BEHAVIOR OF POLYMERS IN HIGH PRESSURE HYDROGEN, HELIUM, AND ARGON AS APPLICABLE TO THE HYDROGEN INFRASTRUCTURE

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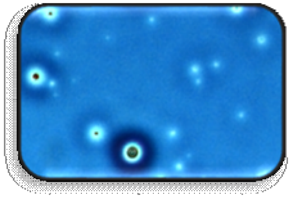

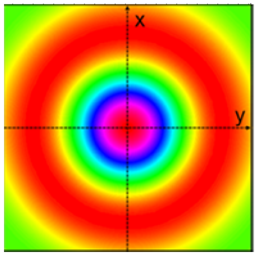

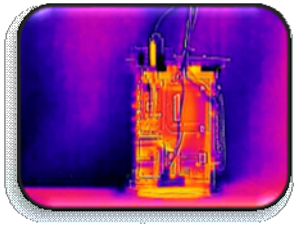

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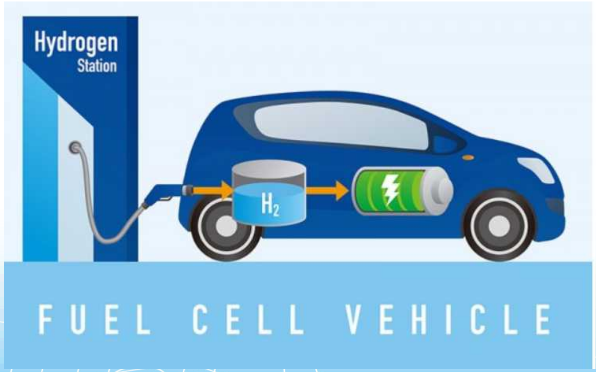
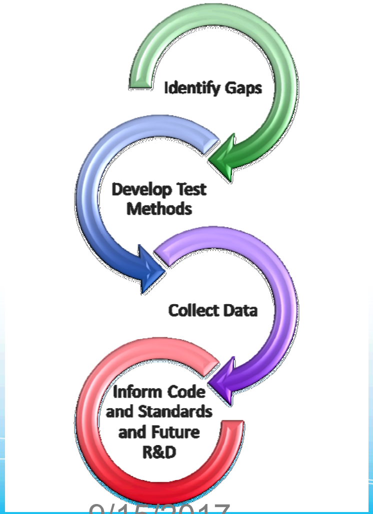
Hydrogen Safety, Codes, and Standards FCTO (DOE) Sub-Program: Objectives

- 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
- Develop standard test protocols for polymeric materials to evaluate their H_2 compatibility for conditions, applications, and polymers of interest by the hydrogen community.
- Disseminate test protocols and compatibility information to SDOs and support the deployment of H_2 infrastructure.





Polymers in Hydrogen Environment: Current Applications

- Polymers are used extensively in the hydrogen infrastructure for :
  - ❑ Distribution and Delivery (Piping and Pipelines)
  - ❑ Fueling Stations
  - ❑ Vehicle Fuel Systems

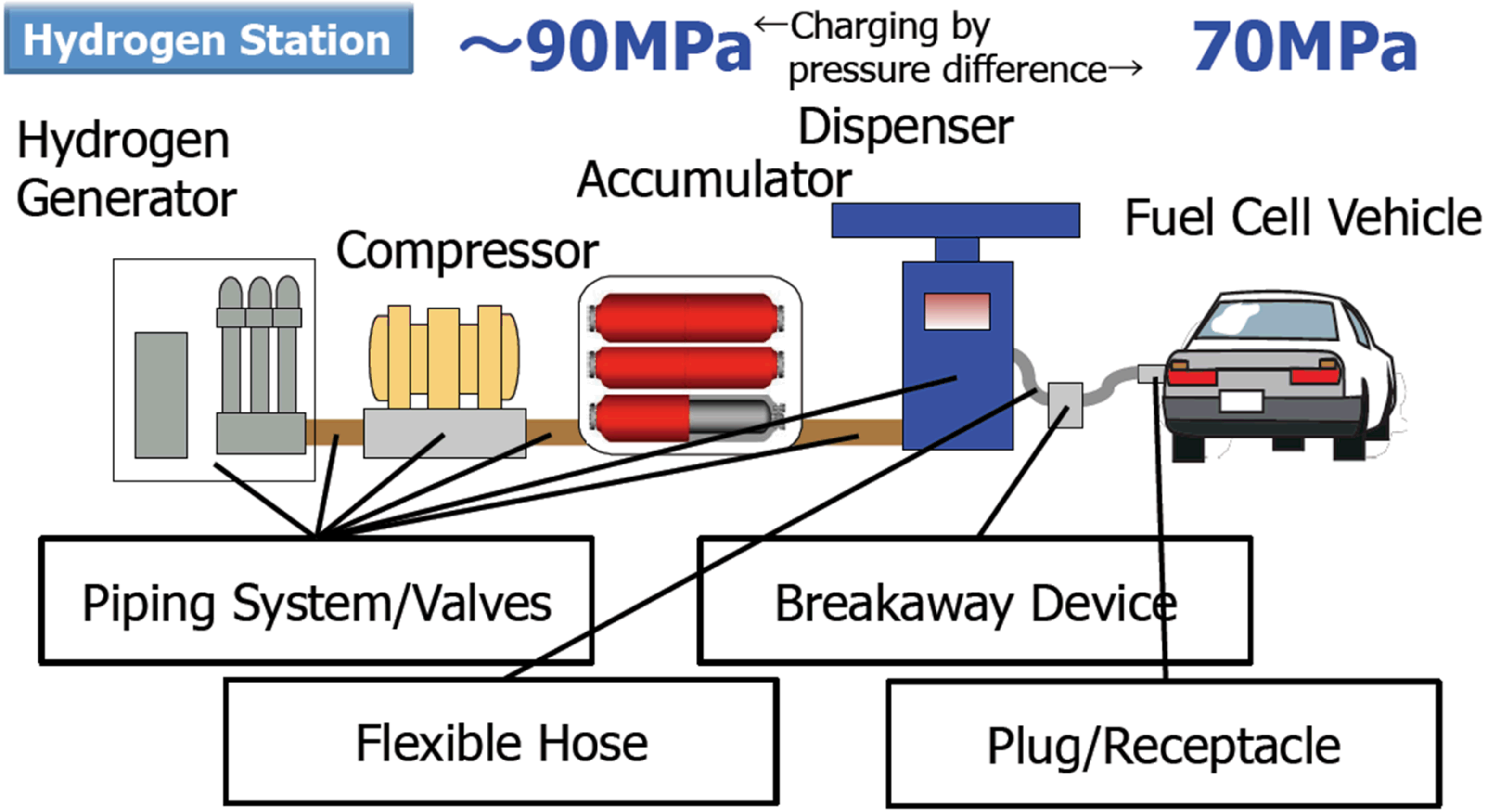
- Component designs such as tanks, pipeline liners, valves, O-rings, gaskets, regulators, pistons, and other fittings are made of polymers
- Conditions of high pressures (0.1 to 100 MPa) and rapid cycling of temperatures (-40˚C to +85˚C) possible during service

Elastomers
EPDM, NBR/HNBR Levapren, Silicone, Viton, Neoprene

Thermoplastics
HDPE, Polybutene, Nylon, PEEK, PEKK, PET, PEI, PVDF, Teflon, PCTFE, POM

Thermosetting polymers
Epoxy, PI, NBR, Polyurethane

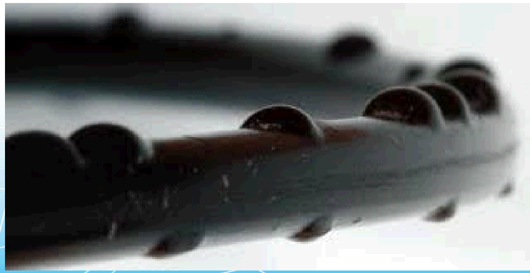
Polymeric Materials for Hydrogen Equipment



Rubbers and polymeric materials are used for gas seals and liners in the hydrogen equipment.

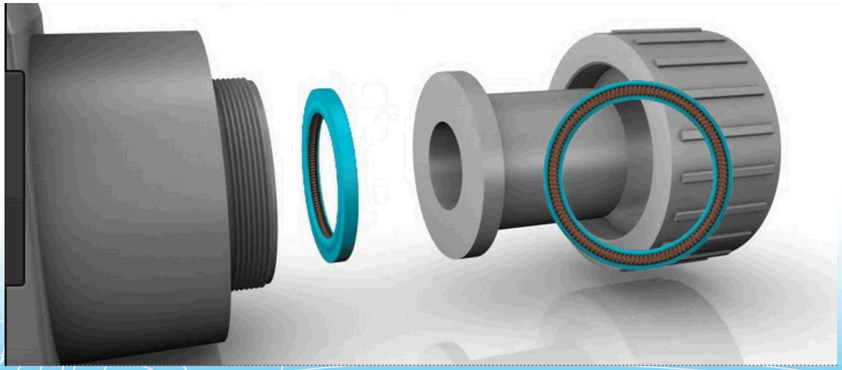
Polymers in Hydrogen Environment: Gap Analysis for Characterization and Test Methodology

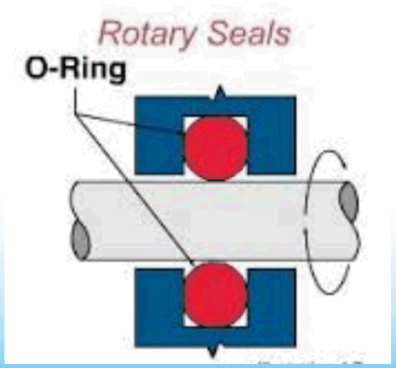
- High-pressure hydrogen and related transport properties in polymers: assessment of effect of plasticization through mechanical properties
- Effect of high pressure hydrogen on fracture and fatigue
- Friction and wear characterization effects, methods, and test facilities
- Rapid gas decompression of elastomers with combined effects of temperature and pressure cycling: metrics for assessing damage and mitigation through development of damage-resistant materials
- Low-pressure hydrogen transport data (permeation) through epoxies and composites used in the hydrogen infrastructure
- Effects of volatiles from polymers in the hydrogen stream



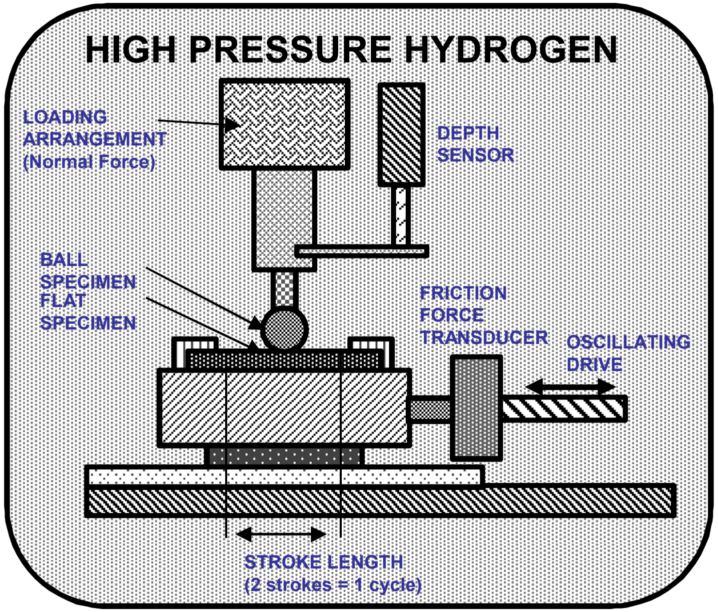
Why are friction characteristics important?

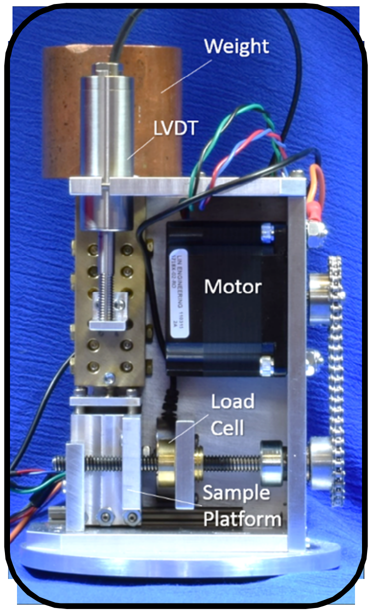
- Tribology of polymers in hydrogen is important in dynamic sealing applications
- A low coefficient of friction can mean less wear and tear and therefore longer lifetimes for polymers in high-pressure hydrogen environments
- Friction behavior of polymers can differ in air vs. other gases depending on permeation characteristics of the polymers
- Fillers in polymers can play a large role in increasing or decreasing susceptibility to hydrogen

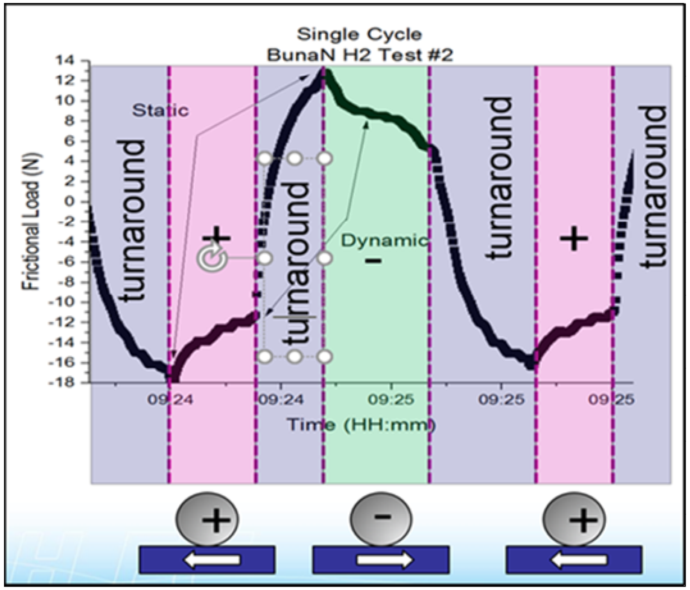


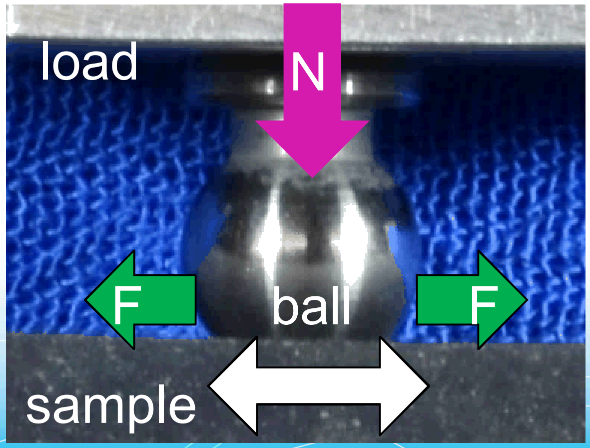


In-situ friction and wear in high-pressure hydrogen (PNNL): Unique In-situ Tribometer





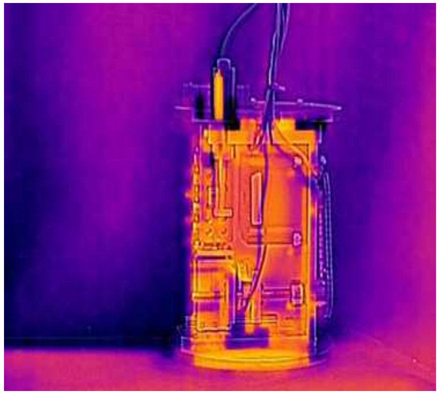




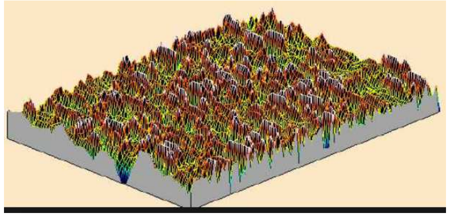
- Linear reciprocating adapted from ASTM G133
- Normal load (using weights) presses steel ball into moving sample
- Frictional force and vertical wear depth profiles measured in situ
- Pressures up to 5,000 psi hydrogen
- Ambient air and high pressure argon tests run for comparison

In-situ friction and wear in high-pressure hydrogen at PNNL: Data (in-situ and ex-situ measurements)

- Initial calibration experiments for air, high-pressure argon and high-pressure hydrogen completed with HNBR
- In-situ measurements
  - Coefficient of friction
  - Penetration wear depth
  - Wear factor
- Ex-situ: Optical microscopy and profilometry
- In-situ vs ex-situ depth profiles enable separation of pressure vs gas species effects
- For in-situ measurements:
  - dimensional changes are pressure driven
  - friction and wear are gas species driven – possibly due to lubricity (gas absorption) and filler interactions

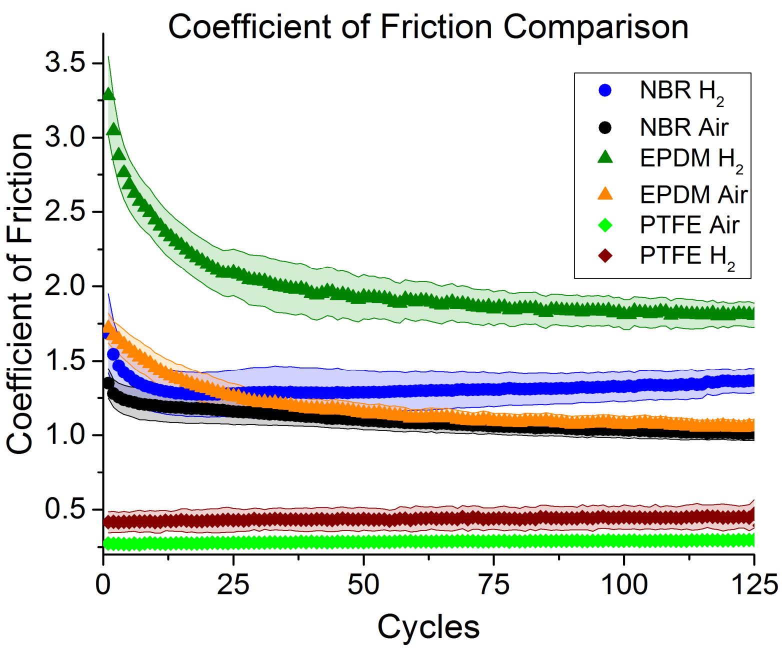


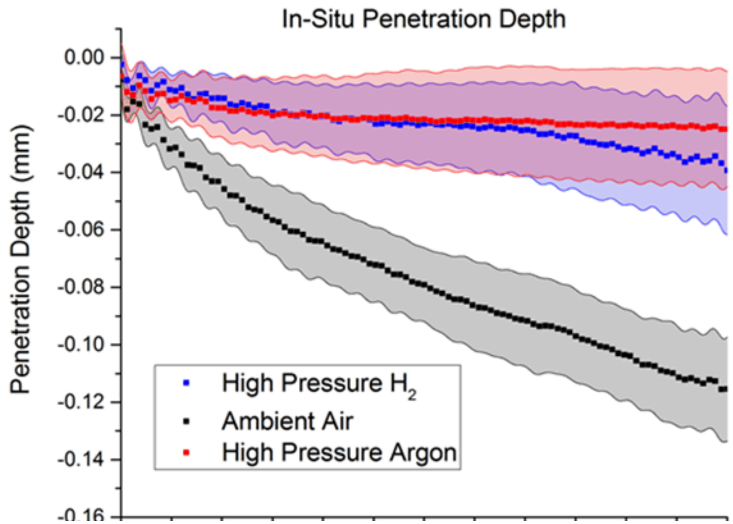
IR image of tribometer after multiple cycles (air)

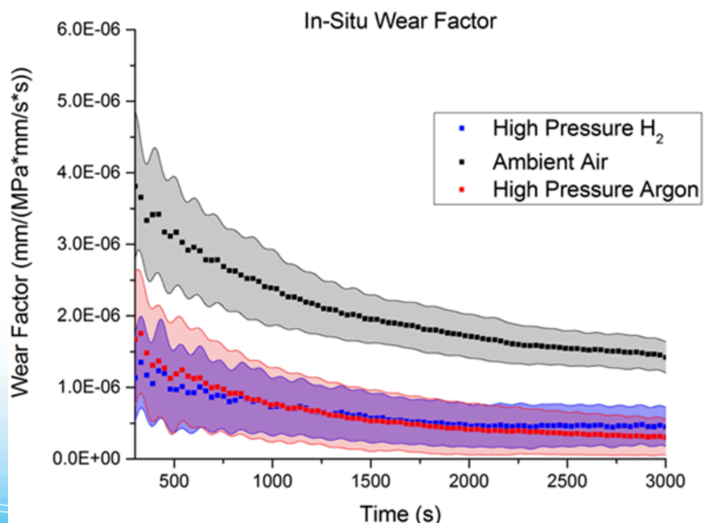


In-situ friction and wear in high-pressure hydrogen at PNNL: In-situ data

For NBR only



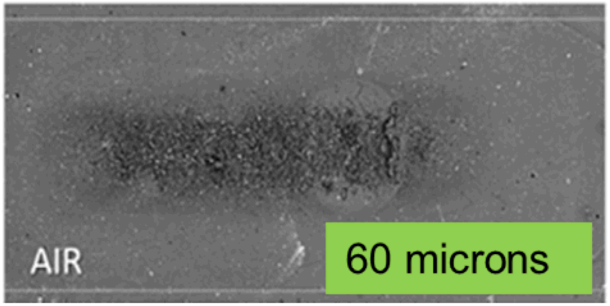


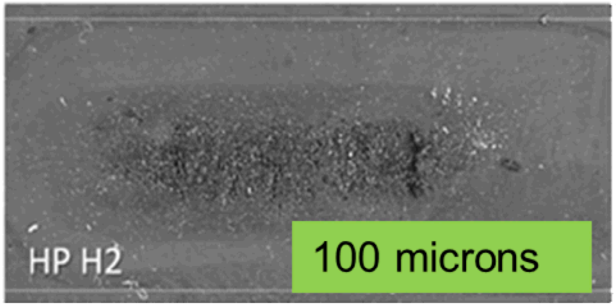


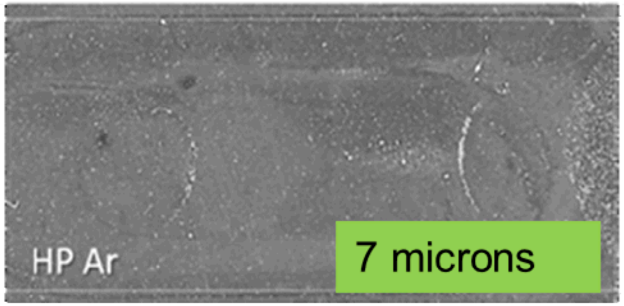
- NBR, EPDM, and PTFE show an increase in coefficient of friction in 4,000 psi hydrogen by factors of 1.4, 1.8, and 1.5 respectively as compared to ambient air
- Penetration depth drops in H_2 and Ar
- Wear factor lower in H_2 and Ar

In-situ friction and wear in high pressure hydrogen at PNNL: Ex-situ depth profile data

- Ex-situ optical microscopy shows clear increase in wear for hydrogen and ambient air over high pressure argon for NBR
- Ex-situ optical profilometry (interference) shows clear increased wear in high pressure hydrogen over ambient air
- Ex-situ hardness and swelling measurements on elastomers shows hydrogen effects for NBR and EPDM



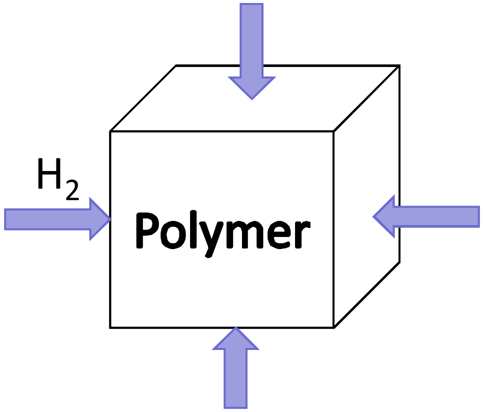


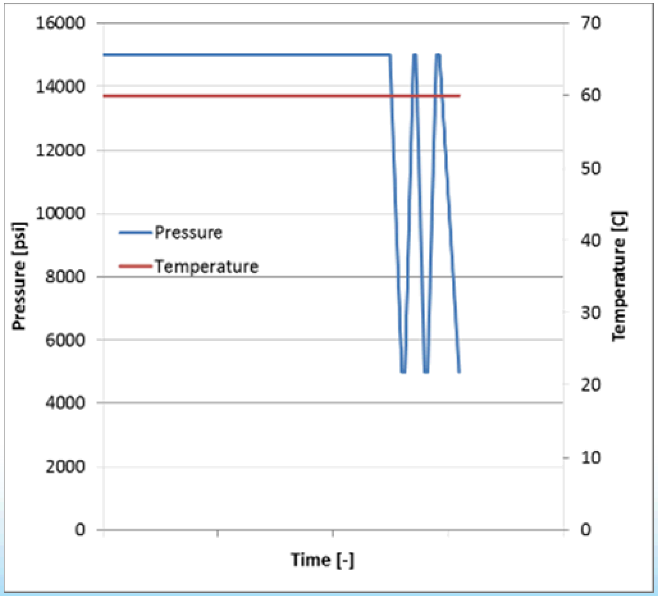


Ex-situ optical microscopy wear tracks in NBR (depths shown)

High-pressure hydrogen studies at SNL: Pressure cycling of polymers under HP hydrogen, argon, and helium

- Construction of a one-of-a-kind high-pressure hydrogen cycling manifold in progress (Sandia National Labs)
- Understand rapid decompression effects and build for controlled decompression rate in cycling experiments aimed at mitigation
- Material characterization of thermal and pressure cycling effects from high pressure exposure with mitigation by new material selection/development
- Use of purge gas or leak detection gas at high pressures in cycling manifolds
- Isolate the influences of purge gas or leak detection gas from influences of hydrogen on polymer properties



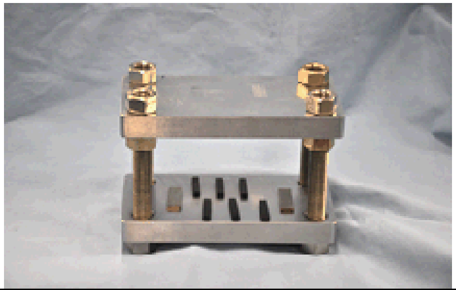


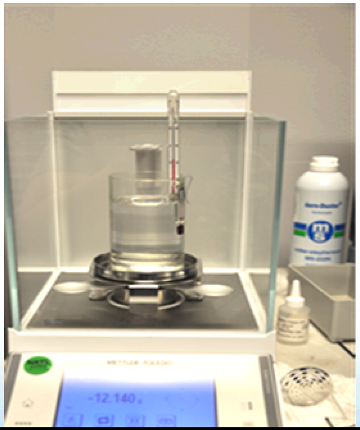
High-pressure hydrogen studies at SNL: Experimental details

- Polymers tested:
  PTFE, Nylon-11, POM, EPDM, NBR, Viton A, HDPE
- O-rings and sheets of all polymers used
- Static exposure, 20°C, dwell times shown below
- All specimens were kept at 3 mm (0.12 inches) thickness regardless of other dimensions
- No pre-treatment before exposure; except for thermoplastics
- Specimens of PTFE and HDPE were annealed prior to use to remove residual thermal stresses from processing
- Experiment 1: Helium gas at 100 MPa for 40.5 hrs followed by hydrogen at 100 MPa for 168 hrs
- Experiment 2: Helium gas at 100 MPa for 40.5 hrs*
- Experiment 3: Argon gas at 100 MPa for 108 hrs followed by hydrogen at 100 MPa for 168 hrs

* = Data from this experiment is shown minimally in this presentation because the effect of helium on polymers was negligible


Sample holder with O ring specimens


Compression set test for elastomers


Density measurements set-up

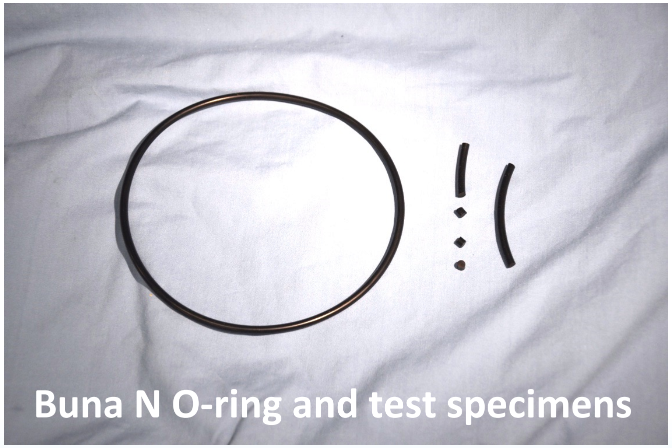
High-pressure hydrogen studies at SNL: Experimental details

- Static isobaric (100 MPa) and isothermal (20ºC) conditions of exposure
- Time of exposure: 1 week for saturation of 3 mm thick specimens for all polymer types (calculated based on DIFFUSE#)
- Specimens removed from test and characterized

Elastomers (Viton A and Buna N)
- T_g and Modulus
- Compression Set
- Specific volume changes
- Mass loss (TGA and TDS)

Thermoplastics (HDPE and PTFE)
- T_g and Modulus
- Specific volume changes
- Tensile Testing


Pressure vessel in secondary containment


Buna N O-ring and test specimens

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

High-pressure hydrogen studies at SNL: Permeability characteristics (H_2 transport)

Polymer	Permeability coefficient, 10^{-9} mol H_2/m·s·MPa	Diffusivity coefficient, 10^{-10} m^2/s	Solubility coefficient, mol H_2/m^3·MPa
Perbunan (Buna N)	5.1	4.2	12
FKM (Viton A)	3.5	1.9	19
EPDM	17	5.0	33
Nylon 11	0.4	0.65	6.2
PTFE	3.2	-	-
HDPE	0.82	1.9	4.3

POM = No data for behavior in hydrogen in literature

Source: Hydrogen transport properties for HDPE, PTFE, Buna N, and Viton A (Source: Sandia Report 2013-8904)

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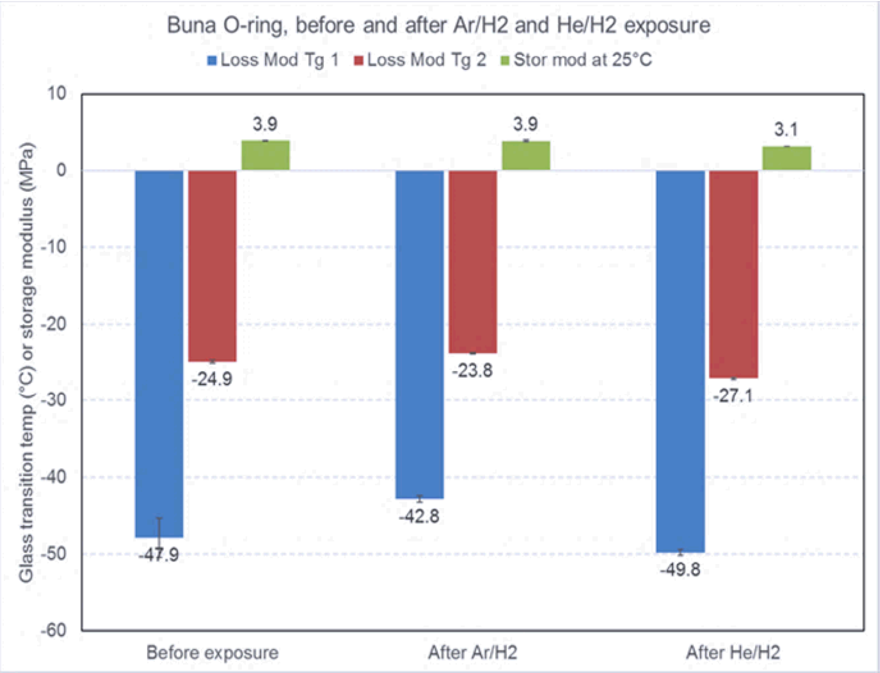
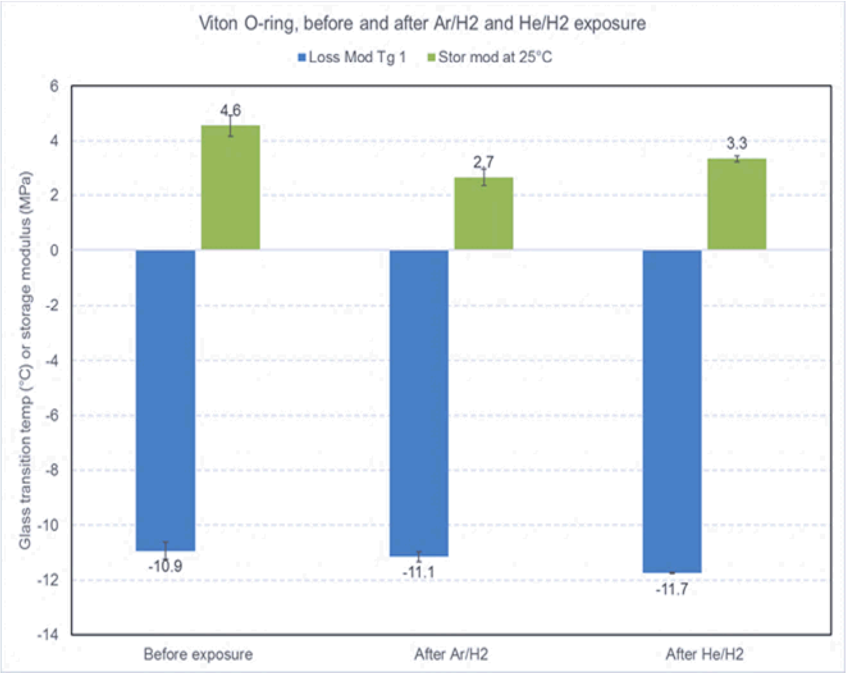
DMTA data for polymers in hydrogen

	Before He/H_2 exposure		After He/H_2 exposure		After Ar/H_2 exposure	
Polymer properties	T_g (˚C) (Tan Delta peak)	Storage Modulus (MPa)	T_g (˚C) (Tan Delta peak)	Storage Modulus (MPa)	T_g (˚C) (Tan Delta peak)	Storage Modulus (MPa)
Buna N	-36	3.9 ± 0.0	-39	3.1 ± 0.0	-43	3.9 ± 0.2
Viton A	-11	4.6 ± 0.4	-12	3.3 ± 0.1	-11	2.7 ± 0.3
EPDM	-48	4.1 ± 0.4	Not tested	Not tested	-49	3.6 ± 0.2
PTFE	32	225 ± 1	27	234 ± 4	31	266 ± 0
HDPE	-110	848 ± 7	-111	913 ± 25	Not tested	Not tested
POM	-65	1695 ± 5	Not tested	Not tested	-65	1664 ± 9
Nylon 11	70	1118 ± 92	Not tested	Not tested	67	1189 ± 11

High-pressure cycle aging-related studies at SNL: Storage modulus changes for elastomers

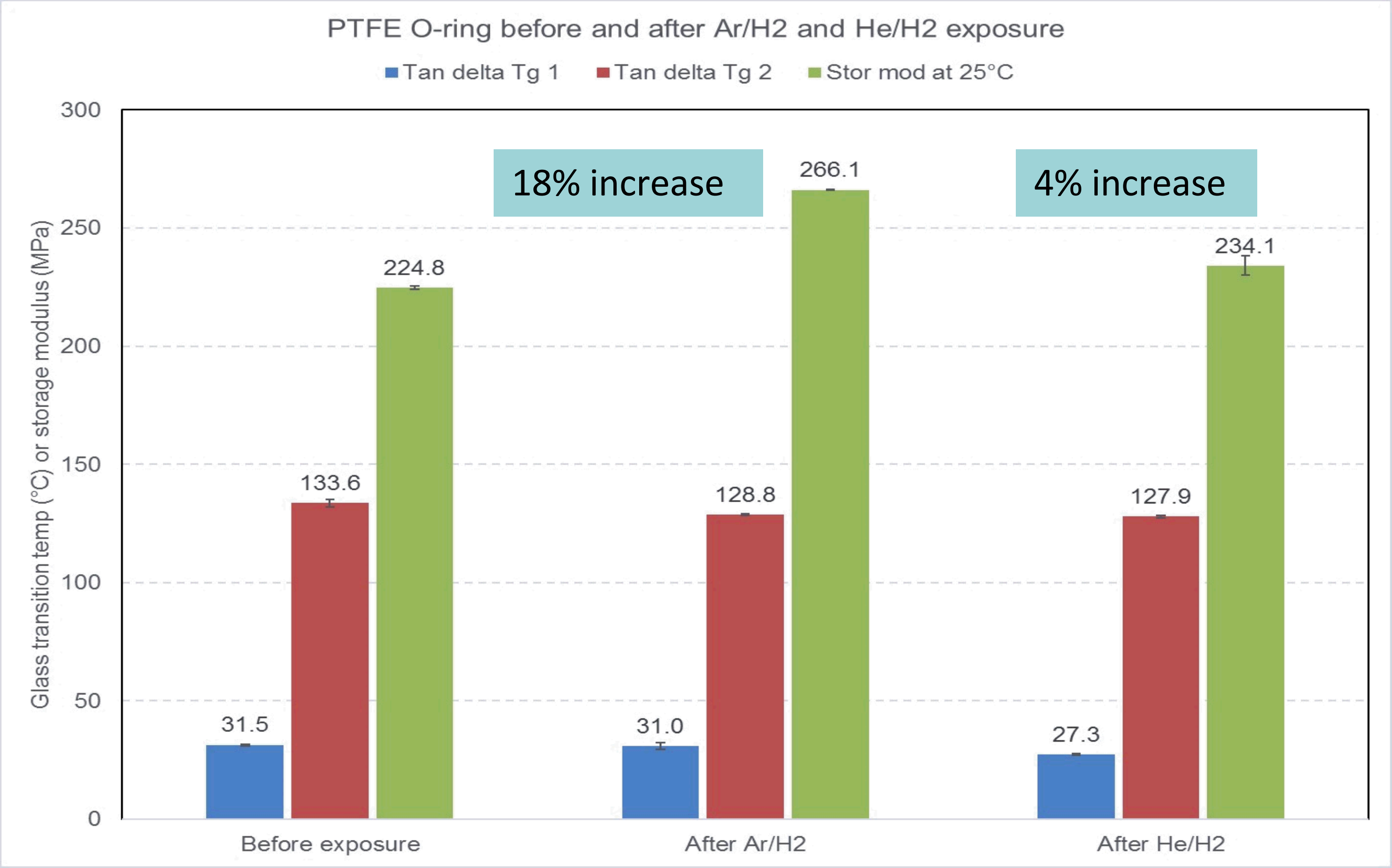




Buna N (left) and Viton A (right) before exposure and after exposure to Ar/H_2 and He/H_2 (DMTA test conditions: 0.1% strain, 1 Hz, 5°C/minute)

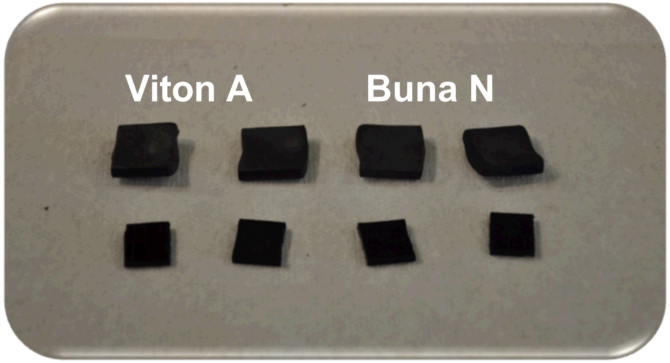
Polymer	He/H_2 exposure	Ar/H_2 exposure
Buna N	20% decrease	No change
Viton A	28% decrease	41% decrease

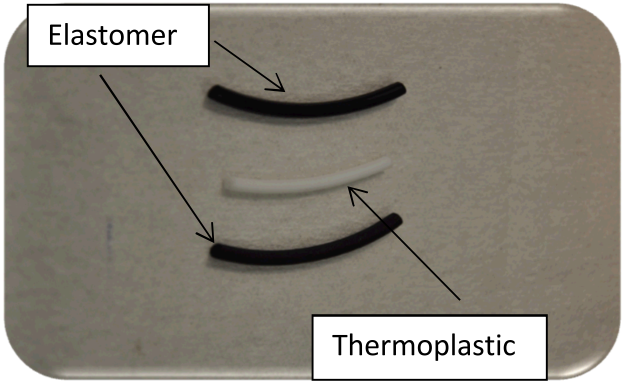
High-pressure cycle aging-related studies at SNL: Storage modulus changes in PTFE



PTFE before exposure and after exposure to Ar/H_2 and He/H_2
(DMTA test conditions: 0.1% strain, 1 Hz, 5°C/minute)

Specific volume changes in hydrogen: Degree of swell in elastomers and thermoplastics





Polymer	He/H_2 exposure	Ar/H_2 exposure
Buna N	74%	14%
Viton A	34%	34%*
EPDM	TBD	2%
Nylon 11	TBD	0%
PTFE	0%	-4%
POM	TBD	0%

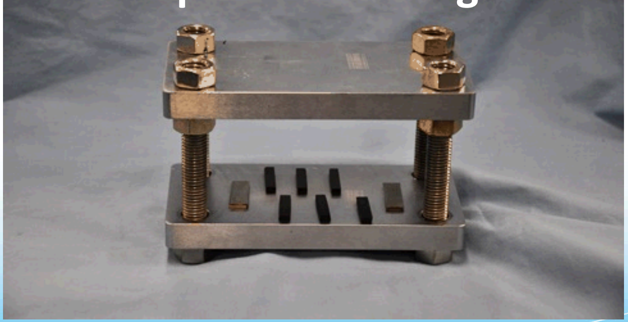
All numbers shown are the percent increase in dimensions for specimens immediately after removal from the pressure vessel. All the polymers with the exception of Viton A returned to original dimensions. Viton A retained 10% swell

High-pressure hydrogen studies at SNL: Compression set for elastomers

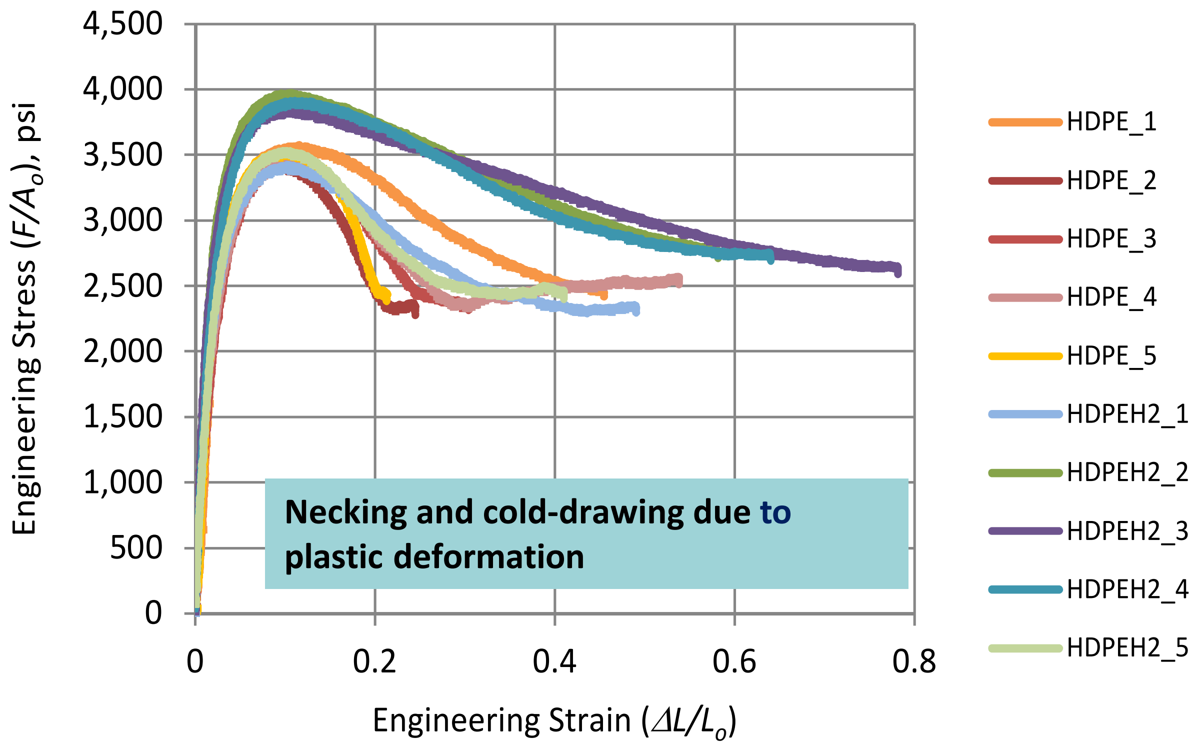
Polymer	Before exposure	After exposure to He/H_2	After exposure to Ar/H_2
Buna N	14%	15%	22%
Viton A	5%	9%	28%
EPDM	7%	Did not test	8%

Viton A shows 5.3x increase in compression set in Ar/H_2 compared to Buna N (1.6x) and EPDM (1.2x)

Compression Set Jig

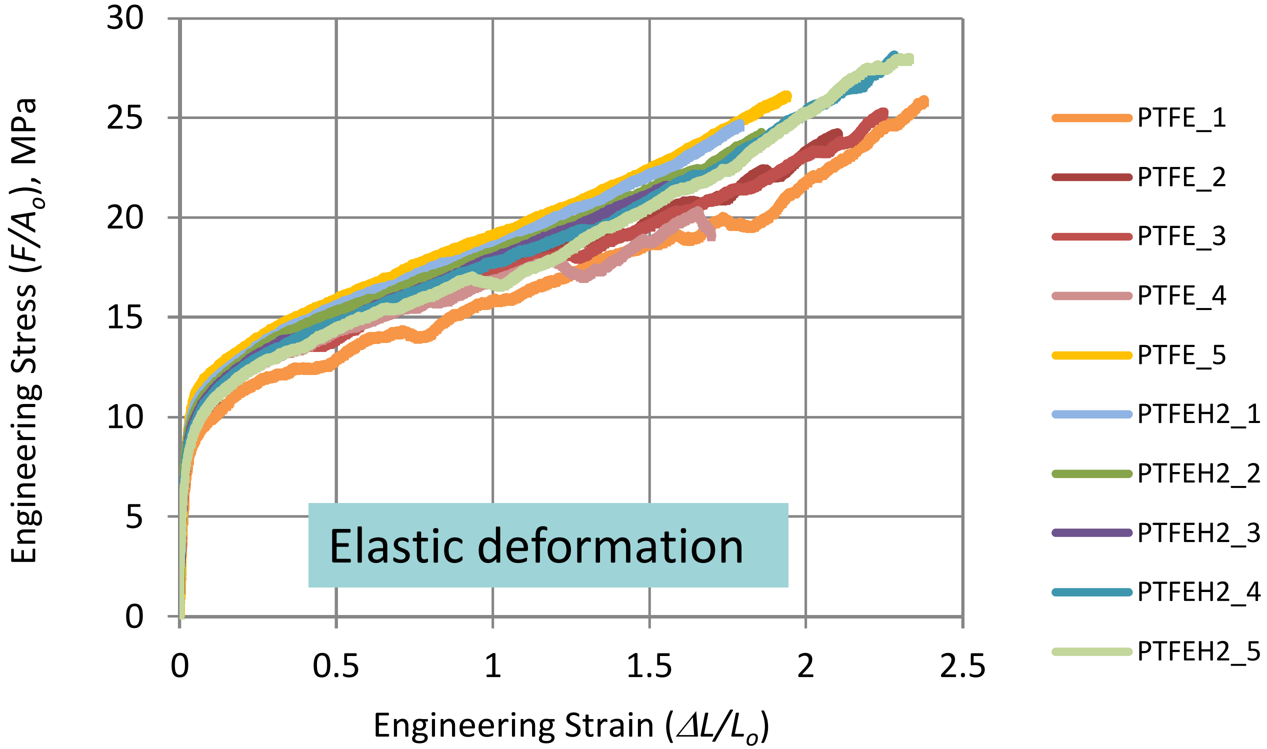


Mechanical Testing of HDPE exposed to hydrogen



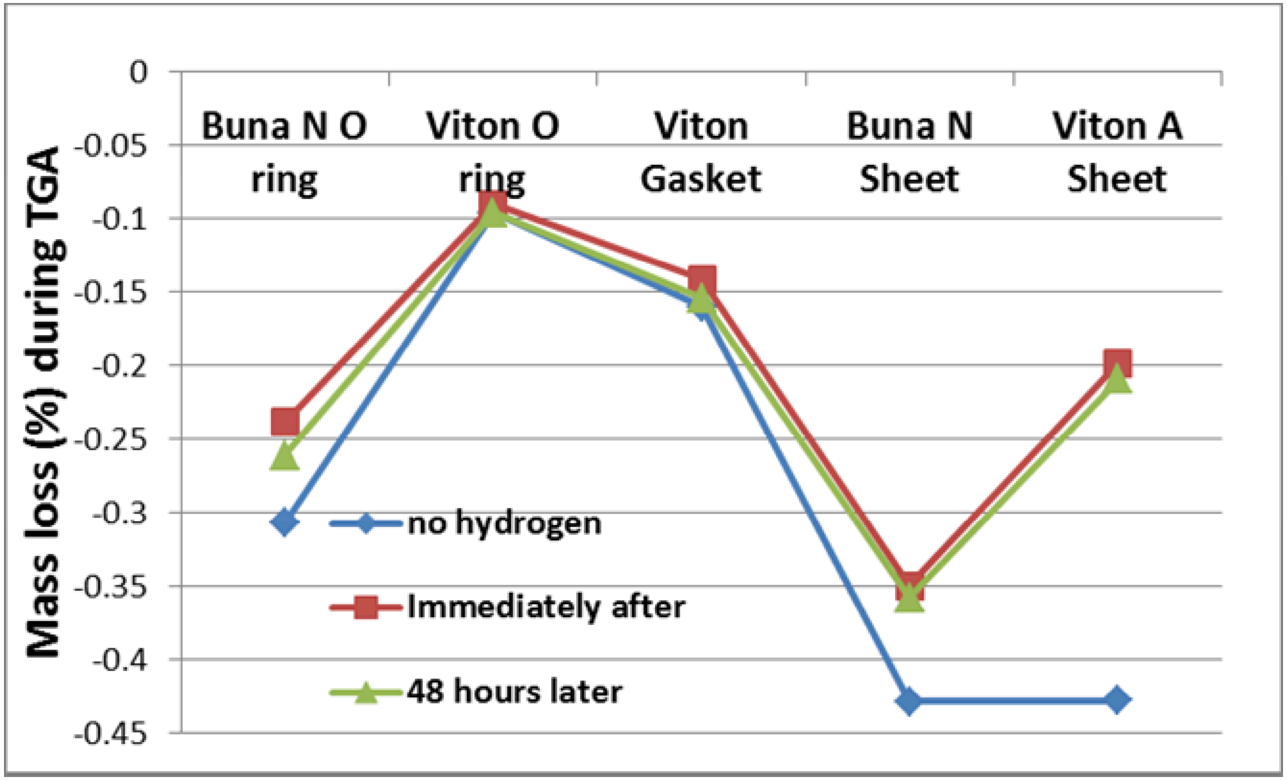
Sample	Young's modulus (MPa)	Yield Stress (MPa)	Strength (MPa)
HDPE	863 ± 225	20 ± 0.7	24 ± 0.6
HDPE Hydrogen	990 ± 235	22 ± 1.9	26 ± 1.6

Mechanical Testing of PTFE exposed to hydrogen



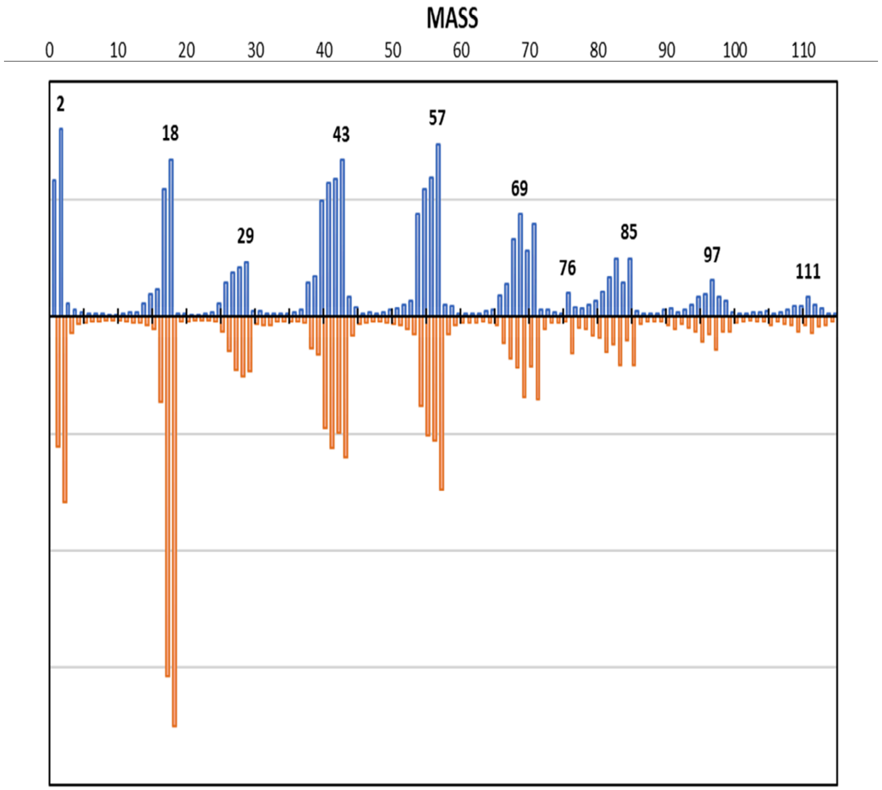
Sample	Young's modulus (MPa)	Yield Stress (MPa)	Strength (MPa)
PTFE	493 ± 127	8.8 ± 1.1	24.4 ± 1.1
PTFE Hydrogen	667 ± 40	8.1 ± 0.6	25.4 ± 0.5

Thermogravimetric Analysis of Buna N and Viton A after He/H_2 exposure

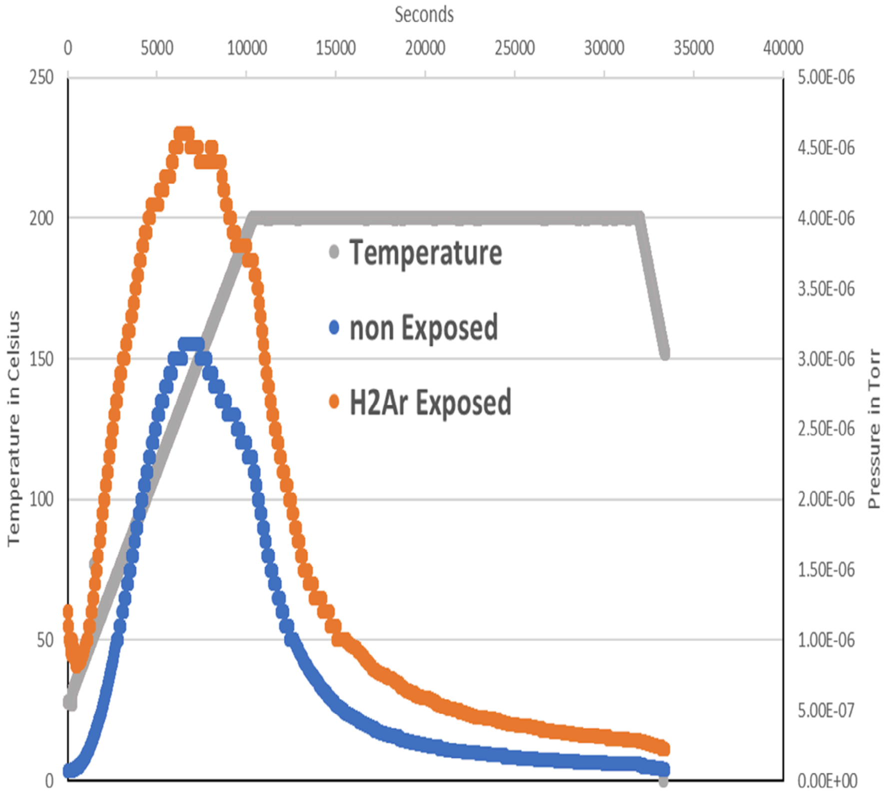


Mass loss immediately after and 48 hours later similar in all cases and lower than with no exposure – retention of hydrogen or did volatiles get driven out along with hydrogen?

Longer term effects: e.g. EPDM after Ar/H_2 exposure



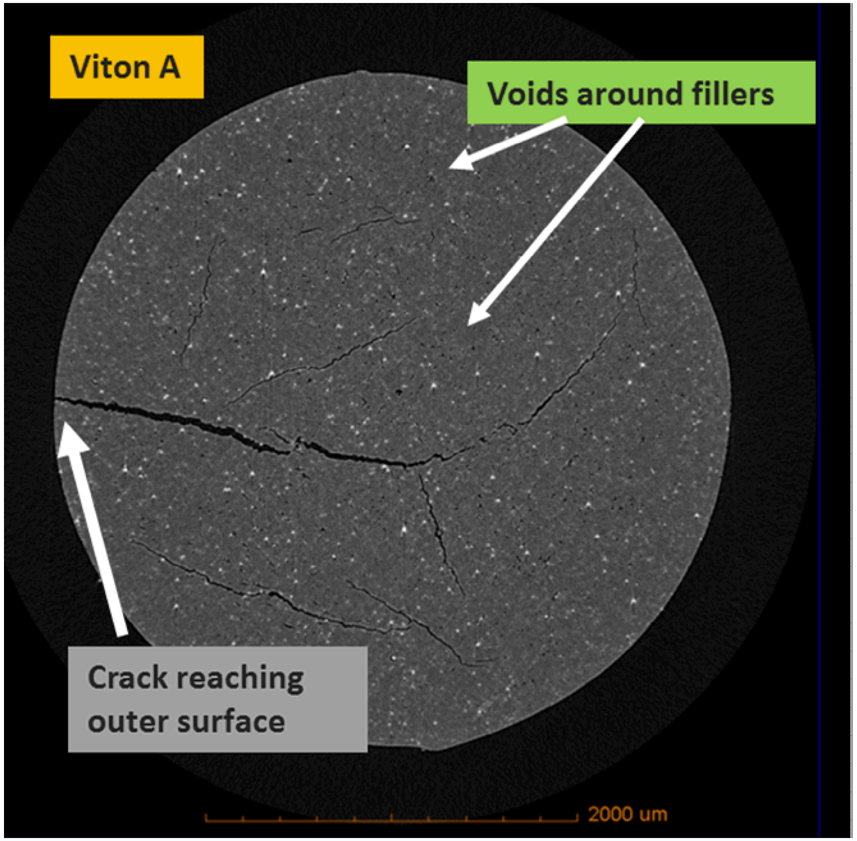
Maximum mass spectra of the exposed and the unexposed EPDM are shown in a mirror plot; major peaks are labeled

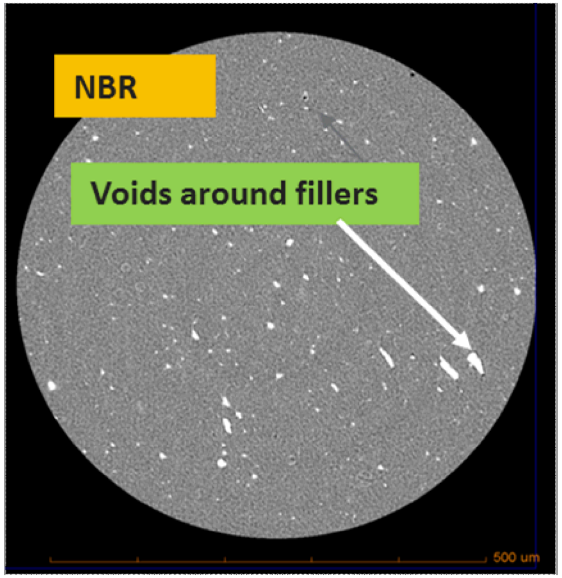


Total pressure as a function of time for both the EPDM samples; temperature ramp is shown in grey

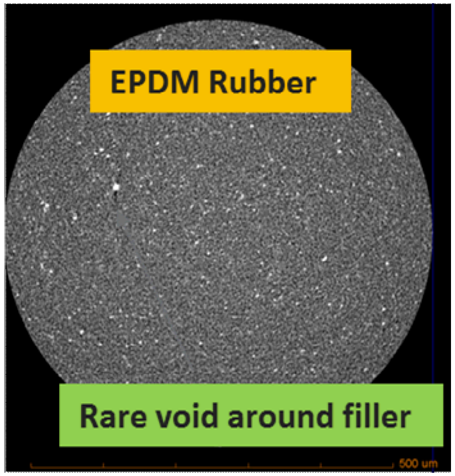
Hydrogen may be driving some of the volatiles out during decompression: polymer turning brittle with time, contaminants in hydrogen stream?

High-pressure cycle hydrogen studies at SNL: Micro-CT images for elastomers after Ar/H_2 exposure

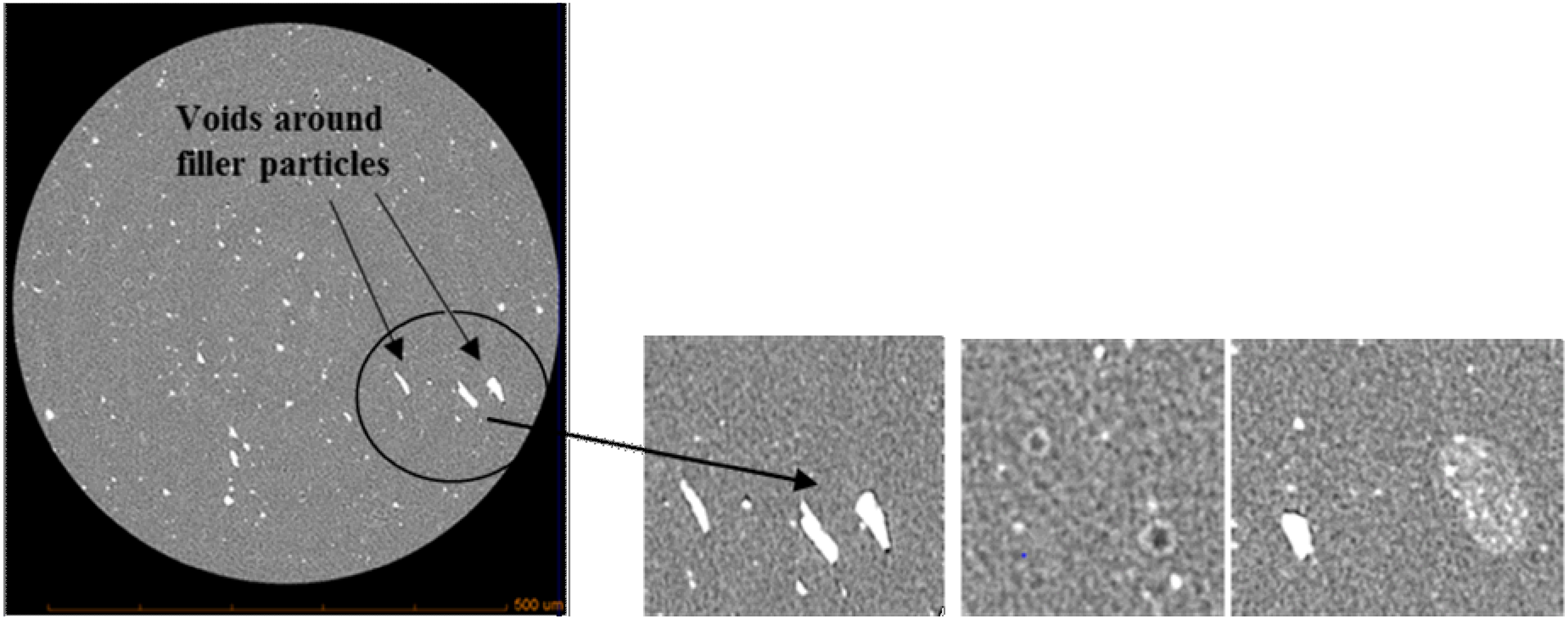




NBR and EPDM shown at 500 microns to magnify any voids or cracks



High-pressure hydrogen studies at SNL: Micro-CT images for Buna N after Ar/H_2 exposure



Micro-CT imaging reveals microstructure damage in Buna N after Ar/H_2 exposure seen as (a) voids around filler particles, (b) voids in the matrix, and (c) blister areas

Micro-CT movies: Void distribution in elastomer samples

Movie showing Viton A after hydrogen exposure; large voids seen surrounding the largest filler particle

20160307_0641_A168c_2D_XY_100_18389_36778_scale_movie.mpg

Movie showing Buna N after hydrogen exposure; no discernable voids seen around fillers

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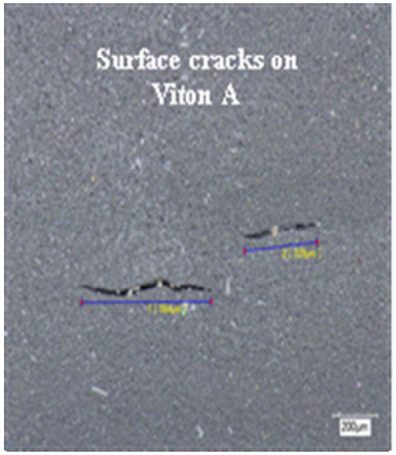
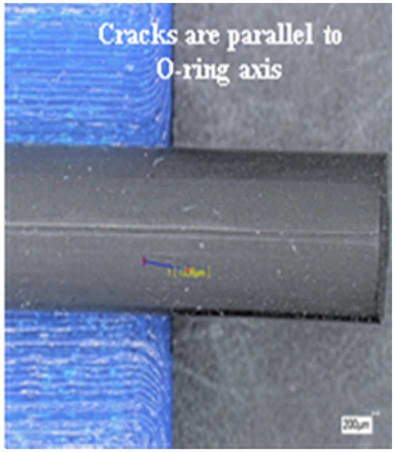
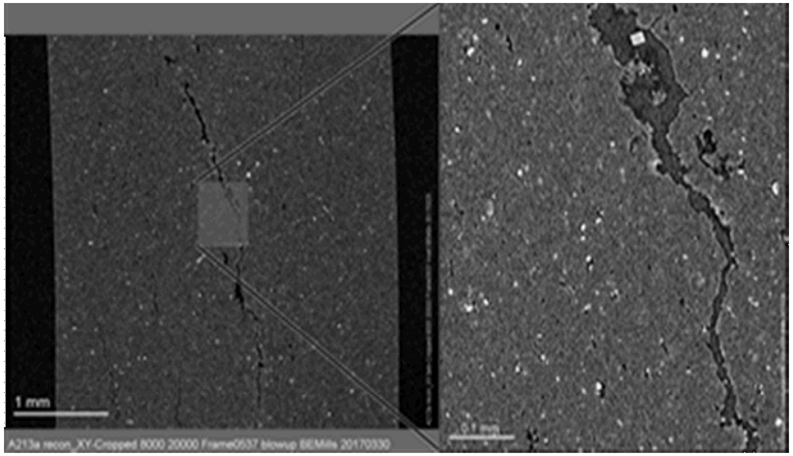
Partnering with polymer suppliers critical towards understanding polymer compositions and influences on hydrogen compatibility

High-pressure hydrogen studies at SNL: Crack formation in Viton A after Ar/H_2 exposure



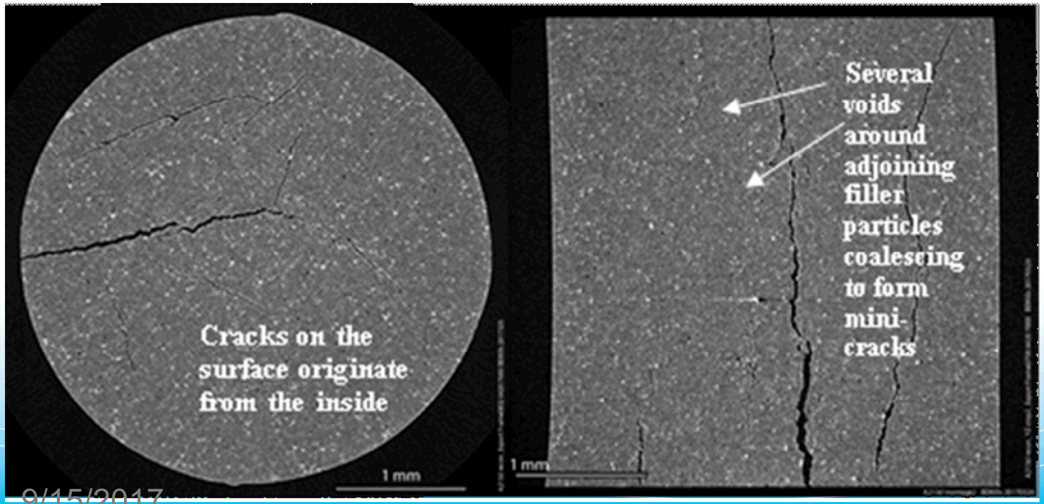


Optical micrographs: cracks parallel to o-ring axis on the surface after Ar/H_2 exposure



Micro-CT cross sections : large cracks in Viton A from smaller cracks

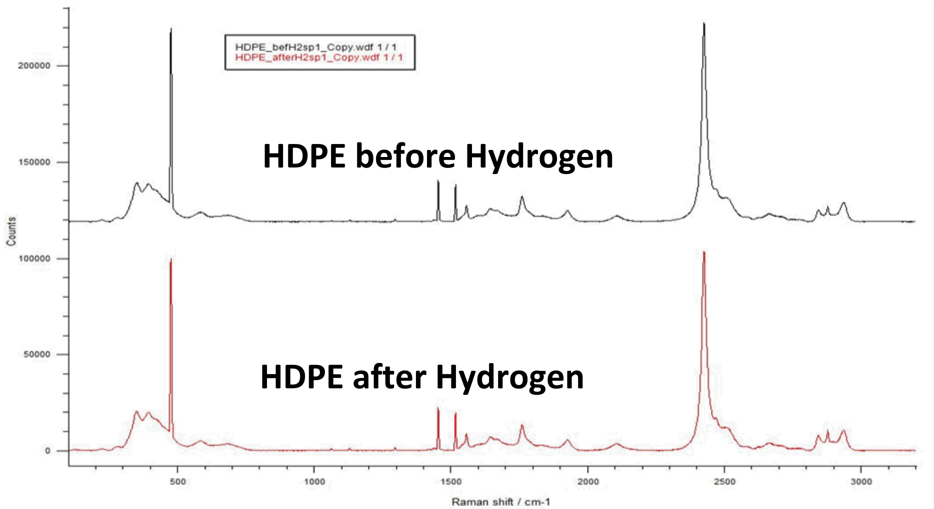
Micro-CT: Cracks seem to originate from the internal microstructure where voids appear to nucleate around filler particles and coalesce to form micro cracks

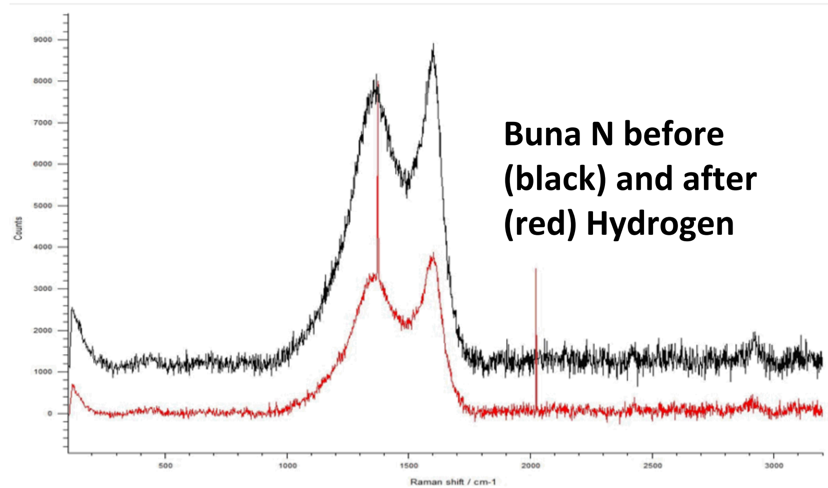


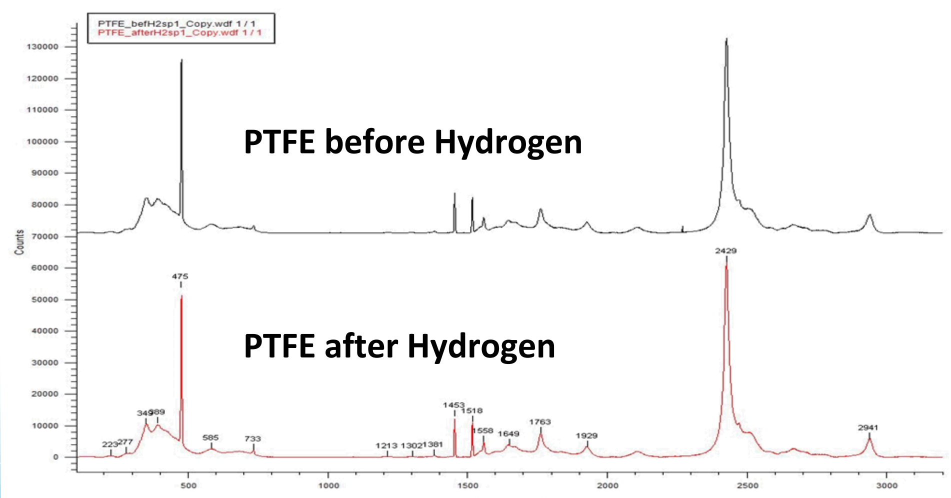
High-pressure hydrogen studies at SNL: Summary

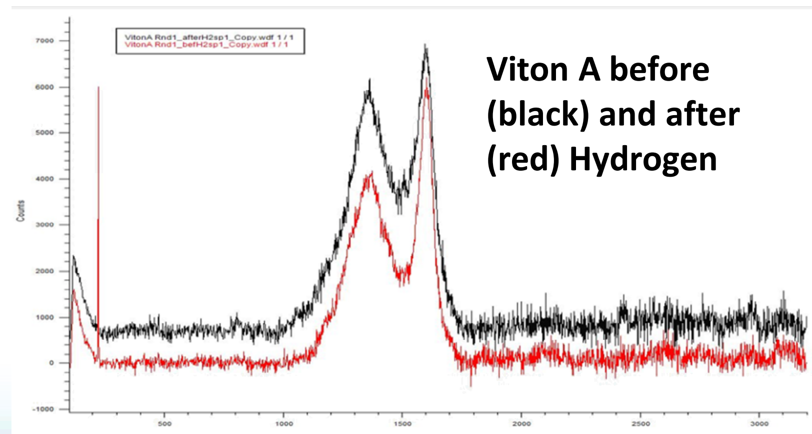
Polymer properties (Characterization methods)	Maximum Effects seen in gas environments	
	Argon/Hydrogen	Helium/Hydrogen
Swelling (Density measurements)	74% volume increase with 100% recovery in 48 hrs seen with Buna N	36% volume increase with 90% recovery in 48 hrs seen with Viton A
Storage Modulus changes (DMTA)	41% decrease for Viton A	20% decrease for Buna N
Compression set (Elastomers only)	5 times increase seen for Viton A	1.6 times increase with seen for Viton A
Explosive Decompression (Micro-CT)	Viton A shows severe damage; significant effects with Buna N and EPDM	Viton A shows voids around specific fillers; Buna N and EPDM unaffected
CHOICE OF PURGE GAS/LEAK DETECTION GAS PRIOR TO CYCLING	GOOD FOR THERMOPLASTICS; NOT FOR ELASTOMERS	GOOD FOR ELASTOMERS AND THERMOPLASTICS

Raman spectroscopy before and after H_2 exposure



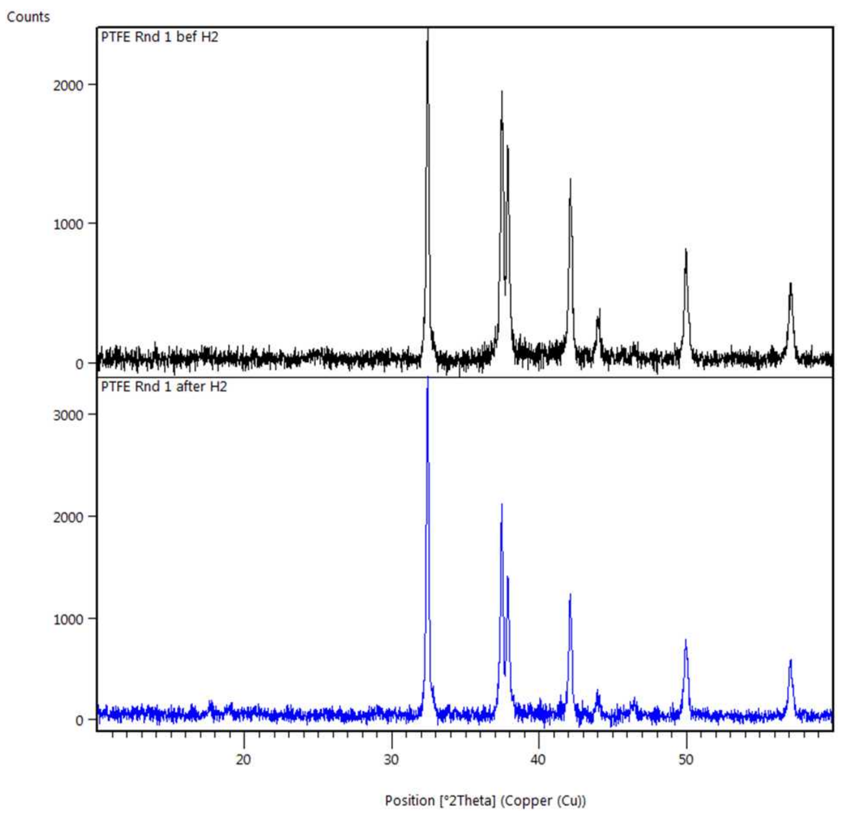


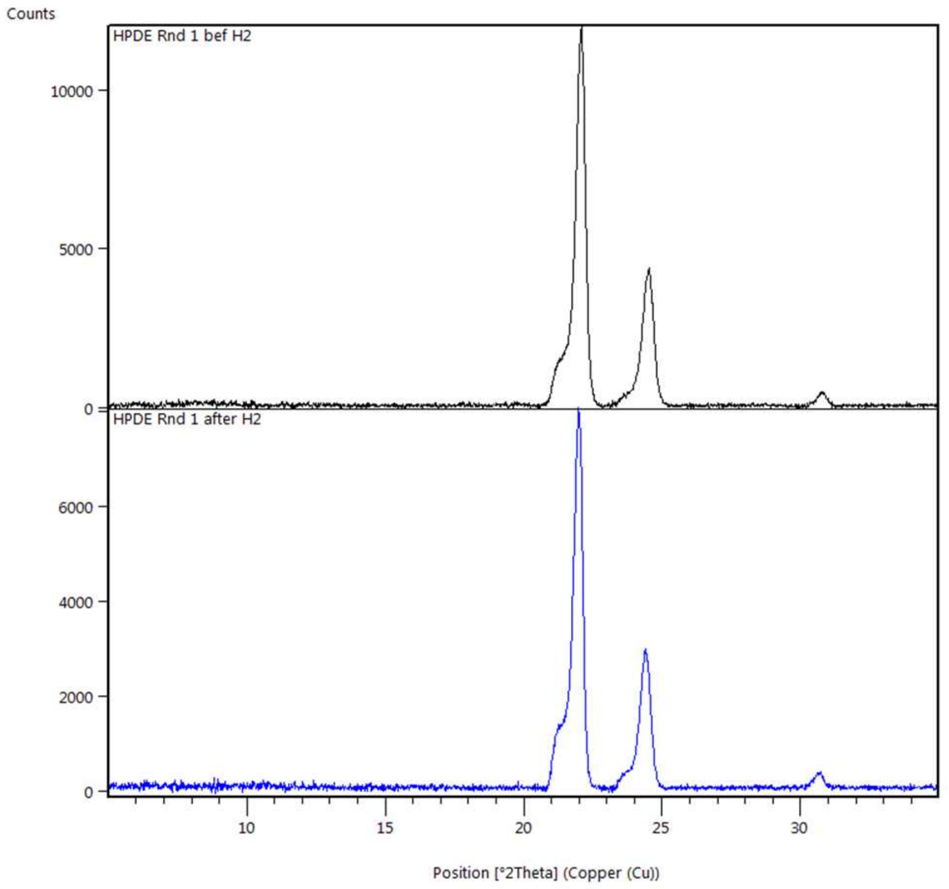




NO FREE OR BOUND HYDROGEN DETECTED IN ANY OF THE POLYMERS

X-Ray Diffraction on thermoplastics before and after hydrogen





No significant changes in HDPE and PTFE after exposure

FUTURE STEPS:
Addressing knowledge gaps for polymers in H_2

- Tribology work to continue at PNNL for different polymers, gas environments at different temperatures for science-based understanding of wear and friction in polymers in hydrogen
- Cycling of polymers in high pressure hydrogen with the goal of understanding explosive decompression mechanisms and control
- Mitigation of hydrogen influences on polymeric materials used in the hydrogen infrastructure through new material selection/development

Collaborative Activities

Partner		Project Roles
U.S. DEPARTMENT OF ENERGY	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

Thank you for your attention.

Questions?

Hydrogen and Fuel Cells Program

Technical Back-Up Slides

Experimental Details: Polymer selection

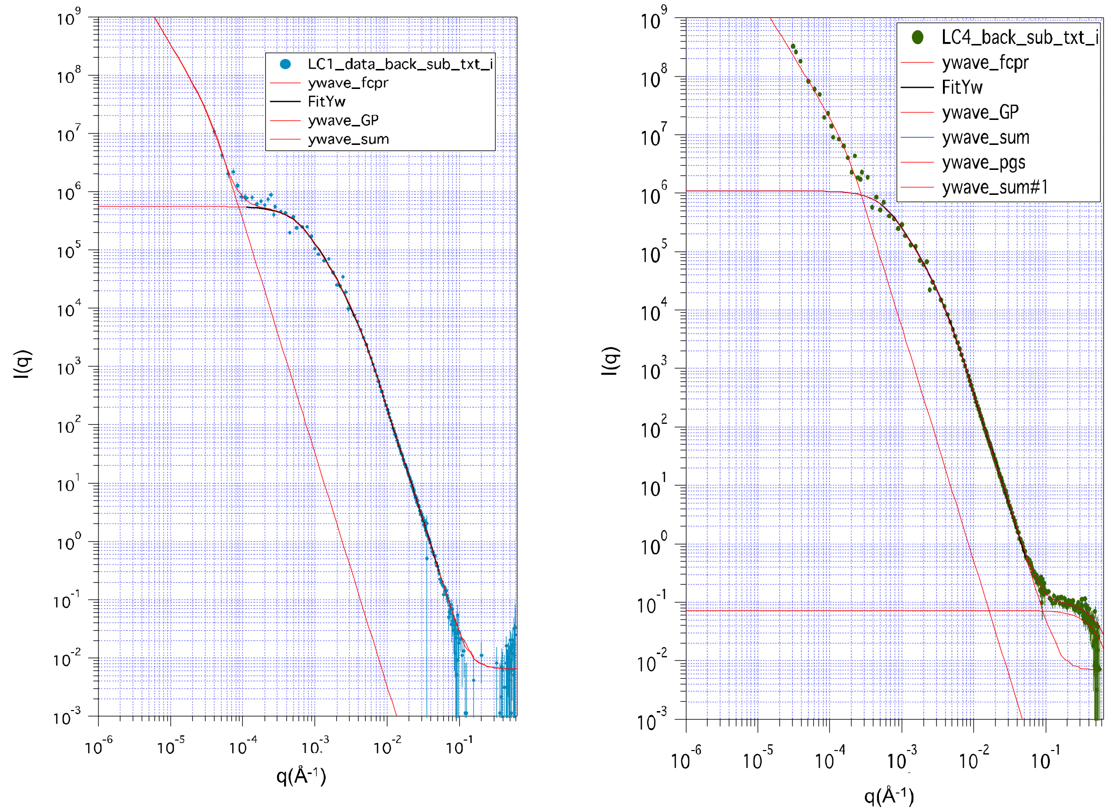
Polymer	Component in Hydrogen Infrastructure	Properties
Viton A	O-rings, gaskets,	Fluoroelastomer with 66% fluorine, 75 Shore A hardness high chemical resistance wide service temperature (-29˚C to 204˚C) low compression set
Buna-N (Nitrile Butadiene Rubber)	O-rings, gaskets	High acrylonitrile-content grade rubber superior chemical resistance medium-low flexibility
HDPE (High Density Poly Ethylene)	Tank liners	Possibly a filled PE80/PE100 grade High impact strength Excellent chemical resistance low moisture absorption properties
PTFE (Poly Tetrafluoroethylene)	O-rings, seals	Premium virgin Type 1, grade I, unfilled High temperature resistance Chemically inert Low coefficient of friction

Results of earlier *ex situ* (U)SANS measurements on HDPE revealed microstructural changes

Specimens of HDPE tank liner were cycled 4000 times between -30 and 85° C while differentially pressurized with 43 MPa H_2

Analysis of low-*q* scattering appearing in the post-cycling specimen revealed an emergence of scattering features (1nm-30μm) that correlated with long-term exposure to H_2 or increasing number of temperature cycles or both

Temperature cycling in H_2 produced progressive reductions in the permeation coefficient at all temperatures



(U)SANS curves for HDPE tank liner specimens, before temperature cycling (left) and after 4000 temperature cycles (right)

Oak Ridge National Laboratory
Managed by UT-Battelle for the U.S. Department of Energy

DIFFUSE details

- The thickness of all specimens in all tests was kept constant at 3 mm. This was adopted based on diffusion calculations that specified this thickness for complete penetration over a period of a week for all polymer types and specimen shapes in this study.
- The Sandia National Laboratories code DIFFUSE was used to determine exposure time (Baskes, Michael I. DIFFUSE 83, SAND83-8231, 1983). This program numerically determines the diffusion rate of hydrogen through a given material.
- A planar geometry using Sievert's Law as the boundary condition was employed. The lowest diffusion coefficient of the four polymers was chosen (1.9e-6 cm^2/s for HDPE) as all materials were simultaneously exposed.
- Time for the hydrogen concentration to increase from effectively zero to equilibrium was determined for a 20 ksi external pressure at 25° C. Calculations showed that 13 hours are sufficient to achieve complete saturation in all polymers, but to be conservative samples were exposed for 7 days (13 times more).