

# Polymer compatibility in high pressure static and cycling hydrogen for hydrogen infrastructure applications




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PRESENTED BY

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- Polymers in the hydrogen infrastructure
  - Distribution and Delivery (Piping and Pipelines)
  - Storage and Transportation
  - Fueling/dispensing stations
  - Vehicle fuel Systems



- Present as liners and sheath materials for storage tanks and pipelines, as flexible hoses, as O-rings, gaskets in pistons, regulators and other fittings



#### Thermoplastics

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

#### Elastomers

EPDM, NBR, HNBR, EVM, Silicone, Viton, Neoprene

- Conditions of high pressures (875 bar/~13,000 psi) and rapid cycling of temperatures (-40°C to +85°C) possible during service

#### H-MAT Tasks

**Task P1**  
Mechanisms of hydrogen-induced degradation of polymers

**Task P2**  
Computational multiscale modeling

**Task P3**  
Hydrogen-resistant polymeric formulations

#### CRITICAL GAPS

Degradation failure modes  
Explosive decompression  
Transport properties Friction and wear  
Fracture and fatigue

#### VARIABLES

Polymer sources  
Polymer types  
Composition (additives)  
Compounding methods  
Environments (cycling)

#### MODELING

Atomistic scale  
Micro scale  
Phase Field  
Modeling  
Continuum scale

### Summary of high pressure hydrogen exposures

- Polymers were exposed to high pressure hydrogen under static and cycling conditions cycling H<sub>2</sub>
  - one week-long exposure to static high pressure (100 MPa) @ ambient temperature
  - 100 cycles, 86 MPa to 17 MPa and back, ambient temperature, rate of pressurization = 13.79 MPa/min; rate of depressurization = 2.29 MPa/min
- Ex-situ characterization of polymer physical and chemical properties
- Polymer microstructural changes to “hydrogen effects” and modes of failure, degradation analyses and lifetime prediction

#### Ex-situ characterization methods

•Hardness  
•Modulus  
•Volume changes

Density  
Nanoindentation

DMTA  
Mechanical Test

•Glass transition temperature  
•Storage and loss moduli  
•Tensile strength

NMR  
ATR-FTIR

XRD  
Micro CT

•Chemical structure in bulk  
•Chemical changes on the surface

•Expansion of free volume space  
•Changing orientation of polymer chains  
•Presence of cracks and voids

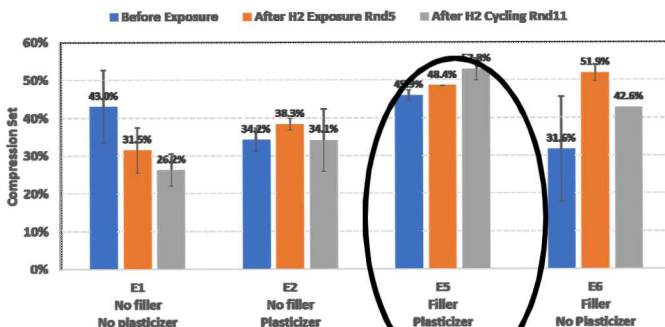


# Compatibility of elastomers in hydrogen

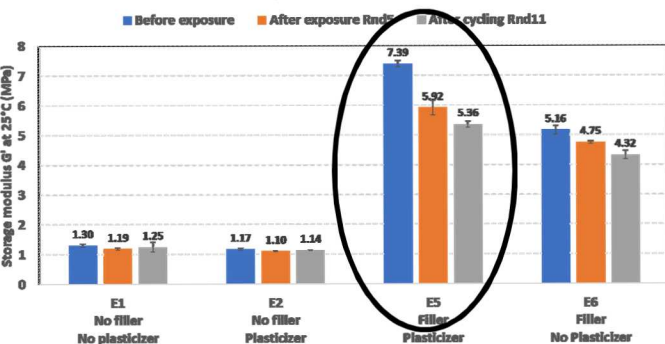


Nanoindentation

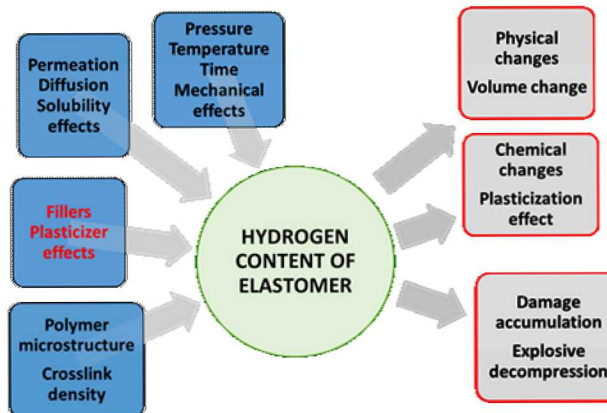
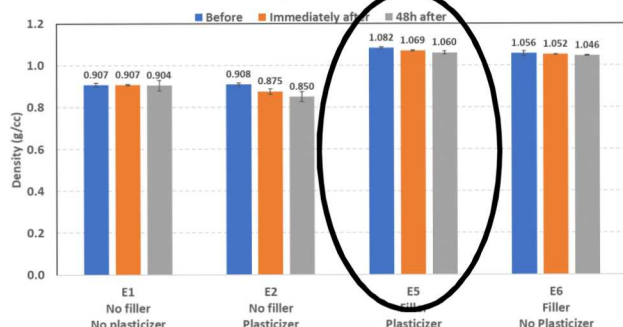
PNNL EPDM formulations  
effect of H<sub>2</sub> exposure (Rnd5) and H<sub>2</sub> cycling (Rnd11) on compression set  
Compressed to 75% for 22 hours at 110°C, recovered 30 minutes



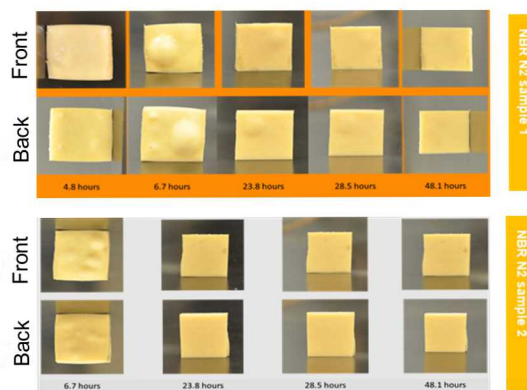
PNNL EPDM Formulations, effect of H<sub>2</sub> exposure (Rnd 5) and H<sub>2</sub> cycling (Rnd 11) on modulus  
DMTA, 1 Hz, 5°C/min, average of two specimens



H2 MAT Round 11, Takaishi EPDM, change in density after 100 cycles  
average of 2 specimens



#	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%



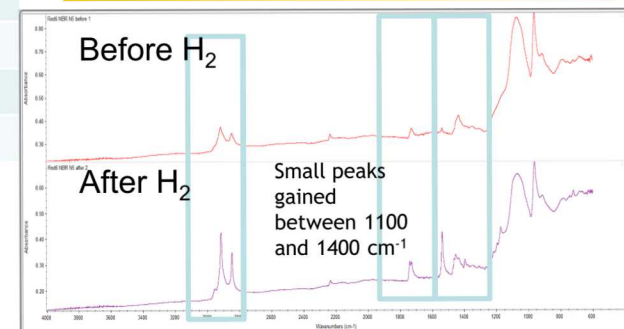
Picture showing the evolution of H<sub>2</sub> from NBR N2 over 48 hours

PNNL NBR N5	Avg Friction
Before H <sub>2</sub>	0.53±0.043
After H <sub>2</sub> cyclic	0.81±0.095
After H <sub>2</sub> static	0.81±0.101

PNNL EPDM E5	Avg Friction
Before H <sub>2</sub>	0.41±0.091
After H <sub>2</sub> cyclic	0.49±0.094
After H <sub>2</sub> static	0.63±0.095

FTIR of NBR showing chemical changes



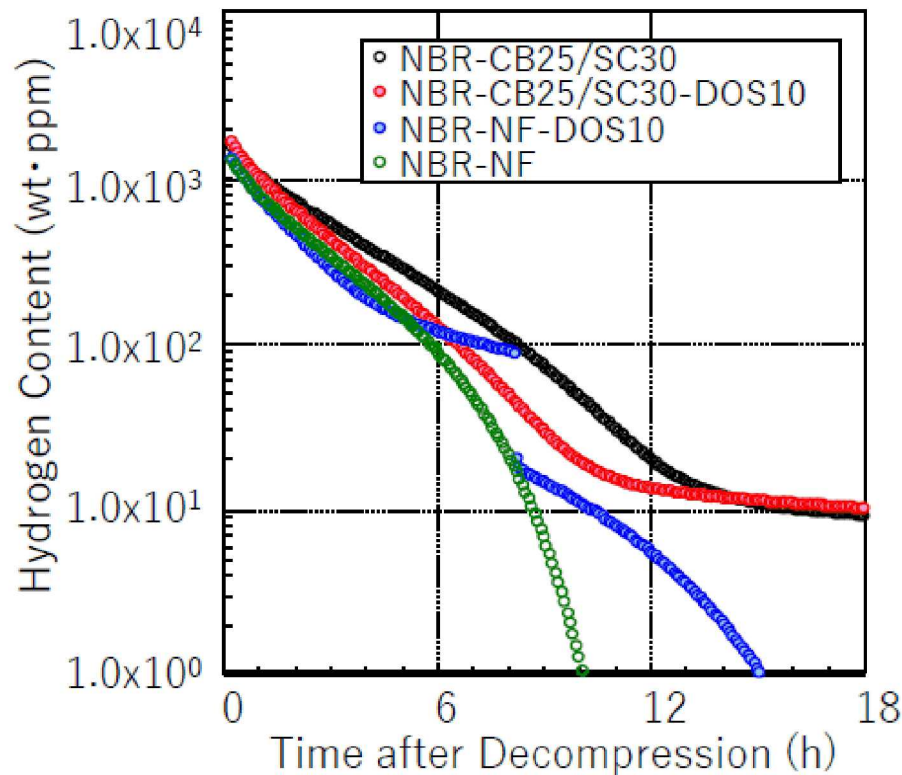
- Compression set increase indicates plasticization and softening of matrix
- Significant decrease in storage modulus and hardness indicates plasticization of matrix
- Filler-containing formulations show maximum change indicating interaction of carbon and silica with H<sub>2</sub>



# Compatibility of EPDM and NBR with $H_2$ environments

EPDM no filler

EPDM no



fewer cracks

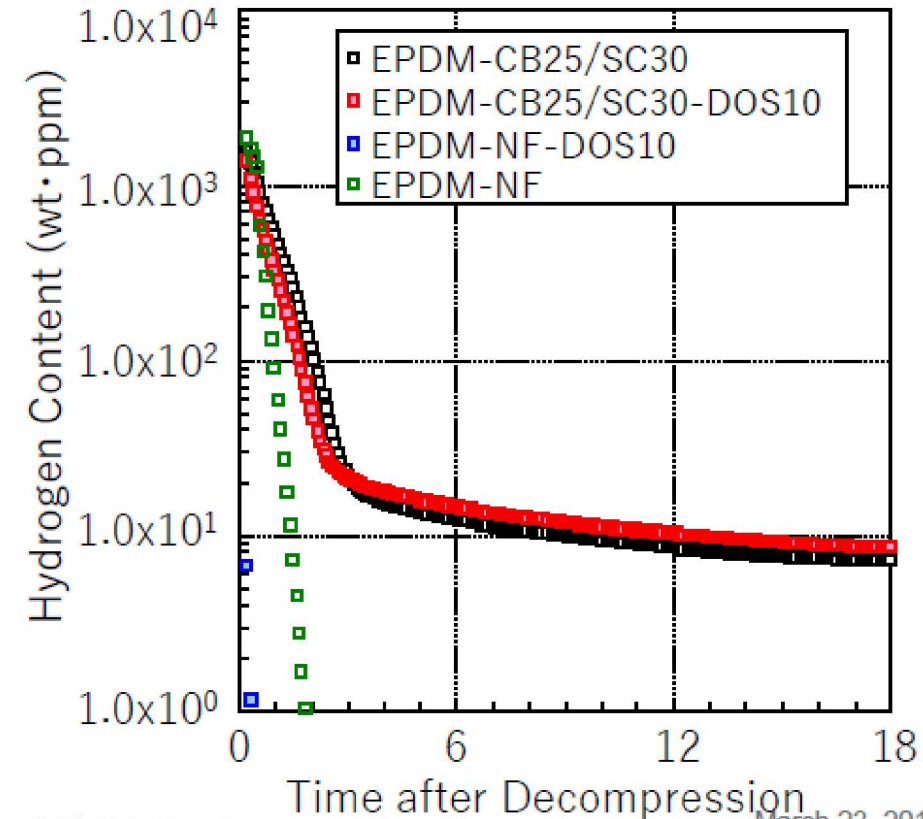
100  $\mu$ m

A3321

100  $\mu$ m

EPDM filler, no

EPDM filler,



voids

100  $\mu$ m

A3331

cracks

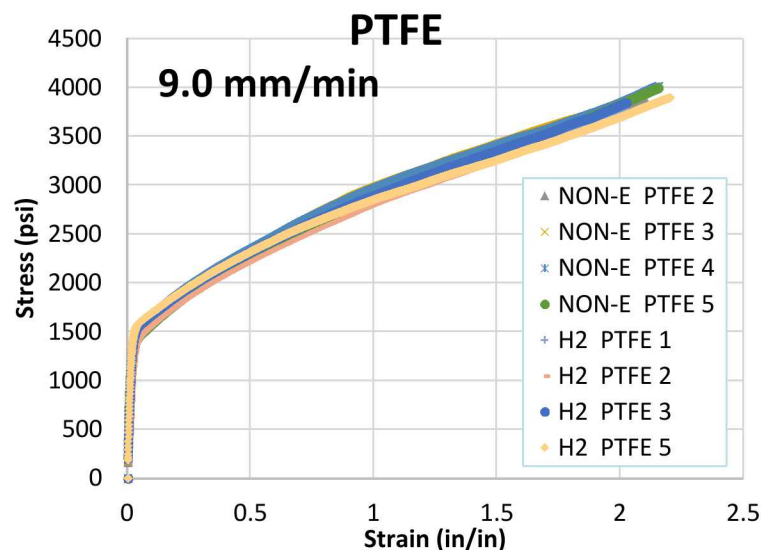
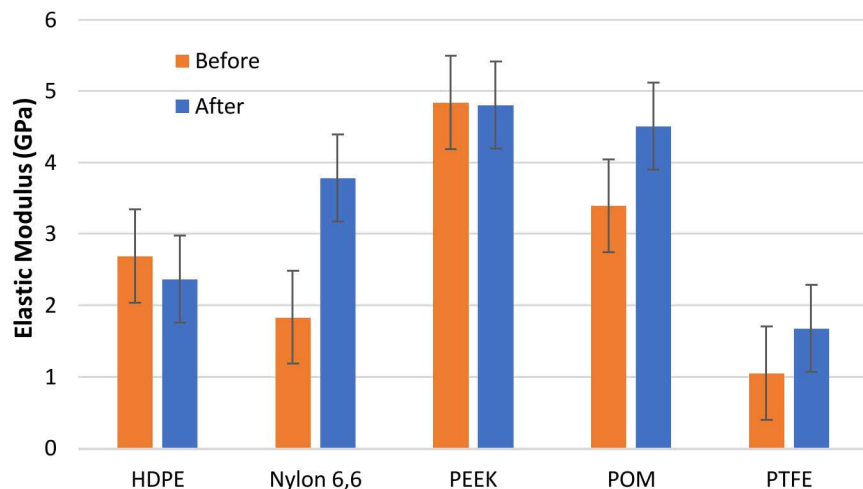
100  $\mu$ m

- Micro CT comparisons show differences in behavior of the two elastomers in  $H_2$
- Polymer compositions matter to  $H_2$ -resistance
- Fillers mitigate  $H_2$  effects in both elastomers

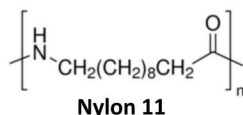
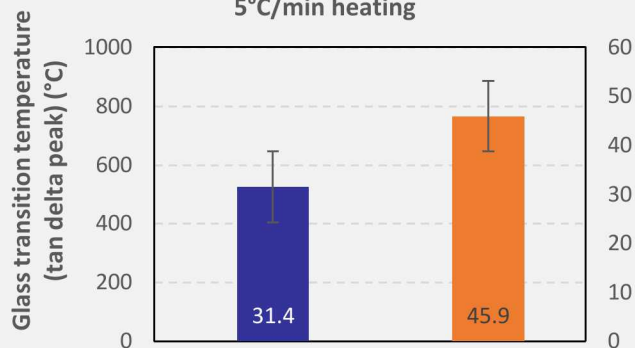


# Compatibility of thermoplastics: Change in mechanical properties

Elastic Modulus before and after 100 cycles H<sub>2</sub>

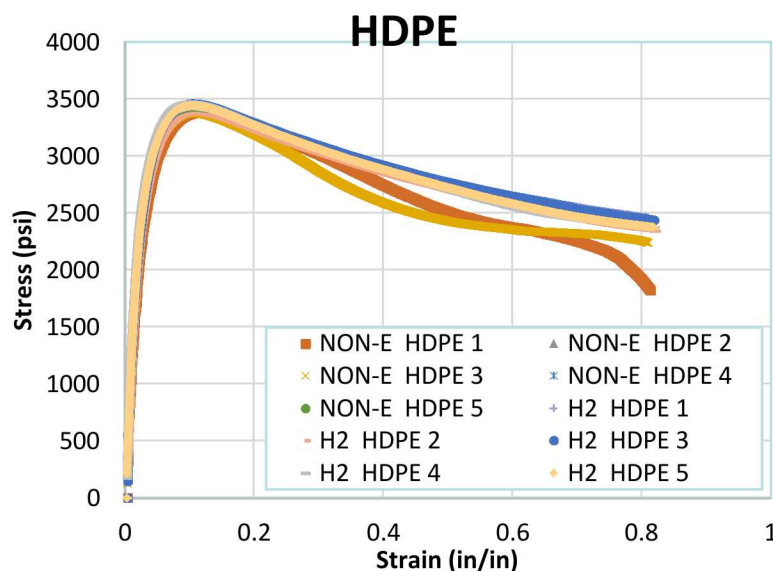


H<sub>2</sub> MAT Round 10, Nylon-11, 100 H<sub>2</sub> cycles  
DMTA Rectangular Torsion, 0.03% strain, 1 Hz,  
5°C/min heating



Most notable changes for physical properties of thermoplastics

T<sub>g</sub> changes due to H<sub>2</sub> exposure - 46% increase for Nylon 11  
Tensile strength does not change for PTFE and HDPE

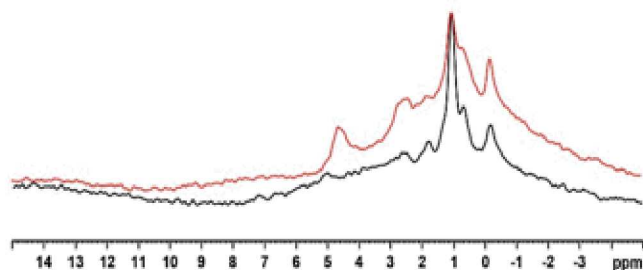




# NMR Analyses of thermoplastics for H<sub>2</sub> environments

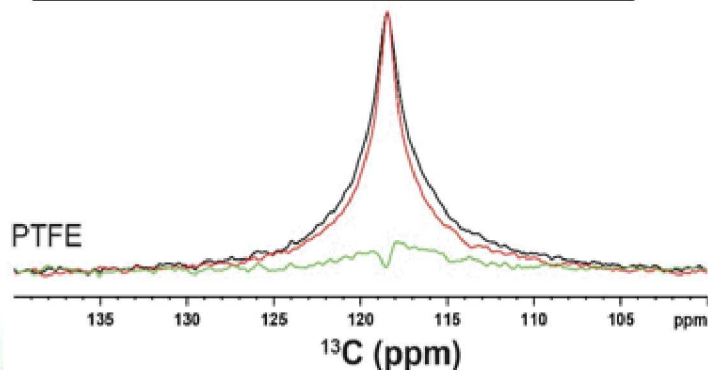


## Solid State <sup>1</sup>H MAS NMR of thermoplastics: 100 cycles of H<sub>2</sub>

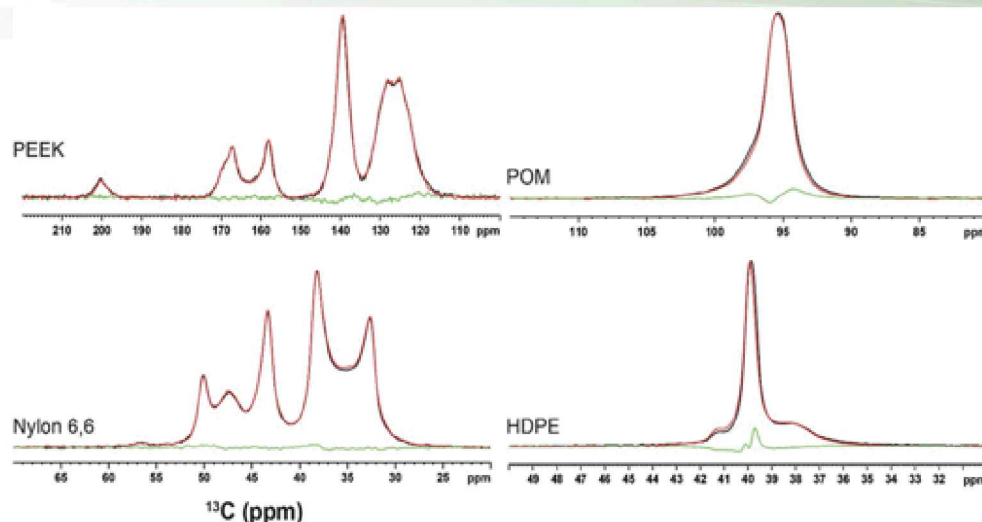


- <sup>1</sup>H NMR chemical shifts experimentally observed for these materials have resonances consistent with the H in the different materials
- There is a minor resonance at  $\delta = 4.3$  ppm that grows in with exposure in the PTFE.

## Solid state <sup>13</sup>C CPMAS NMR of PTFE

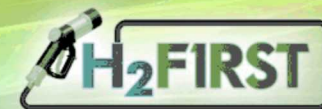


## Solid state <sup>13</sup>C CPMAS NMR of polymers



- The PEEK and Nylon-6,6 polymers revealed no differences due to exposure.
- Both the POM and PTFE polymers revealed a *minor* decrease in the line width (most notably in the PTFE) suggesting an increase in the mobile (amorphous fraction) for those polymers.
- The HDPE polymer also revealed some variation following exposure demonstrating small changes in the chain conformations for this polymer with exposure.
- All these changes are considered minor but may show up in subtle changes of the DMA analysis.

# Compatibility of thermoplastics in H<sub>2</sub> environments

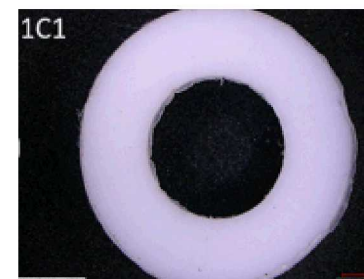


## XRD analyses after H<sub>2</sub>

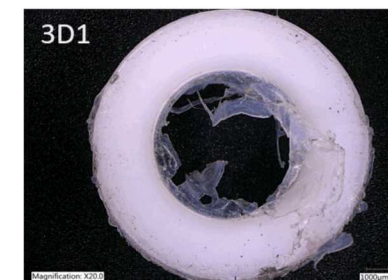
## FTIR analyses after H<sub>2</sub>

## Optical microscopy

PTFE in normally open valves before hydrogen

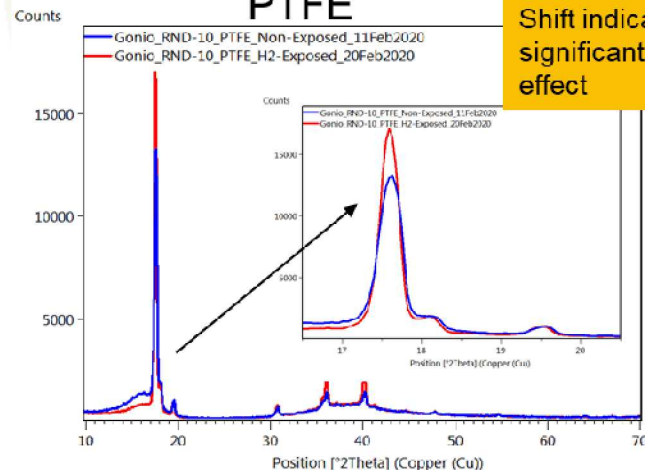


PTFE in normally open valves after hydrogen



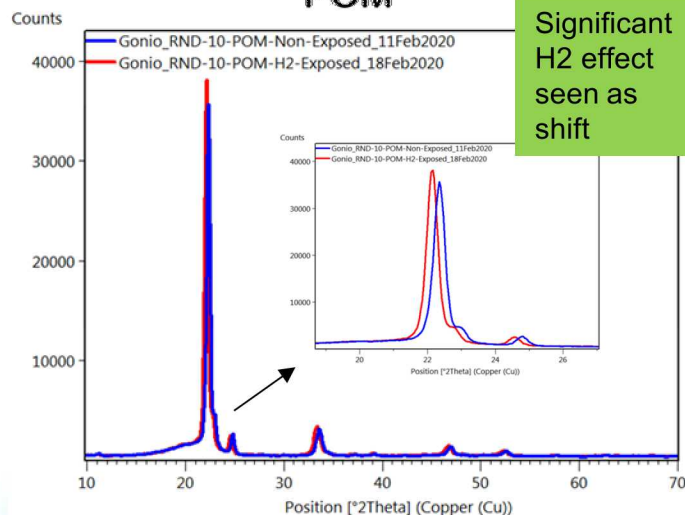
### PTFE

Shift indicates a significant H<sub>2</sub> effect

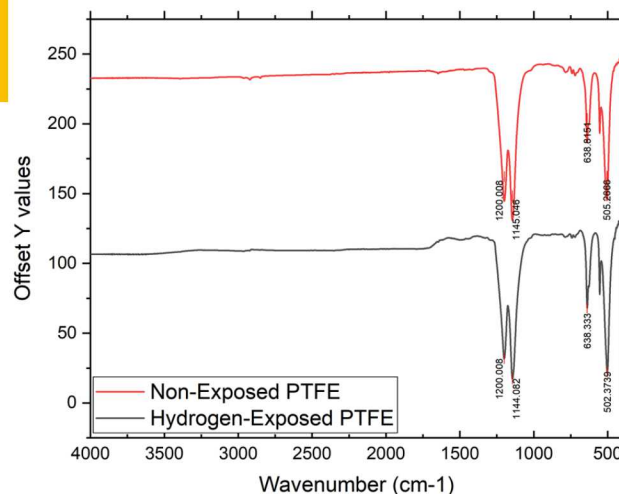


### POM

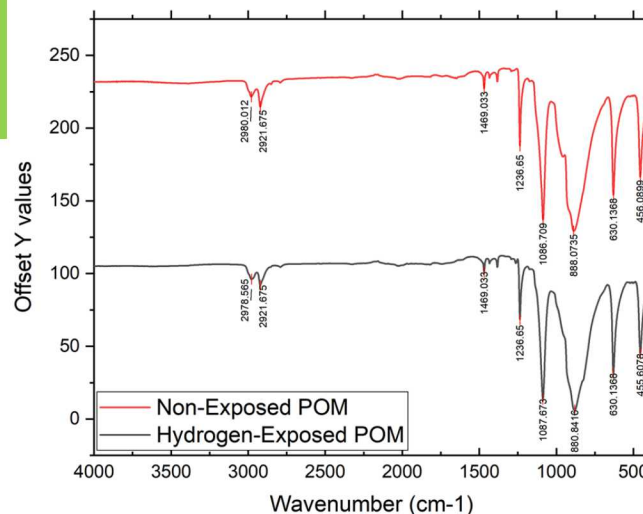
Significant H<sub>2</sub> effect seen as shift



### PTFE Side 1 FTIR



### POM Side 1 FTIR





# Conclusions

- Elastomers and thermoplastics subjected to high pressure cycling H<sub>2</sub> behave differently
- For elastomers, a highly cross-linked tight polymer network with limited free volume and the presence of fillers and plasticizers play a significant role in providing H<sub>2</sub> resistance
- Plasticization of the matrix can be a possible mechanism for H<sub>2</sub> attack while filler-containing formulations show maximum change, indicating interaction of carbon and silica with H<sub>2</sub>
- The six thermoplastics tested (POM, PTFE, HDPE, PEEK, Nylon-6,6 and Nylon-11) for different physical, chemical and mechanical properties do not show substantial changes; however,
  - Onset of chemical changes was identified for H<sub>2</sub> cycled polymers
  - Chemical changes were seen best with Fourier Transform Infrared Spectroscopy (FTIR), Solid state <sup>1</sup>H MAS NMR and X-ray Diffraction (XRD)

**THANK YOU FOR YOUR ATTENTION !!**