H_2FC Hydrogen and Fuel Cells Program

SAND2017-9743C

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

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Laboratories

Ford

OAK RIDGE
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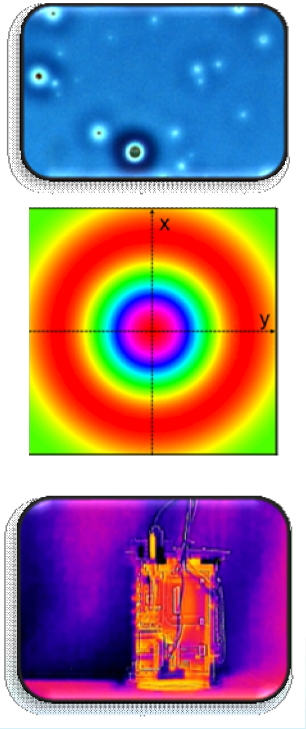


Collaborative Activities

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

Polymers in Hydrogen Environments: Current Applications

- Polymers are used extensively in the hydrogen systems
  - ❑ Distribution and Delivery (Piping and Pipelines)
  - ❑ Fueling Stations
  - ❑ Vehicle Fuel Systems
- Component designs such as tanks, pipeline liners, hoses, valves, O-rings, gaskets, regulators, pistons, and other fittings are made of polymers
- Conditions of ambient temperature (-40˚C to +85˚C) and high pressure (0.1 to 100 MPa) with rapid transitions in temperature and pressure are possible during service

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

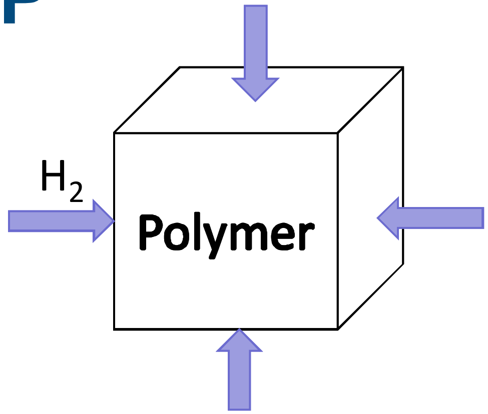
Thermoplastics
HDPE, Polybutene, Nylon,
PEEK, PEKK, PET, PEI,
PVDF, Teflon, PCTFE, POM

Thermosetting polymers
Epoxy, PI, NBR,
Polyurethane

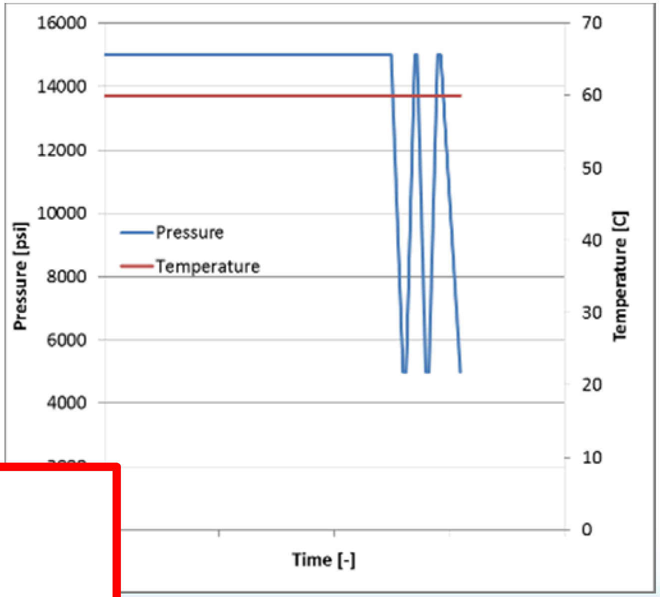
Polymers in Hydrogen Environments: Gap Analysis for Characterization and Testing

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

Pressure cycling of polymers under HP hydrogen, argon, and helium



- Construction of one-of-a-kind high-pressure hydrogen cycling manifold
  - Controlled decompression rate at controlled temperature
- Understand damage accumulation due to cycling and effects of rapid gas decompression
  - Materials characterization
  - Mitigation of failure modes through materials design



- Isolate the effect of purge gas during experimental setup from hydrogen effects on polymer properties

High-pressure testing: materials and exposure

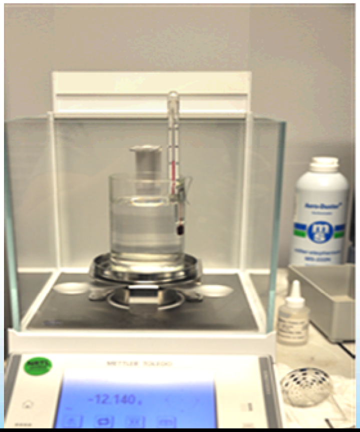
- **Polymers tested:**

  PTFE, Nylon-11, POM, EPDM, NBR, Viton A, HDPE
- **O-rings and sheets of all polymers used**
- **Static exposure at temperature of 20°C**
- **All specimens were 3 mm thick regardless of other dimensions**
- **No pre-treatment before exposure; except for thermoplastics**
- **Specimens of PTFE and HDPE were annealed**
  - **removal residual thermal stresses**
- **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

Characterization and methods

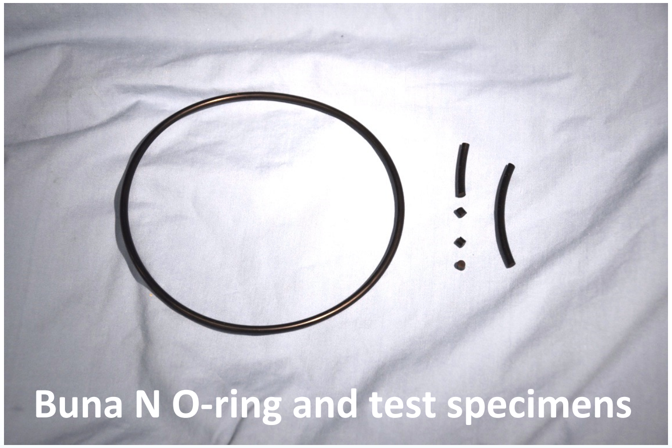
Elastomers
Viton A
Buna N

- Mass loss & Spectroscopy
- T_g and Modulus
- Compression Set
- Specific volume changes
- Microstructure

Thermoplastics
HDPE
PTFE

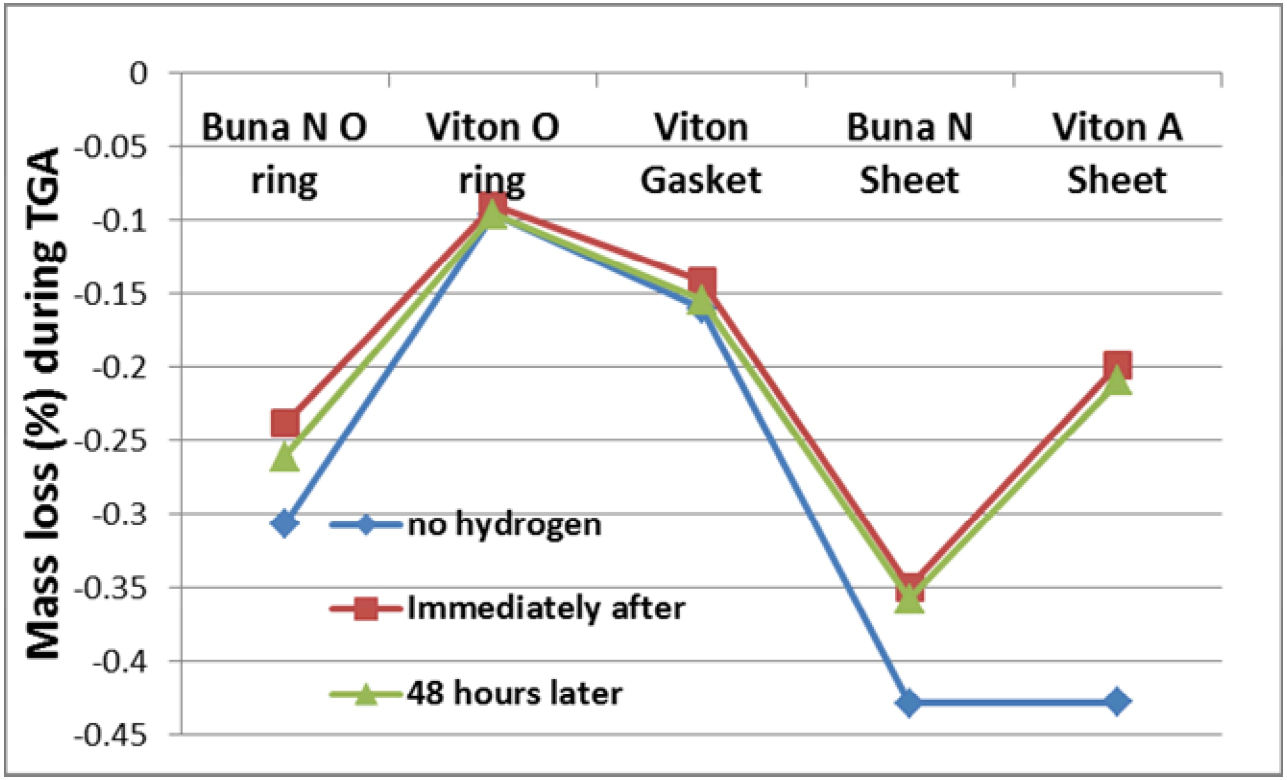
- Spectroscopy
- T_g and Modulus
- Specific volume changes
- Microstructure

Pressure vessel in secondary containment



Buna N O-ring and test specimens

Mass loss from Buna N and Viton A after He/H_2 exposure

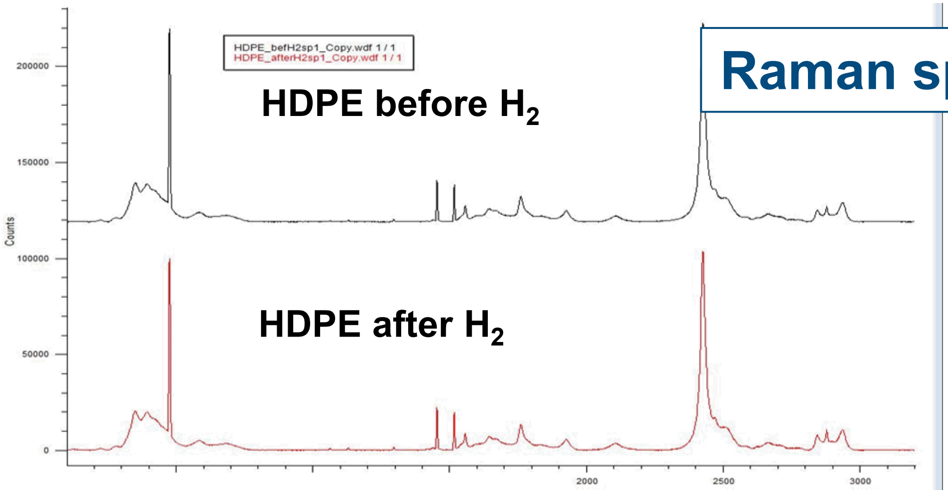


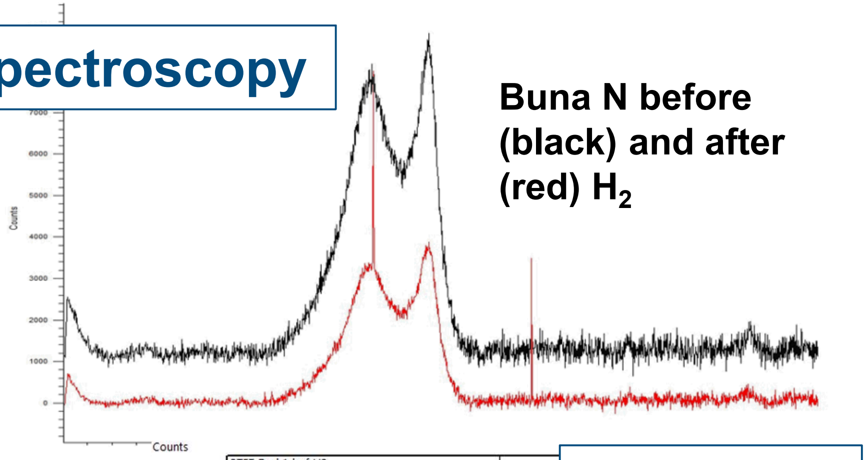
- Mass loss not sensitive to time after exposure
- Greater mass loss prior to exposure

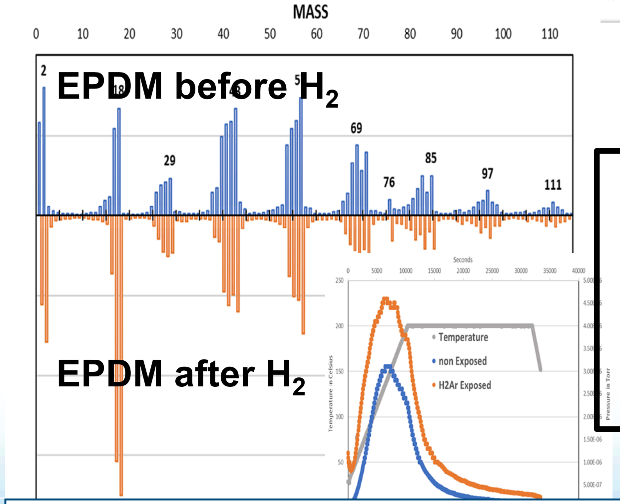
Were volatiles driven out with hydrogen decompression?

Spectroscopy shows no structural changes in polymeric materials after high-pressure exposure

Raman spectroscopy



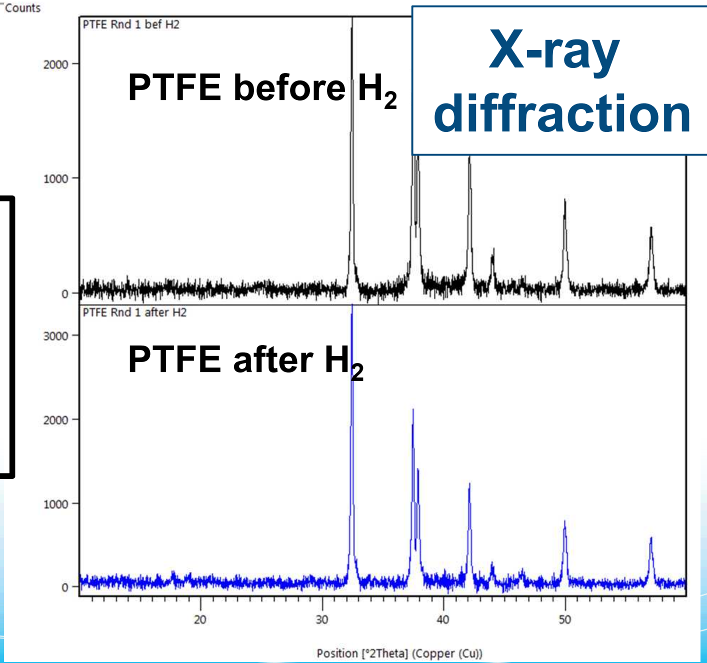




Suggestion of additional volatility after Ar/H2 exposure

Thermal desorption spectroscopy

X-ray diffraction

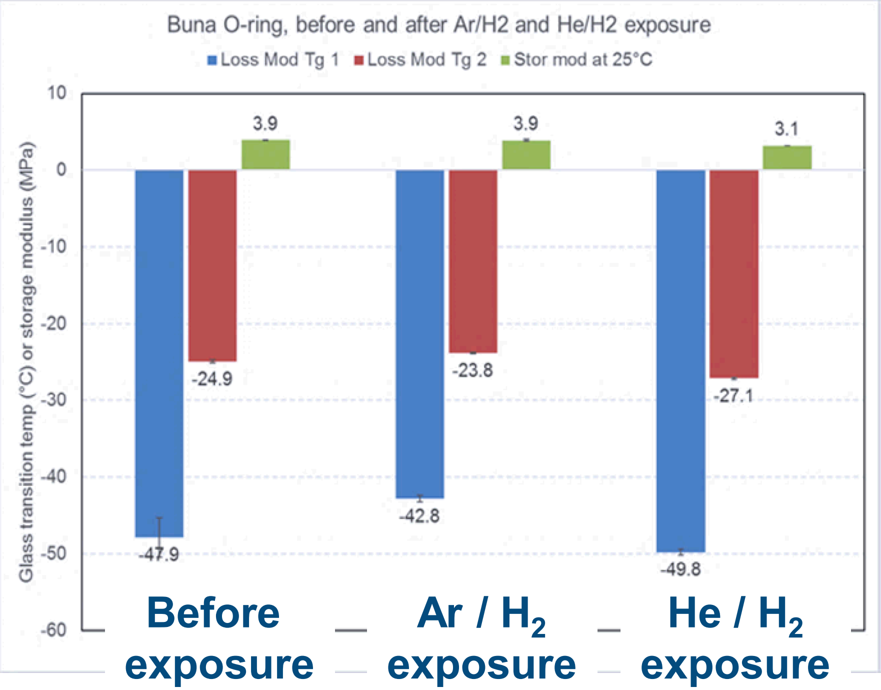


Storage modulus and T_g measurements

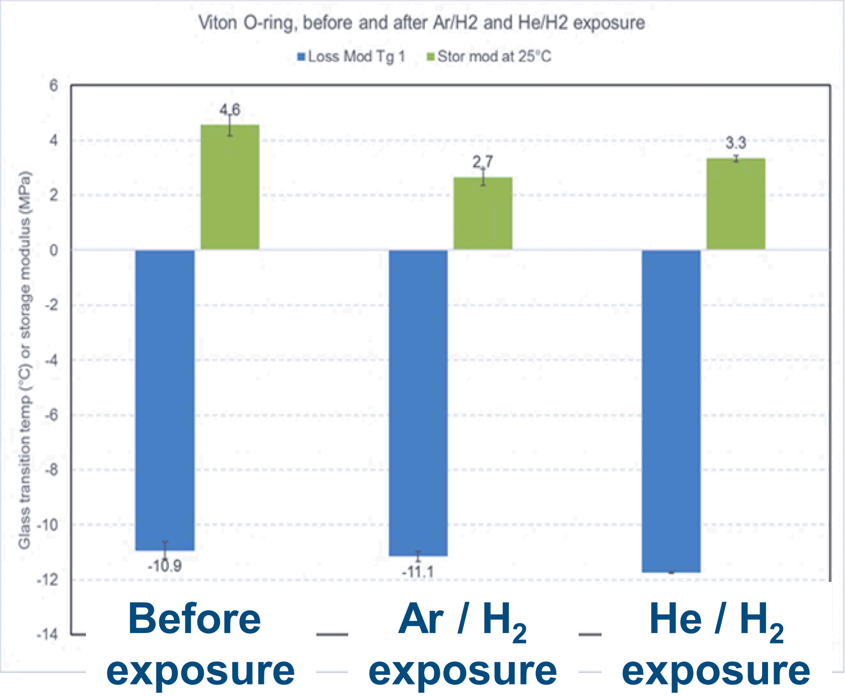
	Before exposure		After Ar / H_2 exposure		After He / H_2 exposure	
Polymer properties	T_g (˚C)	Storage Modulus (MPa)	T_g (˚C)	Storage Modulus (MPa)	T_g (˚C)	Storage Modulus (MPa)
Buna N	-36	3.9 ± 0.0	-43	3.9 ± 0.2	-39	3.1 ± 0.0
Viton A	-11	4.6 ± 0.4	-11	2.7 ± 0.3	-12	3.3 ± 0.1
EPDM	-48	4.1 ± 0.4	-49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

Storage modulus changes for elastomers

Buna N



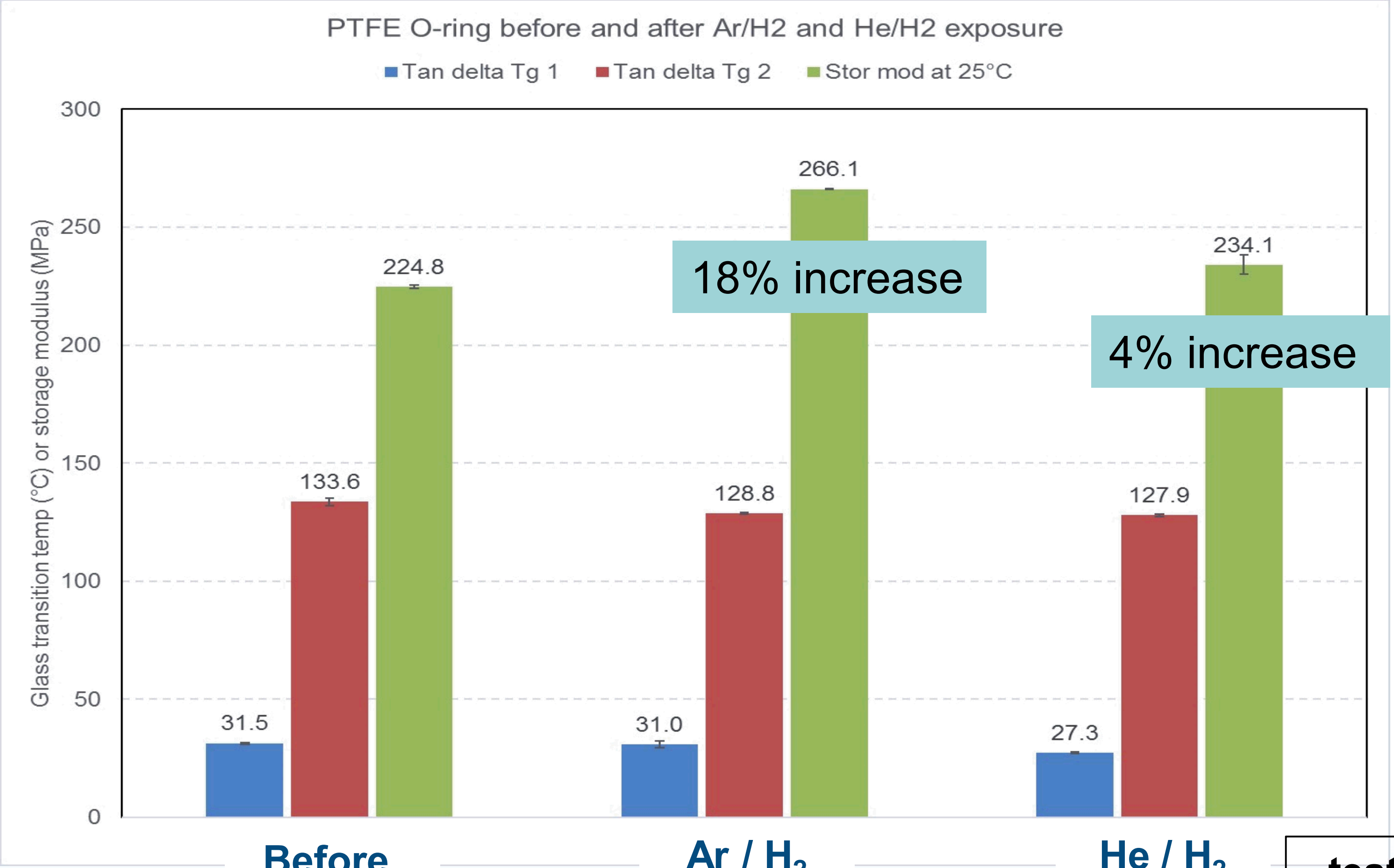
Viton A



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

test conditions
0.1% strain
1 Hz
5°C/minute

Storage modulus changes for PTFE



18% increase

4% increase

Before exposure

Ar / H_2 exposure

He / H_2 exposure

test conditions
0.1% strain
1 Hz
5°C/minute

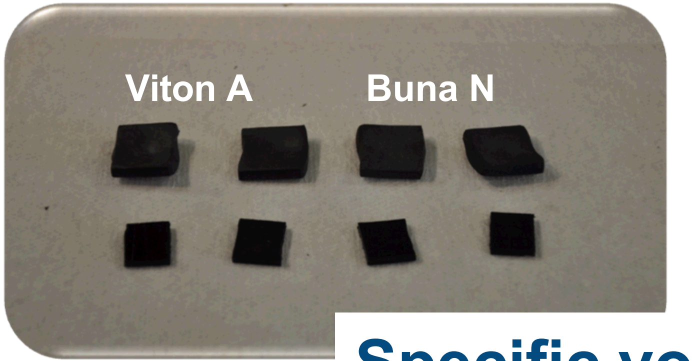
Compression set of elastomers

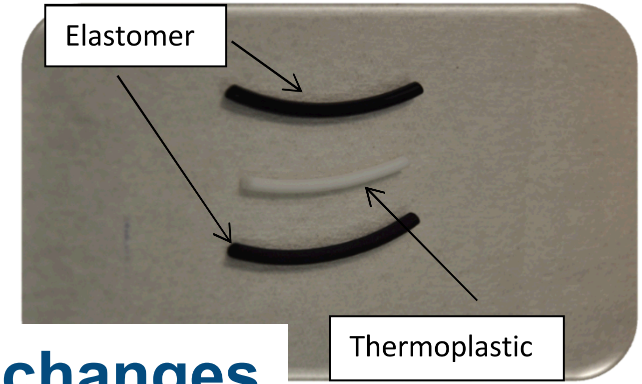
Polymer	Before exposure	Ar / H_2 exposure	He / H_2 exposure
Buna N	14%	22%	15%
Viton A	5%	28%	9%
EPDM	7%	8%	Did not test

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


Compression Set Jig

Swelling in elastomers and thermoplastics



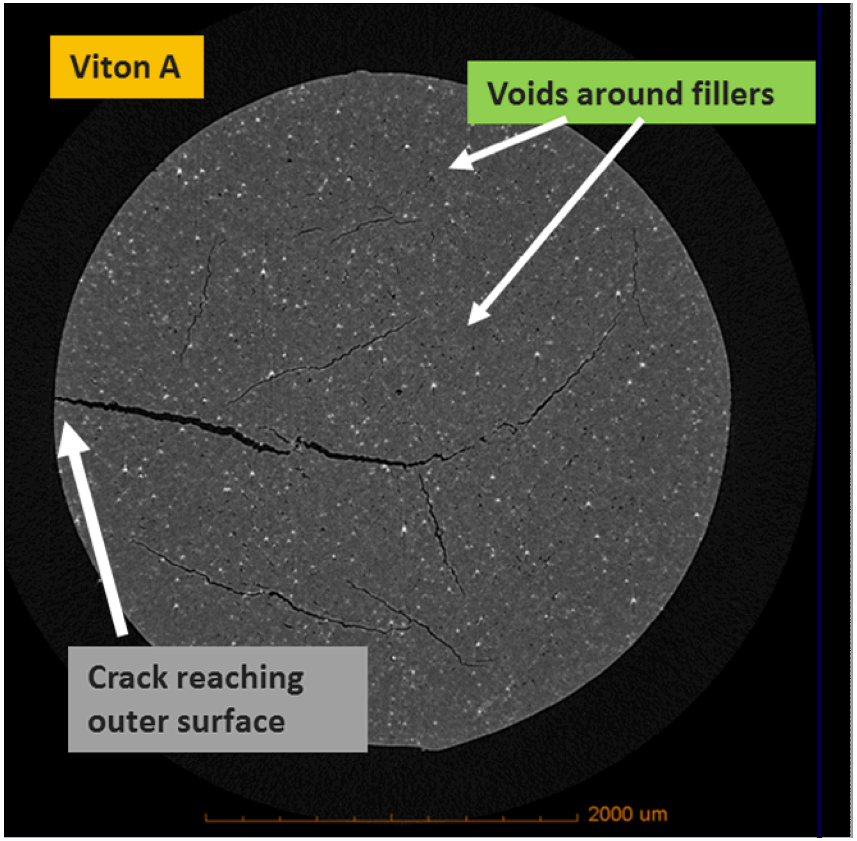


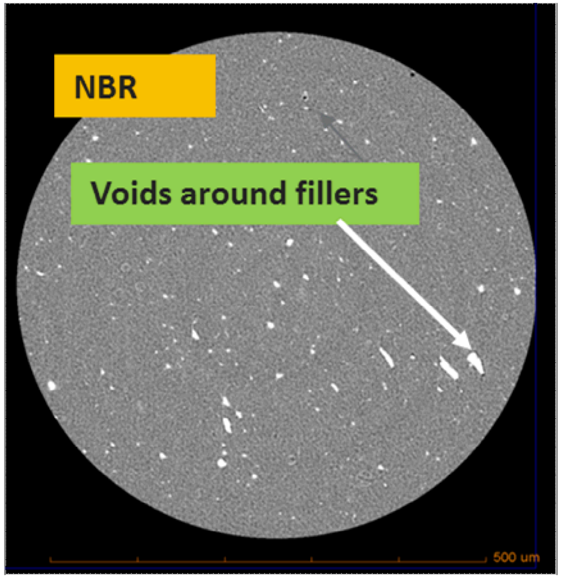
Specific volume changes

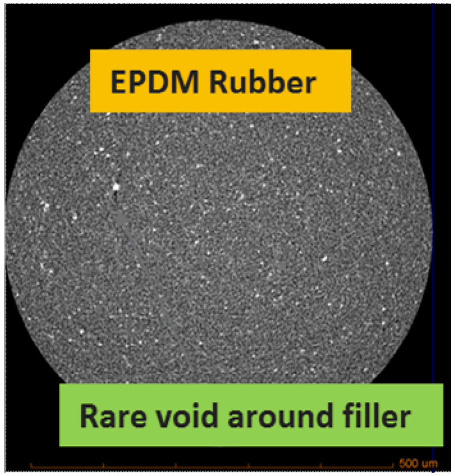
Polymer	Ar / H_2 exposure	He / H_2 exposure
Buna N	14%	74%
Viton A	34%	34%
EPDM	2%	TBD
Nylon 11	0%	TBD
PTFE	-4%	0%
POM	0%	TBD

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

Micro-CT reveals voids and cracks in elastomers after Ar/H_2 exposure

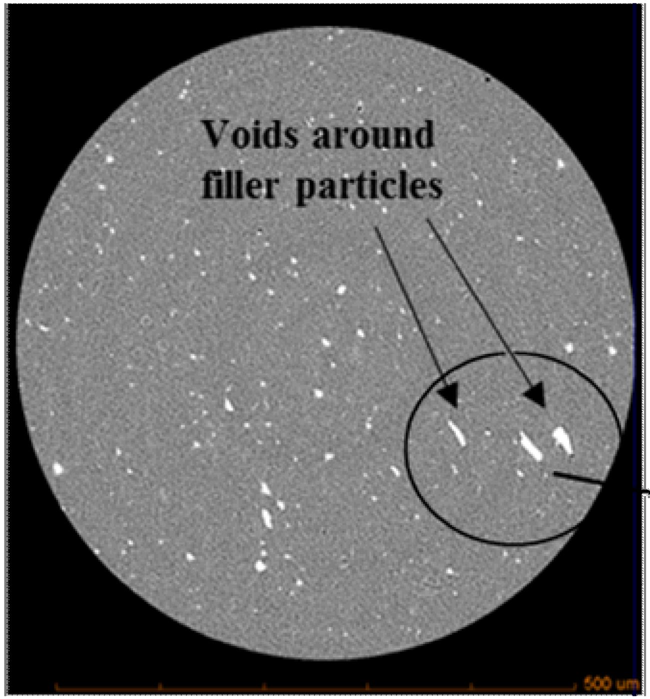






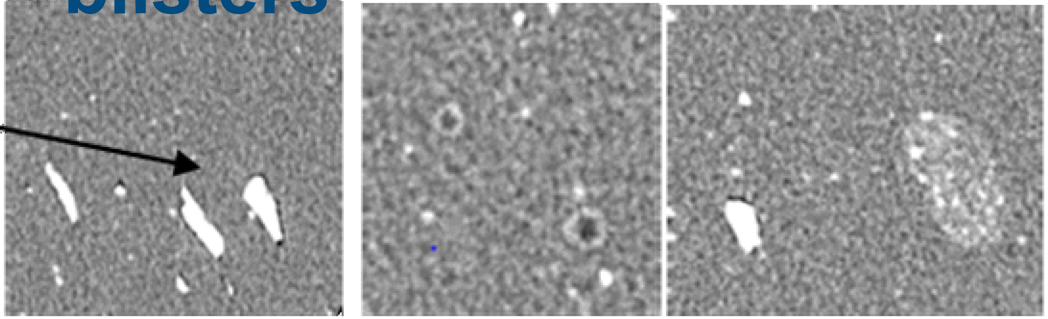
NBR and EPDM at higher magnification show voids around fillers

Micro-CT reveals damage in Buna N after Ar/H_2 exposure



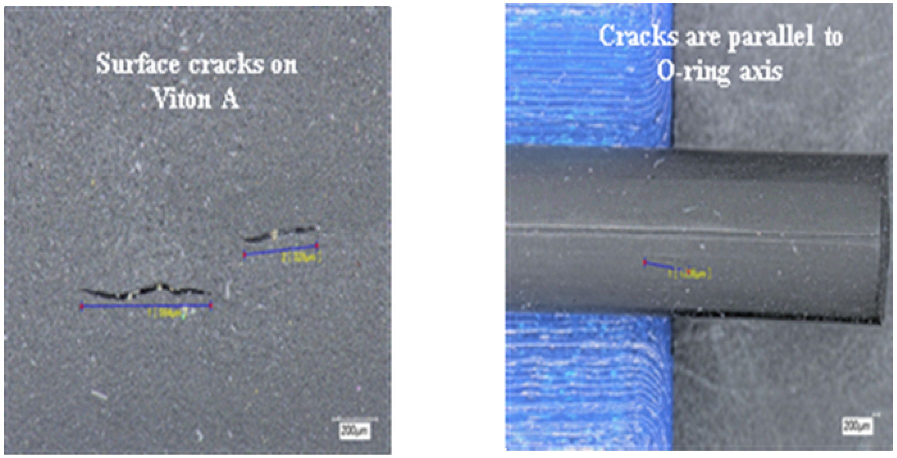
Several types of damage are evident in Buna N

- Voids around filler particles
- Voids in the matrix
- blisters

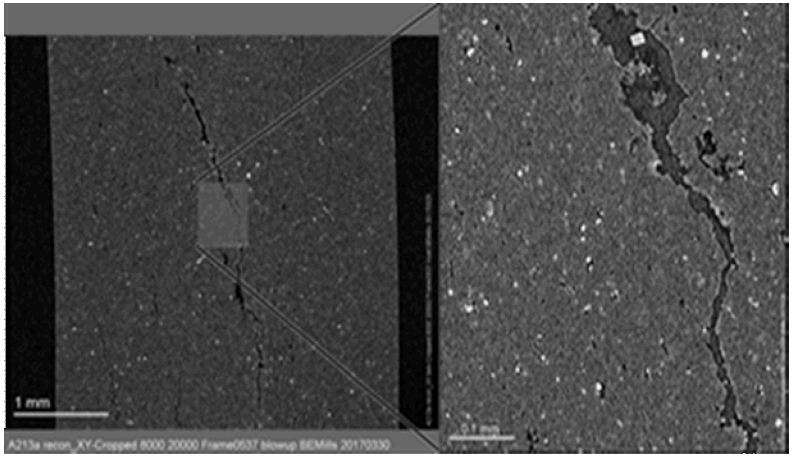


Damage not observed in Buna N after He/H2 exposure

Formation of voids and cracks in Viton A

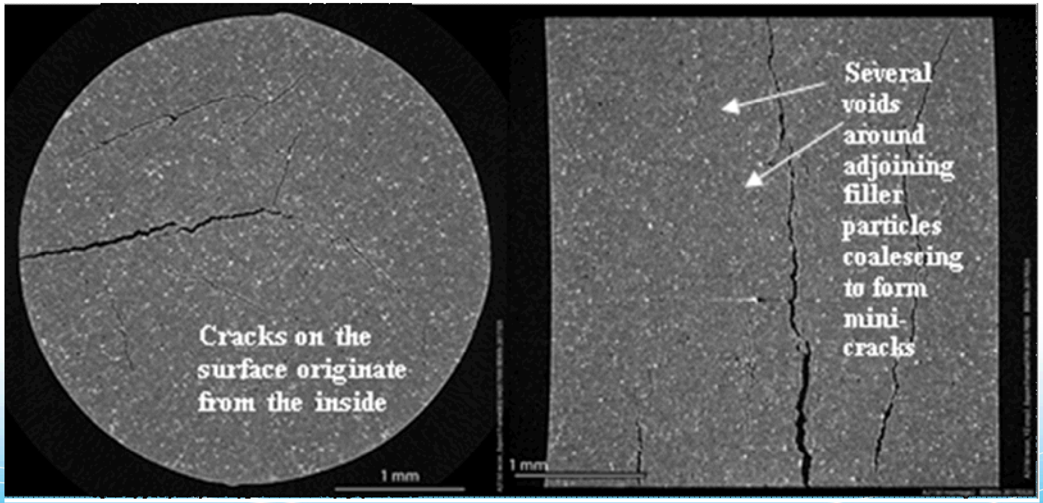


Cracks parallel to O-ring axis on the surface after Ar/H_2 exposure



Large cracks extend from smaller cracks after Ar/H_2 exposure

- Voids appear to nucleate around filler particles and coalesce to form microcracks in Viton A after Ar/H_2 exposure
- Some voids at fillers after He/H_2 exposure



Summary

Polymer property	Maximum Effects seen in gas environments	
	Argon/Hydrogen	Helium/Hydrogen
Swelling	74% volume increase 100% recovery in 48 hrs for Buna N	36% volume increase 90% recovery in 48 hrs for Viton A
Storage Modulus	41% decrease for Viton A	20% decrease for Buna N
Compression set (Elastomers only)	5 times increase for Viton A	1.6 times increase for Viton A
Damage evolution	Severe damage in Viton A; significant damage in Buna N and EPDM	Voids around some fillers in Viton A; 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

The observed behaviors can be rationalized based on the basic character of the gases and the materials

- Structural changes in the polymers were not observed, therefore behaviors appear to be governed by damage evolution and accumulation
- Damage appears to evolve from formation of voids within the polymer
  - Presumably due to precipitation of dissolved gases when the overpressure is removed (ie during decompression)
- Damage coalesces into microcracks in advanced stages of damage evolution
- Damage evolution should depend on the materials microstructure as well as on the character of the gases
  - Atomic size: Ar > H_2 > H2
  - Diffusivity: He > H_2 > Ar
  - Solubility: Ar > H_2 > He

Conclusions

- Ar/H_2 exposure appears to result in more damage than He/H_2 exposure
  - Slow diffusion of Ar, combined with greater solubility results in void formation during decompression
  - In contrast, He moves rapidly and has comparatively lower solubility, resulting in less damage
- Viton A displays more damage than Buna N or EPDM
  - More highly crosslinked microstructure can resist damage as observed for thermoplastics as well as Buna N and EPDM
- The presence of fillers and the strength of the bond between the filler and the polymer matrix will likely also affect damage evolution
- Other characteristics can also be explained by the evolution or lack of damage

Future steps: Addressing knowledge gaps for polymers in H_2

- Pressure cycling of polymers at high pressure with the goal of characterizing damage accumulation and understanding mechanisms of failure (RGD)
- Materials design to mitigate effects of pressure cycling on polymeric materials for use in hydrogen technologies

Thank you for your attention.

Questions?

Technical Back-Up Slides

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: SAND2013-8904, Literature review by Sandia National Laboratories, Livermore CA)