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# Compatibility of Polymeric Materials Used in the Hydrogen Infrastructure

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Project Start Date: October 1, 2015  
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.
- Develop an understanding of material interaction with hydrogen to mitigate impacts on reliability and durability.
- Develop experimental test methodologies that provide material performance under hydrogen infrastructure environments.
- Disseminate material characteristics to the community to begin discussions on how to improve materials in the hydrogen infrastructure environment.

## Fiscal Year (FY) 2018 Objectives

- Complete the test methodology for in-situ high pressure hydrogen testing of friction and wear of polymers.

- Investigate the effects of fillers in nitrile butyl rubber (NBR) and ethylene propylenediamene (EPDM) model elastomer compounds.
- Disseminate test methodologies in hydrogen testing through Compressed Hydrogen Materials Compatibility 2 (CHMC 2) polymers standards.
- 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<sup>1</sup>:

- (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 Hydrogen Safety, Codes and 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)

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<sup>1</sup> <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

## **FY 2018 Accomplishments**

- Developed six EPDM and six NBR model compound materials for investigation of hydrogen effects with fillers. Carbon and silica fillers indicate 10 ppm of hydrogen absorption in the material.
- Performed friction and wear testing on all 12 compounds in ambient air, high-pressure argon, and hydrogen environmental conditions.
- Performed R&D to determine that the desorption rate of the EPDM polymer is nearly five times faster than that of the NBR polymer without any additives or fillers. Compression set of NBR is significantly influenced by hydrogen with a 37% increase whereas EPDM compression set was insignificant.

## 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, databases of acceptable conditions, and hydrogen-compatible 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 stakeholders, (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.

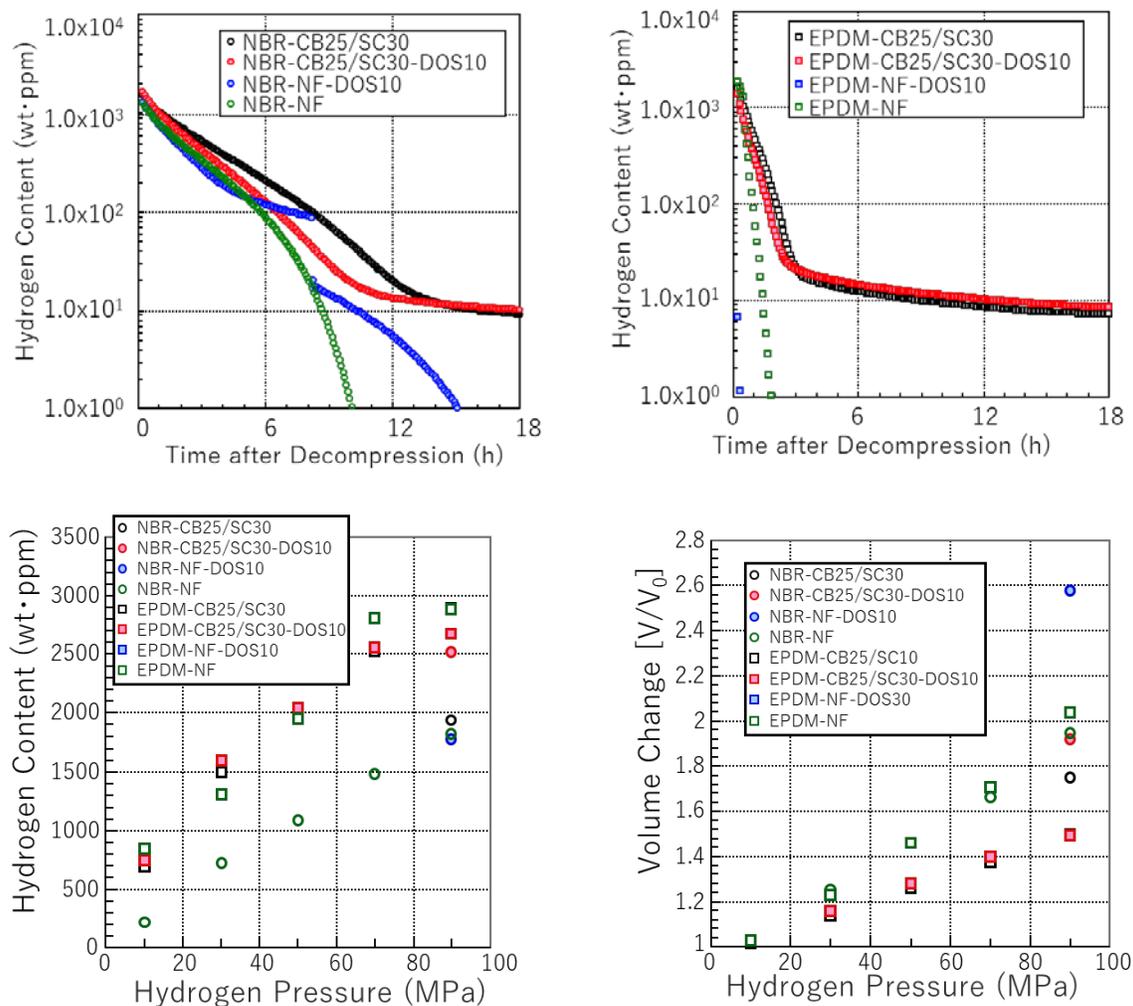
## RESULTS

The team has been working with stakeholders on the Canadian Standards Association (CSA) committee for developing the new CHMC 2 standard for hydrogen compatibility in polymers. The scope of this standard is to provide uniform test methods for the industry to compare the performance of polymers in applications utilizing hydrogen. During this fiscal year, significant progress was made in advancing the test methods from conceptual approaches to a comprehensive document that is being prepared for an industry review and ballot. The committee consists of more than 25 stakeholders from various parts of the hydrogen community. There were numerous opportunities to exchange experiences in the area of test method development under the auspices of the CSA CHMC 2 committee's meetings that benefited the community and the project team. The development of the CSA CHMC 2 document for hydrogen polymer capability is greatly benefiting from the leadership and technical contribution of this project team.

This fiscal year, the team worked with Kyushu University on developing a set of model material compounds of NBR and EPDM for investigating the effects of known additives and fillers in the elastomer materials with hydrogen. There was a total of six compounds for each material:

- No filler, crosslinked elastomer
- Crosslinked elastomer with plasticizer only
- Crosslinked elastomer with carbon black only
- Crosslinked elastomer with silica filler only
- Crosslinked elastomer with plasticizer, carbon black, and silica filler
- Crosslinked elastomer with carbon black and silica filler.

Kyushu University provided thermal desorption data (Figure 1) to the team on their hydrogen content as a function of pressure, time after decompression, and their volume change. The results of the thermal desorption data demonstrate the effects of the polymer, plasticizer, and the fillers. The desorption rate of the EPDM polymer is nearly five times faster than that of the NBR polymer without any additives or fillers. The addition of the plasticizer significantly increased the desorption of hydrogen in the EPDM, whereas the data was inconclusive for NBR due to a measurement error. The inorganic fillers of silica and carbon black show an absorption behavior in both materials (of 10 ppm of hydrogen), which will be investigated in the future.



**Figure 1. Hydrogen thermal desorption and hydrogen effects related to pressure**

The filler material used in these model material compounds shows a decrease in volume change for NBR by 10% and 30% in EPDM from unfilled baseline compound, while the plasticizer only increased by nearly 40% in volume at 90 MPa.

A final draft has been developed for the in-situ friction and wear testing capability at PNNL. The test methodology was an adaptation of ASTM G-133 and has demonstrated differences in hydrogen, argon, and ambient air. This fiscal year all 12 of the model material compounds were tested following a newly developed test method using the in-situ friction and wear testing capability. Results of the test shown in Table 1 demonstrate the effect that hydrogen has on NBR and EPDM. The hydrogen exposure actually decreased the coefficient of friction (CoF) with the exception of compound N6. These results are different than what has

been compared to in the past with commercial off-the-shelf material and indicate that the compounds can alter the performance of the materials’ frictional and wear behavior.

**Table 1. Tribology Results of Ambient Air and High-Pressure Hydrogen**

EPDM	PNNL#E1	PNNL#E2	PNNL#E5	PNNL#E6
<b>Features</b>	No filler No plasticizer	No filler Plasticizer	Carbon black Inorganic Plasticizer	Carbon black Inorganic No plasticizer
<b>Air In-situ Tribo (CoF)</b>	1.24	1.01	1.65	1.57
<b>HP-H2 In-situ Tribo (CoF)</b>	1.11	0.84	1.04	1.26
NBR	PNNL#N1	PNNL#N2	PNNL#N5	PNNL#N6
<b>Air In-situ Tribo (CoF)</b>	2.17	1.47	1.44	1.15
<b>HP-H2 In-situ Tribo (CoF)</b>	1.74	1.12	.681	2.73

Tribo – tribology

HP-H2 – high-pressure hydrogen

The development of the high-pressure in-situ dynamic mechanical analysis (DMA) was designed and an autoclave was procured. The autoclave frame was constructed, and the autoclave was mounted in place. The DMA components for the internal design are in fabrication. The new in-situ DMA will allow research into the effects of polymer property changes in relation to gas and pressure effects. This will provide insight into compressibility of materials of during charging and discharging, volume changes in material during high-pressure soaking as gas diffuses into the polymer, and material expansion during decompression.

The compression set of NBR compounds N1, N2, N5, and N6 and EPDM compounds E1, E2, E3, and E4 were investigated for polymer property changes before and after hydrogen. N1 and E2 were rubbers with no filler or plasticizer, N2 and E2 had filler and no plasticizer, N5 and E5 had both filler and plasticizer, and N6 and E6 had fillers and no plasticizer. The compression set for the filled, plasticized EPDM system is insignificant. However, the compression set increased by ~37% due to hydrogen exposure for the filled plasticized NBR system. The material systems were then analyzed with DMA storage modulus measurements. In general, both EPDM and NBR show a decrease in storage modulus upon hydrogen exposure. A 20% decrease in modulus was seen in the filled plasticized EPDM after hydrogen exposure, whereas the modulus change in the NBR equivalent system was insignificant. There were also no indications of changes to the glass transition temperatures in all the compounds tested before and after exposure. For unexposed and exposed rubbers, fillers contribute heavily to the storage modulus of EPDM and NBR whereas plasticizers significantly lower the glass transition temperature.

The volumetric change before and after exposure was significantly different between the two model compounds. The NBR material expansion after exposure increased in volume by 72% of the filled plasticized compound compared to 8% in the EPDM (Table 2). It was observed that the volume change was much slower in recovery with the NBR compared to the EPDM, which correlates to the desorption curves discussed above. For filled and unfilled EPDM and NBR, volume change was lower with filler present than with no filler.

Micro-computed-tomography images of the NBR and EPDM rubbers were compared. For EPDM formulation E1, a large number of cracks that were not aligned in any particular direction were seen all over the sample after hydrogen exposure. When filled, EPDM E6 showed complete crack mitigation after hydrogen exposure. For exposed N1 samples, far fewer cracks (again not aligned in any particular direction) were seen in the sample. Overall, NBR seemed more resistant to hydrogen exposure without filler or plasticizer help, whereas for EPDM, filler addition is a must for crack mitigation.

**Table 2. Filler Effects on Volumetric Changes after Hydrogen Exposure**

		Filler	Plasticizer	Percent increase in volume	Recovery in volume
NBR	N1	No	No	79%	99%
	N2	No	Yes	85%	97%
	N5	Yes	Yes	72%	97%
	N6	Yes	No	55%	101%
EPDM	E1	No	No	4%	102%
	E2	No	Yes	2%	103%
	E5	Yes	Yes	8%	100%
	E6	Yes	No	16%	102%

## CONCLUSIONS AND UPCOMING ACTIVITIES

The team has contributed to the advancement of test methodologies for polymer compatibility in hydrogen with involvement in the CSA CHMC 2 standard. The model material compounds provided detailed insight as to the difference in hydrogen diffusion behaviors between polymers and fillers. The carbon and silica fillers both indicate a hydrogen absorption around 10 ppm hydrogen. The plasticizer additive increases the hydrogen diffusion with its addition. The coefficient of friction decreased in hydrogen atmosphere with these specific compounds compared to past off-the-shelf commercial materials, indicating that the filler materials in hydrogen can influence the wear and friction of the material compounds. The effect of filler and plasticizer as additives with respect to hydrogen exposure of NBR and EPDM rubbers were studied, and conclusions useful toward compression set, volumetric swelling, and mitigating damage accumulation were drawn.

The upcoming activities include the following:

- Build up material properties in a database
- Long term aging effects of hydrogen
- Material contamination of hydrogen
- Complete neutron scattering experiments on pressure cycle aged polymers
- Material damage effects from hydrogen and pressure
- Polymeric material damage model
- New material development approaches for improved durability of elastomers.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. K.L. Simmons, “Hydrogen Compatibility of Polymers Program,” 2018 HYDROGENIUS Research Symposium, Fukuoka, Japan (February 2, 2018).
2. N.C. Menon, “Compatibility of Polymeric Materials in Hydrogen Service,” 2018 HYDROGENIUS Research Symposium, Fukuoka, Japan (February 2, 2018).
3. N. Menon, K. Simmons, D. Smith, A. Naskar, M. Veenstra, “Influence of Fillers and Plasticizers on Polymer Behavior in High-Pressure Hydrogen Environments,” Poster presentation to Material Science Research Foundation External Review Board, Sandia National Laboratories, Albuquerque, NM (April 19, 2018).
4. K.L. Simmons, N. Menon, D. Smith, A. Naskar, M. Veenstra, “Compatibility of Polymeric Materials Used in the Hydrogen Infrastructure,” 2018 Hydrogen and Fuel Cells Program Annual Merit Review, Washington, DC (June 2018).