Association to contribute to the next generation documents such as CHMC 2 or SAE 2579. We will continue to be involved in this effort, and these standards documents will be developed in synergy with our technical accomplishments.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Alvine, K., K. Brooks, et al, “Hydrogen Compatibility of Polymers for Infrastructure Applications,” presentation accepted for the 2016 International Hydrogen Conference, Moran, WY, September 2016.

2. Alvine, Brooks, et al., “Hydrogen Compatibility with Polymers: Tribology and Cycle Aging,” presentation accepted for ASME 2016 Pressure Vessels and Piping Conference, July 17–21, 2016, Vancouver, British Columbia, Canada, July 2016.

3. Menon, N., A. Kruizenga, A. Nissen, C. San Marchi, K. Alvine, K. Brooks, “Behavior of Polymers in High Pressure Environments as Applicable to the Hydrogen Infrastructure,” PVP2016-63713, Proceedings of the ASME 2016 Pressure Vessels and Piping Conference, July 17–21, 2016, Vancouver, British Columbia, Canada, July 2016.