Compatibility of Polymeric Materials Used in the Hydrogen Infrastructure

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PNNL-SA-117520

Overview

Timeline

- Project Start Date: October 2015
- Project End Date: September 2018
- % Completed:14%

Budget

- Total Project Budget: $1800K
  - Total Funds Spent (as of 3/31/16)
    - $82K (PNNL)
    - $129K (SNL)
    - $17K (ORNL)

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

- SNL
- ORNL
- Ford Motor Company

Relevance and Objectives

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Project Objective

- Provide scientific and technical basis to enable full deployment of H_2 and fuel cell technologies by filling the critical knowledge gap for polymer performance in H_2 environments.

Barrier	Project Goal for this Year
Barrier J: Limited Participation of Business	Gather and assess stakeholder input for their challenges and materials and conditions of interest for H_2 compatibility.
Barrier G: Insufficient Technical Data	Develop three standard test protocols for evaluating polymer compatibility with high pressure H_2: (1) cycling tests, (2) in-situ tribology tests, and (3) neutron scattering.
A. Safety Data and Information: Limited Access and Availability	Develop an approach to disseminate test protocols and compatibility information to SDOs and support the deployment of H_2 infrastructure.

Overall Technical Approach: Reporting Period

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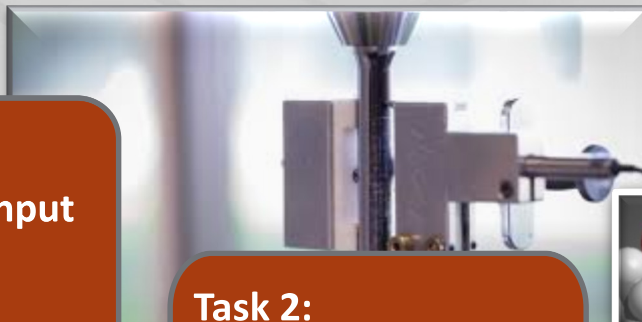
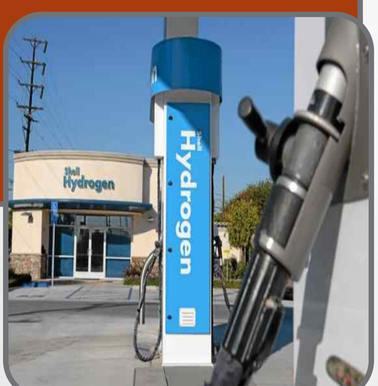


Task 1:

Stakeholders' Input

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

(On-Going)

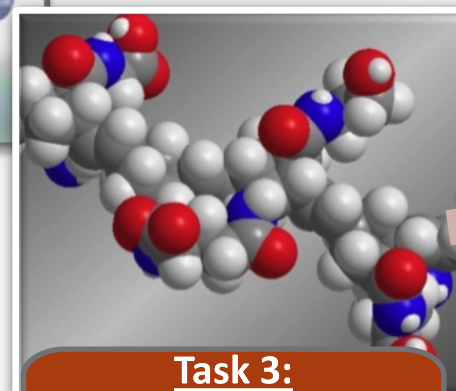


Task 2:

Test Methodology Development

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

(On-Going)



Task 3:

Characterization of Polymers

- Baseline properties before and after exposure to H_2

(Future Work)

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

(Future Work)

Approach
Task: 1 Gather and Assess Stakeholder Input
(Barrier J: Limited Participation of Business)

- Stakeholders (20 participants to date)
  - System Users
    - Automotive, Aerospace, Stationary
  - System Suppliers
    - Tanks, H_2 gas
  - Component Manufacturers
    - Valves, Compressors
  - Seal Producers
    - O-rings, seals, tubes, liners
  - Polymer Manufacturers
  - Consultants
    - CSA, ASME
    - Academia

Task 1:

Stakeholders' Input

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

Task 1: Stakeholder Input

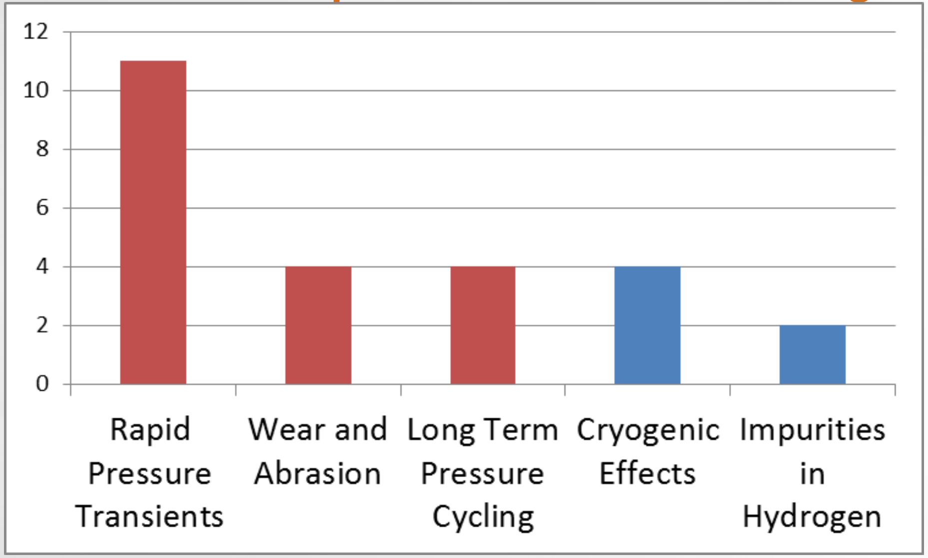
(Barrier J: Limited Participation of Business)

- Questions Asked for Stakeholders
  - Challenges Related to H_2 Compatibility
    - What failure mechanisms or degradation have you observed or are concerned about?
  - Operating Conditions of Interest
    - What operating conditions are you most concerned about for polymers in hydrogen service for your application (e.g. temperature extremes, pressure cycles)?
  - Suggested Polymers
    - What polymers or applications are most needed for hydrogen compatibility of polymers?
  - Availability of Compatibility Information
    - Is the compatibility information in the literature is sufficient to meet your needs?
    - What tests do you use to evaluate hydrogen compatibility?
  - Method of Collecting and Disseminating Information on Polymer Compatibility
    - What is the most valuable method to disseminate hydrogen compatibility for polymers information to your sector?

Task 1: Stakeholder Input

- Challenges Related to H_2 Compatibility
  - Rapid Pressure Transients
    - Explosive decompression, blistering, liner collapse
  - Long Term Pressure Cycling
    - Fatigue, change in mechanical properties
  - Wear and Abrasion changes from H_2 permeation in the material
    - O-ring and valve seat leakage)
  - Dimensional and Mechanical Properties changes
    - O-ring and valve seat leakage)

Number of Respondents for Each Challenge



Some Stakeholder Challenges may be **Unrelated** to H_2 Compatibility

- Temperature effects associated with sub-ambient and cryogenic temperatures
- Impurities in the hydrogen impacting fuel cell use

Task 1: Stakeholder Input

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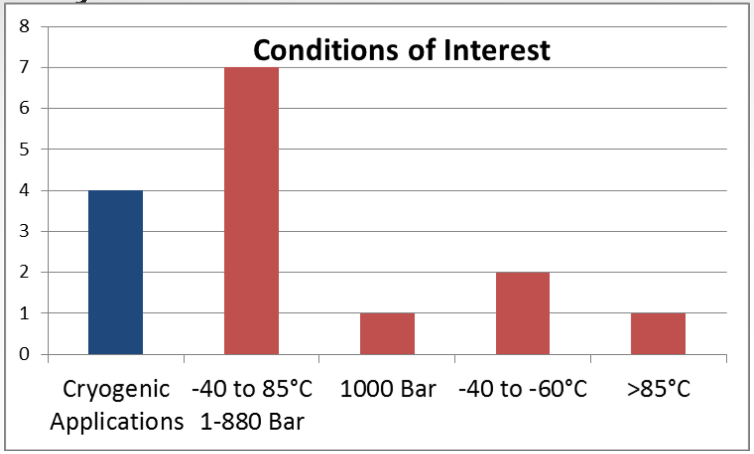
- Take-away messages from stakeholder survey:
  - Wide range of suggested polymers
  - Conditions of Interest:
    - -40 to +85 degrees C
    - 1(atm.) to 880 bar (13,000 psi)
    - Cryogenic applications
  - All agree that more testing is required
  - Continued Discussions with Stakeholders



Number of Respondents for Each Condition

Thermoplastics of Interest:
HDPE, PB-1, PA, PEEK, PP-R/PP-RCT, PEKK, PET, PEI, PVDF, **PTFE**, PCTFE

Elastomers of Interest:
EPDM, **NBR/HNBR**, Viton, **Levapren**

Thermosetting polymers of Interest:
Epoxy, PI, NBR, Polyurethane

Polymers in hydrogen service selected for test methodology development:

Elastomers: Viton A ,NBR

Low Temperature Seal: PTFE

Tank liner Material: HDPE

Hose Material: Delrin (future)

Approach
Task 2: Test Methodology Development
(Barrier G: Insufficient Technical Data)

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- Tests Currently Being Developed:

  a. Pacific Northwest National Laboratory

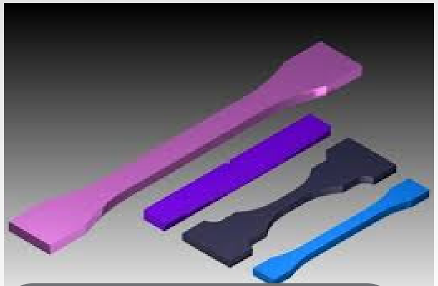
  Wear and tribology studies on polymers in H_2

  b. Sandia National Laboratories

  Characterization studies (baseline)
  High pressure H_2 cycling of polymers

  c. Oak Ridge National Laboratory

  Evaluation of H_2 exposed polymers
  with neutron and X-ray scattering methods



<u>Task 2:</u>

Test Methodology Development

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

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Task 2a: Test Methodology Development: Tribology

- PNNL is developing test methodologies for in-situ high pressure hydrogen tribology
  - Application is valves and seals for infrastructure applications
  - Damage and failure mechanisms are increased wear and leakage
- Current status – Tribometer is functional and active
  - Sample is reciprocating pin configuration
  - In-situ testing with pure H_2 up to 4,000 psi done; 5,000 psi capable,
  - Current system designed for room temperature – future upgrades may include sample heating or cooling
  - Current measurement is frictional load
- Upgrade planned May 2016
  - Planned upgrade to machine will add vertical LVDT to measure wear track depth in-situ
  - Requires modification of the tribometer and the autoclave

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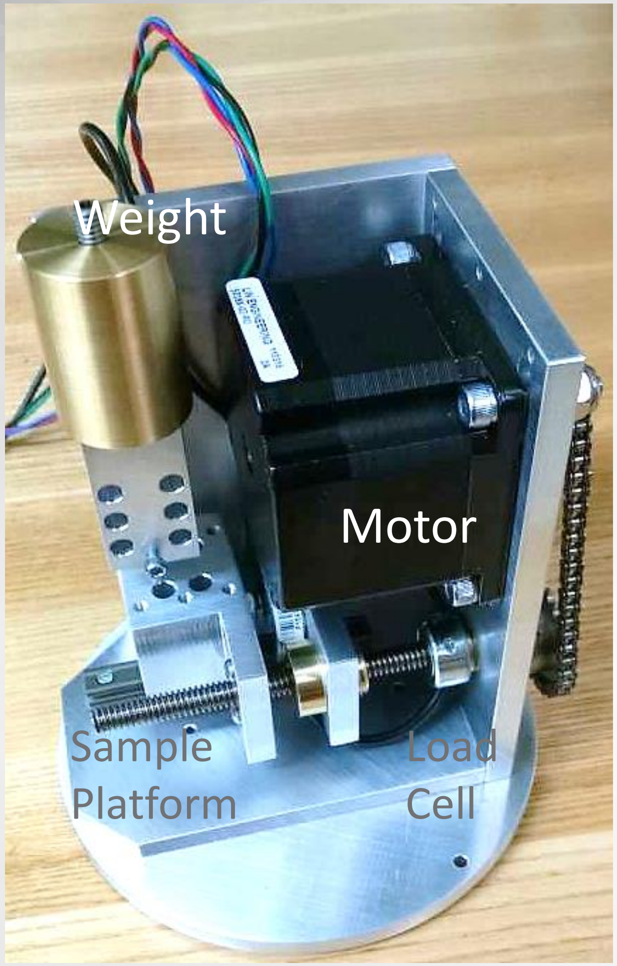
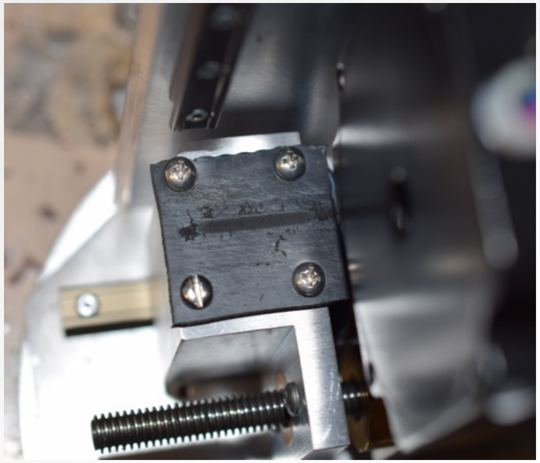
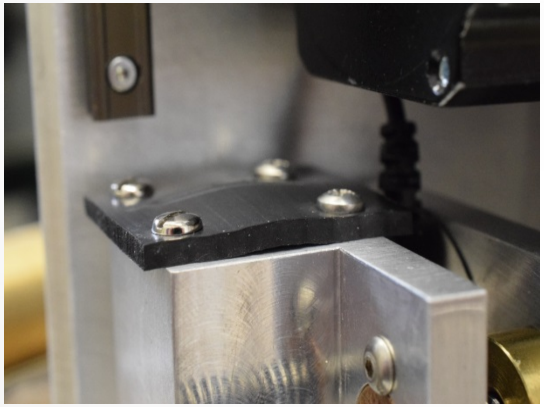
Task 2a: Test Methodology Development: Tribology

In-situ H_2 Tribometer

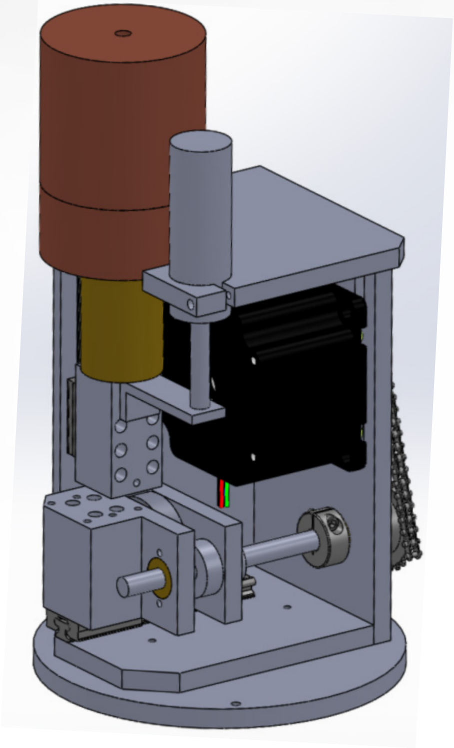


Viton sample with wear track after hydrogen





Planned upgrade with vertical LVDT for in-situ wear track measurement



Task 2a: Test Methodology Development: Tribology

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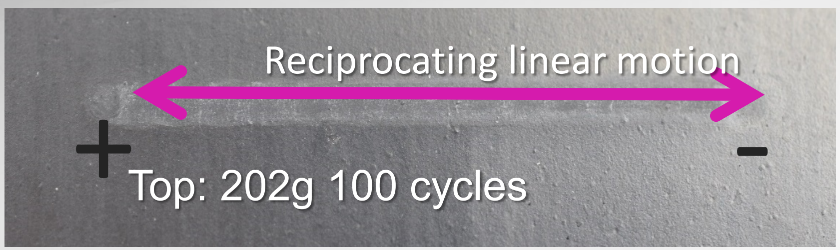
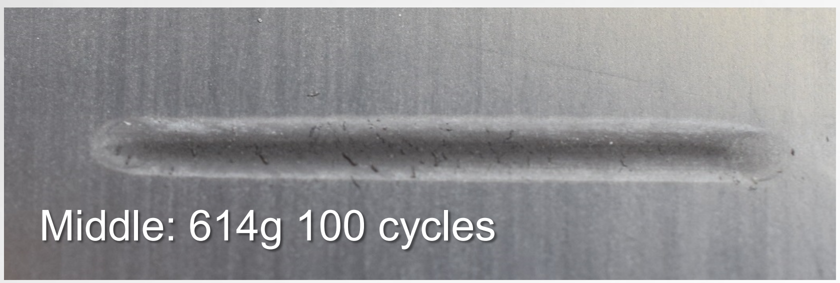
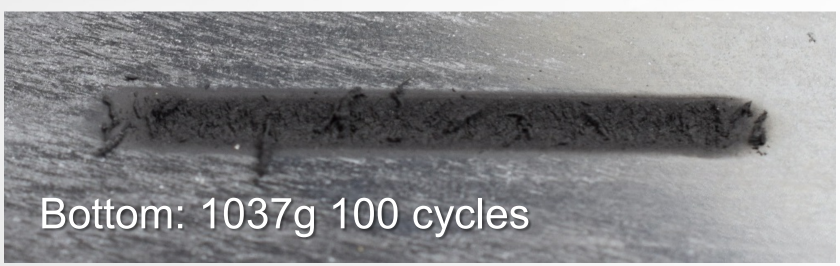
Capability to adjust the weight of the Tribometer

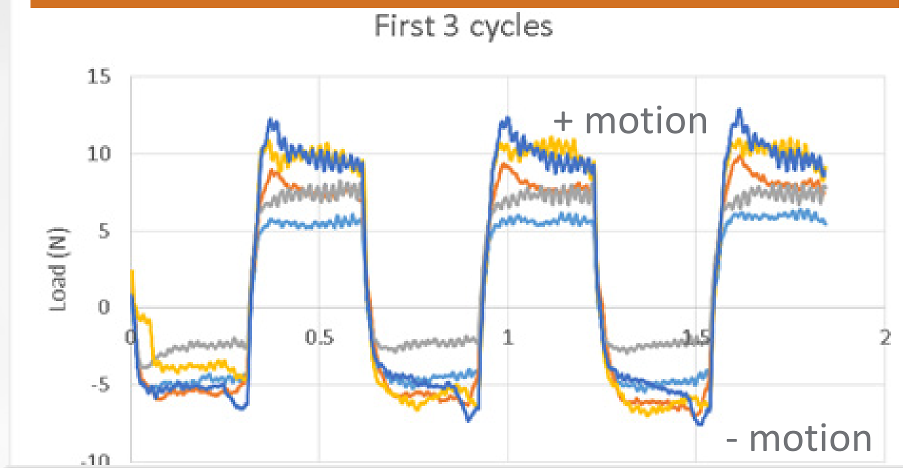


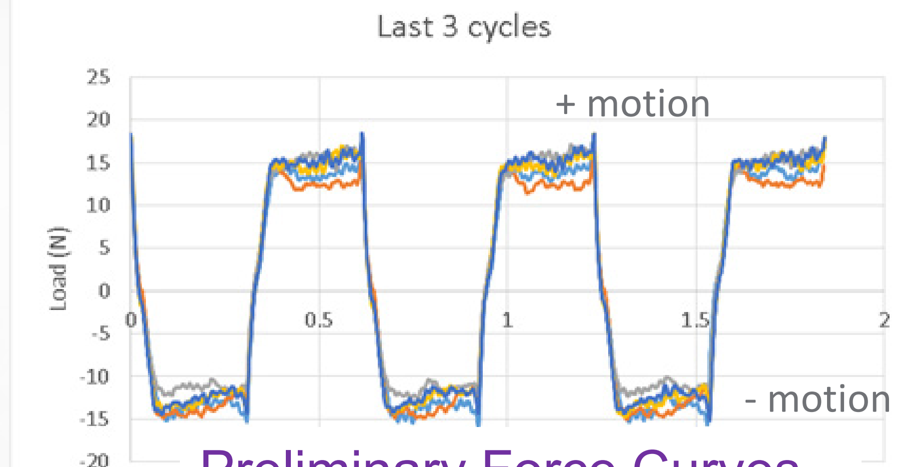




Wear Tracks in Viton in H_2 Autoclave

Initial variation in load response much higher than after 100 cycles





Preliminary Force Curves

Accomplishments

Task 2a: Test Methodology Development: Tribology

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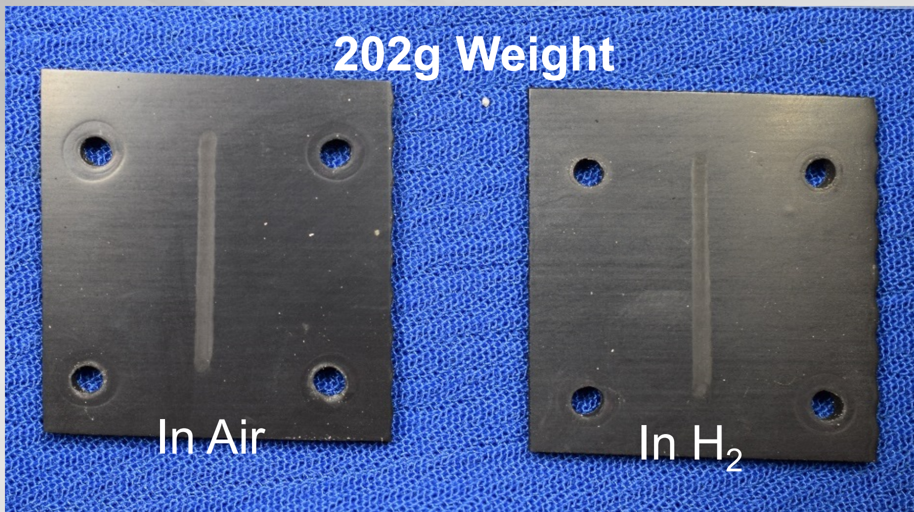
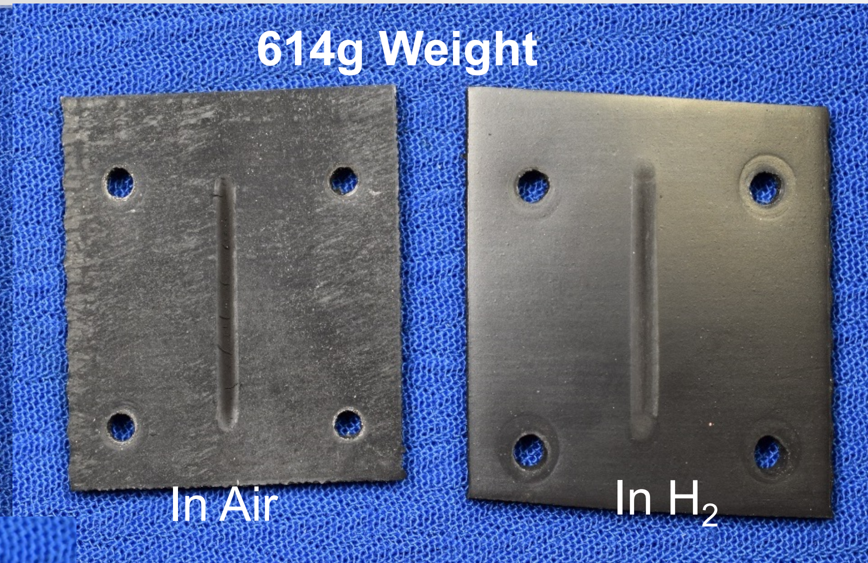
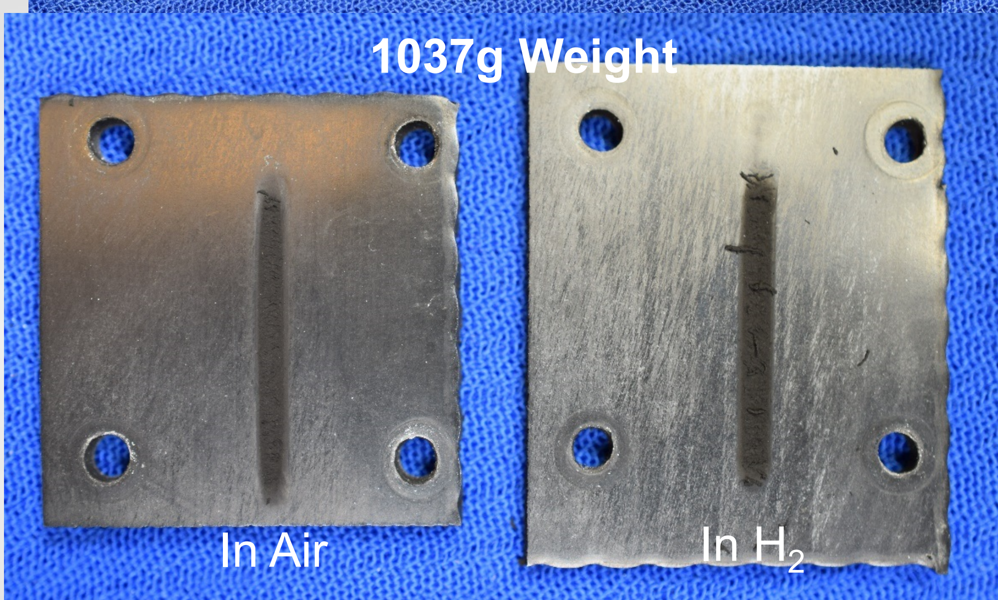
Wear Track Comparison Between Air and Hydrogen for Various Weights







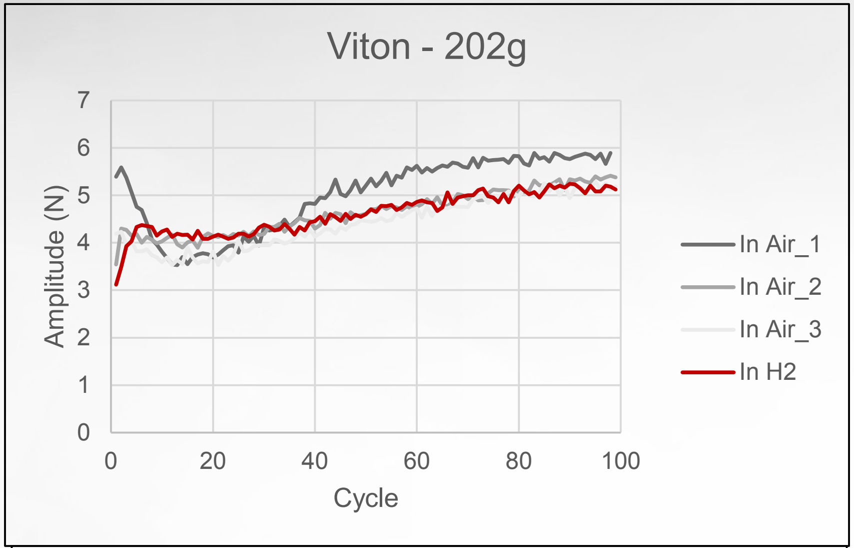
Preliminary Data Results:

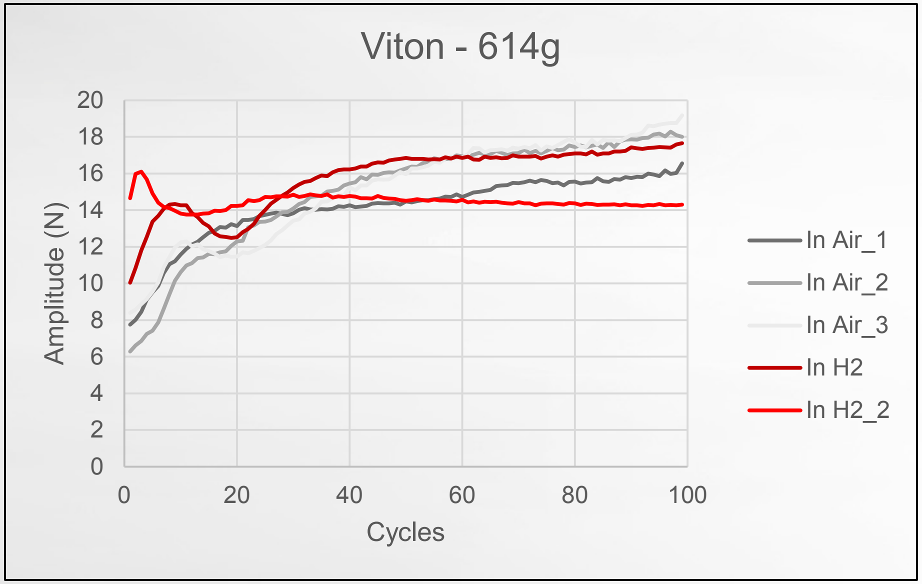
No obvious difference at low weights, damage more prominent in H_2 at higher weights

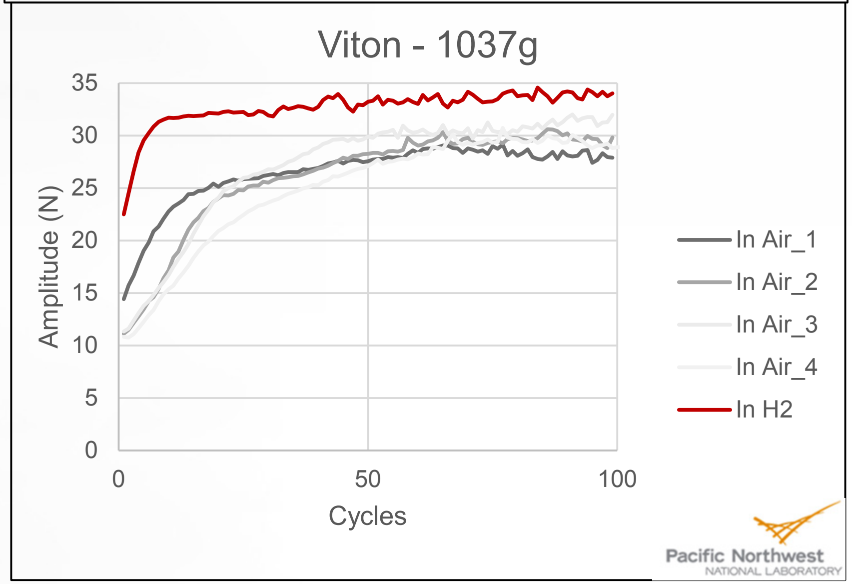
Task 2a: Test Methodology Development: Tribology

Viton Frictional Load Comparison: Weights vs. Number of Cycles

Preliminary Results:
We are still trying to understand the correct operational parameters needed for best results. (weight, pin size, etc.)







Task 2b: Test Methodology Development: High Pressure Hydrogen Exposure

Preliminary experiment to investigate testing parameters of a high pressure hydrogen system for Polymers

- Four polymers selected based on components in hydrogen infrastructure - **NBR** , **Viton A** (seals, gaskets, O-rings), **HDPE** (tank liners), and **PTFE** (seals, gaskets, O-rings)
- Molded specimens (O-rings, gaskets) vs sheets; off-the-shelf grades
- Static isobaric (100 Mpa), and isothermal (25ºC) conditions of exposure
- Time of exposure: 1 week for saturation of 3 mm thick specimens of all polymer types (calculated based on DIFFUSE*)
- Characterization tests performed: DMTA, Compression set (elastomers only), Polymer volume change, TGA/DSC, tensile strength (thermoplastics only), Micro CT analysis before and after exposure

* Sandia National Laboratories Code, M.I. Baskes, DIFFUSE 83, SAND83-8231, 1983)

Task 2b: Test Methodology Development: High Pressure Hydrogen Exposure

Sandia National Laboratories

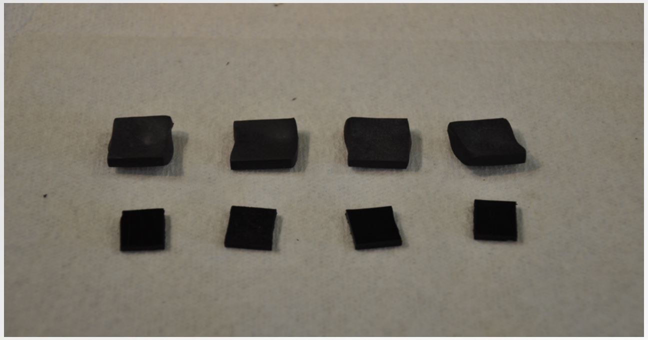
General trends observed:

- Polymer structure-property relationships explain trends in hydrogen environments
- As expected, Viton A and Buna N (elastomers) showed greater H_2 effects than HDPE and PTFE (thermoplastics) within the scope of the experiment
- With hydrogen exposure, elastomers exhibited
  - a decrease in storage modulus
  - significant change in densities with recovery afterwards (swelling)
  - increased compression set (Viton A)
- Thermoplastics did not exhibit significant changes with hydrogen, except for mechanical properties
  - Young's Modulus 35% higher for PTFE and 15% higher for HDPE
  - HDPE exhibited cold-drawing (plastic deformation); PTFE failed in the elastic region

Task 2b: Test Methodology Development: High Pressure Hydrogen Exposure

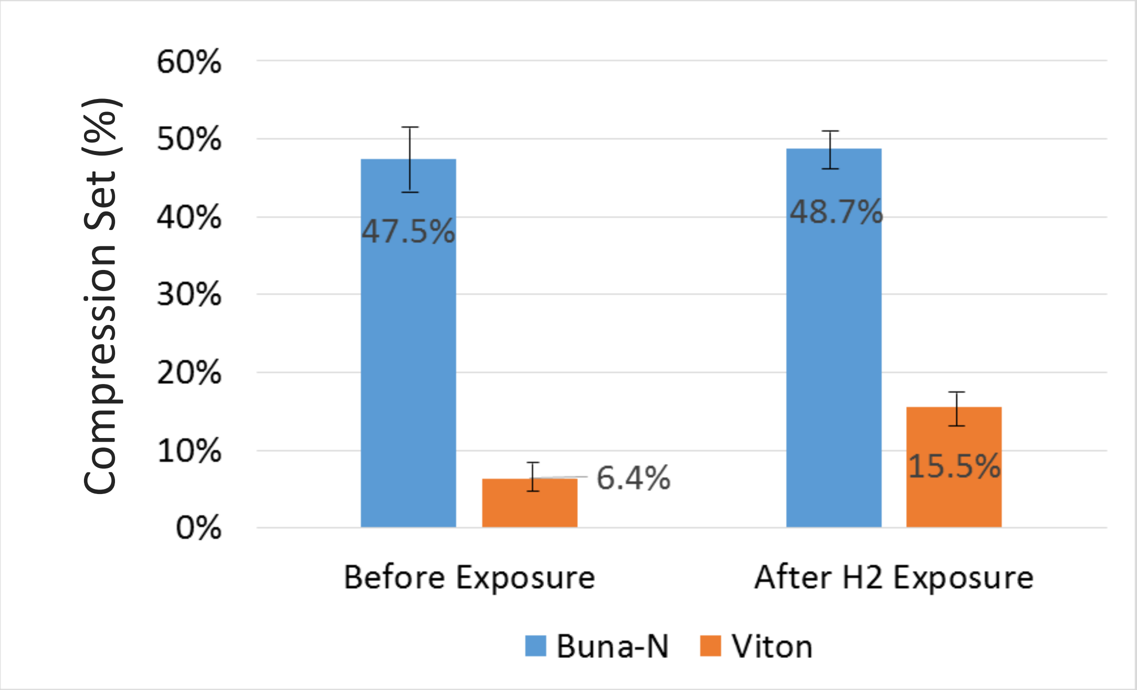
ELASTOMERS IN HYDROGEN

Viton A and Buna N swelling evident from comparing before hydrogen (bottom row) and after hydrogen exposure (top row)



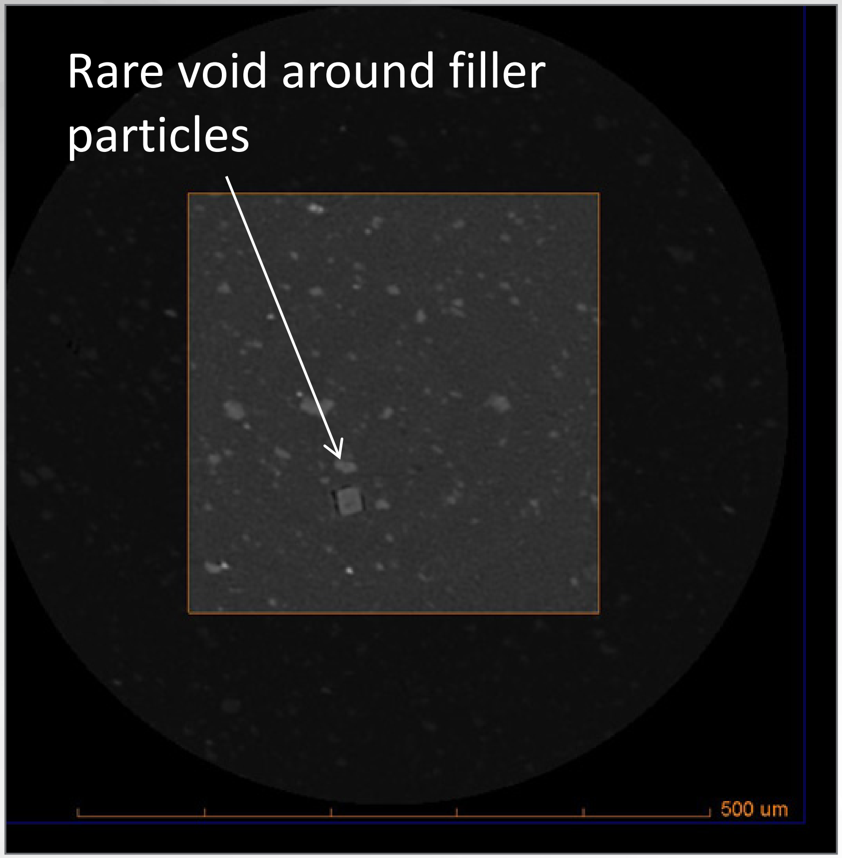
Polymer	% Volume Change/gram upon Hydrogen Exposure	
	Immediately	48 hours
Buna N	57.2%	3.9%
Viton A	69.0%	11.5%

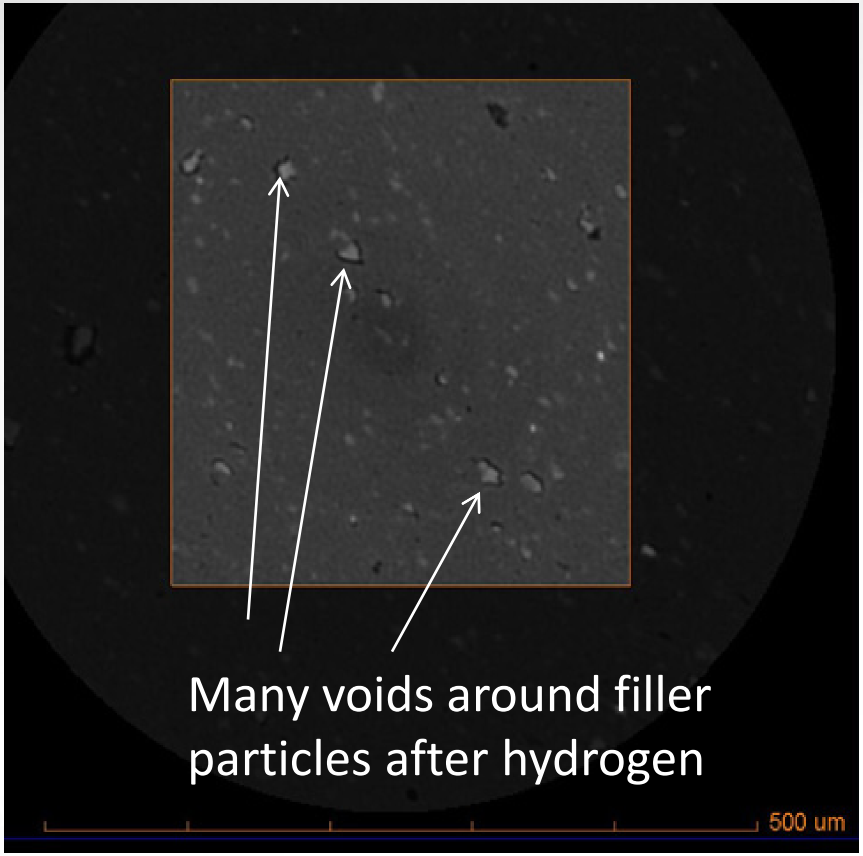
Compression Set: Different responses to hydrogen for Viton A and Buna N



(1/8" thick sheets, Round 1 H_2 exposure removed after 7 days, compression set measured on 3 specimens under 75% compression at 110°C for 21 hours, recover 38 min)

Task 2b: Test Methodology Development: High Pressure Hydrogen Exposure

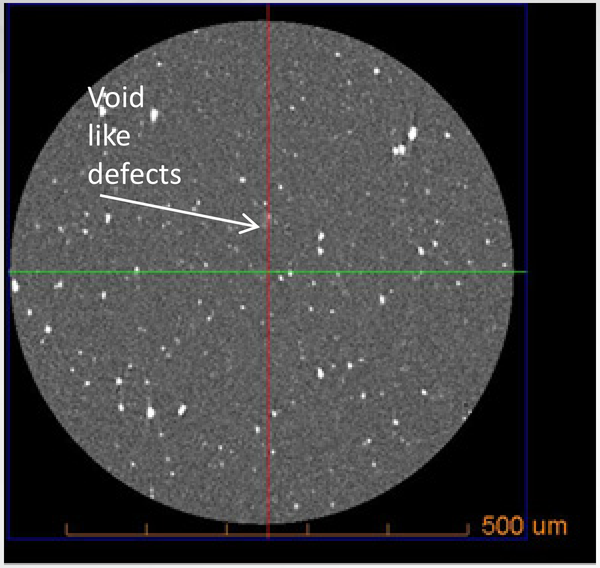


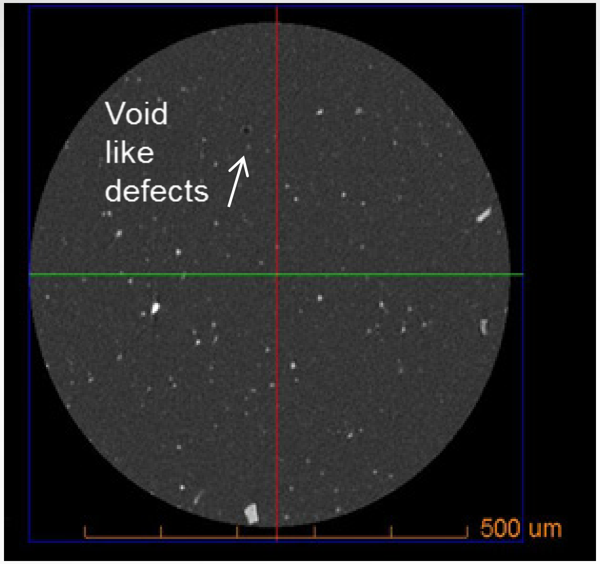


Micro-CT of Viton A before and after hydrogen: Voids seen around filler particles

Accomplishments

Task 2b: Test Methodology Development: High Pressure Hydrogen Exposure





Micro CT of Buna N before and after Hydrogen exposure

No void encapsulation of filler particles, no new defects after hydrogen in Buna N

Accomplishments

Task 2b: Test Methodology Development: High Pressure Hydrogen Exposure

THERMOPLASTICS IN HYDROGEN

Thermoplastics are less impacted by high pressure H_2 soak than elastomers: little impact on Yield Stress and Strength, Swelling, and DMTA properties. Young's Modulus is increased.

DMTA Results for Thermoplastics

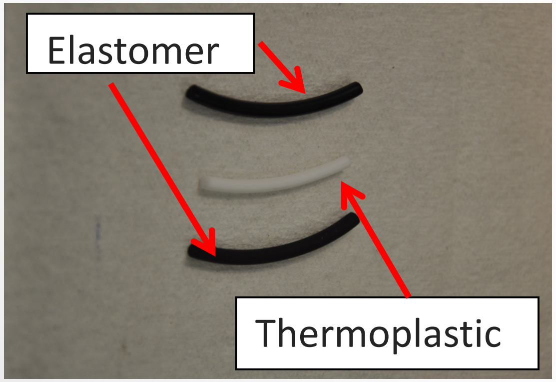
	Before Hydrogen exposure		After Hydrogen exposure	
Polymer properties	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)
HDPE	-110	848±7	-111	913±25
PTFE	34, 137*	431±12	36, 137*	441±14

* PTFE shows two T_gs because of possible separation of components

PTFE Stress Strain Results

Sample	Young's Modulus MPa	Yield Stress MPa	Strength MPa
Ave. No H_2 Soak	**493**	**8.8**	**24.4**
Ave. With H_2 Soak	**667**	**9.1**	**25.4**

Degree of Swelling for Thermoplastics as Compared to Elastomers



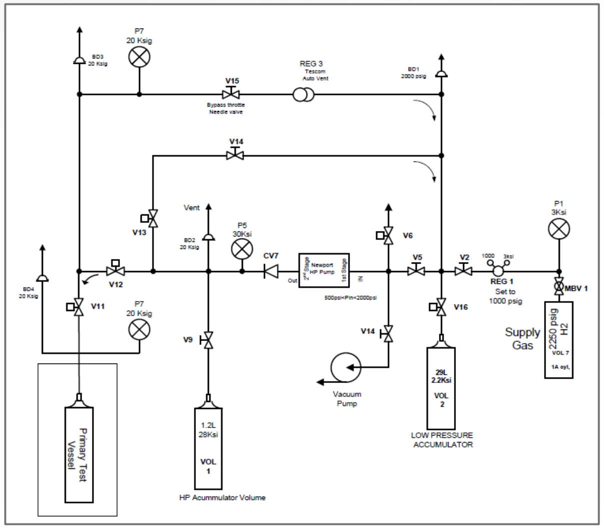
HDPE Stress Strain Results

Sample	Young's Modulus MPa	Yield Stress MPa	Strength MPa
Ave. No H_2 Soak	**863**	**20.3**	**24.0**
Ave. With H_2 Soak	**990**	**22.3**	**25.8**

Task 2b: Test Methodology Development: High Pressure Hydrogen Exposure

▶ **Deliverables (present-end of FY 16)**

- Basic design of a high pressure manifold is ready and necessary steps to build are in progress at SNL's Hydrogen Materials Laboratory



- Based on stakeholder meetings:
  - Finalize "most desirable" polymer selection
  - Identify potential suppliers, different grades
  - Selection of test parameters mimicking actual operating conditions

▶ **Proposed additions for FY 17**

- Addition of a environmental test chamber to pressure manifold capable of operating between -40ºC and 100ºC to study pressure and temperature effects in hydrogen

Task 2c: Test Methodology Development: Neutron and X Ray Scattering

- Objective
  - Use neutron and x-ray scattering to investigate molecular dynamics of hydrogen solvated polymers and additive-modified polymer composites
  - Understand effect of temperature and high-pressure H_2 at the interface of crystalline and amorphous regions within semi-crystalline polymers, at the interface of solvated hydrogen and the polymer matrix, and the loaded additive and the matrix
  - Identify microscopic properties critical to polymer performance, and predict failure modes

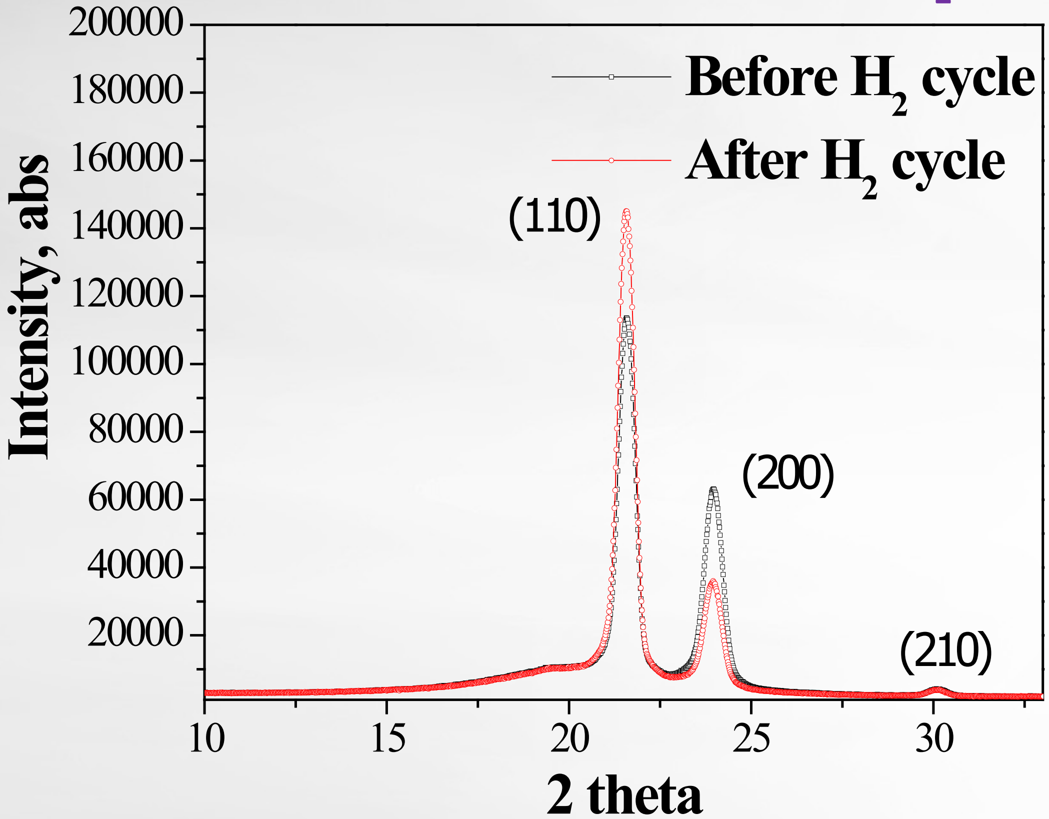
Task 2c: Test Methodology Development: Neutron and X Ray Scattering

- Ex situ (U)SANS provides information about final pore structure **after** sample treatment
- In situ (U)SANS provides **real-time** information during solvation, compression, swelling and depressurization processes
  - Determines pore-size distribution in a polymer structure
- Use *in situ* neutron reflectometry (NR) provides **real-time** information during solvation, compression, swelling and depressurization processes
  - Determines pore-size distribution along the vertical direction of a polymer film
  - Discover morphology of the polymer crystal and amorphous regions
  - Determine local solvation of the polymer matrix
  - Examine effect of high-pressure hydrogen on interface between the loaded additive and the matrix

Task 2c: Test Methodology Development: Neutron and X Ray Scattering

- Sandia National Laboratories has provided high pressure-cycled polymers samples for scattering studies
  - Selected thermoplastics (PTFE, HDPE) and elastomers (FKM, NBR)

WAXD Patterns of HDPE Before and After H_2 Cycle



- Different intensity ratios of orthorhombic (110) and (200) HDPE diffraction peaks suggest that applied high pressure H_2 induced lamellar rotation along the in-plane direction.
- No martensitic deformation peak (monoclinic peak) was observed implying that no crystal deformation. Only crystal rotation.

Approach
Task 3: Characterization of Polymers

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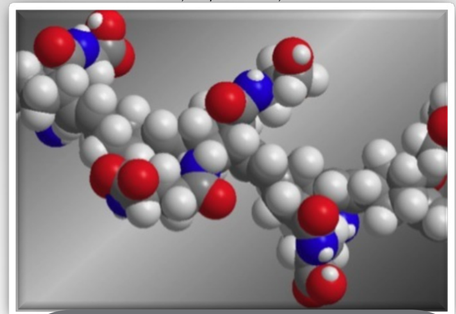
- Characterize polymers selected based on stakeholder input and preliminary test methodology development
  - Large variations in materials properties for a given polymer purchased from different suppliers
  - Establish baseline performance of select polymers in H_2 environment
  - Understand the impact of thermal history, processing aids, additives such as fillers etc. of polymers on H_2 compatibility



Task 3:

Characterization of Polymers

- Baseline properties before and after exposure to H_2

Thermal Techniques		Spectroscopy Techniques		Rheological Techniques	
Technique	**Purpose**	**Technique**	**Purpose**	**Technique**	**Purpose**
DSC	Glass transition (Tg), melt temperature (Tm), percent crystallinity, aging, hardness, mechanical properties	FT-IR	chemical structure, molecular characterization, degree of crystallinity	Rotary vane	filler loading and cure kinetics
DTA		Raman		Cone and Plate	
TMA		UV/VIS/NIR		Parallel Plate	
DMA		XRD		Twin Screw	
Dilatometry					

Collaborative Activities

Partner		Project Roles
	DOE	Sponsorship, steering
	PNNL	Project Lead, Polymer Characterization, Wear and Tribological Studies, Mechanical Properties and Moderate Pressure
	SNL	Exposure Pressure Cycling studies, Mechanical Properties and High Pressure, Develop Technical Reference Documentation and Database
	ORNL	Neutron and x-ray scattering studies
	Ford	Subcontracted Participant and Consultant, Represent OEM Perspective
Air Liquide Parker		Stakeholder Participant and Consultant

Remaining Challenges and Barriers

- Large gaps exist in knowledge base for performance and degradation of polymers in hydrogen environments
- A wide range of polymeric materials for components, operating conditions and applications exist in the hydrogen infrastructure
- Large variations in material properties of a single polymeric material from suppliers is common
- Standardized tests to identify polymer compatibility have not been developed
- There is a tremendous need to develop methods for the dissemination of information on the hydrogen compatibility of polymers and standardized tests developed on this program to stakeholders and SDOs

Proposed Future Work

- Remainder of FY16
  - Develop test procedure and conditions for tribological tests and high pressure cycling tests
    - Gather preliminary information about scoping study materials
  - Evaluate hydrogen surface affects using neutron scattering and XRD
    - Publication of comparative porosity data on SNL/PNNL polymer specimens using SAXS,WAXS and ex situ small angle neutron scattering data
  - Identify and characterize 3-5 materials to be used in future tests
    - Use results of stakeholder evaluation and preliminary tests to identify materials
    - Characterize baseline initial polymers for molecular weight, Tg, Tm, degree of crystallinity, thermal history
  - Develop the framework for an initial database of compatibility results
    - Approach may be similar to that done for metallic materials compatibility
- Next Year (FY17)
  - Refine test procedure and conditions for characterized materials
    - Produce statistically meaningful results that can be compiled in database
  - Expand the range of temperatures, pressures or cycling rates

Project Summary

Relevance	Information will fill critical knowledge gap for polymer performance in H_2 environments by developing standard test protocols for key applications and disseminating both the test methods and results to the H_2 infrastructure stakeholders.
Approach	• Obtain input from H_2 infrastructure stakeholders • Characterize the materials to be tested • Develop appropriate test protocols • Provide dissemination tools to share results
Technical Accomplishments and Progress	• Gathered information from Stakeholders on materials and conditions of interest • Preliminary results of tribology and high pressure soak testing demonstrate impact of hydrogen • Preparing for pressure cycling and neutron scattering tests
Collaborations	• PNNL/SNL/ORNL/Ford Team with Stakeholder Input
Proposed Future Research	• Continue to refine and develop of test methods • Expand temperature, pressure and cycling range • Develop approach to disseminating information collected

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Questions?

Response to previous year's reviewers' comments

- This project was not reviewed last year.

Technology Transfer Activities

- Stakeholders
  - Maintain contact with survey participants
  - Present and publish results
- Code and Standards Committees
  - Share approach to information dissemination with Committee members
- Industrial Collaborators (e.g. Ford)
  - Maintain dialog with Collaborators to discuss pathways for qualification and technology transfer

Technical Back-Up Slides

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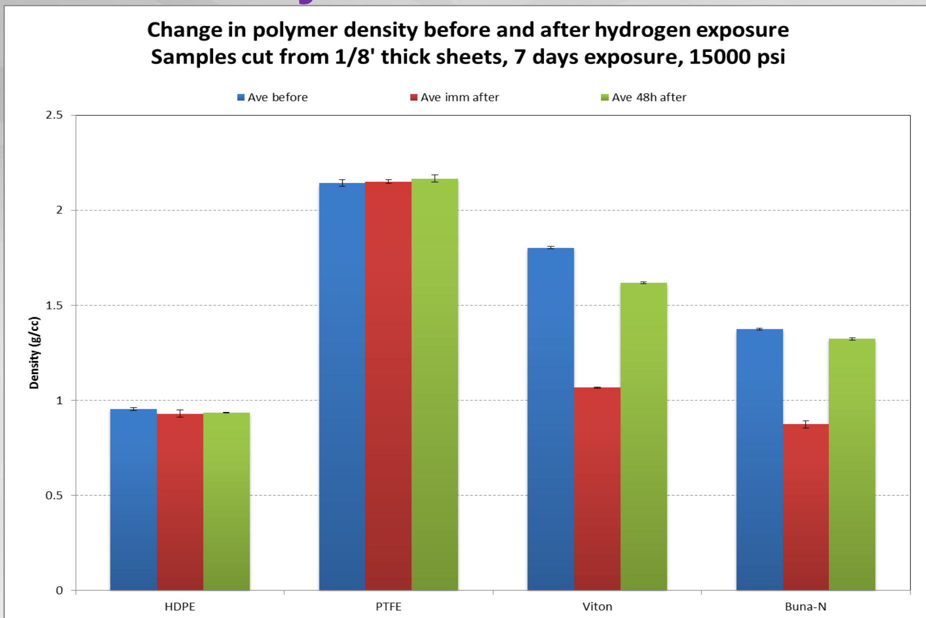
Task 2b: Test Methodology Development, High Pressure Hydrogen Exposure

Permeability and related information on polymers



Polymer	Permeability Coefficient X 10^{-9} (mol.H_2/m.s.MPa)	Diffusion Coefficient X 10^{-10} (m^2/s)	Solubility coefficient (mol.H_2/m^3.MPa)
HDPE	0.82	1.9	4.3
PTFE	3.2	-	-
Buna N	5.0	4.3	11.4
Viton A	3.5	1.9	19

	Before Hydrogen exposure		After Hydrogen exposure	
Polymer properties	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)
Buna N	-32	34.0±2	-31	19.9±3.7
Viton A	-2	10.7±0.5	-3	5.4±1.4