Compatibility of Polymeric Materials Used in the Hydrogen Infrastructure

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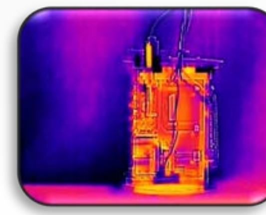

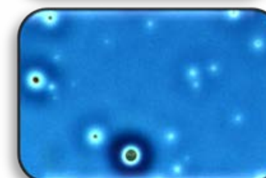

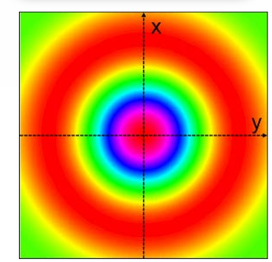

Overview

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Timeline

- Project Start Date: October 2015
- Project End Date: September 2018
- % Completed: 75%

Budget

- Total Project Budget: $1800K
  - Total Federal Share: 100%
  - Total DOE Funds Spent**:

    $196K (PNNL) – includes Ford subcontract

    $75K(SNL)

    $27.4K (ORNL)

* *As of 3/24/17

Barriers

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

Partners

- PNNL (Project Lead)
- SNL
- ORNL
- Ford Motor Company

Relevance

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Objectives: To develop a knowledge base of polymer and elastomer materials hydrogen compatibility through development of test methodologies that will enable a better understanding of material interaction in infrastructure that will guide future research and development activities

- Provide scientific and technical basis to enable full deployment of H2 and fuel cell technologies by filling the critical knowledge gap for polymer performance in H2 environments
- Develop standard test protocols for polymeric materials to evaluate their H2 compatibility for conditions, applications, and polymers of need by the hydrogen community
- Disseminate test protocols and compatibility information and support the deployment of H2 infrastructure

Barriers	Project Impact
A. Safety Data and Information: Limited Access and Availability	Develop H2 Tools webpage for data dissemination and hydrogen compatibility guidance
G. Insufficient Technical Data to Revise Standards	Develop test methodologies for evaluating polymer compatibility with high pressure H_2: (1) in situ tribology, (2) pressure cycle aging. Understand fundamental aspects of hydrogen damage in polymers through techniques like neutron scattering.
J. Limited Participation of Business in the Code Development Process	Performed FMEA analysis from technical experts and stakeholder input to prioritize required material attributes for test methods to evaluate conditions of interest for H2 compatibility. Disseminate project findings through conferences, publications, and website
K. No consistent codification plan and process for synchronization of R&D and Code Development	Engaging codes and standards community (CSA and others) early on and having discussions to synchronize our data collection and test method development with new codes and standards development like CHMC 2

Approach

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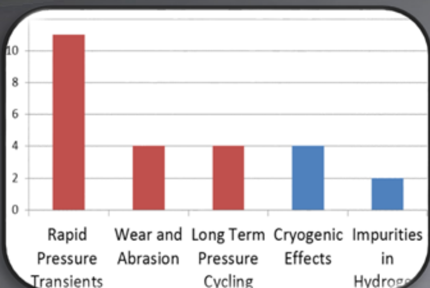
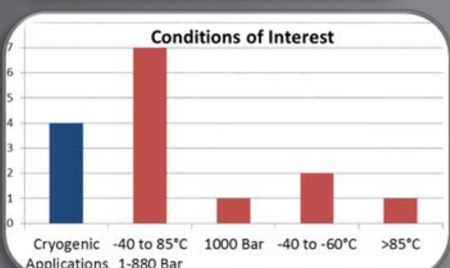
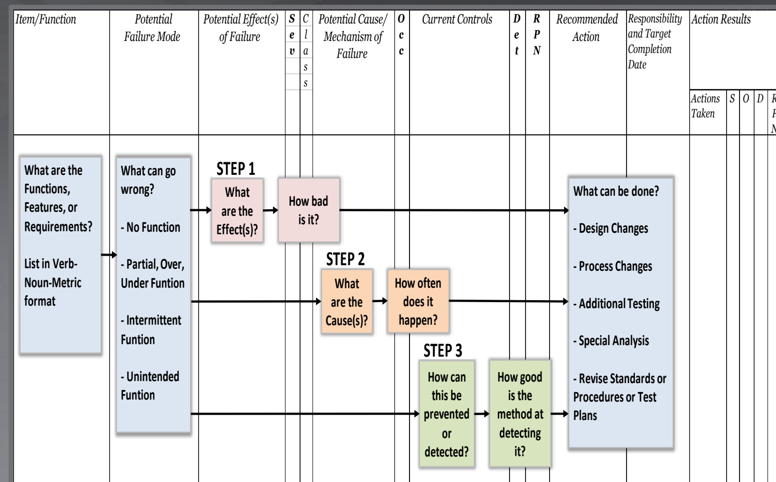
Identify the issues: Stakeholder Engagement (1st round complete)

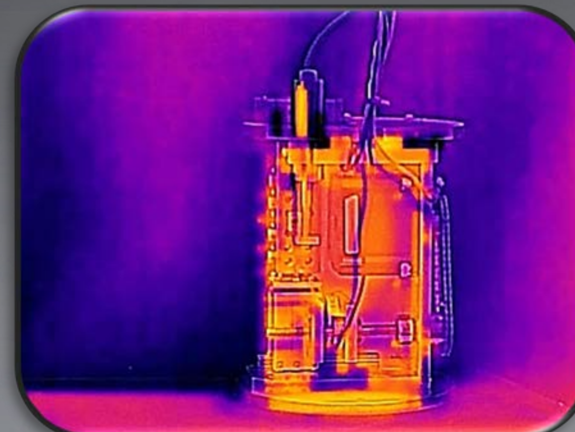




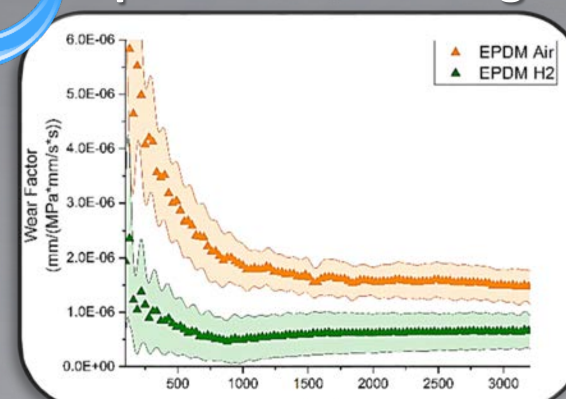
FMEA Prioritization of Critical Attributes



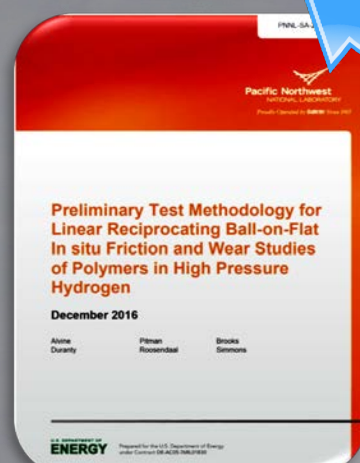
Test Method Development



Build the Database: Experimental Testing



Disseminate: Standards, Test Methods, Publications

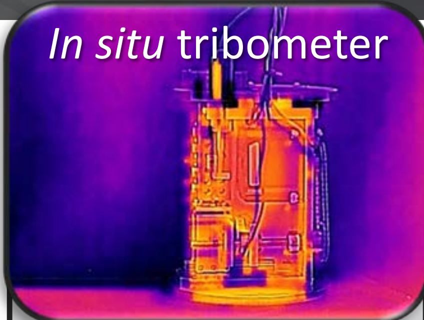


Project Tasks

Task 1:

Stakeholder Engagement

- Materials of Interest
- Operating Conditions of Interest
- Challenges faced
- Test methods currently employed by them



In situ tribometer

Task 2:

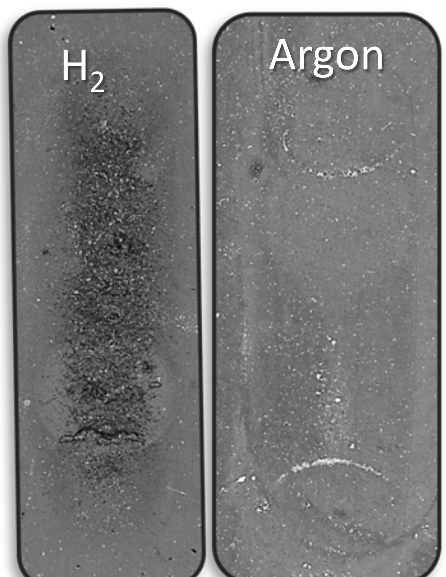
Test Methodology Development & Data Collection

- Selection of relevant polymers
- Determining preliminary test parameters
- Conducting preliminary tests and establishing optimum conditions of operation

Task 3:

Characterization of Polymers

- Baseline properties before and after exposure to H_2



Task 4:

Disseminate Information

- Lay the groundwork and deliver preliminary data for a database
- Share results with stakeholders
- Feedback from them to improve/modify test methodologies
- Identify dissemination approaches: Technical Reference

Approach
Work Flow

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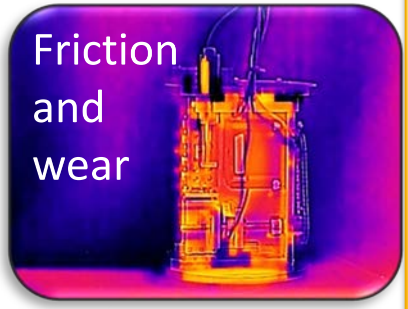


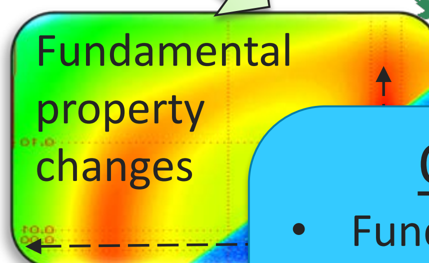
PNNL
- Project lead
- Friction and wear in hydrogen tests
- Dynamic Mechanical Analysis

Ford
- Subcontractor to PNNL
- Consulting on code and standards engagement

Critical handoffs:
SNL provides ORNL with samples for testing

Consultation

Consultation



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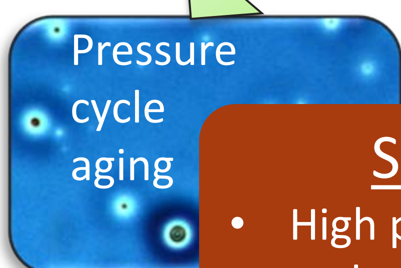
ORNL
- Fundamental property changes like porosity with neutron and X-ray scattering techniques



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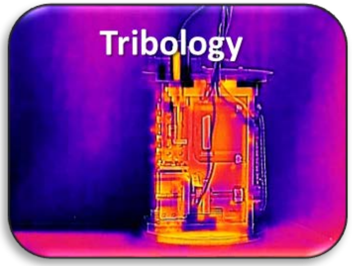
SNL
- High pressure cycle aging tests

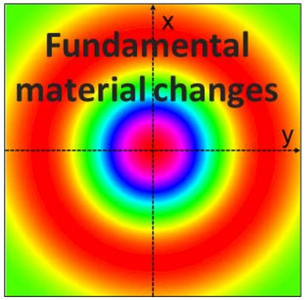
SNL provides samples to ORNL

Industry Stakeholders and FMEA Influenced Test Methodology Development

- Industry survey confirmed knowledge on hydrogen compatibility of polymers is lacking and provided input regarding pressure and temperature priorities.
- The team completed a Failure Mode and Effects Analysis (FMEA) and identified the top failure causes:
  - Polymer seal (dynamic) material experiences a change in properties (strength, modulus, shear, hardness, etc.) due to hydrogen exposure
  - Polymer barrier material degrades from rapid high pressure differentials (explosive decompression) due to hydrogen exposure
  - Polymer seal (static & dynamic) material selected exceeds hydrogen permeation rate
  - Polymer seal (static & dynamic) material geometry changes and volume swells or reduction due to hydrogen exposure

Project task approach:





Project test methodology development directly aligns with industry stakeholder and FMEA input.

Model Elastomer Material Compounds

- Transitioned from purchased commercial materials to controlled material compounds for research
- Developed model EPDM and NBR compounds with Kyushu University and Takaishi Industries
- Controlled compound additives in six different formulations 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

Used to evaluate the effects of hydrogen on polymers and known additives

Accomplishments and Progress

Model Elastomer Compounds Hydrogen Content

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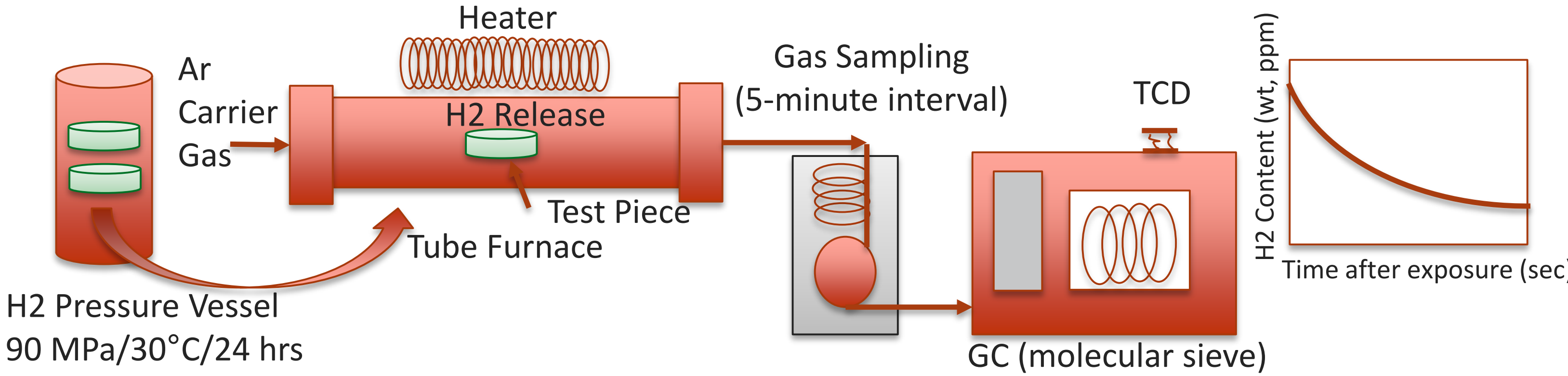
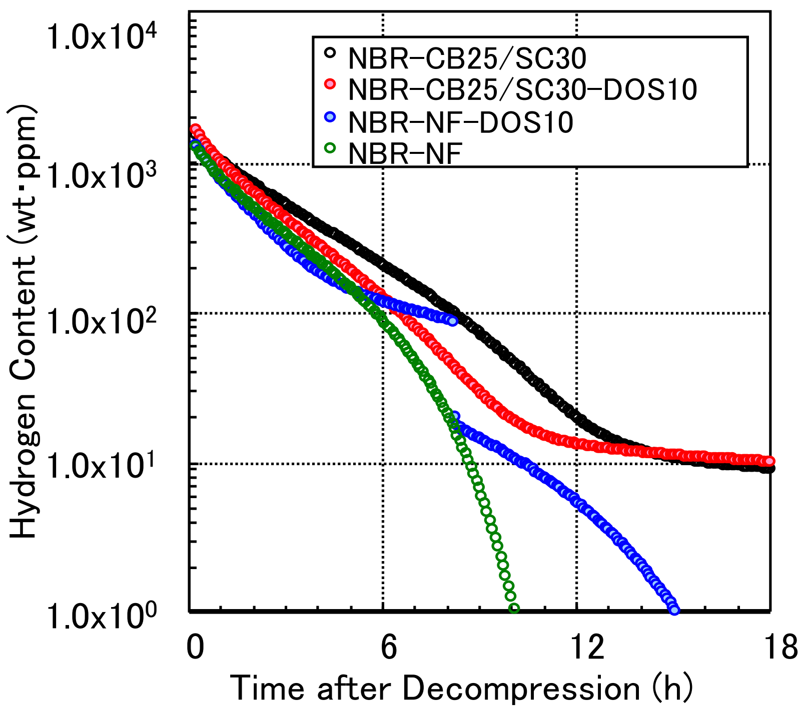
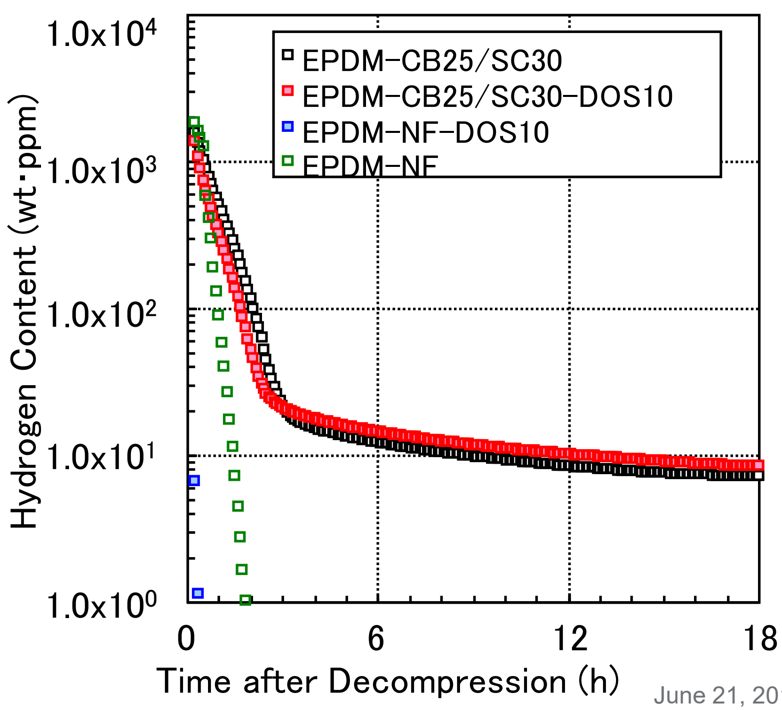
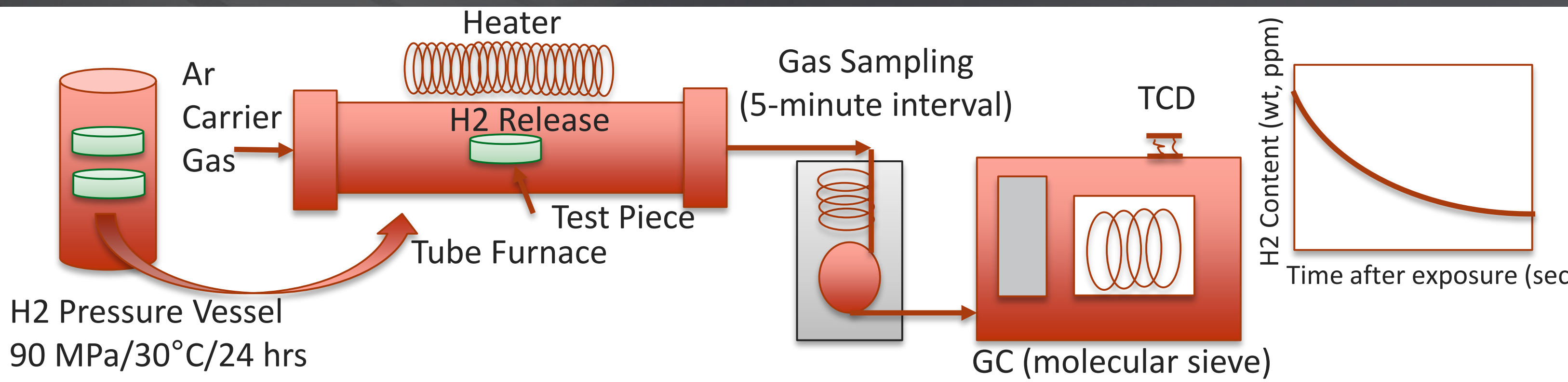


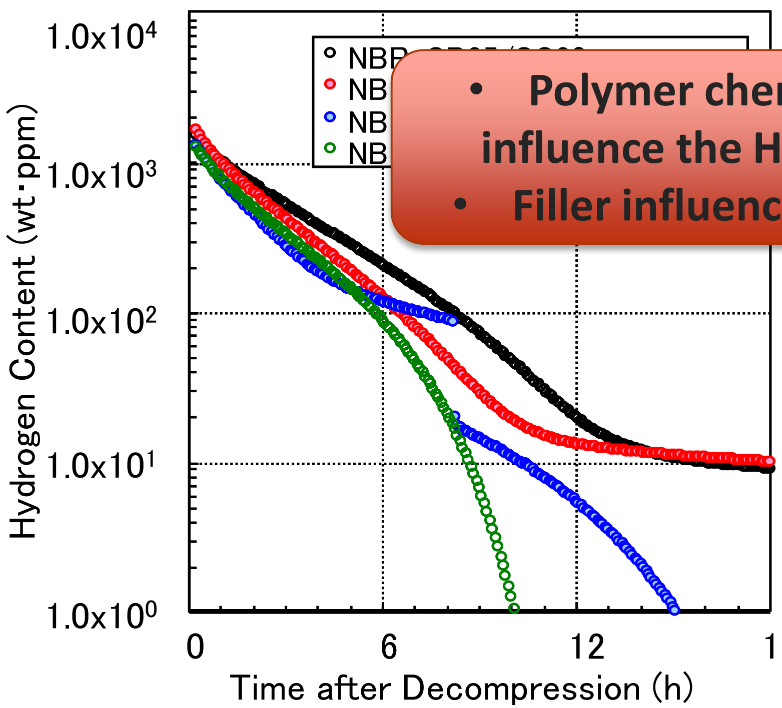




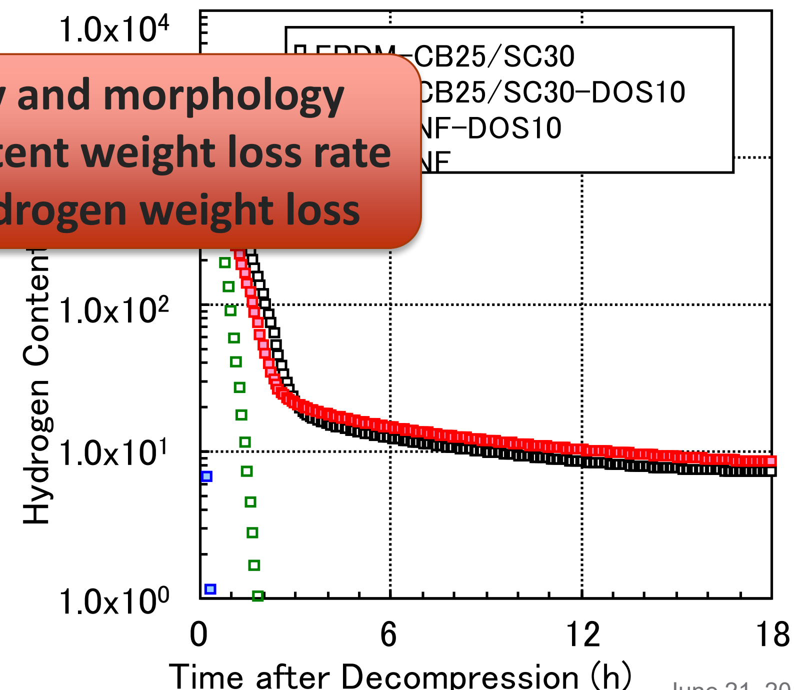
Accomplishments and Progress

Model Elastomer Compounds Hydrogen Content





- **Polymer chemistry and morphology influence the H_2 content weight loss rate**
- **Filler influences hydrogen weight loss**



Accomplishments and Progress

Hydrogen Content and Volume Change Related to Pressure

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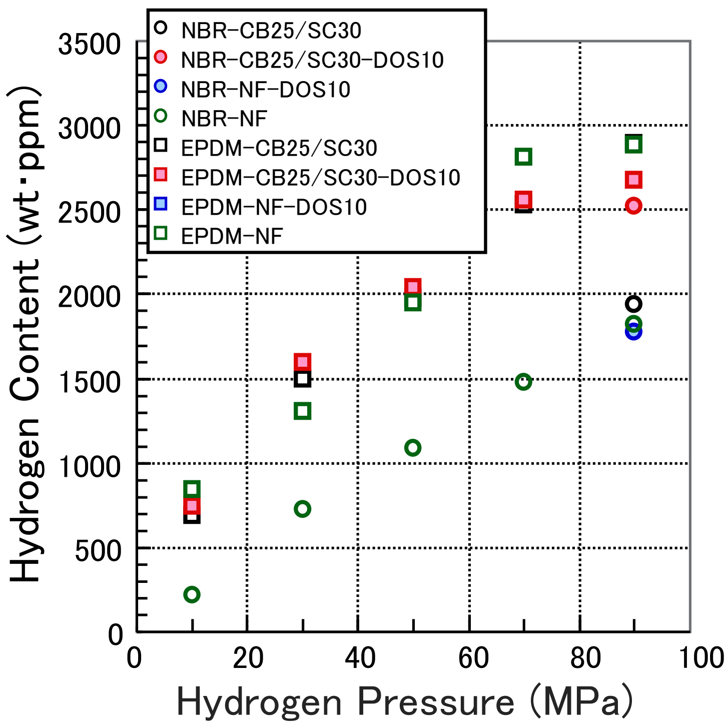
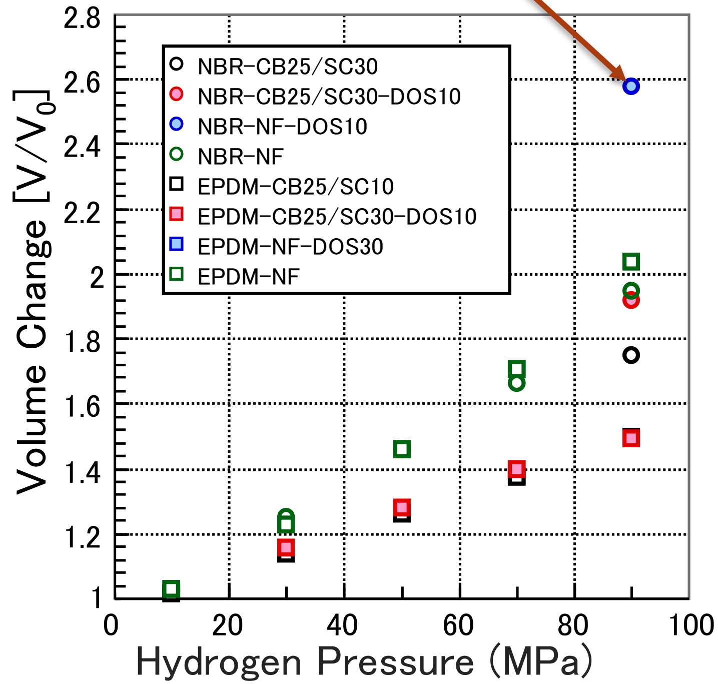
40% volume change with plasticizer additive in NBR





The filler material used in these model material compounds show a decrease in volume change for NBR by 10% and 30% in EPDM from unfilled baseline compound

Approach
PNNL Unique In situ Tribometer

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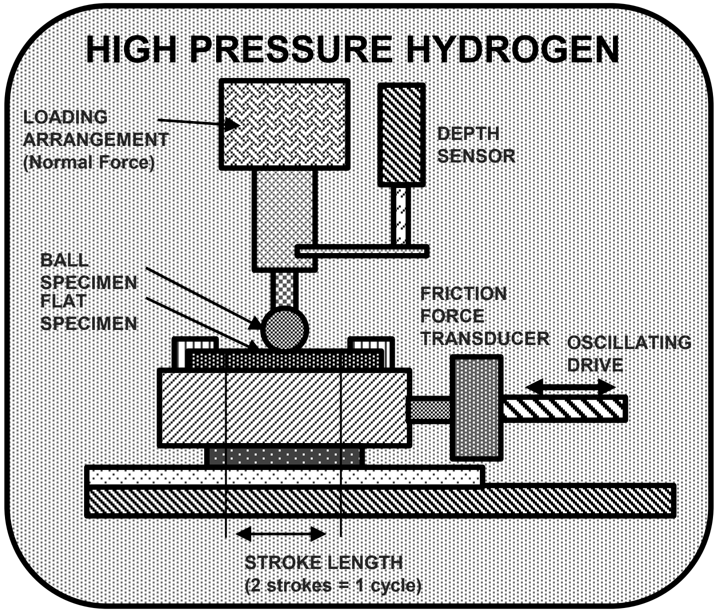

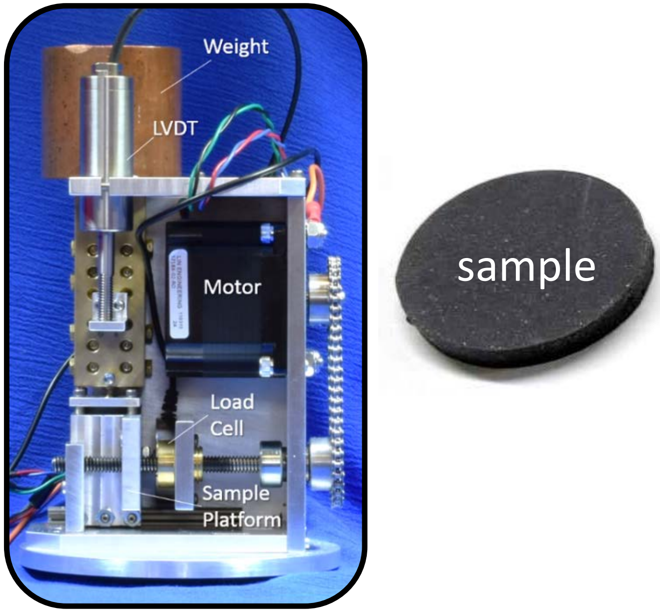

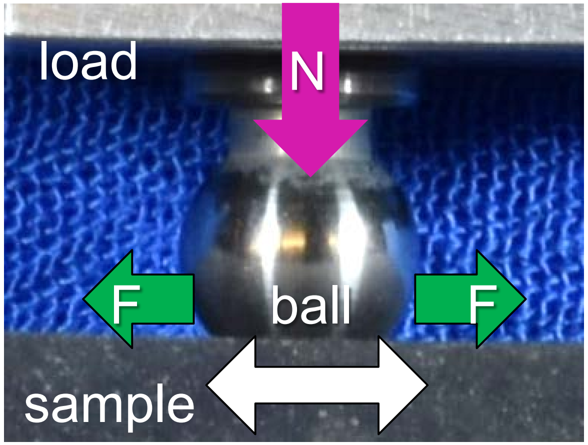

Overview of Tribometer

- Linear reciprocating adapted from ASTM G133
- Normal load (using weights) presses steel ball into moving sample
- Frictional force and vertical wear depth profiles measured in situ
- Pressures up to 5,000 psi hydrogen
- Ambient air and high pressure argon tests run for comparison

Accomplishments and Progress
EPDM and NBR Model Compound Series

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EPDM	PNNL ref.#											
ITEMS	PNNL#E1		PNNL#E2		PNNL#E3		PNNL#E4		PNNL#E5		PNNL#E6	
Features	No Filler No Plasticizer		No Filler Plasticizer		Carbon black No Plasticizer		Inorganic No Plasticizer		Carbon black Inorganic Plasticizer		Carbon black Inorganic No Plasticizer	
	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL
Density	0.921	0.93	.919	0.886	1.013	1.010	1.039	1.035	1.073	1.065	1.053	1.05
Hardness (Duro)	55.3	A52	48.3	A49	67.2	A65	76.3	A71	72	A69	71.9	A69
CSM Tribo (COF)	1.33		.997		1.29		1.89		1.31		1.6	

NBR	PNNL ref.#											
ITEMS	PNNL#N1		PNNL#N2		PNNL#N3		PNNL#N4		PNNL#N5		PNNL#N6	
Features	No Filler No Plasticizer		No Filler Plasticizer		Carbon black No Plasticizer		Inorganic No Plasticizer		Carbon black Inorganic Plasticizer		Carbon black Inorganic No Plasticizer	
	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL	TI (IRHD)	PNNL
Density	1.032	1.018	1.015	1.013	1.118	1.1	1.152	1.137	1.182	1.180	1.175	1.167
Hardness (Duro)	51	A53	43.4	A47	66	A65	66.1	A65	65.8	A68	68.7	A72
CSM Tribo (COF)	1.95		1.33		1.55		1.76		.60		1.35	

Plasticizer and Filler has significant influence on hardness and CoF

Accomplishments and Progress

Optical Evaluations of EPDM Tribology Wear

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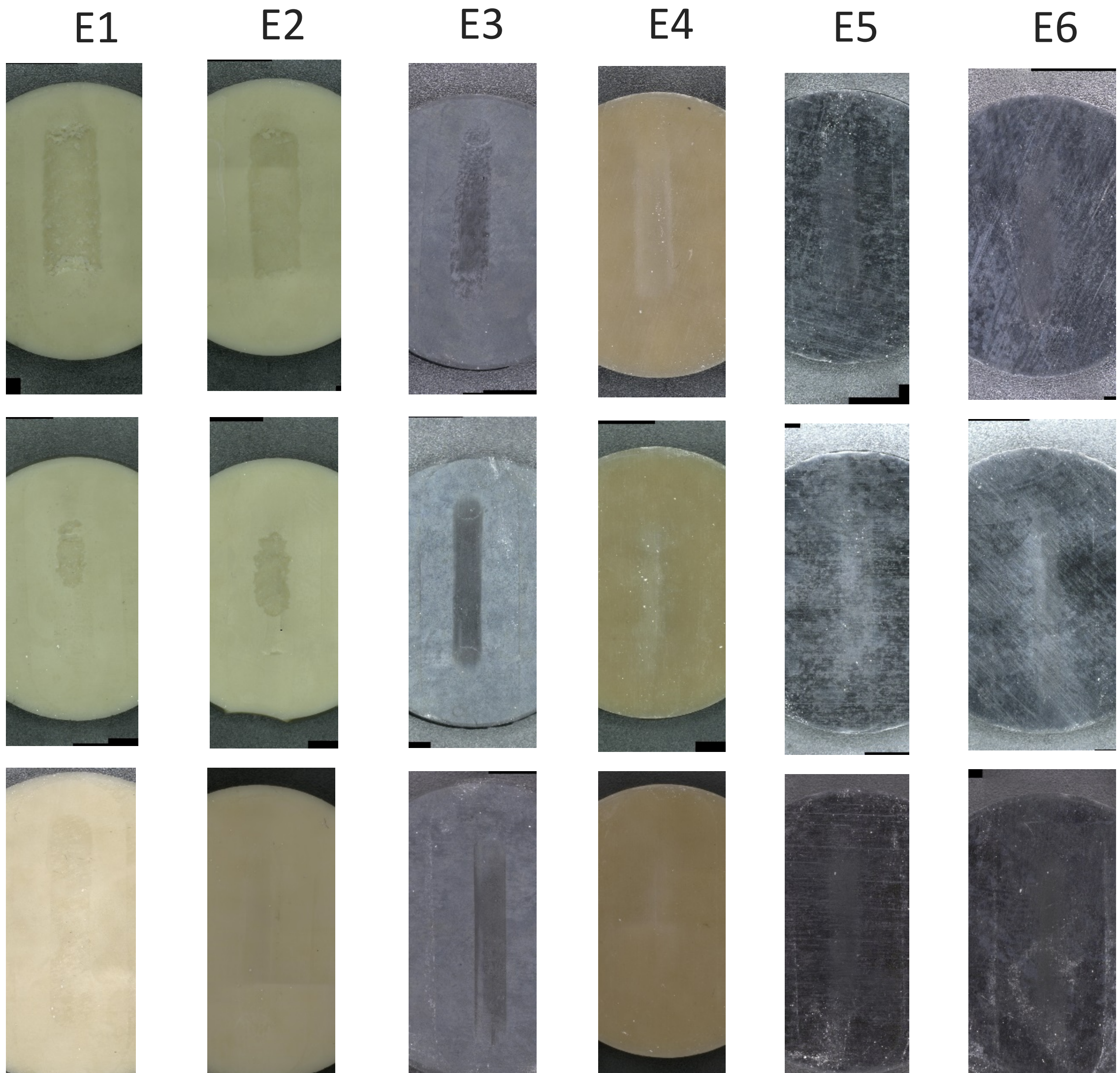

In situ
7.5N Load
60 minutes
3.36 meters
Ambient air

CSM
7N Load
60 minutes
3.36 meters
Ambient air

CSM
5N Load
60 minutes
3.36 meters
Ambient air

Filler has significant influence on wear and elastomer durability

Optical Evaluations of NBR Tribology Wear

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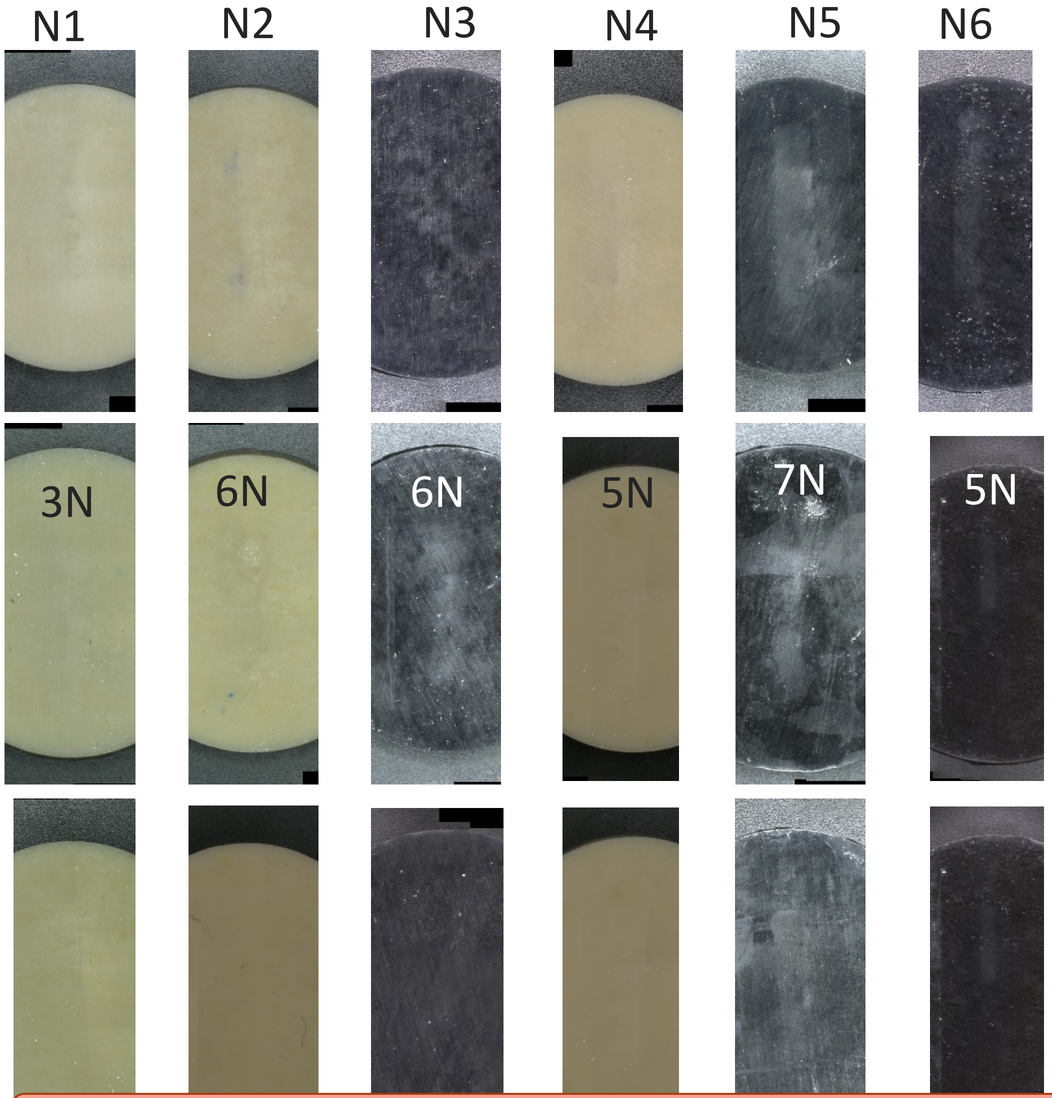


In situ
7.5N Load
60 minutes
3.36 meters
Ambient air

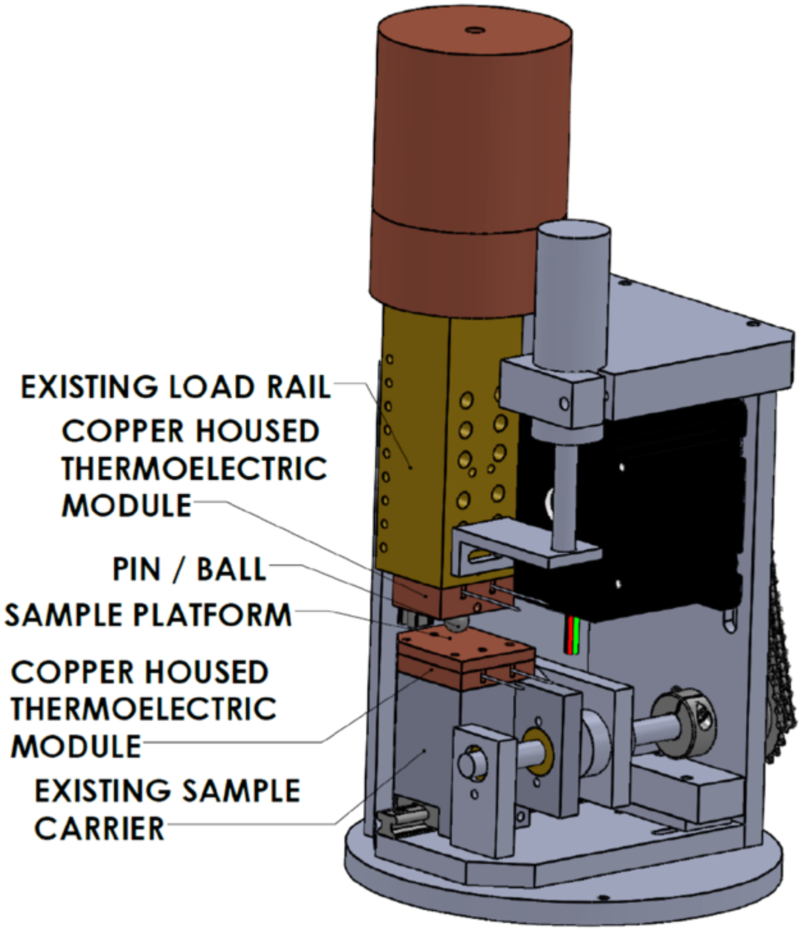
CSM
Varied Load
60 minutes
3.36 meters
Ambient air

CSM
5N Load
60 minutes
3.36 meters
Ambient air

Hardness and load have significant effect Cof

Tribometer Upgrade for In Situ Heating & Cooling

- Target temperatures above or below ambient (-40 to +85°C) for infrastructure applications
- Previous design was to use thermoelectric heater/cooler stage for the system
  - Testing of heaters, Peltier's, thermocouples, etc. complete
  - Peltier were compatible with H2 but were unable to reach target temperatures
  - Redesign underway that integrates new autoclave for lower temperature capability (-50 to +200°C)
  - New design expected to be completed in two months
  - Module will be tested after ambient tests are complete to ensure identical testing conditions



Accomplishments and Progress

Compression Set changes for EPDM and NBR with H2 Exposure

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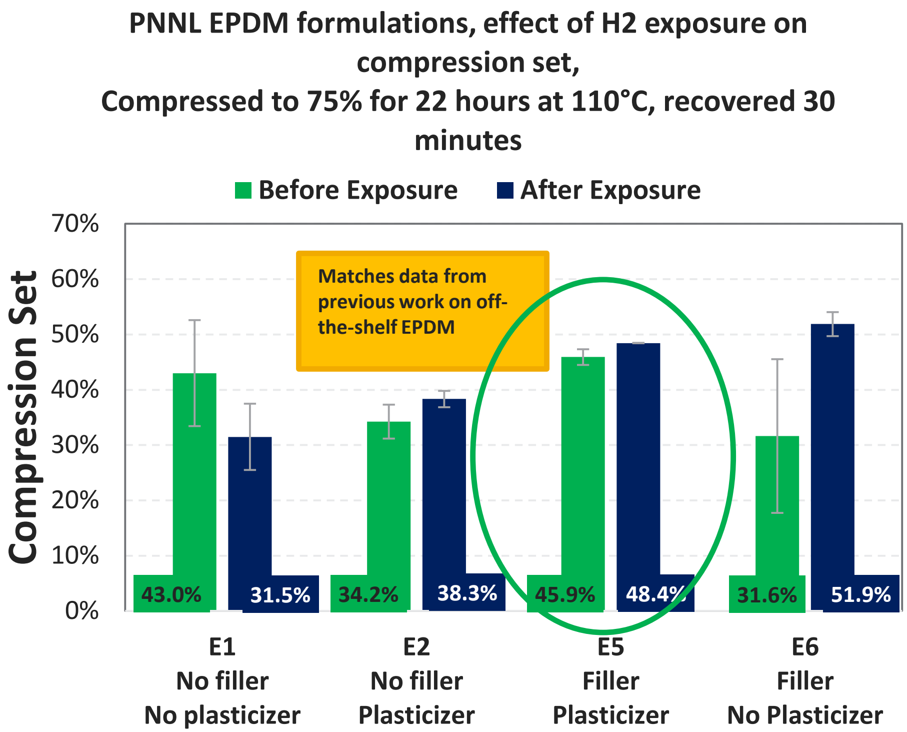

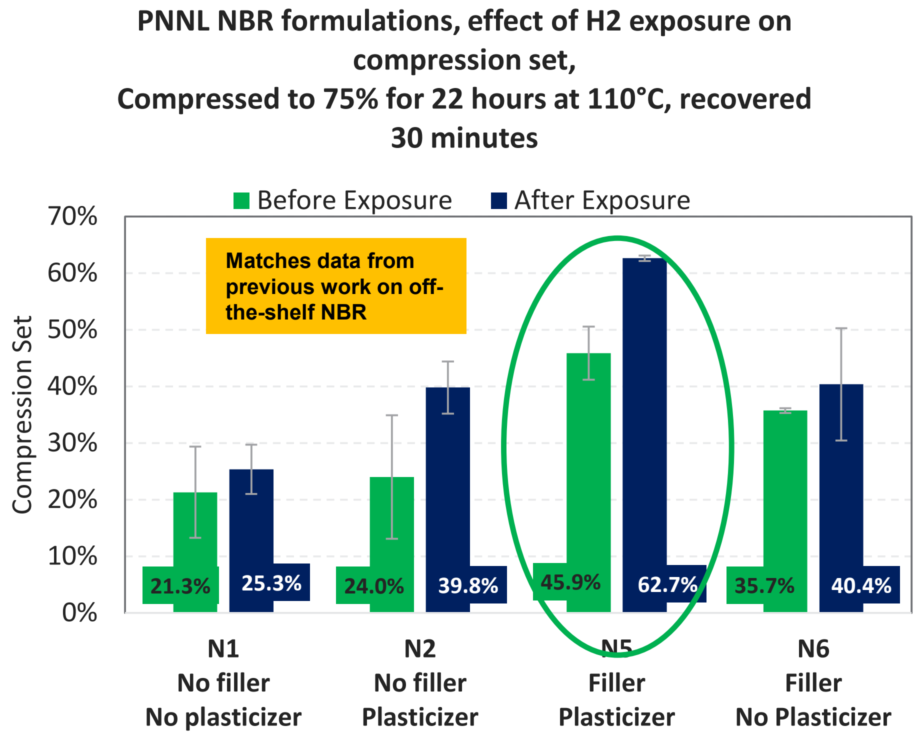

Compression set change due to H2 exposure for a filled, plasticized EPDM system is insignificant

Compression set increase by ~37% due to H2 exposure for a filled plasticized NBR system

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Accomplishments and Progress

Storage Modulus changes for EPDM with H2 Exposure

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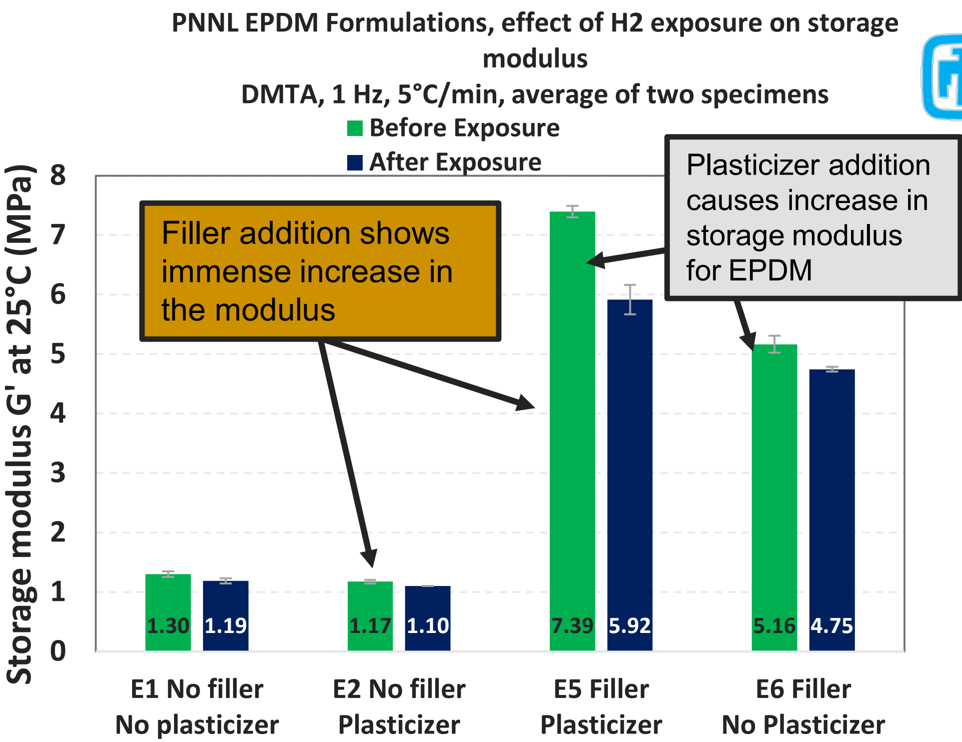

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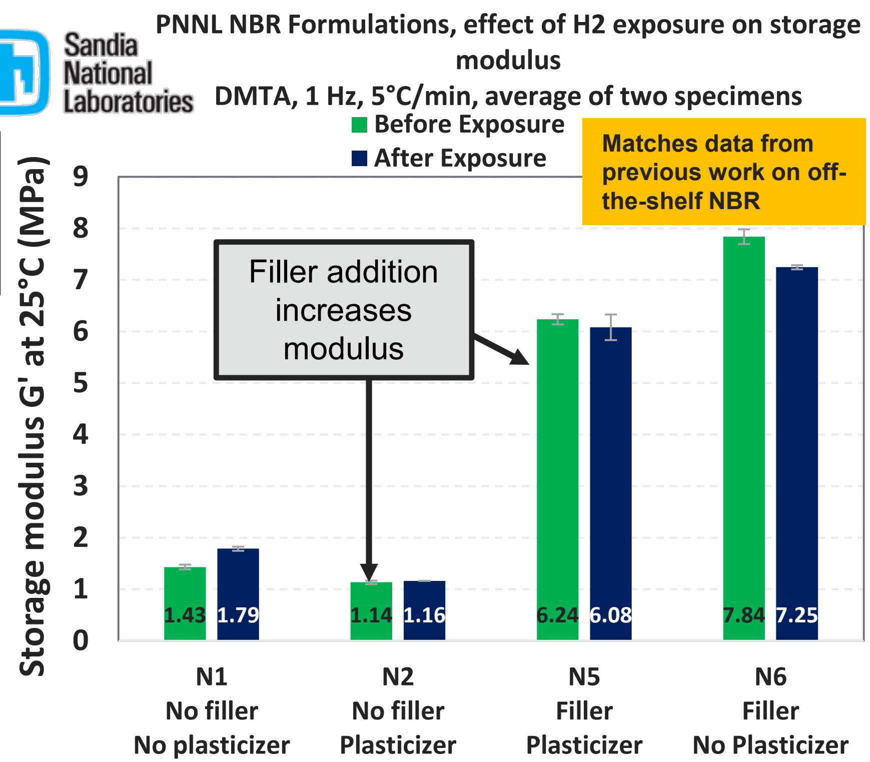

New finding

A 20% decrease in modulus is seen in filled plasticized EPDM after H2 exposure

Modulus decrease due to H2 exposure for filled plasticized NBR is insignificant

Accomplishments and Progress
Glass transition temperature changes after H2 exposure

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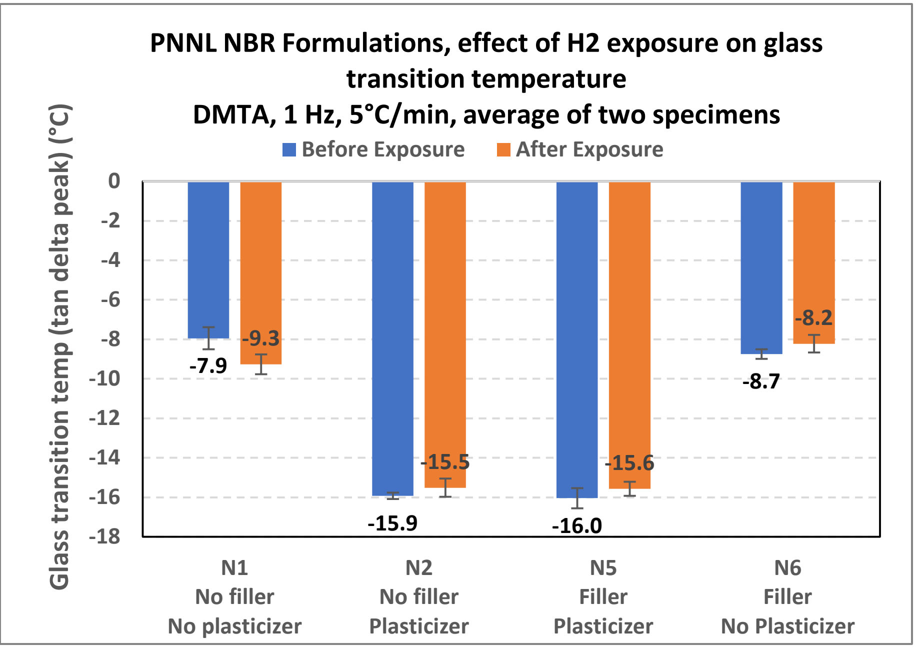
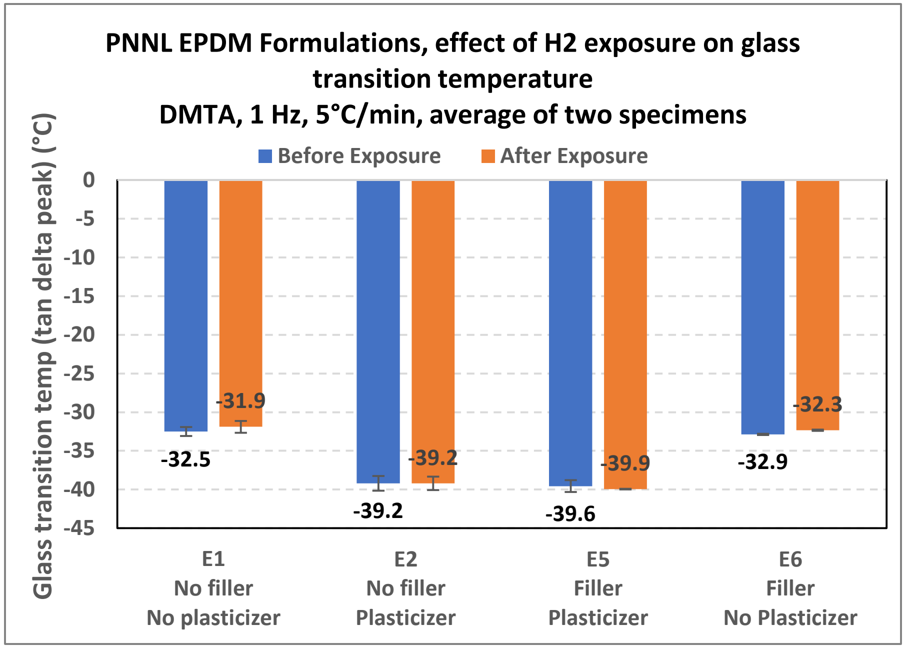
Matches data from previous work





- **For filled, plasticized EPDM and NBR systems, there is no significant change in T_g due to H2 exposure**
- **The addition of plasticizer decreases the Tg of EPDM and NBR significantly**

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Accomplishments and Progress
Density changes for NBR and EPDM with H2 exposure

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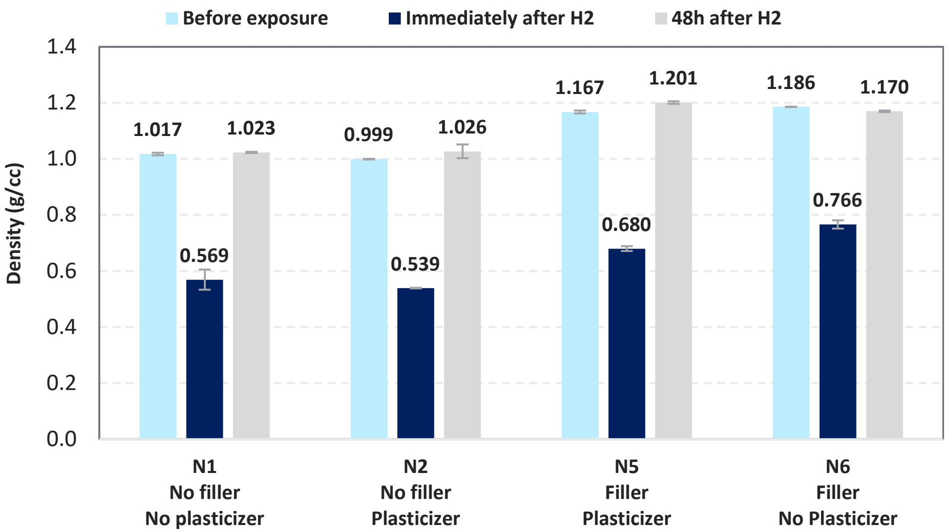
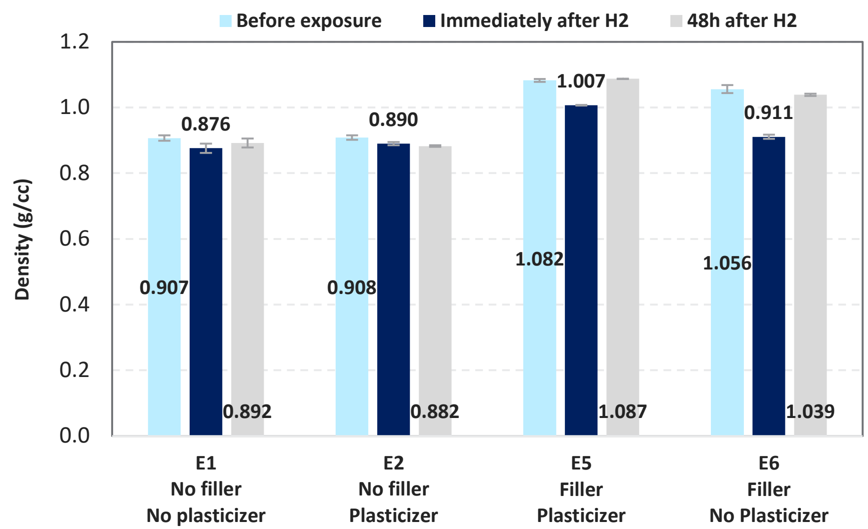


#	Filler	Plasticizer	Percent increase in volume	Recovery in volume
N1	No	No	79%	99%
N2	No	Yes	85%	97%
N5	Yes	Yes	72%	97%
N6	Yes	No	55%	101%

NBR N2 sample 1

Picture showing the evolution of H2 from NBR N2 over 48 hours

Significant swelling after H2 exposure



#	Filler	Plasticizer	Percent increase in volume	Recovery in volume
E1	No	No	4%	102%
E2	No	Yes	2%	103%
E5	Yes	Yes	8%	100%
E6	Yes	No	16%	102%

EPDM swells much less upon H2 exposure compared to NBR, which matches previous work on off-the-shelf materials

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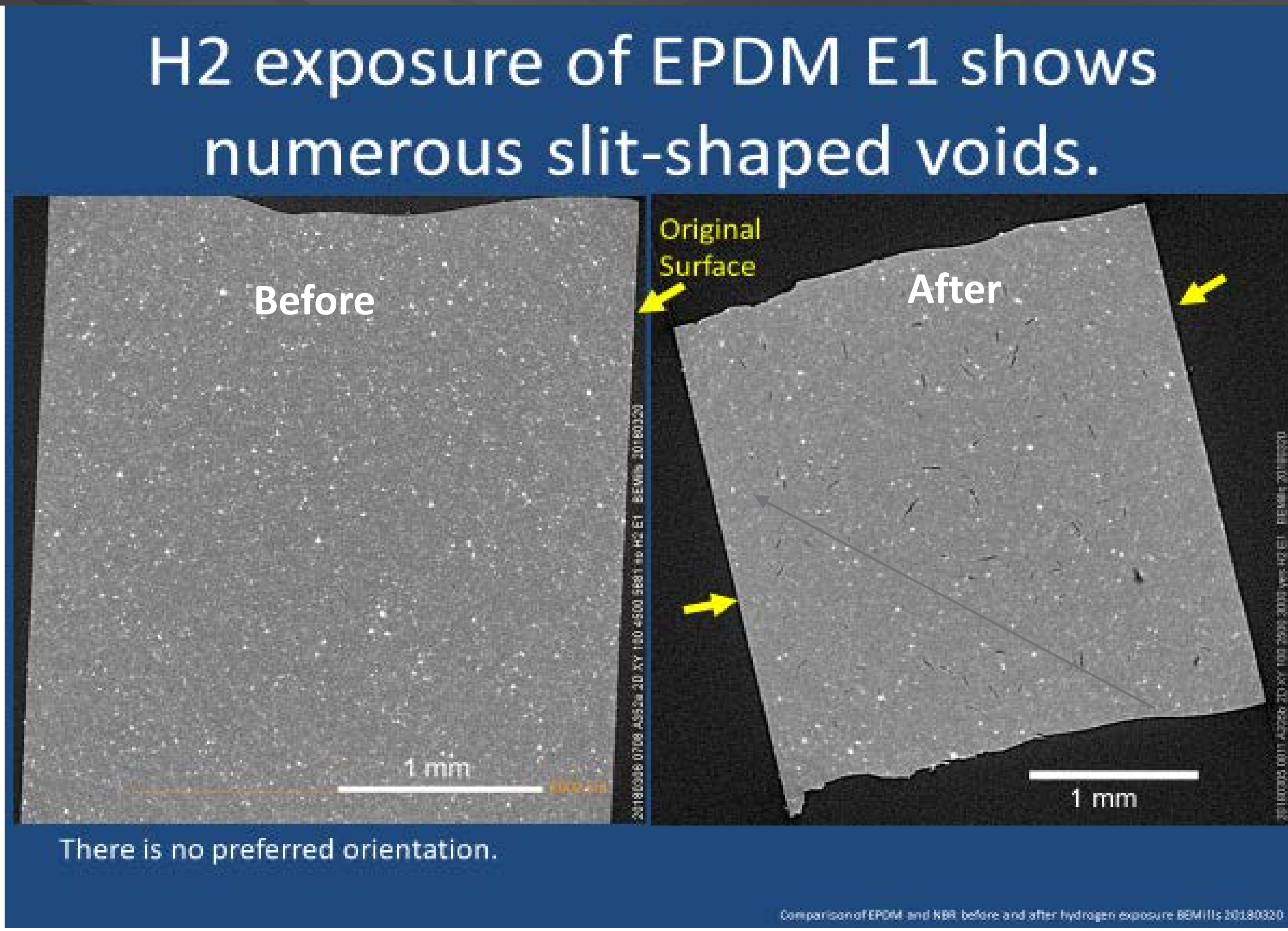
Accomplishments and Progress

Micro-CT images for EPDM after H2 exposure



- Formulation EPDM E1 has no filler or plasticizer
- Both formulations contain high Z particles (5% by wt. ZnO)

Microcracks in picture are not aligned in any particular direction and seem more or less distributed all over

Unfilled EPDM after H2 exposure has significant microcrack damage

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Accomplishments and Progress

Micro-CT images for EPDM after H2 exposure

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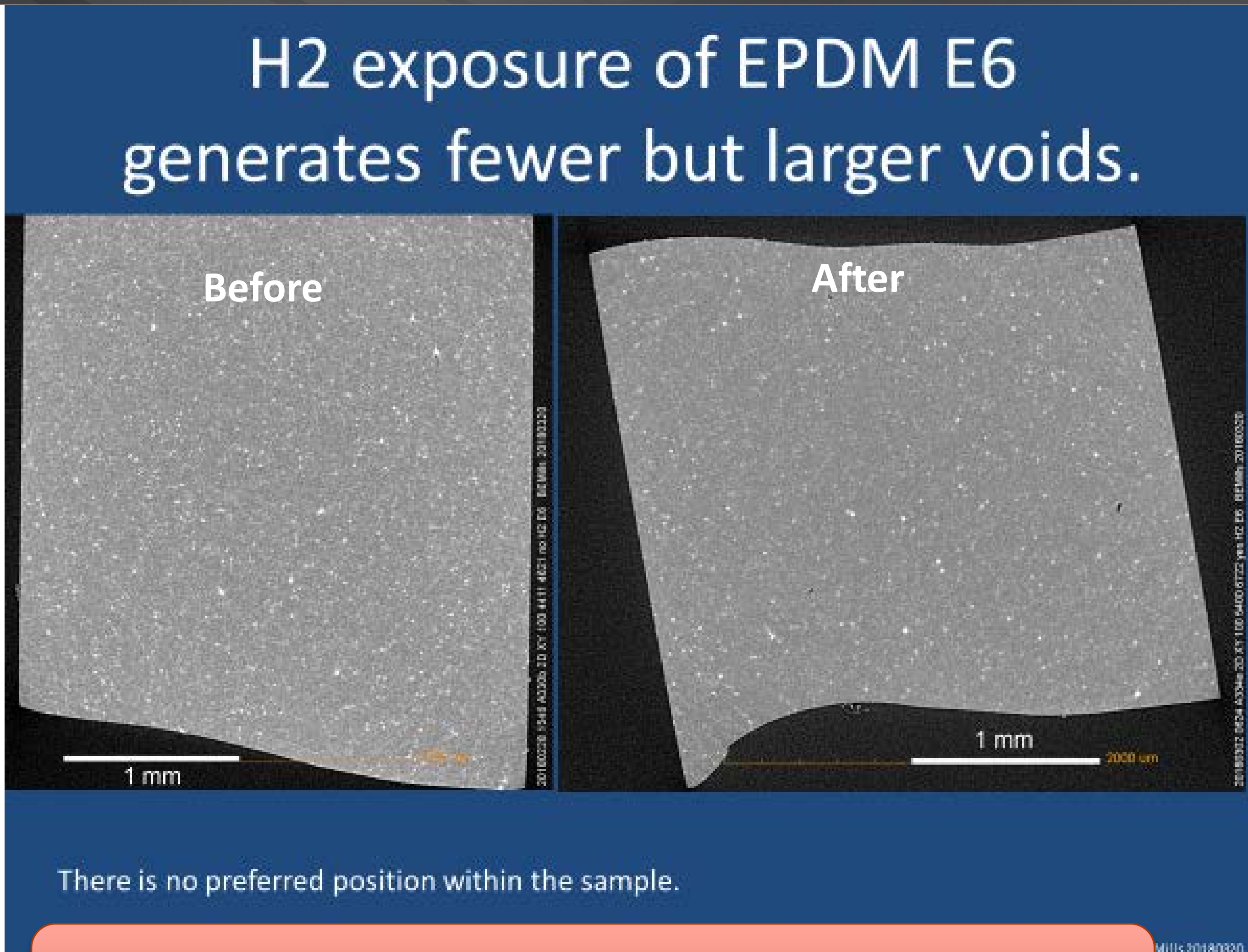

- Formulation EPDM E6 has filler but no plasticizer
- Fillers in EPDM E6 are: carbon black (300 nm) and Silica
- Both formulations contain high Z particles (5% by wt. ZnO)

Fillers appear to help with crack mitigation in EPDM after H2 exposure

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Construction of a one-of-a-kind High Pressure Cycling Manifold at Sandia

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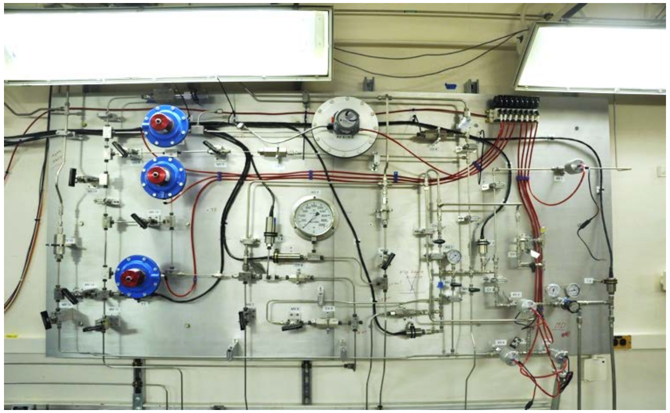

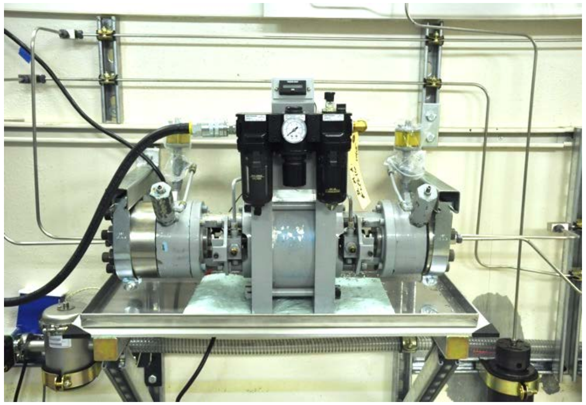

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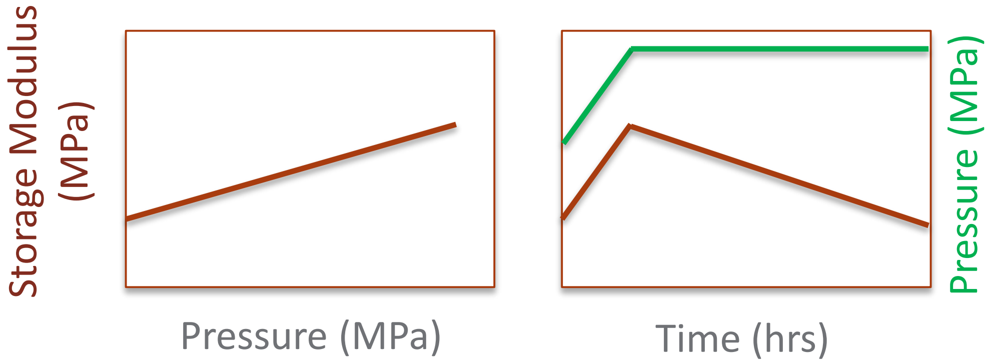
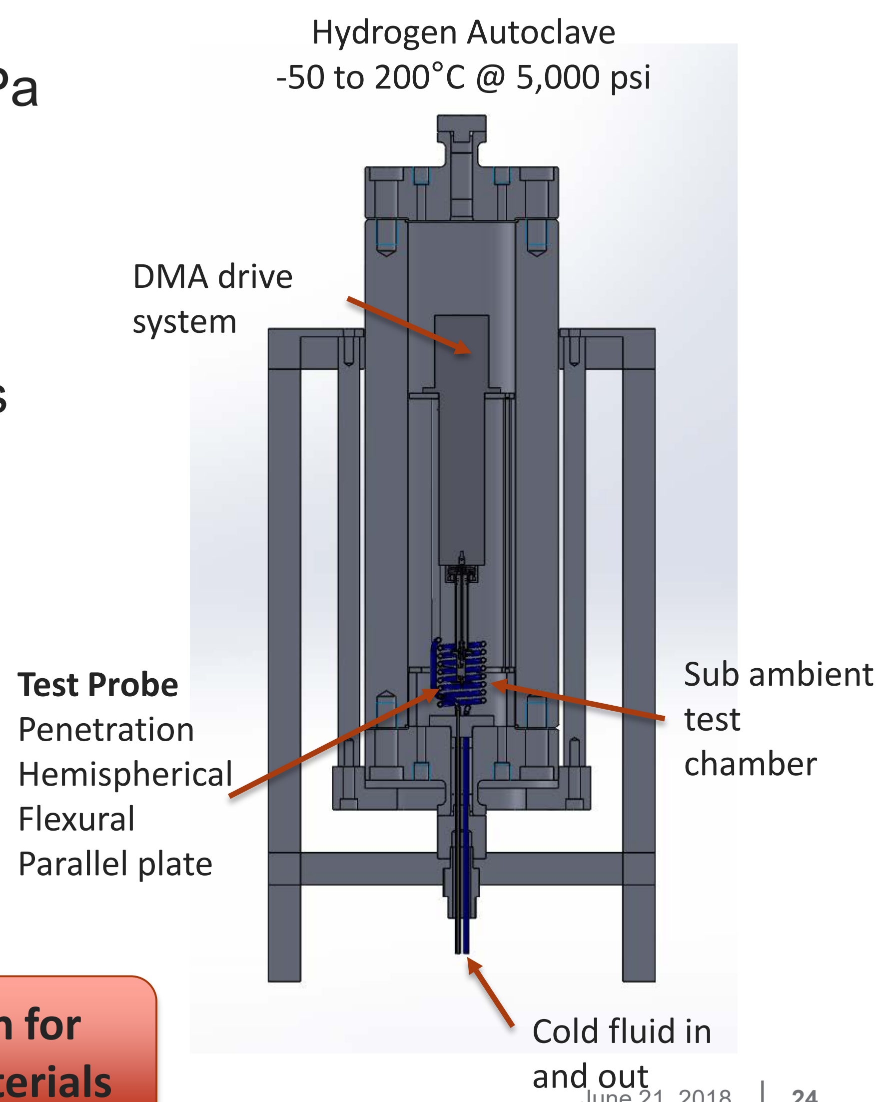
Pressure cycling manifold installed and undergoing safety tests for controlled decompression rates at controlled temperatures

In situ Dynamic Mechanical Analysis

- Pressure range atmospheric to 30 MPa
- Frequency sweeps
- Creep and recovery
- Temperature range -50°C to 125°C
- Isothermal runs with pressure sweeps to investigate pressure effects on material with gas variable





New novel in situ DMA under construction for evaluating hydrogen pressure effects in materials

CHMC 2 – High Priority Tests

Pacific Northwest NATIONAL LABORATORY

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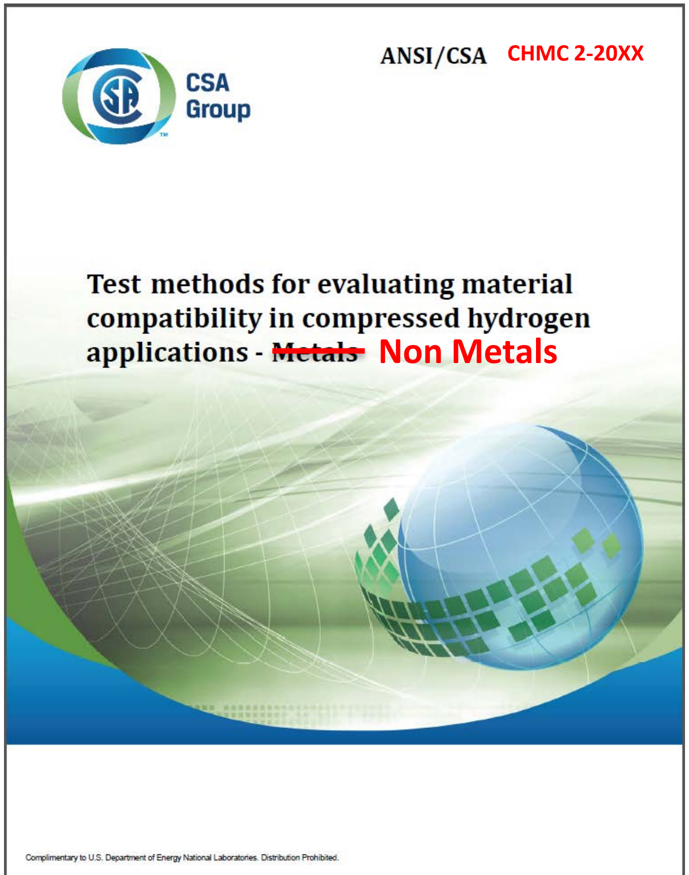
Scope: This standard provides **uniform test methods** for evaluating material compatibility with compressed hydrogen applications. The results of these tests are intended to provide a basic **comparison of materials performance** in applications utilizing compressed hydrogen.



Contents

0. Introduction
1. Scope
2. Reference Publications
3. Definitions
4. General Requirements
5. Test Methods
6. Material Qualifications

Annex

Potential Test Methods

1. Polymer Permeation
2. Physical Stability and Property Changes
3. Rapid Cycling Effects
4. Dynamic Frictional Wear
5. Material Contamination

Accomplishments and Progress

CHMC 2 – Development of Test Method Document Sections

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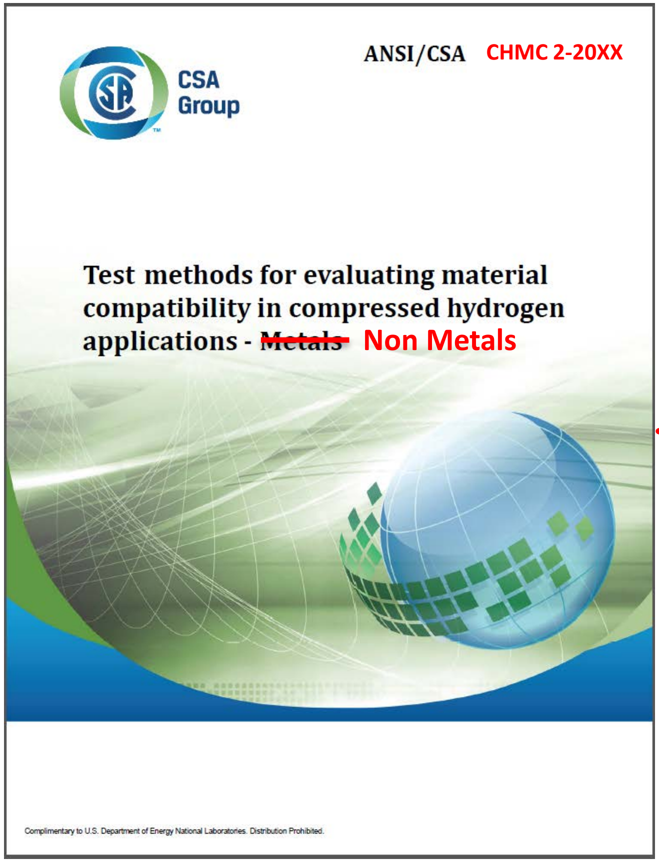

CHMC 2 Test Method

→ Describe test pur

1.1 Apparatus

→ Describe test equ

1.2 Test environm

→ Describe pressur

1.3 Specimen Prep

→ Describe test sam

1.4 Test Procedur

→ Describe test step

1.5 Reporting

→ Describe test resu

CHMC 2 Test Method: Physical Stability of Polymers in Hydrogen Environments

Density or Specific Gravity Measurements of Polymers

Test Purpose

This test method gives the details of the procedure to evaluate the density changes of specimens of elastomeric or solid polymeric materials due to swelling or shrinking upon exposure to hydrogen environments. Dimensional and density measurements will be made prior to and after conditioning in the designated test gas (in this case hydrogen).

1.1 Apparatus

Test equipment will

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1.2 Test environm

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Component
Hydrogen
CO + CO2
Nitrogen
Oxygen
THC
Water

Table 1. Compo

CHMC 2 Test Method: Physical Stability of Polymers in Hydrogen Environments

Test Purpose

This test method gives the details of the procedure to evaluate the change in dimensions and mass of specimens of elastomeric or rubbery materials due to swelling or shrinking upon exposure to hydrogen environments. Dimensional and mass measurements will be made prior to and after conditioning in the designated test gas

1.1 Apparatus

Test equipment wi

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Hydrogen
CO + CO2
Nitrogen
Oxygen
THC
Water

Table 1. Com

1.2.2 Pressure o psi) durin

1.2.3 Temperatu the end of

1.3 Specimen Pr

The following

CHMC 2 Test Method: Dynamic Wear of Polymers in Hydrogen Environments

1.1 Test Method

This test method covers laboratory procedures for determining the coefficient of friction, wear volumes, and wear rates for polymers and elastomers that have been subjected hydrogen environments. The method covers two conditions of testing: a) in-situ testing in a high-pressure hydrogen environment and b) ex-situ testing of post-exposure specimens of polymeric and elastomeric materials using a ball-on-flat linear reciprocating geometry similar to ASTM G133-95 (reapproved 2002).

1.2 Apparatus

→ Describe test equipment: in-situ vs. ex-situ

1.1.1 General description of liner reciprocating tribometer for wear and friction property testing

Figure 1A shows the general schematic of a linear reciprocating tribometer. The tribometer shown in Figure 1B is the final design of one-such device that can be used in-situ in a high-pressure hydrogen autoclave. **Error! Reference source not found.** shows the pin and sample geometry in greater detail. The system works by pressing a steel ball (See **Error! Reference source not found.**A, B) normally into an elastomeric sample that is horizontally-mounted on a linear reciprocating stage. w. The loading on the ball is applied through a series of dead weights set on top of the ball carriage system which is free to move in the vertical direction while a computer controlled stepper motor drive provides the horizontal linear motion of the sample stage up to 14 mm. Wear depth of the ball into the sample is measured in the vertical direction by means of a linear position sensor mounted on the ball carriage The motor drive is coupled to the sample stage by means of a capacitive load cell which measures the horizontal force on the stage induced by the friction of the ball on the sample. . The linear reciprocating motion of the sample stage achieves nearly constant velocity over 95% of the travel in both directions.

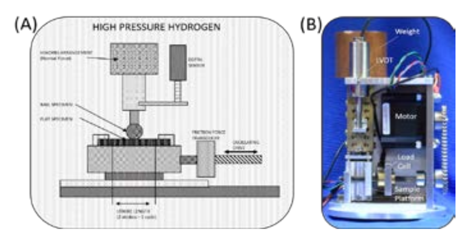

Figure 1. (A) Schematic of the in situ tribometer to measure friction and wear in a high-pressure hydrogen environment.

Accomplishment and Progress

Dissemination of Information
H2Tools.org Website and Database

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https://aws-beta.h2tools.org/resources/h2cop

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HOME / HYDROGEN COMPATIBILITY OF POLYMERS

Hydrogen Compatibility of Polymers

Sub Pages
- Tribology
- Pressure Cycle Aging
- Scattering

While much is known about damaging embrittlement effects of hydrogen on me
the effects of high pressure hydrogen on polymers. The hydrogen infrastructure
(1) distribution and delivery, (2) fueling stations, and (3) fuel cell systems of which
materials to meet the rigorous demands of the environment that they are subje
materials in the most effective combinations allow for safe and cost-effective de
Using non-metallic materials are an essential element in this mix of material. Th
the high-pressure hydrogen environment is important to the myriad of applicati
infrastructure including applications of compressors, seals, valves, and actuators
conditions range from cryogenic storage 77K (-196°C) and 70 MPa to as high as 4
typical application temperature range for gaseous hydrogen systems is 233K (-4
interests of hydrogen effects are:

- Permeation
- Physical Stability (property changes)
- Dynamic Frictional Wear
- Rapid Cycling Effects
- Material Contamination

To support the needs of the hydrogen community, Pacific Northwest National La
Laboratory, and Oak Ridge National Laboratory, have been developing test meth
for hydrogen compatibility. The team has been collaborating with international r
methods and collecting data for development of a non-metallic database referer

H2 Tools is intended for public use. It was built, and is maintained, by the Pacific Northwest National Laboratory with funding from the DOE Office of Energy Efficiency and Renewable Energy's Fuel Cell Technologies Office.

tools.org/resources/h2cop/tribology

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HOME / H2COP / TRIBOLOGY

Tribology

In Situ High Pressure Hydrogen Testing Capabilities

PNNL has high pressure hydrogen autoclaves capable of soaking materials up to 5000 psi, and at elevated temperatures. These are large 1 gallon capacity systems capable of accommodating different in situ test systems. Electrical feed-throughs provide power and sensing for the instruments. Short descriptions of available equipment are listed here.

Tribology: A custom built linear reciprocating (ASTM G133) pin on flat system that is capable of testing samples up to approximately 1" wide at XN, and 5Hz with a stroke length of ½". The system was designed primarily for polymeric materials, but could potentially accommodate metals testing.

Autoclave Test Methodology

PNNL Preliminary Test Methodology Report 12-22-16

This test methodology describes in situ testing of friction and wear (tribology) of polymers under high pressure hydrogen. This methodology is based in part on the existing tribological standard ASTM G133 "standard test method for linearly reciprocating ball-on-flat sliding wear". Friction and wear testing under a high-pressure hydrogen environment is critical for hydrogen fueling infrastructure components such as compressors, valves and other actuated devices. Here we present test a methodology for in situ friction andwear studies of polymers under 28 MPa (4,000 psi) hydrogen in a linear reciprocating custom built apparatus. Supporting data from in situ acrylonitrile-butadiene rubber (NBR, commercially Buna-N) tests in 28 MPa (4,000 psi) hydrogen are presented.

Relevant Standards

STANDARD ID (PREFIX "ASTM")	TITLE	STATUS	DEVELOPED BY SUBCOMMITTEE	BOOK OF STANDARDS VOLUME	DOI	ACTIVE STANDARD LINK
G105 - 16	Standard Test Method for Conducting Wet Sand/Rubber Wheel	Active	G02.30	03.02		

Accomplishments and Progress

Database Structure/Query Breakdown

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Filters

Logical Filters

Logical filters can be used to reduce the Data Set prior to analysis

H2 Permeability (Barrer) is Less than 3

Add Filter | Clear Filters

Data Set for Analysis

The following Data Set will be used for the analysis with the parameters defined above. Click the checkboxes to further downselect alternatives before executing the analysis.

Show Excluded Criteria

	100% Tensile Modulus (MPa)	Failure Elogation (%)	Hardness (Shore)	Tg (°C)	Temperature (°C)	Pressure (kPa)	H2 Permeability (Barrer)
Teflon AF 2400	1500	7.9	75	240	77	1013	28
Technoflon P 457	5.9	239	23	-15	77	1013	0.39
Teflon PTFE 850A	496	300	50	117	-16	1724	22.6
Neoflon DF-0050C1	74000	279	85	100	25	6895	0.74
Elastollan C80A	41.4	3000	85	-40	20	100	6
NBR (27% CN)	2.6	250	60	-2	25	100	16
Polybutadiene	1.5	500	15	-100	25	100	41.9

Criteria Weighting

Drag and drop criteria to rank them from best to worst. Criteria can also be excluded from the analysis.

All Items

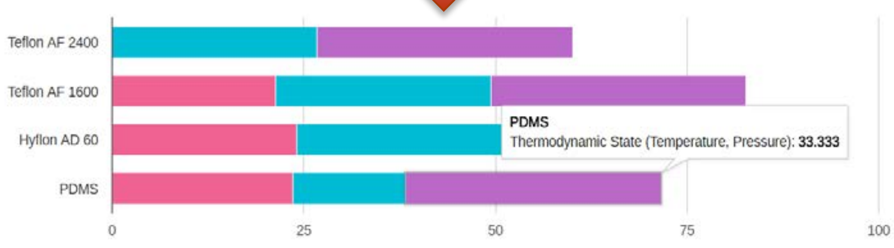
Ranking Order Centroid

- H2 Permeability (Barrer)
- Failure Elogation (%)
- 100% Tensile Modulus (MPa)
- Hardness (Shore)
- Tg (°C)

H2 Permeability (Barrer)	0.46
Failure Elogation (%)	0.26
100% Tensile Modulus (MPa)	0.15
Hardness (Shore)	0.09
Tg (°C)	0.04

	Group Weight	Criterion	Rank	Criterion Weight	Overall Weight
Transport Properties (Permeability)	0.333	Permeability (mol H2/m.s.MPa)	N/A	0.7	0.233
		Diffusivity (cm2/s)	N/A	0.300	0.100
Physical Properties (Density, 100 % Tensile Modulus)	0.333	100% Tensile Modulus (MPa)	N/A	0.500	0.167
		Density (g/cc)	N/A	0.500	0.167
Thermodynamic State (Temperature, Pressure)	0.333	Temperature (K)	N/A	1.000	0.333

Results



Material Database

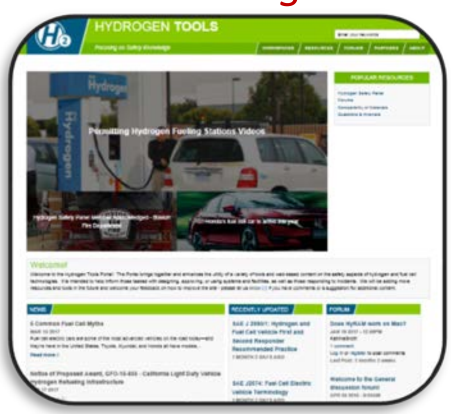
	Ref	Material	Class	Description	Density	Unit[Density]	Hardness	Unit[Hardness]	Temperature	Unit[Temperature]	Pressure	Unit[Pressure]	Diffusing Species	Permeability
0	[1]	Teflon AF 2400	C4	N/A	1.744	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	341723364.4
1	[1]	Teflon AF 1600	C4	N/A	1.836	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	134248464.6
2	[1]	Hyflon AD 60	C4	N/A	1.93	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	69565113.46
3	[1]	Nafion N117	C4	N/A	-	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	5858114.818
4	[1]	Tecnoflon PL 455	C4	N/A	-	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	5369938.583
5	[1]	Tecnoflon PL 457	C4	N/A	-	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	4759718.29
6	[1]	Tecnoflon P 459	C4	N/A	-	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	8176951.933
7	[5]	Viton A-100-1	C4	Original, no post-cure	1.9	g/cm^3	79	Shore A	-	K	-	MPa	Hydrogen	-
8	[5]	Viton A-100-2	C4	Post Cured: 70hr, 200 °C	1.9	g/cm^3	-	Shore A	-	K	-	MPa	Hydrogen	-
9	[5]	Viton A-200-1	C4	Original, no post-cure	1.9	g/cm^3	79	Shore A	-	K	-	MPa	Hydrogen	-
10	[5]	Viton A-200-2	C4	Post Cured: 70hr, 200 °C	1.9	g/cm^3	-	Shore A	-	K	-	MPa	Hydrogen	-
11	[2]	Neoflon PTFE	C4	N/A	-	g/cm^3	-	Shore A	-	K	-	MPa		-
12	[6]	PCTFE-1	C4	N/A	-	g/cm^3	-	Shore A	298	K	-	MPa	Hydrogen	39054.09879
13	[6]	PCTFE-2	C4	N/A	-	g/cm^3	-	Shore A	298	K	-	MPa	Hydrogen	114721.4153
14	[3]	PP	C15	N/A	0.946	g/cm^3	-	Shore A	-	K	-	MPa	Hydrogen	2.5 E-15
15	[2]	PP	C15	N/A	0.946	g/cm^3	-	Shore A	-	K	-	MPa	Hydrogen	-
16	[4]	HDPE‡	C15	K44 Pipe Grade	2.55	g/cm^3	-	Shore A	-	K	-	MPa	Nitrogen/Hydrogen .95/.05	-
17	[4]	HDPE††	C15	K44 Pipe Grade, 2.3% wt carbon black filler	2.55	g/cm^3	-	Shore A	-	K	-	MPa	Nitrogen/Hydrogen .95/.05	-
18	[4]	HDPE††	C15	K44 Pipe Grade	2.55	g/cm^3	-	Shore A	-	K	-	MPa	Nitrogen/Hydrogen .95/.05	-
19	[6]	HDPE	C15	N/A	2.55	g/cm^3	-	Shore A	298	K	-	MPa	Hydrogen	360029.9732
20	[6]	LDPE	C15	N/A	0.917	g/cm^3	-	Shore A	298	K	-	MPa	Hydrogen	1220440.587
21	[1]	Matrimid		N/A	0	g/cm^3	-	Shore A	350	K	-	MPa	Hydrogen	3295189.585
22	[2]	BASF Elastollan-1	C11	C 80A	1.12	g/cm^3	-	Shore A	293	K	-	MPa	Hydrogen	3157477022
23	[2]	BASF Elastollan-2	C11	C 85A	1.12	g/cm^3	-	Shore A	294	K	-	MPa	Hydrogen	2804865375
24	[2]	BASF Elastollan-3	C11	C 90A	1.12	g/cm^3	-	Shore A	294	K	-	MPa	Hydrogen	2107655982
25	[2]	BASF Elastollan-4	C11	C 95A	1.12	g/cm^3	-	Shore A	296	K	-	MPa	Hydrogen	1402432687
26	[2]	Lubrizol Estane TPU	C11	1.14mm thick film	-	g/cm^3	-	Shore A	-	K	-	MPa	Helium	2.33205E+11
27	[6]	Nitrile Rubber		27% acrylonitrile	-	g/cm^3	-	Shore A	298	K	-	MPa	Hydrogen	1952704.939

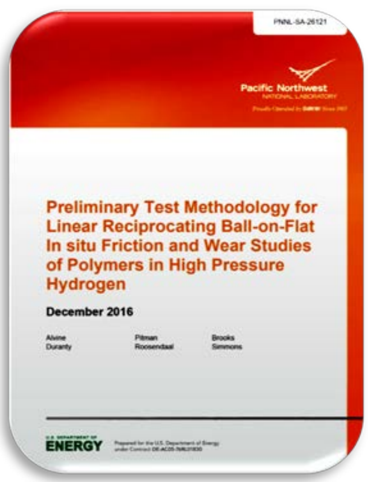
- **Database is populated from agreed upon test methods using ASTM, ISO, CSA and others for consistency in comparing material properties**
- **Analysis tool to query specific information from database for compatibility comparisons**

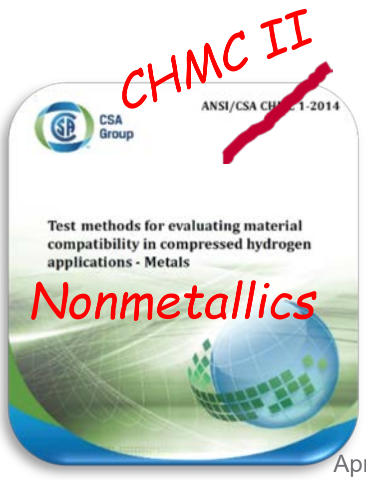
Dissemination of Information

- The team continues to work on disseminating the information gathered on this project through presentations, publications, and involvement in code committee work
  - Team member Mike Veenstra is now chair of the CHMC II nonmetallic hydrogen compatibility code committee
  - CHMC-2 working group has 25 active participants involved in developing standards in 5 different test topic areas
  - The continues to engage with international researchers and companies, including a keynote address to the International Hydrogen Energy Development Forum, and an invited talk at the Hydrogenius Research Symposium, both in Fukuoka, Japan
  - The new publication in Review of Scientific Instruments on the Tribology work
  - The H2tools.org webpage is functioning to showcase this work and provide a database/guide on h2tools.org.

h2tools.org

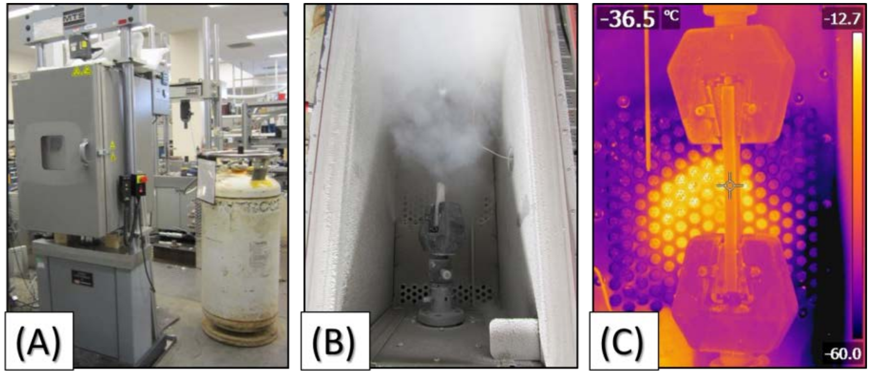


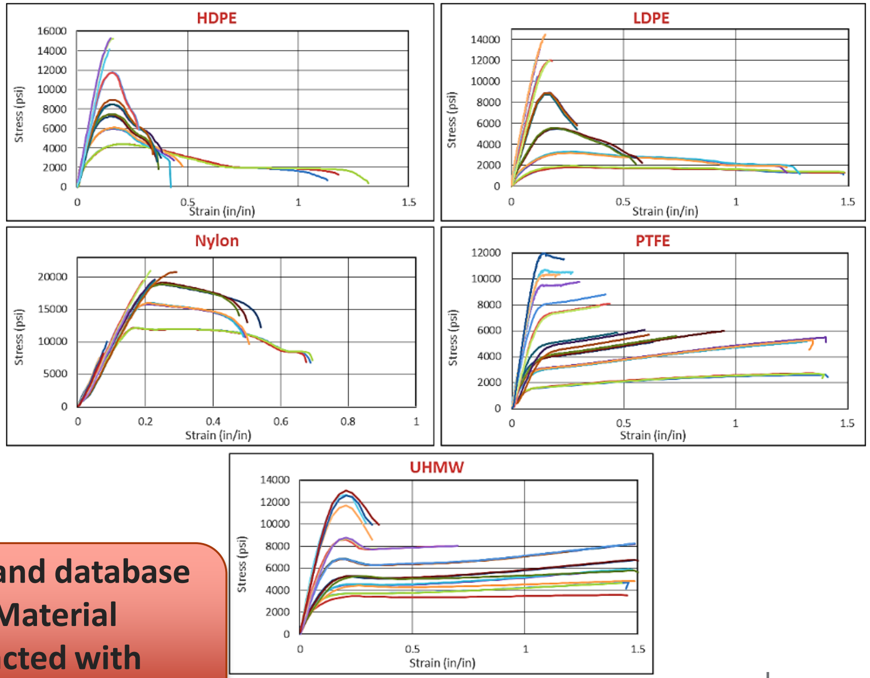




Accelerated Pathway to Tank Qualification

- Develop methods and technologies to test, evaluate, and rapidly screen materials for use in pressurized hydrogen cryogenic storage applications and accelerate the pathway to tank qualification
- Tested cryogenic material properties to provide input to predictive burst test models for high pressure hydrogen cryogenic pressure vessel





Developing material testing protocols and database of cryogenic material properties. Material properties can be significantly impacted with temperature.

Proposed Future Work

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- FY18
  - Continue involvement and leadership in CHMC II
  - Complete heating/cooling tribology testing for NBR, EPDM, and PTFE
  - Update website database/guide and continue publications and presentations
  - Complete pressure cycle aging studies on NBR, EPDM, PTFE, Viton, and POM
  - Complete development of in situ DMA
  - Identify other critical areas of need for polymer/hydrogen testing
- FY19-22
  - Build up material properties in 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

Any proposed future work is subject to change based on funding levels

Accomplishment Summary

- Stakeholder Engagement & Dissemination
  - CHMC 2 committee functioning with over 20 active member participants
  - Industry engagement gives insight of challenges with testing and materials they are being faced with
  - H2tools.org website for Hydrogen Compatibility of Polymers is being published
- Technical Accomplishments
  - PNNL completed design of a novel in situ dynamic mechanical analyzer for high pressure hydrogen
  - Collaboratively developed new model compounds with Kyushu University that are designed to understand the effects of hydrogen on material and additives in EPDM and NBR
  - Hydrogen permeability is influenced material morphology and additives
  - Completed tribology baseline testing of model NBR and EPDM
    - Unfilled materials of EPDM are weak and require reduced normal force loads
    - Filled materials show a small amount of wear compared to previously purchased commercial materials
- Static high pressure hydrogen gas material effects on EPDM and NBR additives
  - Both EPDM and NBR show an increase in compression set after H2 exposure; NBR shows a higher increase
  - Both EPDM and NBR show a decrease in storage modulus upon H2 exposure
  - Swelling upon H2 exposure is less with filler than without
  - Addition of fillers changes damage seen in NBR due to H2 exposure from linear microcracks to pinpoint voids
  - Addition of fillers helps EPDM with respect to H2 resistance – fewer cracks
- Sandia and ORNL have developed rapid cycling test plan for thermoplastic polymers for neutron scattering studies
- Database setup but hydrogen data in polymers is scarce and test methods are inconsistent
- Analysis tool developed to assist in screening materials based on hydrogen material property criteria

Response to previous year's reviewers' comments

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- The project has made significant progress to date: it has developed new test procedures and equipment capabilities and produced new information critical to hydrogen fuel applications
  - *The project is now focusing on material property changes in situ and post exposure to hydrogen to better provide lacking information for stakeholders and to determine the material gaps that need to be addressed for hydrogen infrastructure*
- It is not clear how PNNL and SNL are collaborating on the project. It does not seem that the two laboratories are working on overlapping themes. Collaborative work between ORNL and SNL or PNNL and SNL was not explained during the presentation.
  - *Our collaboration may not have been clearly explained in slide 7. We are highly collaborative in discussion of results and ideas.*
- The collaborations to date are appropriate. The project should consider how to supply this information to the stakeholders. Dr. Shin Nishimura of Kyushu University is doing similar research. Collaboration with Kyushu might be appropriate
  - *We have increased our collaboration with Kyushu University and we are sharing research results and test methodologies*
- The project should focus on characterization of polymers, not screening of polymers as acceptable or unacceptable for use. The key point is understanding hydrogen impact.
  - *We have put more focus into understanding the hydrogen and pressure impacts with the development of EPDM and NBR model compounds with various additives for hydrogen effects*

Collaborative Activities

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Partner		Project Roles
	DOE	Sponsorship, Steering
Pacific Northwest NATIONAL LABORATORY	PNNL	Project Lead, Polymer Characterization, Wear and Tribological Studies, Mechanical Properties and Moderate Pressure
Sandia National Laboratories	SNL	Exposure Pressure Cycling Studies, Mechanical Properties and High Pressure, Develop Technical Reference Documentation and Database
OAK RIDGE National Laboratory	ORNL	Neutron and X-ray Scattering Studies
Ford	Ford	Subcontracted Participant and Consultant, Represent OEM Perspective

Additionally, the team has reached out to over 40 industrial stakeholders for information and had discussions with over 25, including Linde and Parker, and Swagelok Application space includes compressors, valves, refueling stations, seals, liners, and academia.

Remaining Challenges and Barriers

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Challenges and Barriers	Mitigation
Large amount of polymers and elastomers to test	Test methodology developments are material focused from stakeholders
In situ temperature testing (-40 to 85°C)	Redesign of sample cooling to better control and evaluate temperature effect
Testing time is long	When appropriate double up on sample soaking
Dissemination of data is a broad audience	Engagement with stakeholders in working group with CSA, presentation, implementation of h2tools.org with database and guide
Cannot see impact of hydrogen during long term cycling or frictional wear in a short test (Impact may not exist)	Target and test materials that are believed most likely to be impacted prior to evaluating other candidates
Working with high pressure H2	National lab experience working with high pressure hydrogen

Technology Transfer and Outreach

- Stakeholder Engagement
  - Continued outreach internationally with trip to Japan Hydrogenius conference added Japanese stakeholders
  - Continue to present and publish results
  - Webpage on h2tools.org
- Code and Standards Committees
  - Leadership on CSA's new committee on CHMC II Non-Metallics
  - CSA Committee and collaborative interactions with working groups of industry stakeholders
- Industrial Collaborators
  - Maintain dialog with Collaborators to discuss pathways for qualification and technology transfer
  - Automotive and refueling station stakeholders

Contacts

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Mike Veenstra	☎: 313-322-3148	🖂: mveenstr@ford.com

Technical Backup Slides

Approach
Strategy for Polymer Compatibility with Hydrogen

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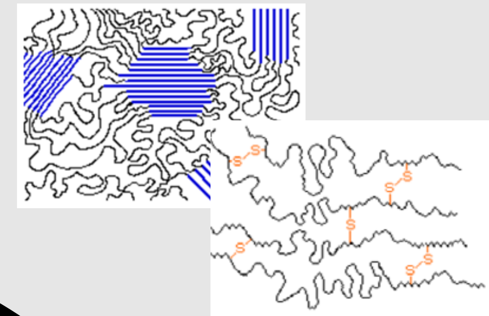
- Polymer microstructure
- Hydrostatic pressure effects
- Plasticization of polymers
- Permeation, diffusion and solubility effects
- Explosive decompression

Polymers

Material selection

(Elastomers, epoxies and thermoplastics)

New materials for hydrogen service



Elucidation of hydrogen effects

Establish material limits enabling new materials development

Database development

Test methods development

Compatibility of Polymers in Hydrogen Environments

Test Environments

Low/high temperatures

Low/high pressures

De-pressurization rates

Rapid cycling (P, T, time)

Long-term aging in H_2

Tribology

Outgassing from polymers

Gas mixtures

Characterization

Density, Weight and Specific volume changes (swelling)

Wear property changes

Hardness (elastomers)

Microscopy (optical & CT)

Compression set (elastomers only)

Mechanical property changes

Thermal desorption spectroscopy

- Collaboration with SDOs (CSA, ASTM, ASME etc.)
- Existing test methods adapted for hydrogen
- Dissemination of test methods

Test Methodology Development

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- PNNL has developed a new test methodology for *in situ* hydrogen measurement of friction and wear of polymers (tribology)
  - Infrastructure applications include:
    - Dynamic seals for compressors, valves (O-rings and seats), regulators
    - Delivery hose liners where frictional contact can occur
  - Failure mechanisms are:
    - Increased leak rates
    - Reduced mechanical efficiency
    - Reduced part lifetime due to part degradation
- Instrument Specifications*
  - Linear reciprocating instrument capable of up to 5,000 psi in situ hydrogen
  - Measures in situ frictional load and wear depth profile
- Tests to date:
  - Model Materials that have been tested or are in process include:
    - NBR (nitrile butadiene rubber or Buna-N) – completed 4,000 psi hydrogen, 4,000 psi argon, ambient air.
    - EPDM (ethylene propylene diene monomer) – In progress 4,000 psi hydrogen, ambient air, 4,000 psi argon completed
  - NBR, EPDM materials are undergoing NMR studies and are expected to be complete by end of summer 2018
- Upgrade planned late 2018 to include in situ heating and cooling
    - Targeted range -40 to +85 C
    - New low temperature autoclave
    - Design complete and fabrication is in progress

Micro-CT images for NBR after H2 exposure

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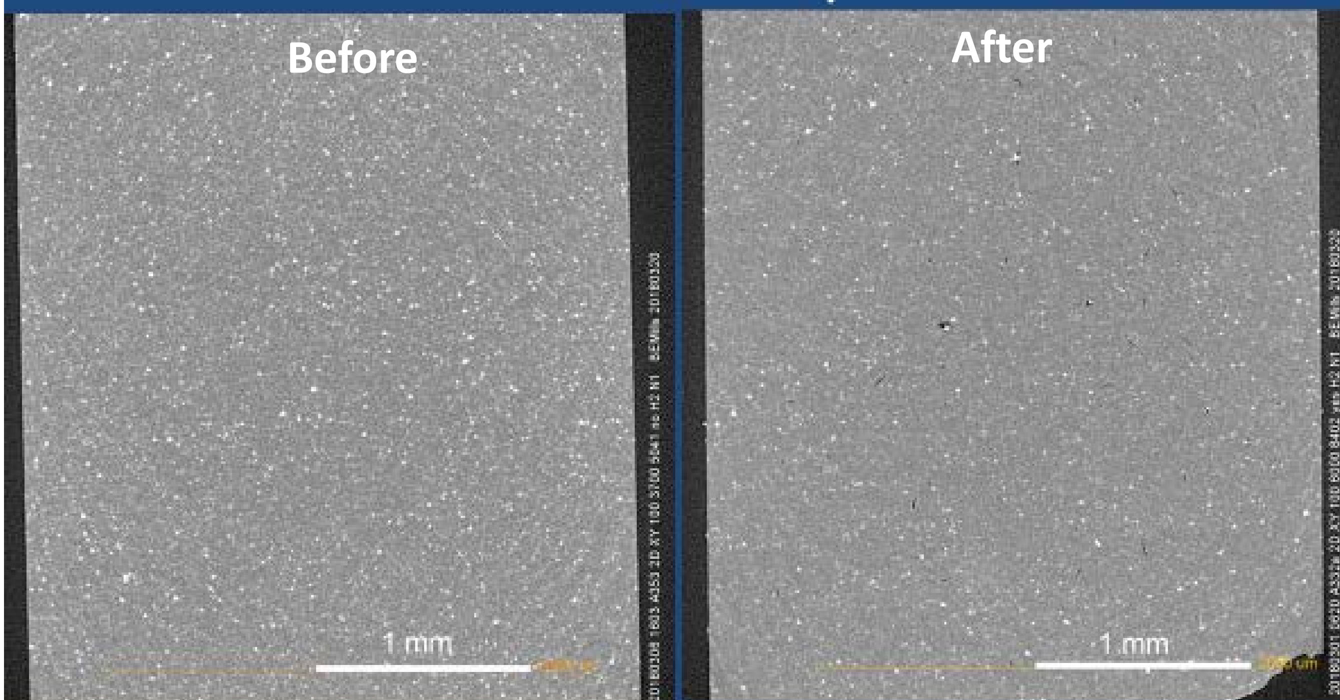
H2 exposure of NBR N1 shows fewer and smaller slit-shaped voids.



There is no preferred orientation. There are perhaps a few more voids in the interior—need to confirm.

Comparison of EPDM and NBR before and after hydrogen exposure BEMills 20180320

- Formulation NBR N1 has no filler or plasticizer
- Both formulations contain high Z particles (5% by wt. ZnO)

Microcracks in left picture changed to more pin-point voids in right picture which are not aligned in any particular direction and seem more or less distributed all over

Microcrack damage is less significant and more pin-point in shape

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Micro-CT images for NBR after H2 exposure

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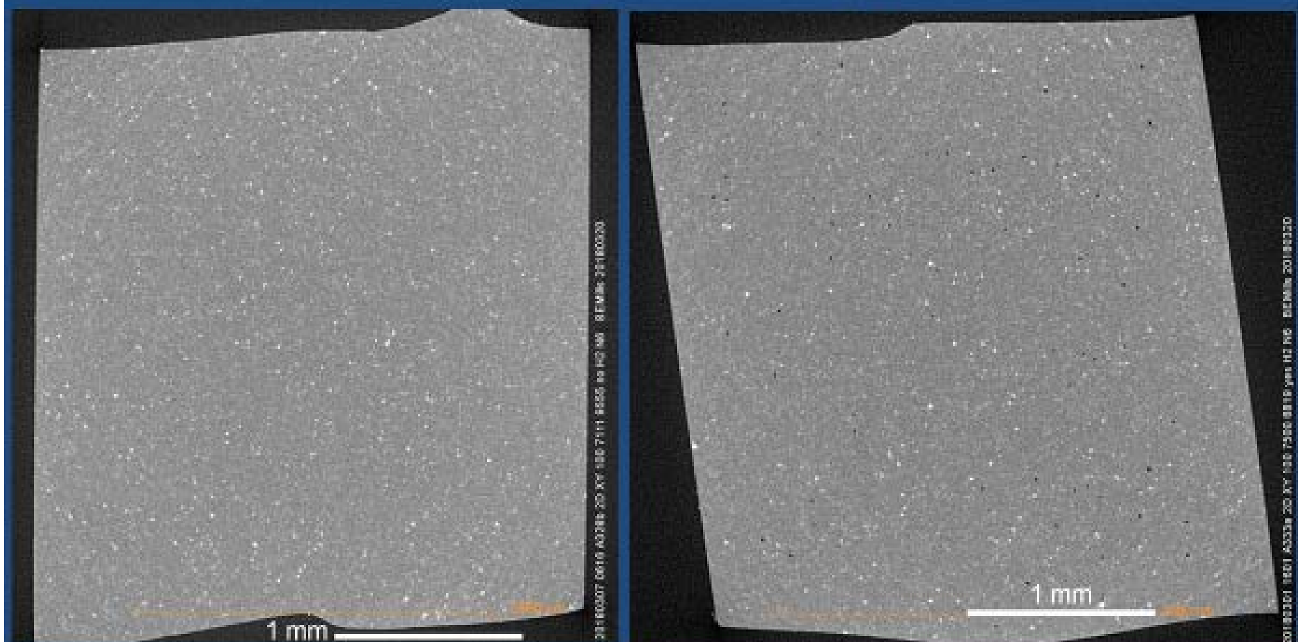
H2 exposure of NBR N6 shows large numbers of small isotropic voids.



There is no preferred position within the sample.

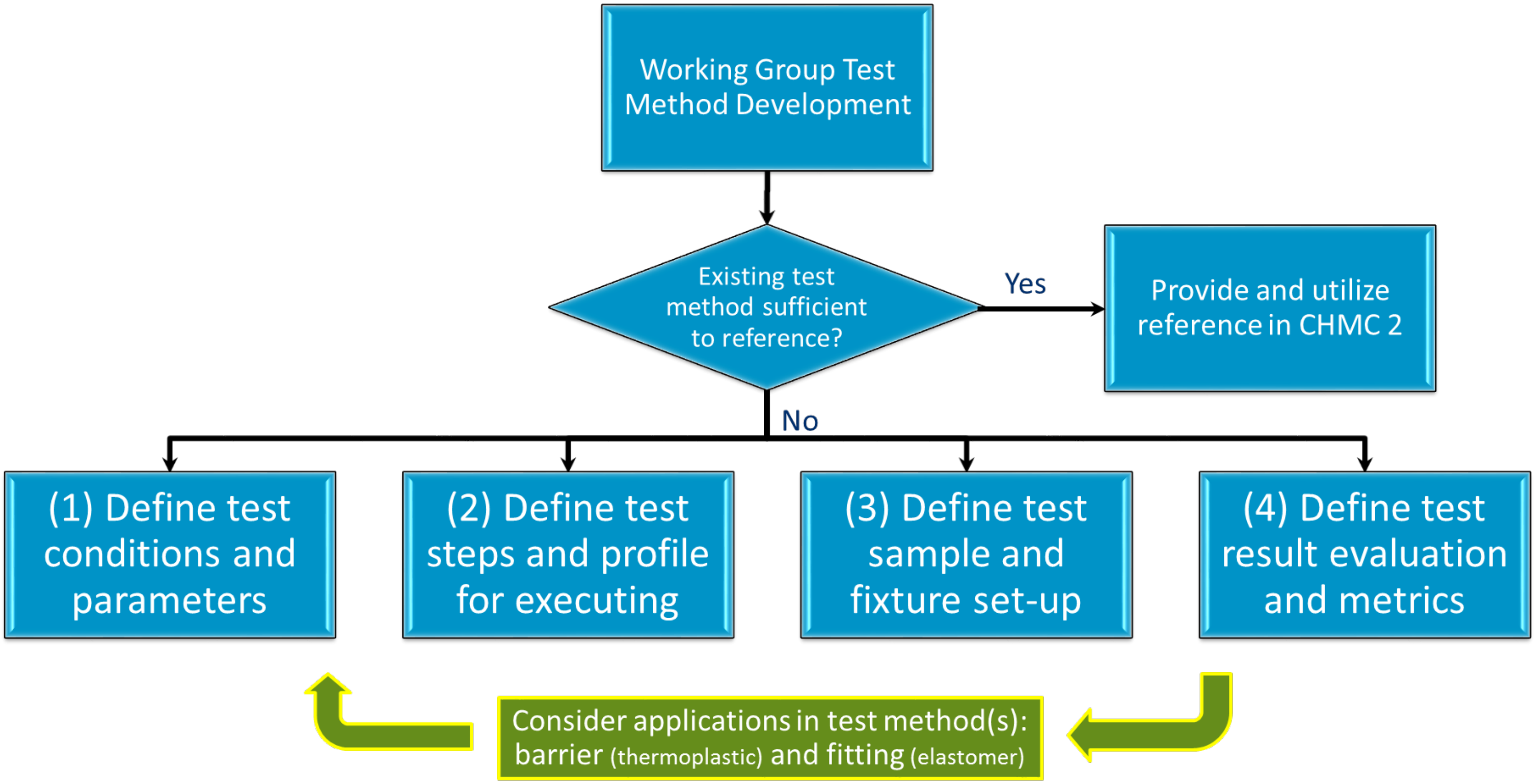
Comparison of EPDM and NBR before and after hydrogen exposure BEMills 20180320

- Fillers in EPDM E6 are: carbon black (300 nm) and Silica
- Both formulations contain high Z particles (5% by wt. ZnO)

Sandia National Laboratories

Fillers appear to change the nature of cracks/voids in NBR after H2 exposure

CHMC 2 – High Priority Tests



Demonstration of Filtering Data and Criteria Weighting

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Logical Filters

Logical filters can be used to reduce the Data Set prior to analysis

H2 Permeability (Barrer) is Less than 3

Add Filter | Clear Filters

Red areas are excluded from the analysis

Data Set for Analysis

The following Data Set will be used for the analysis with the parameters defined above. Click the checkboxes to further downselect alternatives before executing the analysis.

Show Excluded Criteria

	100% Tensile Modulus (MPa)	Failure Elogation (%)	Hardness (Shore)	Tg (°C)	Temperature (°C)	Pressure (kPa)	H2 Permeability (Barrer)
Teflon AF 2400	1500	7.9	75	240	77	1013	28
Technoflon P 457	5.9	239	23	-15	77	1013	0.39
Teflon PTFE 850A	496	300	50	117	-16	1724	22.6
Neoflon DF-0050C1	74000	279	85	100	25	6895	0.74
Elastollan C80A	41.4	3000	85	-40	20	100	6
NBR (27% CN)	2.6	250	60	-2	25	100	16
Polybutadiene	1.5	500	15	-100	25	100	41.9

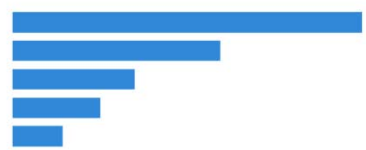
Criteria Weighting

Drag and drop criteria to rank them from best to worst. Criteria can also be excluded from the analysis.

All Items

Ranking Order Centroid

- H2 Permeability (Barrer)
- Failure Elogation (%)
- 100% Tensile Modulus (MPa)
- Hardness (Shore)
- Tg (°C)



H2 Permeability (Barrer)	0.46
Failure Elogation (%)	0.26
100% Tensile Modulus (MPa)	0.15
Hardness (Shore)	0.09
Tg (°C)	0.04

Filters used to define areas of interests and specific weighting of importance

Analysis Outcome

	Group Weight	Criterion	Rank	Criterion Weight	Overall Weight
Transport Properties (Permeability)	0.333	Permeability (mol H2/m.s.MPa)	N/A	0.7	0.233
		Diffusivity (cm2/s)	N/A	0.300	0.100
Physical Properties (Density, 100 % Tensile Modulus)	0.333	100% Tensile Modulus (MPa)	N/A	0.500	0.167
		Density (g/cc)	N/A	0.500	0.167
Thermodynamic State (Temperature, Pressure)	0.333	Temperature (K)	N/A	1.000	0.333