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BEHAVIOR OF POLYMERS IN HIGH PRESSURE ENVIRONMENTS AS APPLICABLE TO THE HYDROGEN INFRASTRUCTURE

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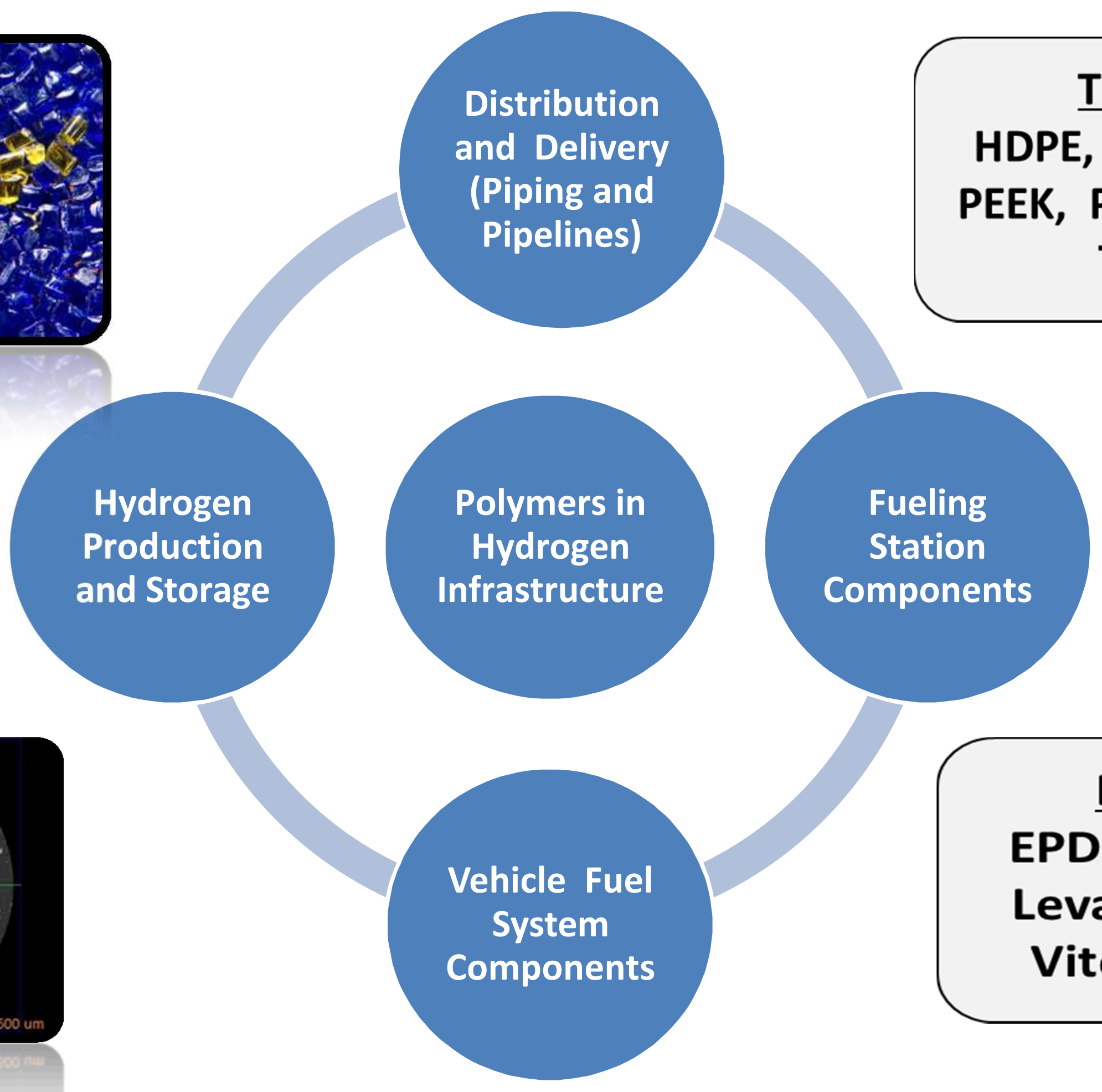
ABSTRACT

Polymeric materials have played a significant role in the adoption of a multi-materials approach towards the development of a safe and cost-effective solution for hydrogen fuel storage in Fuel Cell Vehicles (FCVs). Numerous studies exist with regards to the exposure of polymeric materials to gaseous hydrogen as applicable to the hydrogen infrastructure and related compression, storage, delivery and dispensing operations of hydrogen at fueling stations. However, the behavior of these soft materials under high pressure hydrogen environments has not been well understood. This study involves exposure of select thermoplastic and elastomeric polymers to high pressure hydrogen (70-100 MPa) under static, isothermal, and isobaric conditions followed by characterization of physical properties and mechanical performance. Special attempt has been made to explain hydrogen effects on polymer properties in terms of polymer structure-property relationships, and understand the relationships between polymer composition and microstructure, time of exposure, rate of depressurization, purge and exposure conditions, etc.

POLYMERS IN HYDROGEN INFRASTRUCTURE



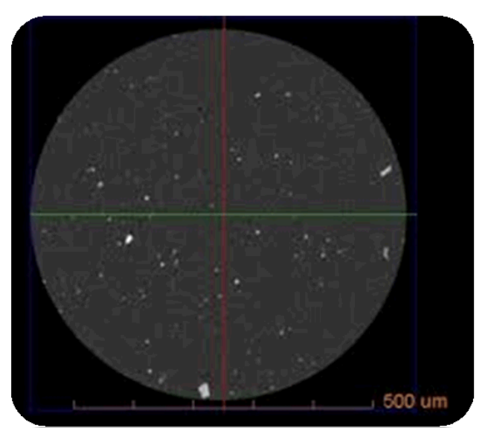
Distribution and Delivery (Piping and Pipelines)

Hydrogen Production and Storage

Polymers in Hydrogen Infrastructure

Fueling Station Components

Vehicle Fuel System Components



<u>Thermoplastics</u>
HDPE, Polybutene, Nylon, PEEK, PEKK, PET, PEI, PVDF, Teflon, PCTFE

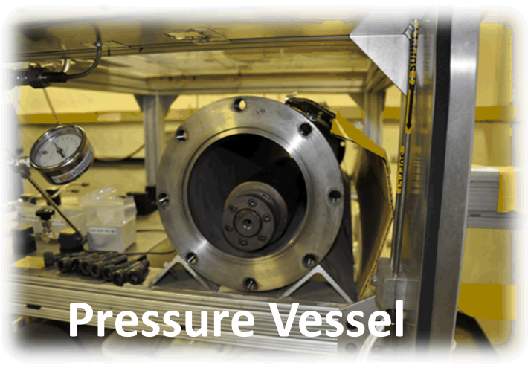
<u>Thermosetting polymers</u>
Epoxy, PI, NBR, Polyurethane

<u>Elastomers</u>
EPDM, NBR/HNBR Levapren, Silicone, Viton, Neoprene

TECHNICAL SCOPE OF CURRENT STUDY

- Four polymers selected based on stakeholder interest:
  - High Density Polyethylene (HDPE) Polytetrafluoroethylene (PTFE) - Thermoplastics
  - Viton A (Fluoroelastomer), and Buna N (Nitrile Butadiene Rubber) - Elastomers
- Investigation of the behavior of these polymers in a static, isobaric high pressure hydrogen environment (100 Mpa) under isothermal (RT/25˚C) conditions was completed
- Influence of hydrogen exposure on polymer properties such as modulus, glass transition temperature (T_g), density, compression set, tensile strength was assessed for given conditions
- Fundamental polymer micro-structure and performance property relationships identified in polymer responses to hydrogen exposure under test conditions

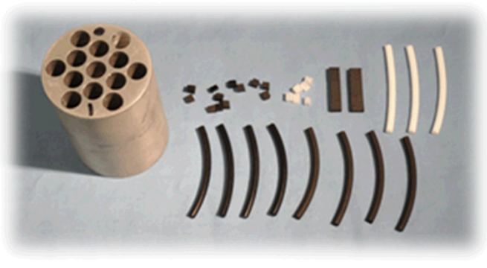
EXPERIMENTAL DETAILS



Pressure Vessel

Specimen details:

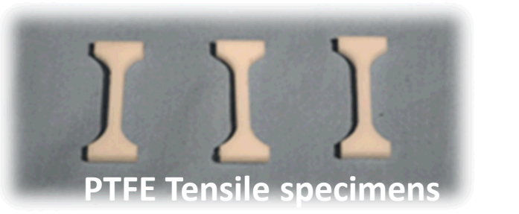
- Molded specimens (O rings, gaskets) vs. sheets; off the shelf grades
- All specimens were kept at 3 mm (0.12 inches) thickness regardless of other dimensions
- No pre-treatment of elastomers before exposure
- Thermoplastic specimens of HDPE and PTFE were annealed
  - HDPE: 25˚C to 93˚C at 1˚C/minute, held at 93˚C for 28 minutes, and then cooled to RT at 0.5˚C/minute
  - PTFE: 25˚C to 273˚C at 1˚C/minute, held at 273˚C for 23 minutes, and then cooled to RT at 0.5˚C/minute



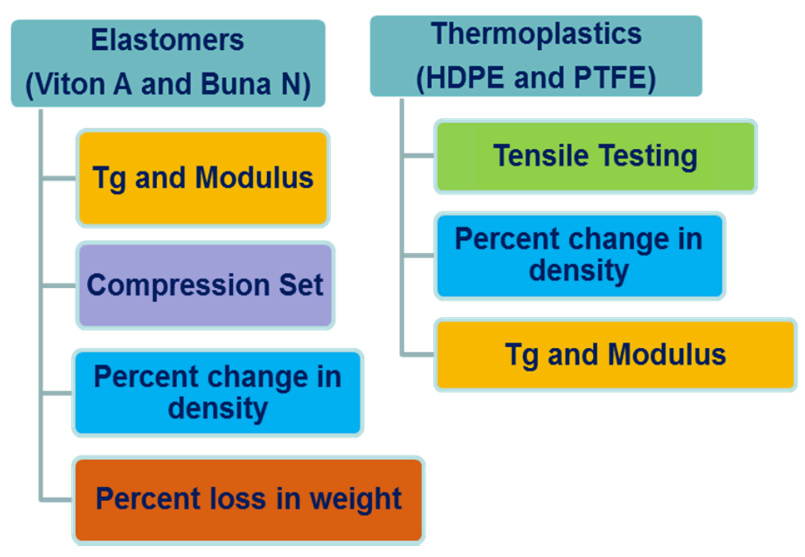
Specimens cut from O rings, sheets and gaskets of various polymers

Testing details:

- Static isobaric (100 Mpa) of hydrogen exposure, under isothermal (25ºC) conditions
- Time of hydrogen exposure: 1 week for saturation of 3 mm thick specimens for all polymer types (calculated based on Sandia National Laboratories Code, M.I. Baskes, DIFFUSE 83, SAND83-8231, 1983)
- Specimens were characterized after exposure to hydrogen



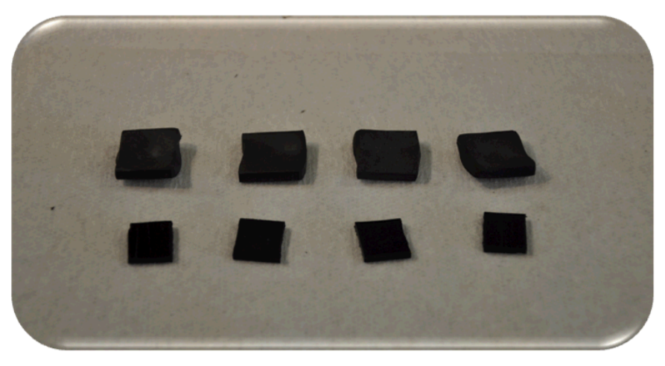
PTFE Tensile specimens



Elastomers (Viton A and Buna N)
- Tg and Modulus
- Compression Set
- Percent change in density
- Percent loss in weight

Thermoplastics (HDPE and PTFE)
- Tensile Testing
- Percent change in density
- Tg and Modulus

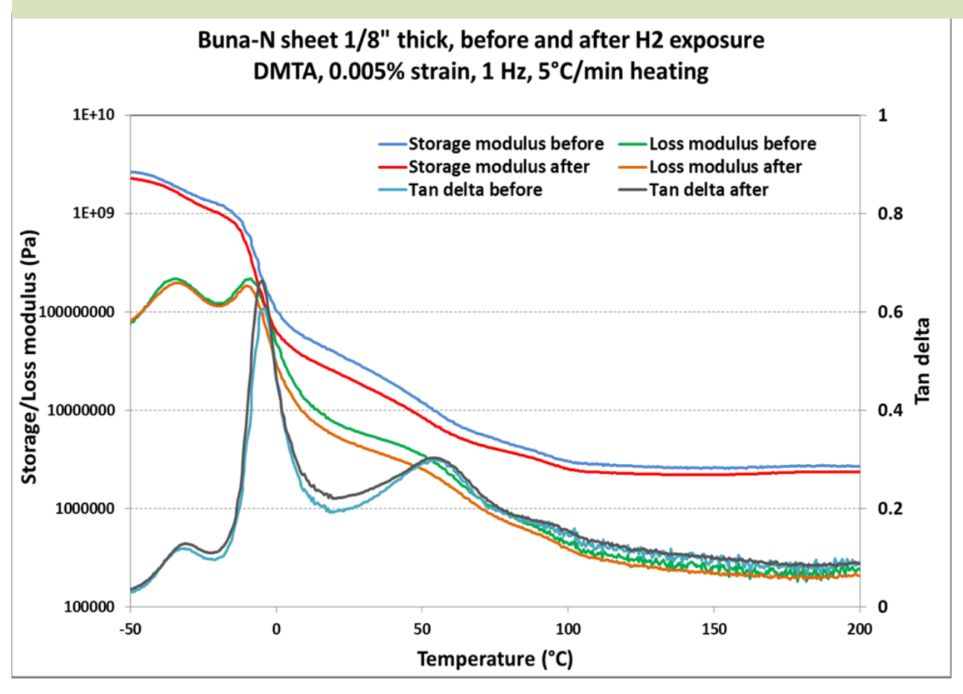
TEST DATA FOR ELASTOMERS AND THERMOPLASTICS

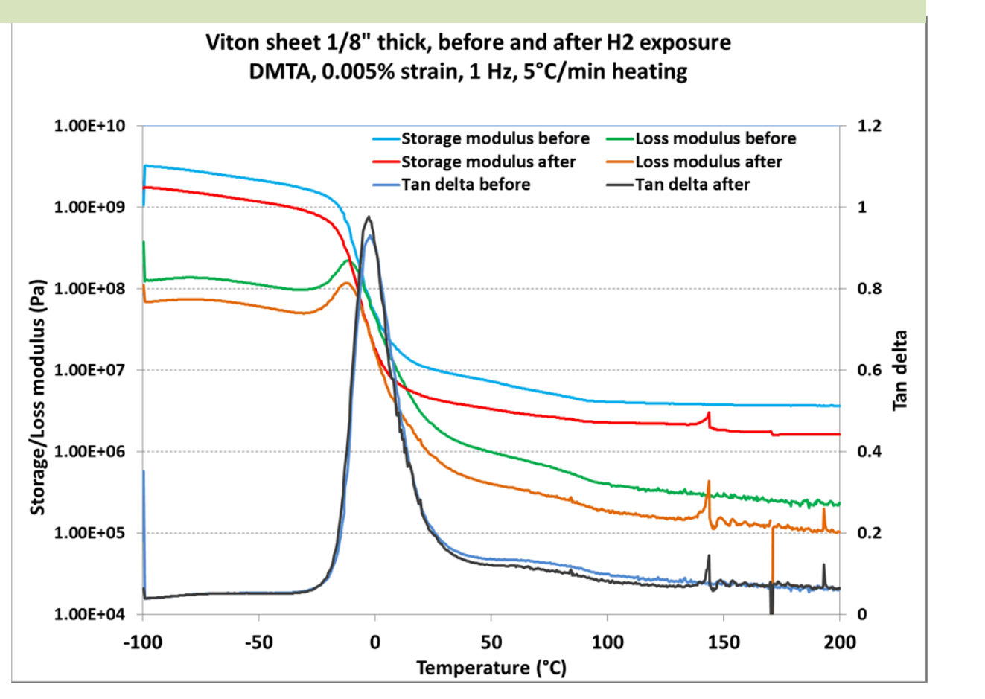


Swelling seen with elastomers :
Before hydrogen (bottom row)
After hydrogen exposure (top row)
No RGD seen because of less cycles

Polymer	Percent Change in Volume per gram upon Hydrogen exposure	
	Immediately after Removal	48 hours after Removal
Buna N Sheet	57.2%	3.9%
Buna N O-ring	22.6%	0.2%
Viton A Sheet	69.0%	11.5%
Viton A O-ring	37.1%	0.8%
Viton A gasket	114.3%	7.0%

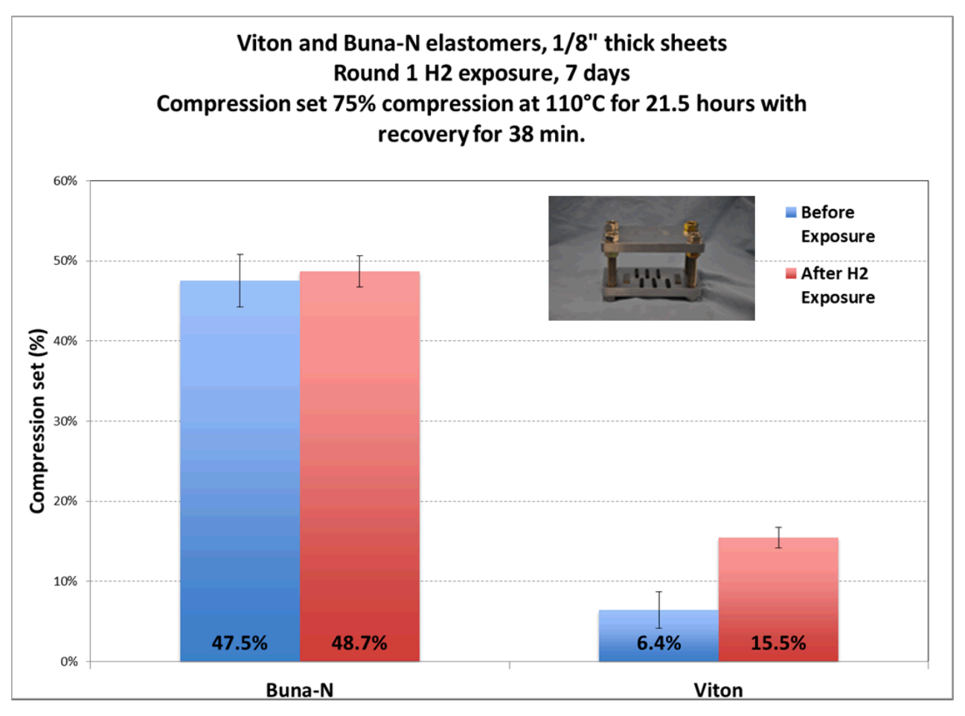
DMTA DATA FOR ELASTOMERS BEFORE AND AFTER HYDROGEN EXPOSURE

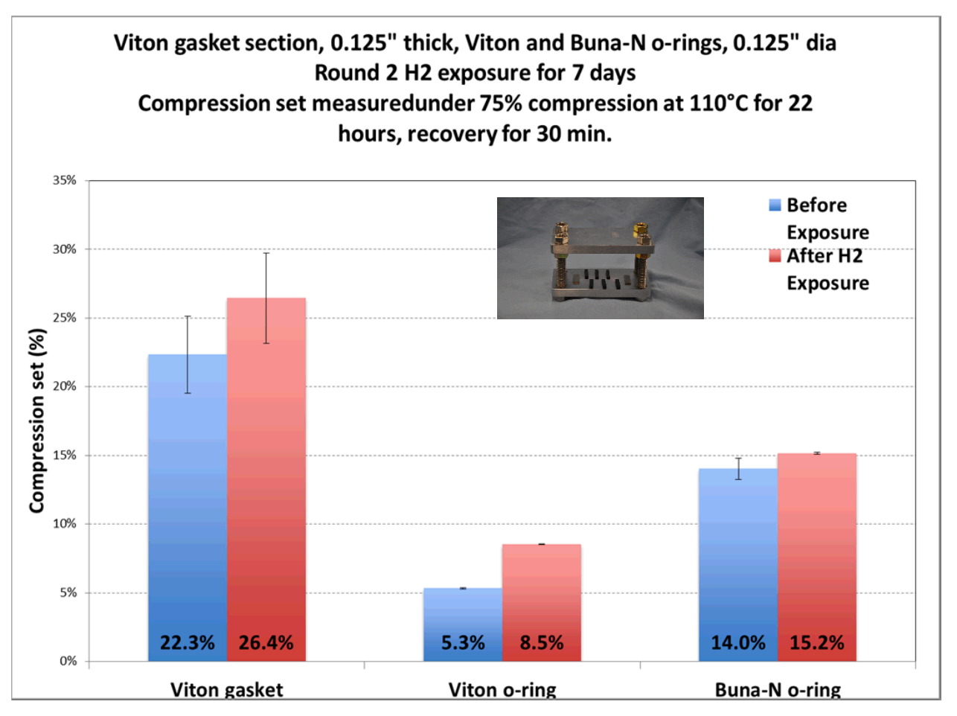

Buna-N sheet 1/8" thick, before and after H2 exposure
DMTA, 0.005% strain, 1 Hz, 5°C/min heating


Viton sheet 1/8" thick, before and after H2 exposure
DMTA, 0.005% strain, 1 Hz, 5°C/min heating

- In case of elastomers, free chain rotations, easy mobility of long polymer chains EQUALS significant free volume allowing easy diffusion of hydrogen into the polymer
- Buna N : unsaturated highly crosslinked
  Viton A : saturated slightly crosslinked
- Viton allows more hydrogen permeation and can also be retaining a significant % compared to Buna N
- Therefore, modulus of Viton A drops more than that of Buna N

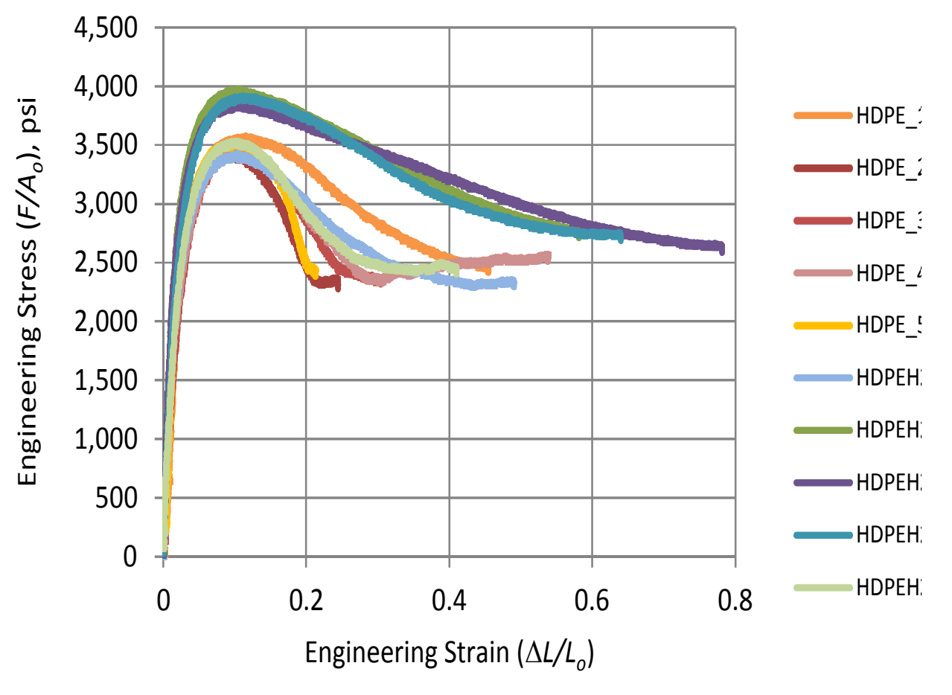
COMPRESSION SET FOR ELASTOMERS BEFORE AND AFTER HYDROGEN EXPOSURE


Viton and Buna-N elastomers, 1/8" thick sheets
Round 1 H2 exposure, 7 days
Compression set 75% compression at 110°C for 21.5 hours with recovery for 38 min.

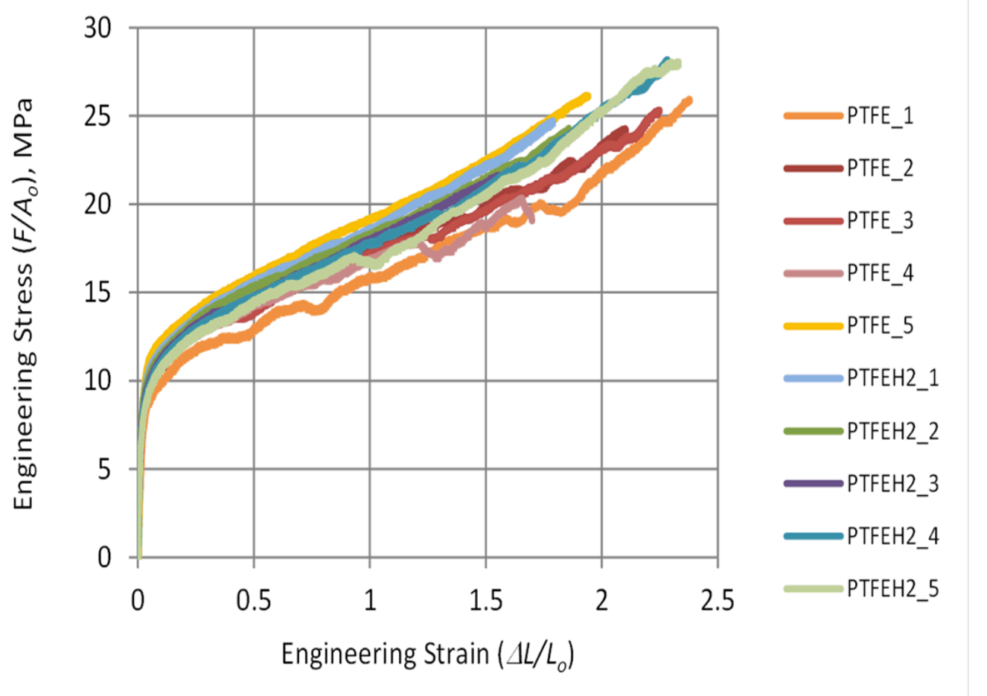

Viton gasket section, 0.125" thick, Viton and Buna-N o-rings, 0.125" dia
Round 2 H2 exposure for 7 days
Compression set measuredunder 75% compression at 110°C for 22 hours, recovery for 30 min.

- Compression set is important for seals and O rings in the hydrogen infrastructure
- Viton A shows 60% whereas Buna N shows 9% increase in compression set
- Viton A, being less crosslinked, allows more hydrogen permeation compared to Buna N
- In the compression set (heating to 110C for 22 hours under 25% deflection), the softer Viton A shows higher set in the sheet form than for gasket or O ring forms
- Buna N shows higher compression set in a sheet form compared to O ring
- The above hydrogen effects has to do with fillers and their alignment in the different forms and the materials response to hydrogen

TENSILE STRENGTH FOR THERMOPLASTICS BEFORE AND AFTER HYDROGEN EXPOSURE



HDPE



PTFE

- Thermoplastics, in general, show less hydrogen effects than elastomers
- The modulus and T_g changes are minimal with hydrogen exposure
- Percent change in volume (swelling) is not seen as much as with elastomers except in the form of formation of blisters in the bulk (seen as increased opacity)
- Tensile modulus goes up for both HDPE and PTFE
- HDPE fails in the elastic mode vs PTFE which fails in the plastic mode
- HDPE fails at a higher stress after hydrogen exposure than before due to possible ordering or alignment of polymer chains under hydrogen pressure
- Bulky fluorine atoms on the PTFE backbone does not permit the alignment

EXECUTIVE SUMMARY OF RESULTS

- Polymer structure-property relationships and permeability 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 (From DMTA)
  - significant change in densities with recovery afterwards (swelling) (ASTM D792-13)
  - increased compression set (ASTM D395 Method B)
- Thermoplastics did not exhibit significant changes with hydrogen, except for mechanical properties
  - Young’s Modulus 35% higher for PTFE and 15% higher for HDPE (ASTM D 638-14)
  - HDPE exhibited more cold-drawing (plastic deformation) after hydrogen exposure than before
  - HDPE exhibited changes in the crystalline regions after hydrogen exposure; degree of crystallinity unchanged, lamellar orientation changed (XRD)
  - PTFE failed in the elastic region before and after hydrogen exposure

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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