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

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Project End Date: September 30, 2018

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 polymer community by interfacing with stakeholders.
- Develop experimental test methodologies that are relevant to the stakeholder's needs.
- Evaluate relevant 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) 2017 Objectives

- Complete analysis of stakeholder feedback utilizing failure mode and effects analysis (FMEA).
- Develop preliminary test methodology for in situ high pressure hydrogen testing of friction and wear of polymers.
- Complete high-pressure hydrogen cycling design and installation for testing polymers.
- Disseminate information to the hydrogen community by participating in committees, journal articles, and conferences.

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 achievement of the following DOE milestones from the 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 2017 Accomplishments

- Identified four polymers and elastomers of interest (Viton™, EPDM, NBR, PTFE), temperature and pressure of interest (-40°C to +85°C, 0–20,000 psi), and tests of interest (pressure transients, wear and abrasion, pressure cycling) through feedback from 25 stakeholders.
- Performed tribology testing on three materials (nitrile butyl rubber [NBR], ethylene propylenediamene [EPDM], and polytetrafluoroethylene [PTFE]) that show an increase in coefficient of friction between 40–80% and an increase in wear by 40% on NBR in high-pressure hydrogen.
- Completed initial study on high-pressure purge and leak test gas to identify influences of gases on startup. Helium identified as the preferred choice of startup gas for purge and leak testing with reduced impact on material.
- Completed FMEA to provide prioritization and future research and development activity focus.

- Disseminated information to the hydrogen community through eight presentations, four publications, and one invention disclosure, including a keynote presentation at International Hydrogen Energy Development Forum in Japan and an invited presentation at the Hydrogenius Research Symposium in Japan.

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INTRODUCTION

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

This will be done by developing a technical foundation to understand the effects of hydrogen on polymers and composites to enable the development of appropriate test protocols for evaluating materials for hydrogen service. The information generated from these tests of target polymeric materials will be disseminated to hydrogen users and standard and code development organizations.

APPROACH

The project consists of four main tasks: (1) gather information from stakeholder, (2) develop test methodologies, (3) characterize polymers, 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 mimic the conditions of interest and accelerate the process to produce meaningful results in a reasonable timeframe. 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 polymers to allow others to compare their materials to those that were tested. Finally, the information generated, both the test protocol and the compatibility results will be disseminated through material databases, standards organizations, and peer-reviewed journals.

RESULTS

The project has engaged over 25 stakeholders from the hydrogen community to provide feedback in how the test and evaluate materials for use in hydrogen, and what are the most important test conditions to evaluate the material in a hydrogen environment. The data from the feedback was developed into 27 failure criteria and used in a FMEA tool to document the risk and to and help prioritize the key actions to reduce failures. The applications include compressors, valves, seals, refueling stations, liners, and others. The failure modes were based on three primary functions/applications, static seals, dynamic seals, and barriers. The team completed the FMEA and the results were presented at the Annual Merit Review and with the Canadian Standards Association committee for developing the new Compressed Hydrogen Materials Compatibility 2 standard for hydrogen compatibility in polymers. The FMEA risk priority number (RPN) value is calculated based on a ranked severity rating, an occurrence rating, and a detection rating that was agreed on prior to ranking. The rankings were based on available information and current test methods developed for hydrogen. The average of the 27 identified failure modes had an average of 300. Table 1 illustrates the top six results that are above the average of the calculated RPN and are in line with our current research. The FMEA is dynamic and is adjusted as new information is learned thereby changing the ranking of priority.

The project developed a preliminary test methodology for in situ high-pressure hydrogen testing of friction and wear and delivered a report to DOE. The test methodology was an adaptation of ASTM G-133 and has demonstrated differences in hydrogen, argon, and ambient air. This fiscal year three materials were tested following newly developed test method, NBR, EPDM, and PTFE. Initial control parameters are load, speed, track length, pin diameter, pin roughness, and pin material. Results of the test demonstrate the effect that hydrogen has on NBR, EPDM, and PTFE which show an increase in coefficient of friction in 4,000 psi hydrogen by factors of 1.4, 1.8, and 1.5, respectively as compared to ambient air as shown in Figure 1. Ex situ optical profilometry (interference) shows a clear increase in wear in high-pressure hydrogen over ambient air, over high-pressure argon for NBR. The ex situ wear track depths are 100 microns, 60 microns, and 7 microns, respectively for high-pressure hydrogen, ambient air, high pressure argon. Figure 2 clearly indicates the difference in wear between the gases and testing condition. Future work for heating and cooling is shown in Figure 3.

The project also assessed the impact of purge and leak test gases on the material being tested. It is important to separate out the effects of other gases used as part to the test method so that the hydrogen effect can be evaluated. Figure 4 illustrates the damage in elastomer seal materials related

TABLE 1. Top Four RPN Items Based on the Initial FMEA Assessment (>300)

Potential Cause	Failure Mode (RPN)	Function
#17 Polymer seal (dynamic) material experiences a change in properties (strength, modulus, shear, hardness, etc.) due to hydrogen exposure	Seal exceeds allowable dynamic performance when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (490)	Contain hydrogen with dynamic seal at all operating pressures (5 bar to 875 bar) and temperatures (-40°C to 85°C) until end of life • Maintain seal dynamic performance
#24 Polymer barrier material degrades from rapid high-pressure differentials (explosive decompression) due to hydrogen exposure • Material extrudes, cracks, or fragments	Liner exceeds allowable external leak rate limit when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (420)	Contain hydrogen with barrier liner at all operating pressures (5 bar to 875 bar) and temperatures (-40°C to 85°C) until end of life • Lower than acceptable external leakage rate of 10 Nml/h
#1 & #9 Polymer seal (static & dynamic) material selected exceeds hydrogen permeation rate • Unable to contain hydrogen through the material	Seal exceeds allowable external and/or external leak rate limit when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (400)	Contain hydrogen with static seal and dynamic seal at all operating pressures (5 bar to 875 bar) and temperatures (-40°C to 85°C) until end of life • Lower than acceptable external and internal leakage rate of 10 Nml/h
#6 & #14 Polymer seal (static & dynamic) material geometry changes and volume swells or reduction due to hydrogen exposure • Unable to maintain seal design and compression (compression set occurs) • Material extrudes, cracks, or fragments	Seal exceeds allowable external and/or external leak rate limit when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (350)	Contain hydrogen with static seal and dynamic seal at all operating pressures (5 bar to 875 bar) and temperatures (-40°C to 85°C) until end of life • Lower than acceptable external and internal leakage rate of 10 Nml/h

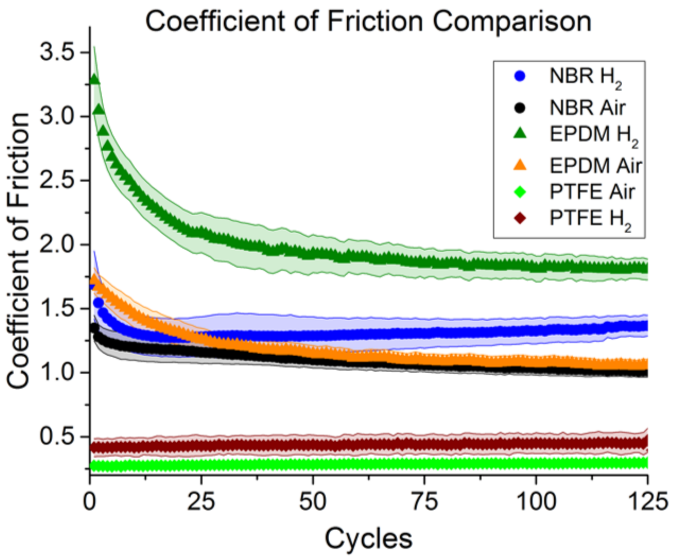

FIGURE 1. Comparing coefficient of friction

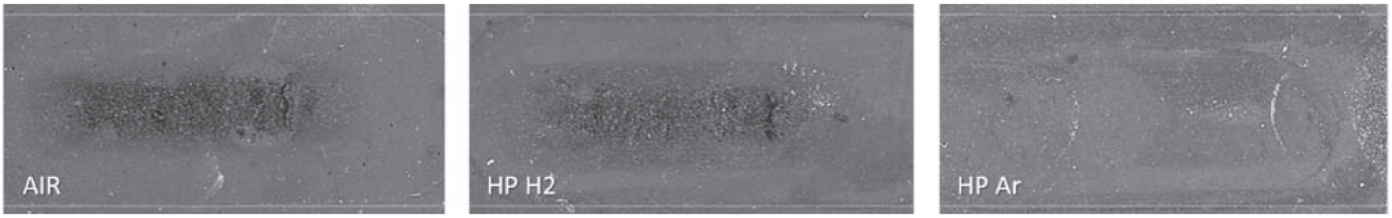

FIGURE 2. Ex situ wear tracks in NBR

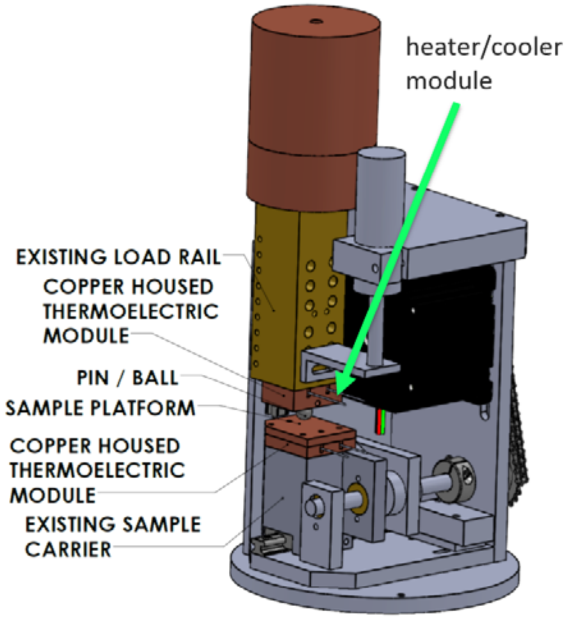

FIGURE 3. Novel high pressure hydrogen in situ tribometer

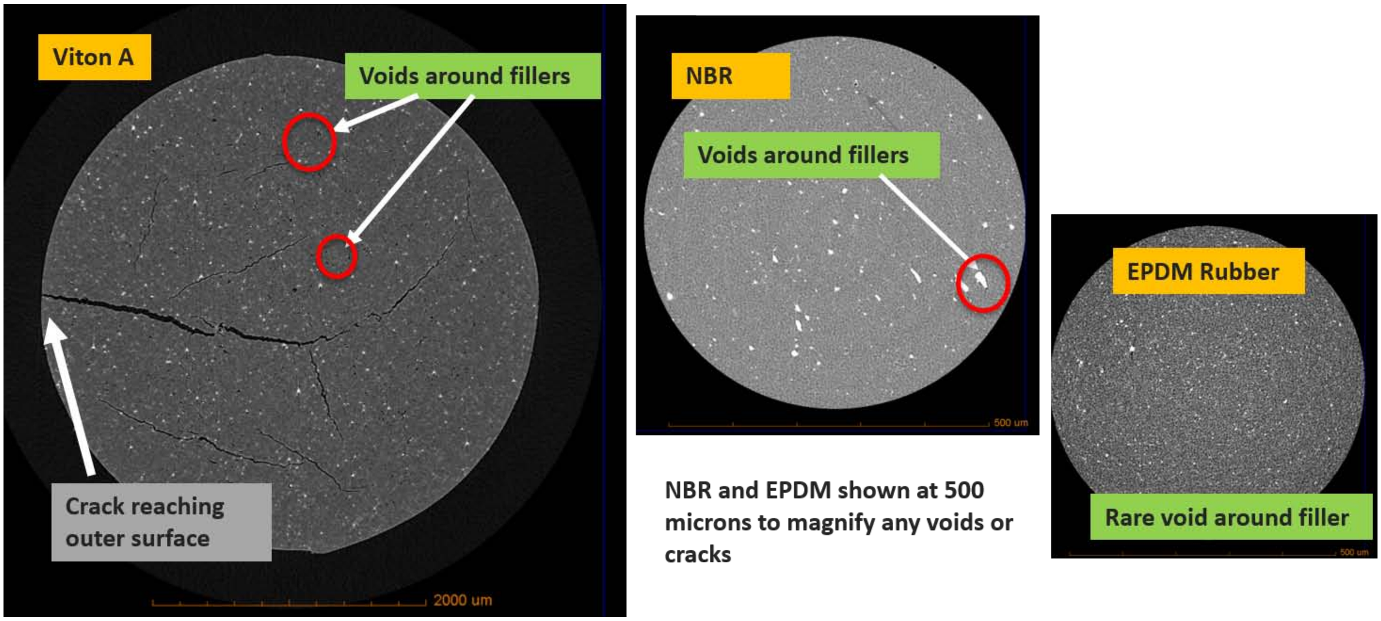

FIGURE 4. Damage in elastomer seal materials related to their purge/leak test gas study

to their purge and leak test gas study. Viton A shows the most damage and influence from argon and argon/hydrogen, whereas helium has a small to negligible effect. It does seem to be polymer/elastomer dependent. Table 2 illustrates the influence of the material properties associated with the gas used. It was also found that compression set can have increased effect based on the gas.

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has prioritized the most important attributes based on the FMEA results and the feedback provided by the stakeholders. Tribology work resulted in delivering an initial test methodology for novel in situ friction and wear testing. The tribology results show hydrogen significantly influence

TABLE 2. Damage or Influence in Elastomer Seal Materials Related Purge and Leak Gas

Polymer properties (characterization methods)	Maximum effects seen in various gas environments		
	Argon/Hydrogen**	Helium/Hydrogen***	Helium
Swelling (Density measurements)	73% with 100% recovery seen with NBR	36% with 100% recovery seen with Viton A	14% with 100% recovery seen with NBR
Storage modulus changes (DMTA)	41% decrease for Viton A	20% decrease with Buna N	No change observed
Compression set (elastomers only)	5 times increase seen for Viton A	1.6 times increase with Viton A	2.0 times increase with Viton A
Mass loss (TGA) indicating gas diffusion out of polymer after 48 h after removal from test	Highest mass loss	Mass loss is lower than unexposed	Lowest
Explosive decompression (micro CT)	Viton A shows severe damage; much less effects on NBR and EPDM	Viton A shows voids around specific fillers; NBR and EPDM unaffected	All polymers are unaffected

Micro CT – micro computed tomography; TGA – thermogravimetric analysis; DMTA – dynamic mechanical thermal analysis

the coefficient of friction in EPDM, NBR, and PTFE. Likewise, the gas species can also influence the friction and the wear. Purge and leak test gases have also shown to have an impact on the material. Viton A was severely impacted with argon gas in several attributes as well as severe cracking. Helium gas shows the least impact, but is also polymer/elastomer dependent on the influence.

The future work includes the following:

- Study heating and cooling impacts on friction and wear.
- Study the influence of material additives in elastomers in both friction and wear, and decompression.
- Complete the cyclic testing experiment build and functional tests.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. N.C. Menon, A.M. Kruizenga, A. Nissen, C. San Marchi, K.J. Alvine, K. Brooks, D.B. Smith, and A.K. Naskar, "Polymer Behavior in High Pressure Hydrogen environments with relevance to the Hydrogen Infrastructure," submitted to International Hydrogen Conference, Moran, WY, September 2016.

2. Alvine K., Brooks K., Duranty E., Menon N., Kruizenga A., San Marchi C., Smith B., Naskar A.,"Hydrogen Compatibility of Polymers for Infrastructure Applications: Friction and Wear." Submitted to the 2016 International Hydrogen Conference, Moran, WY, September 2016.

3. Duranty E., Roosendaal T., Pitman S., Tucker J., Owsley Jr. S., Suter J., Alvine K., "An In Situ Tribometer for Measuring Friction and Wear of Polymers in a High Pressure Hydrogen Environment." Submitted to Review of Scientific Instruments, April 2017.

4. Alvine, Brooks, et al., "Hydrogen Compatibility of Polymers for Infrastructure Applications," submitted to International Hydrogen Conference, Moran, WY, September 2016.

5. Simmons et al., "Hydrogen Compatibility of Polymers Program Overview," International Hydrogen Energy Development Forum,Fukuoka, Japan, February 2017 Invited Keynote Speaker.

6. Alvine et al., "In Situ Friction and Wear of Polymers in High Pressure Hydrogen." HYDROGENIUS Research Symposium, Fukuoka, Japan, February 2017 Invited Speaker.

7. Menon et al., "High Pressure Cycling and Tribology Effects on Polymers in Hydrogen Environments," MSRF Workshop, Livermore, CA, March 2017.