

# H-Mat Overview: Polymers

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**Lab Partners:** SRNL, ORNL, ANL

**Presentation:** Oral Presentation

**Project ID:** IN\_001b

**DOE project award #:** L062-1502

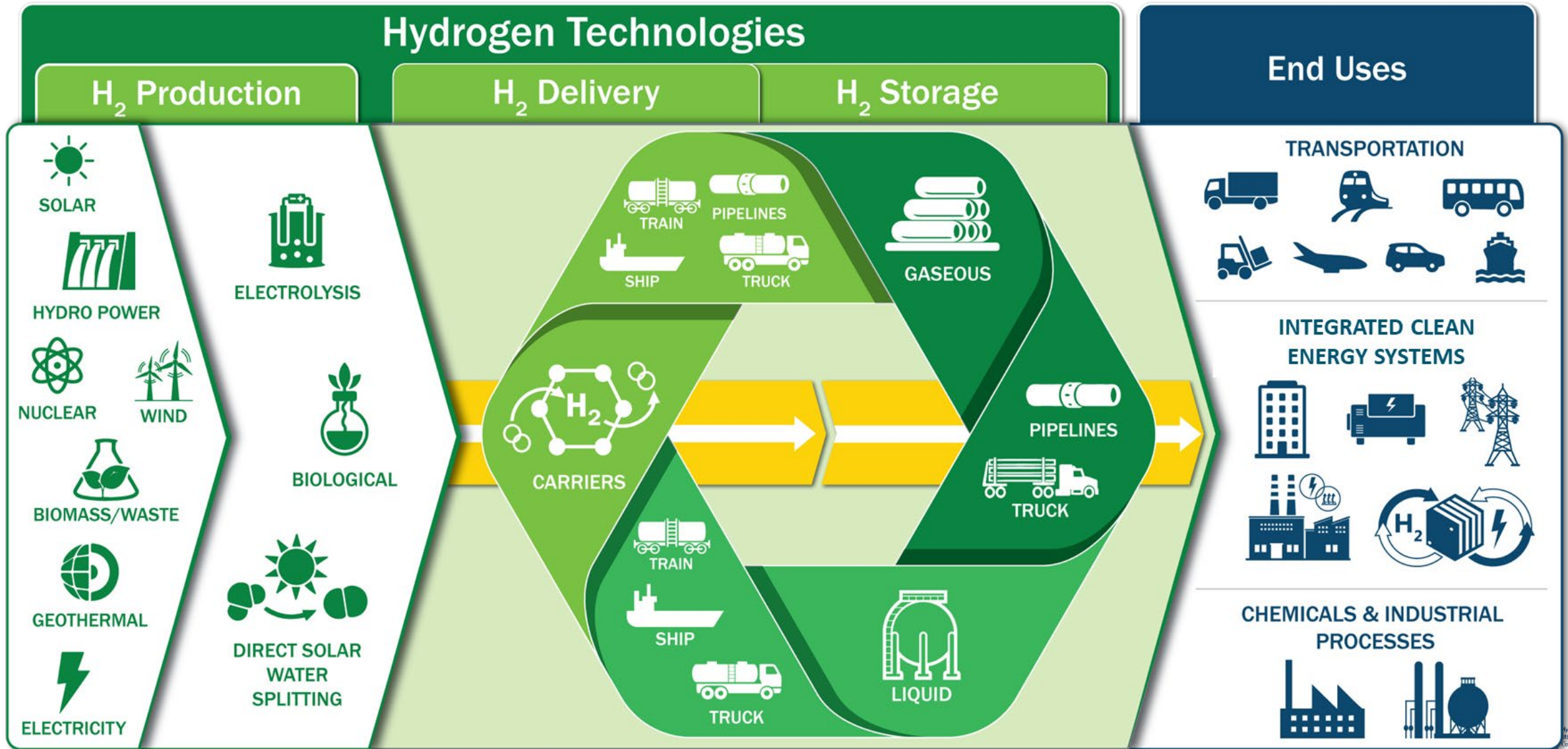
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## 2023 Annual Merit Review & Peer Evaluation Meeting



# DOE program addressing key challenges to achieving the H2@Scale vision

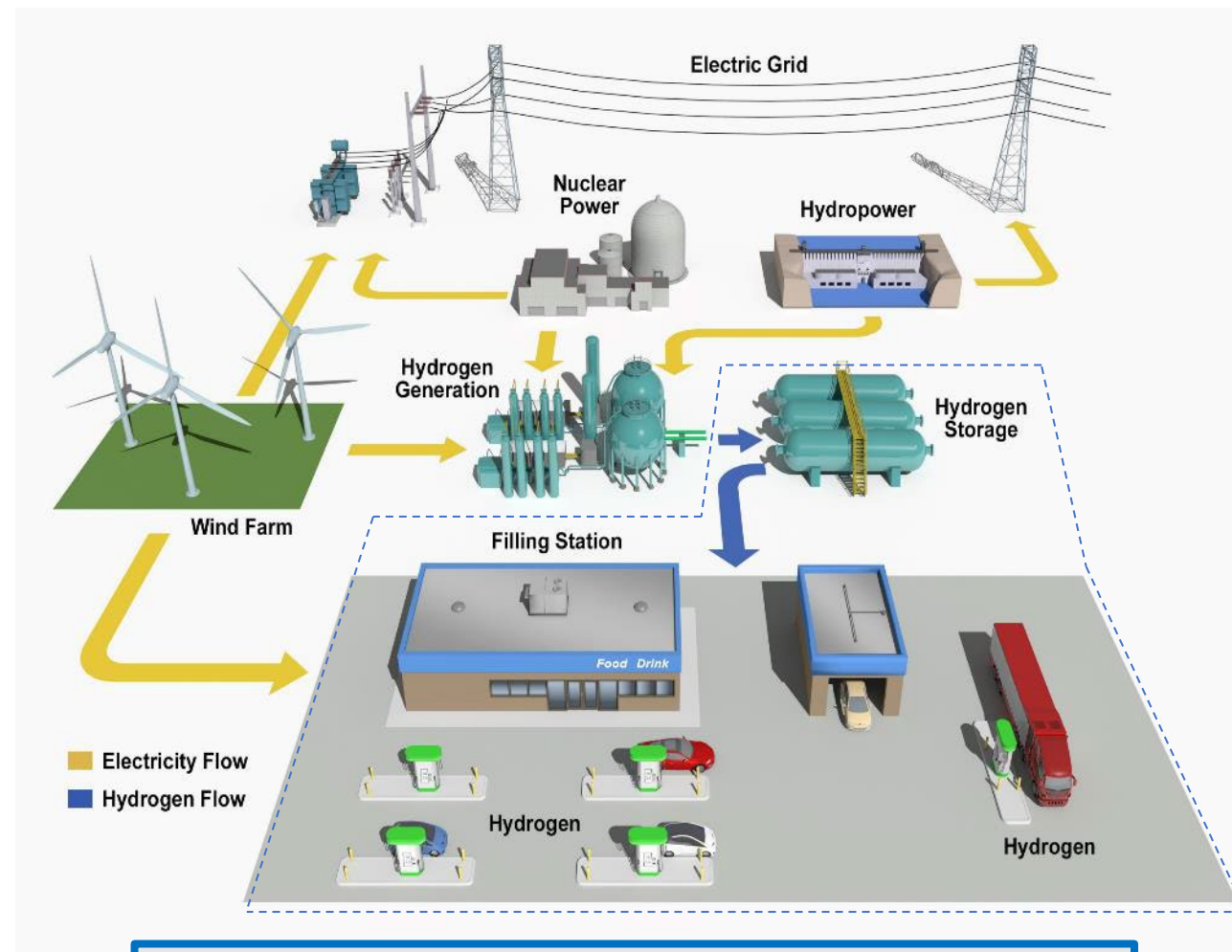


# Project Goal

*H-Mat was formed to address the hydrogen compatibility performance of materials to increase the durability of material thereby providing a more reliable and stable performance of systems in the hydrogen infrastructure.*

- Provide the scientific basis to mitigate failure of polymer elastomers in hydrogen environments.
- Develop computational methodologies that can simulate the polymer behaviors at different material scales and help to understand the interaction between polymers and hydrogen.
- Disseminate material modeling results to the community to begin discussions on how to improve materials in the hydrogen infrastructure environment.

## H2@Scale Infrastructure Example



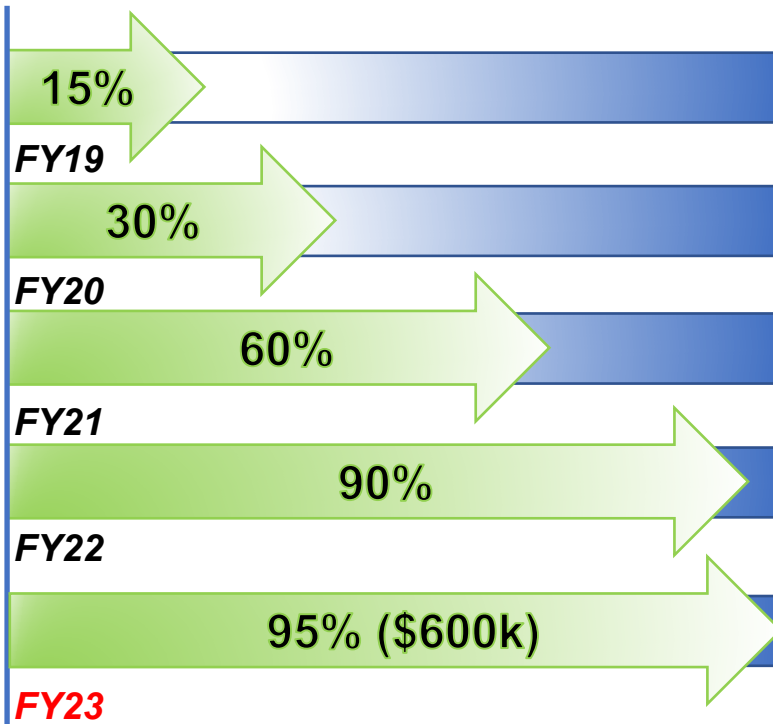
*Question: Can the effects of hydrogen on polymer systems be reduced to provide a more robust and reliable infrastructure?*



# Overview

## Timeline & Budget

- Project Start Date: September 2018
- Initial End Date: September 2022
- Current End Date: September 2023
  - % Completed: 95% with extended scope\*
- Total FY23 Budget: \$600K



## Barriers

### Safety, Codes, and Standards

- 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

### Hydrogen Delivery

- B. Reliability and Costs of Gaseous Hydrogen Compression
- E. Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
- I. Other Fueling Site/Terminal Operations

## Partners



### Collaborators

Swagelok, Takaishi Ind., Burke Ind., Arlanxeo, Zeon, TSE, Chemours, Kyushu University (Hydrogenius), Invista, Ascend, Solvay, St. Gobain, Hummell, Dover, AMPO, Howden, Solar Turbines, Burckhardt, Green Tweed, Arkema, Kepner, NEL, Freudenberg, Evonik



# Relevance

## Objectives:

- Address the challenges of **hydrogen degradation**
- Elucidate the **mechanisms of hydrogen-materials interactions**
- Develop science-based strategies to design material (micro)structures and morphology with improved **resistance to hydrogen degradation**.

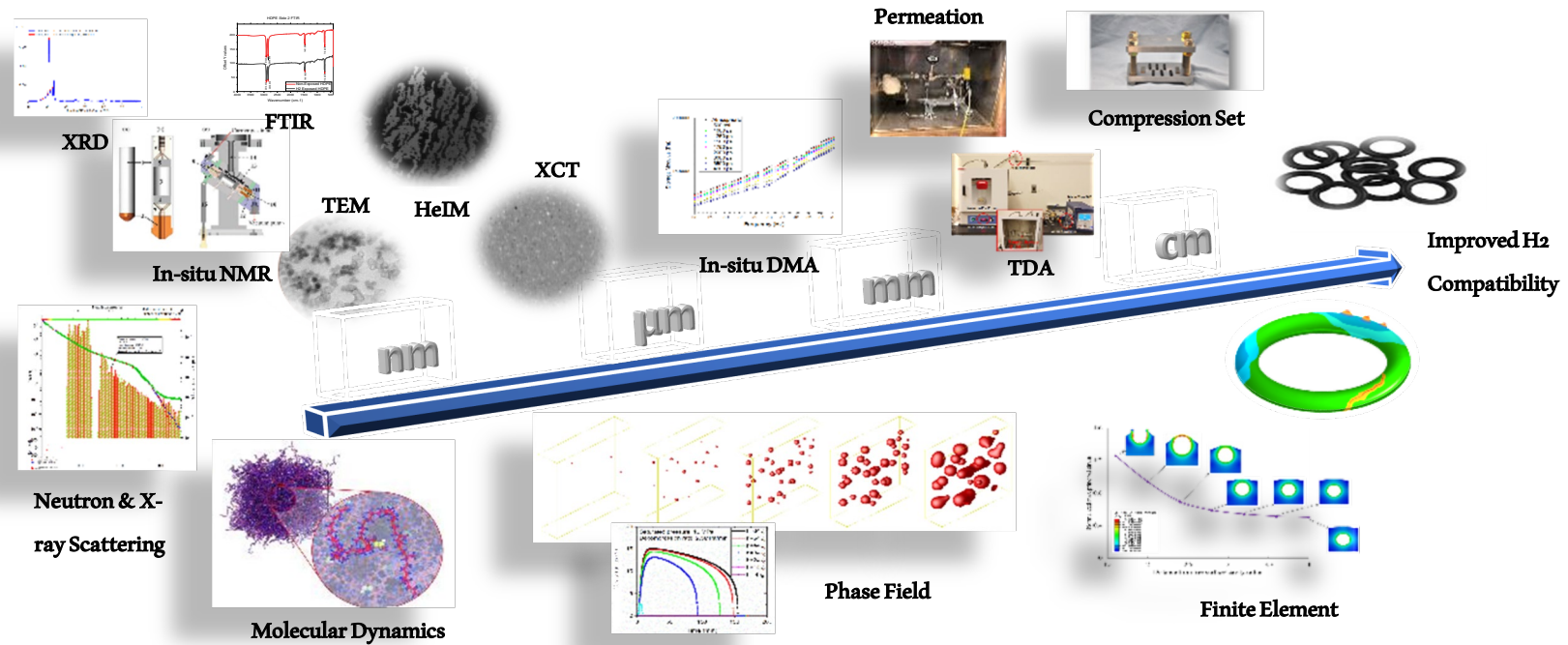
**PROJECT GOAL:** By September 2022, demonstrate an elastomer formulation with 50% less swelling compared to similar off-the-shelf materials

**Complete (HNBR and FKM formulations with >70% improvement in swelling resistance over comparable off-the-shelf materials)**

| Task                                                          | Relevance and Objectives                                                                                                                                                                 |
|---------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Mechanisms of hydrogen-induced degradation of polymers</b> | Quantify the hydrogen pressure-temperature-time-damage relationships of polymers with controlled structure and morphology (to inform models of hydrogen-induced degradation of polymers) |
| <b>Computational multiscale modeling</b>                      | Develop material damage models of process-structure-property performance with the aim of motivating materials formulations that are less sensitive to hydrogen-induced damage            |
| <b>Hydrogen-resistant polymeric formulations</b>              | Discover modified and new materials systems that improve hydrogen compatibility that will increase the reliability of materials and components in hydrogen infrastructure                |
| <b>Materials for cryogenic hydrogen service</b>               | Identify materials for cryo-compressed hydrogen storage onboard vehicles, and develop key technical metrics for viable structural materials in this application                          |

# Approach

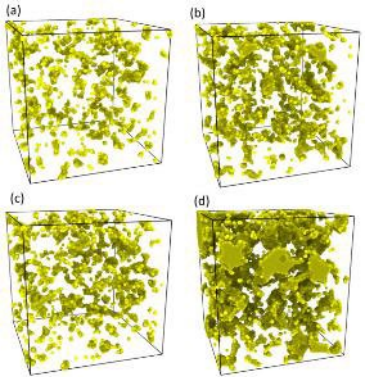
- Experiments provide:
  - Visual observations
  - Material properties
  - Topography of cavities and/or bubbles
  - Validation data
- Simulations provide:
  - Optimum parameters
  - Trends and what to expect
- The science-based understanding will provide direction on material limits and how to develop new materials with improved resistance to hydrogen degradation



*Question: What effects from hydrogen do we see experimentally and computationally that provide insight to the limits of the environmental operating conditions, or how we can modify or develop new material formulation?*

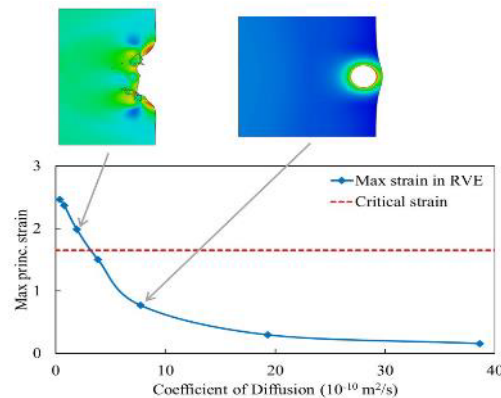


# FY23 Accomplishments Summary

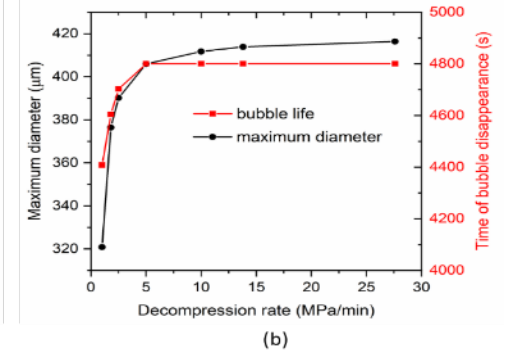
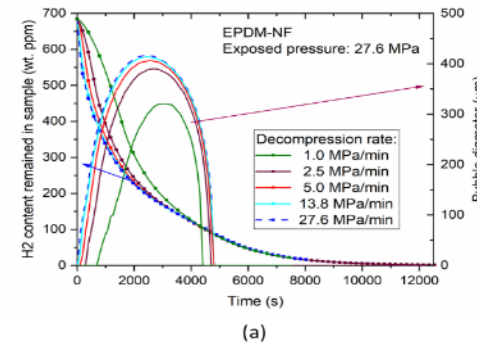


- ❑ *Molecular dynamic modeling of decompression from high-pressure hydrogen suggests higher crosslink densities may help prevent cavitation*

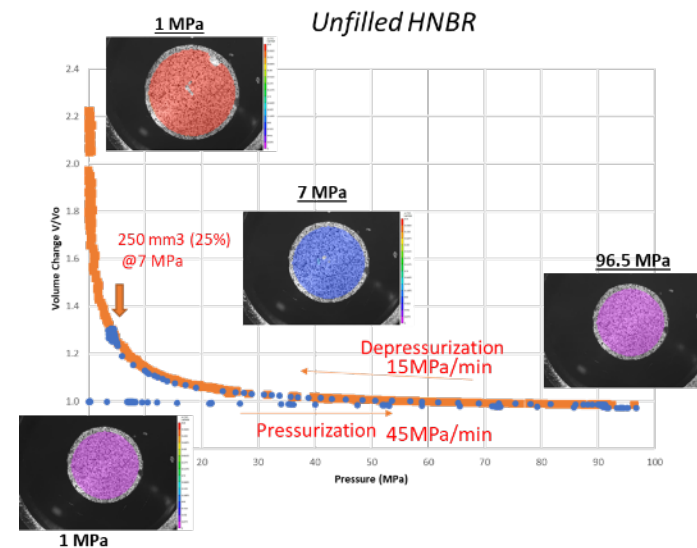
- ❑ *Finite element simulation uses both transport and mechanical properties experimental data to produce critical value of principal strain above which damage occurs*



- ❑ *HNBR and FKM show more favorable hydrogen transport properties than NBR and EPDM*
- ❑ *Hydrogen results in reduced crosslinking density at interior of peroxide-cured FKM*



- ❑ *Phase field modeling informs the maximum size and lifetime of gas bubble reach plateaus at 10 MPa/min*

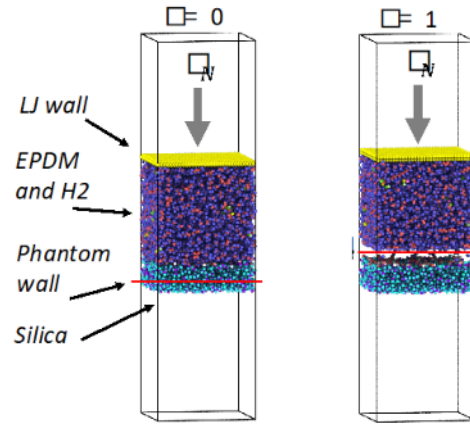


- ❑ *High pressure view cell work indicates a non-linear relationship between volumetric swell and pressure during rapid decompression of hydrogen*

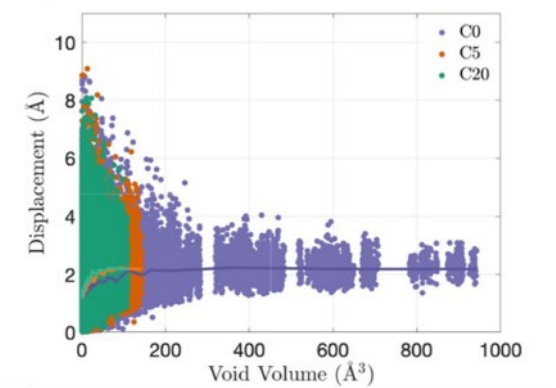
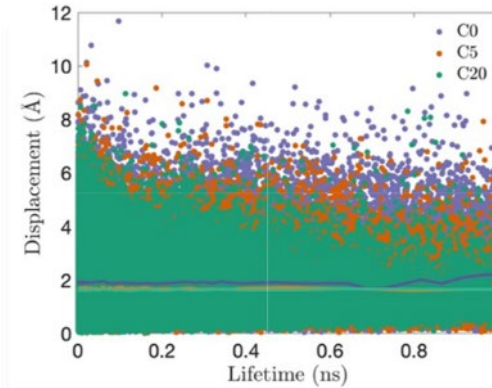
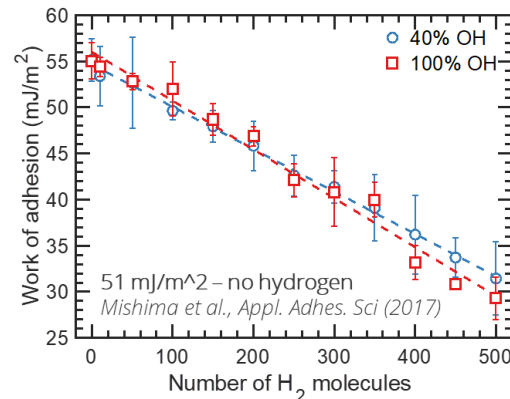
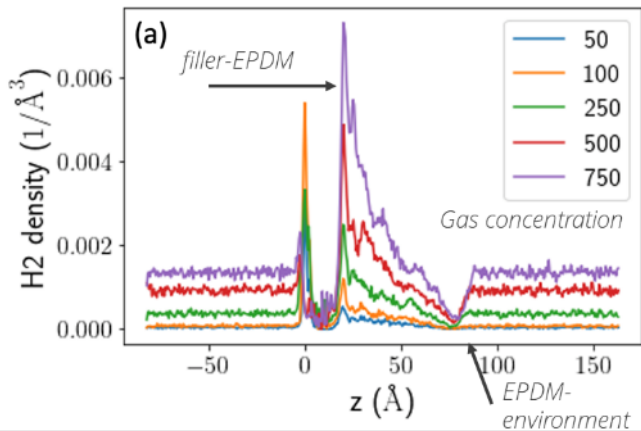
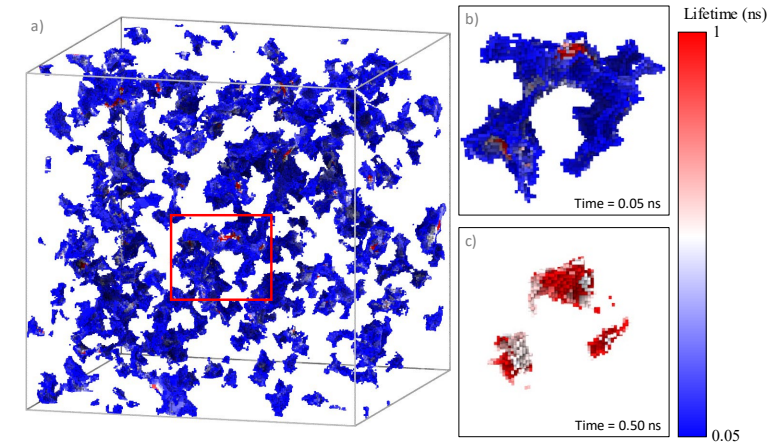
# FY23 Accomplishments

## Molecular Dynamics Studies EPDM-Silica Adhesion Strength and H<sub>2</sub> Diffusion/Pore Size Relationships

Molecular dynamics modeling of decompression from high-pressure hydrogen shows excess gas localization at EPDM-silica filler interface.



*Analysis of molecular dynamics simulations indicate hydrogen accessible free volume is dynamic due to chain mobility.*



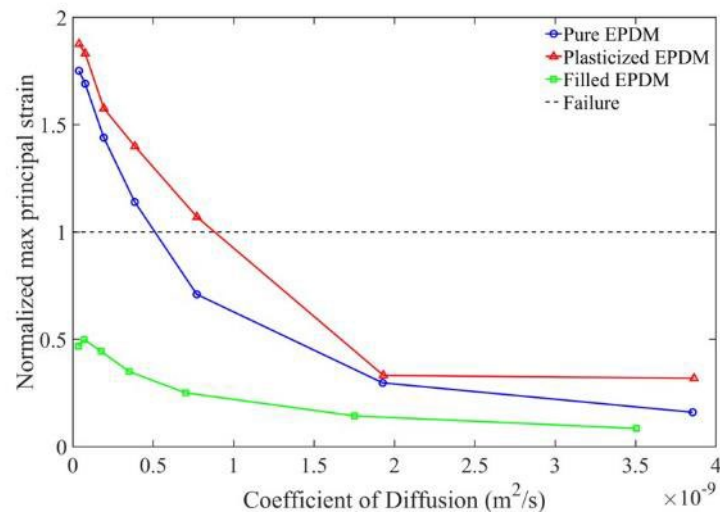
*Greater hydrogen displacement in short-lived, small regions of free volume*

- Predicted linear decrease in adhesive strength with gas concentration – a potential source for cavitation damage
- Hydrogen diffusion in EPDM occurs via a hopping mechanism through free volume; large volume regions are connected by small “channels” with high gas mobility

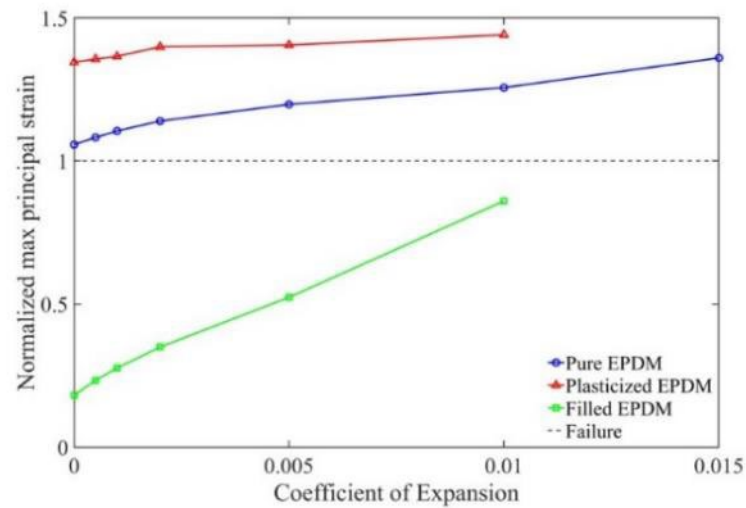
# FY23 Accomplishments

## Finite Element Modeling Delves into Various Effects on Hydrogen Damage Mechanism

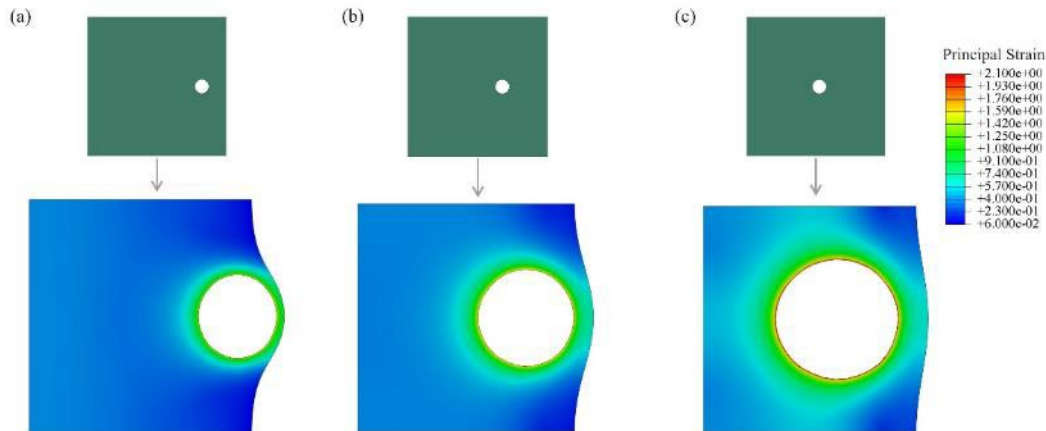
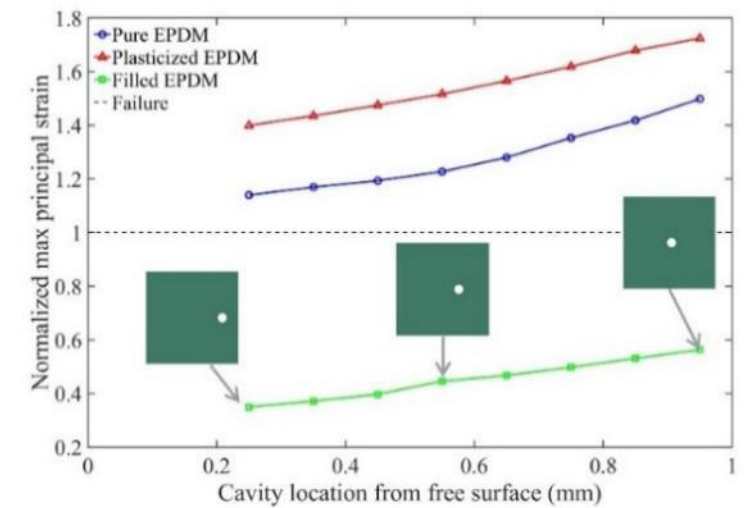
*Effect of coefficient of diffusion*



*Effect of coefficient of swelling*



*Effect of cavity location*



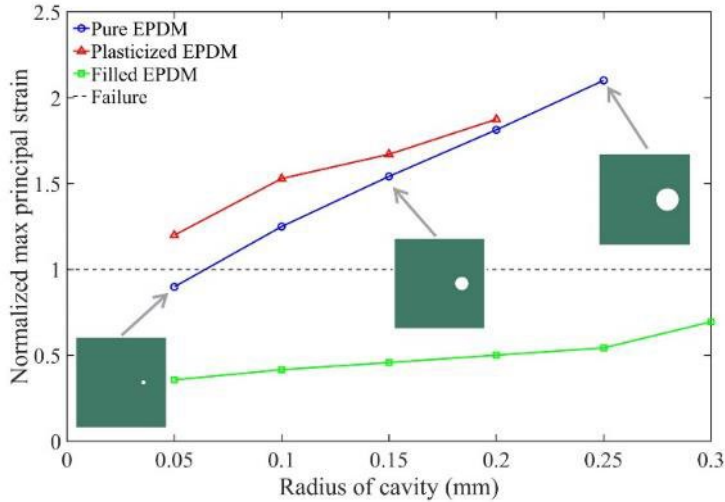
Spatial strain distribution across RVE for cavity located at (a) 0.25 mm, (b) 0.55 mm, and (c) 0.95 mm from the free surface. Plots are shown for pure EPDM material just after depressurization was complete

- Higher coefficient of diffusion lowers risk of causing damage
- Filler mitigates swelling, consistent with experimental results
- Cavities away from free surface are more susceptible to failure due to longer path for hydrogen to diffuse out

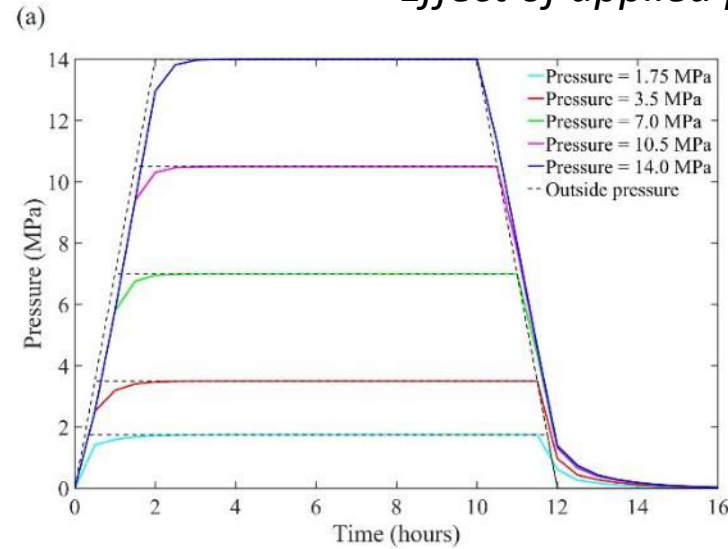
# FY23 Accomplishments

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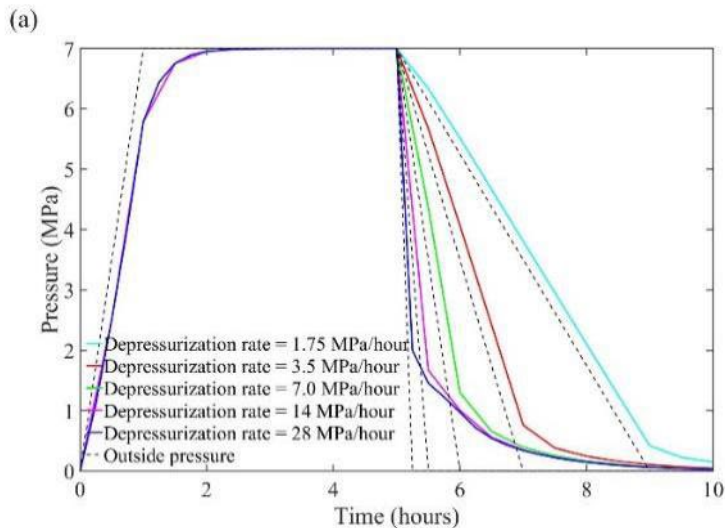
*Effect of cavity size*



*Effect of applied pressure*



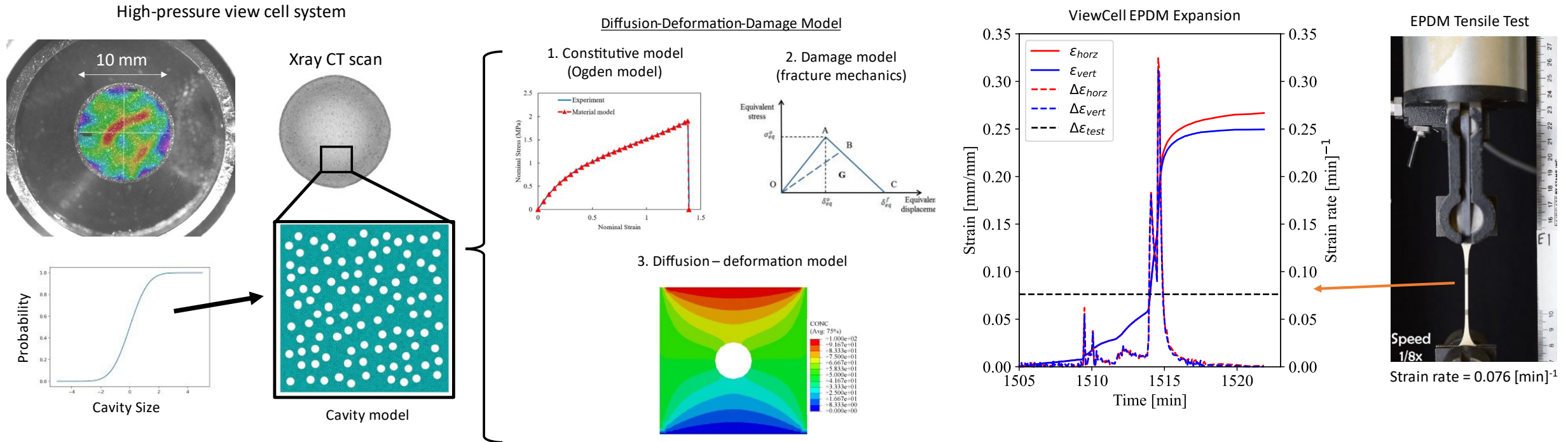
*Effect of depressurization rate*



- Larger cavity size leads to more severe damage in absence of filler
- Max principal strain plateaus at around 10 MPa/min, in agreement with phase field simulation results

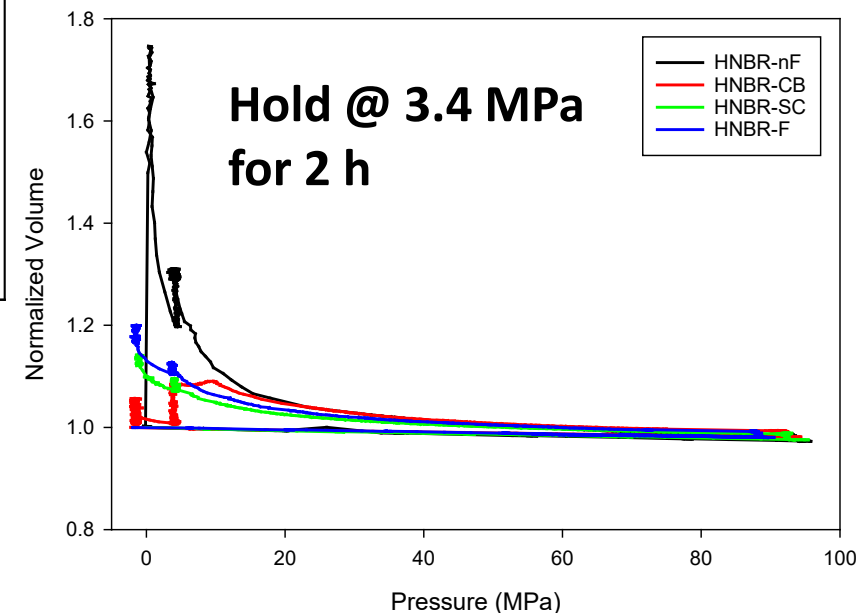
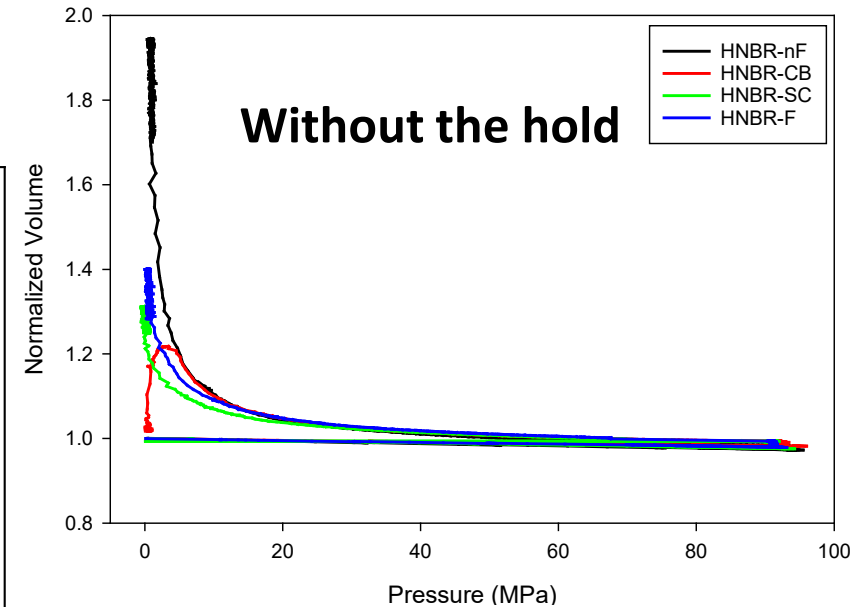
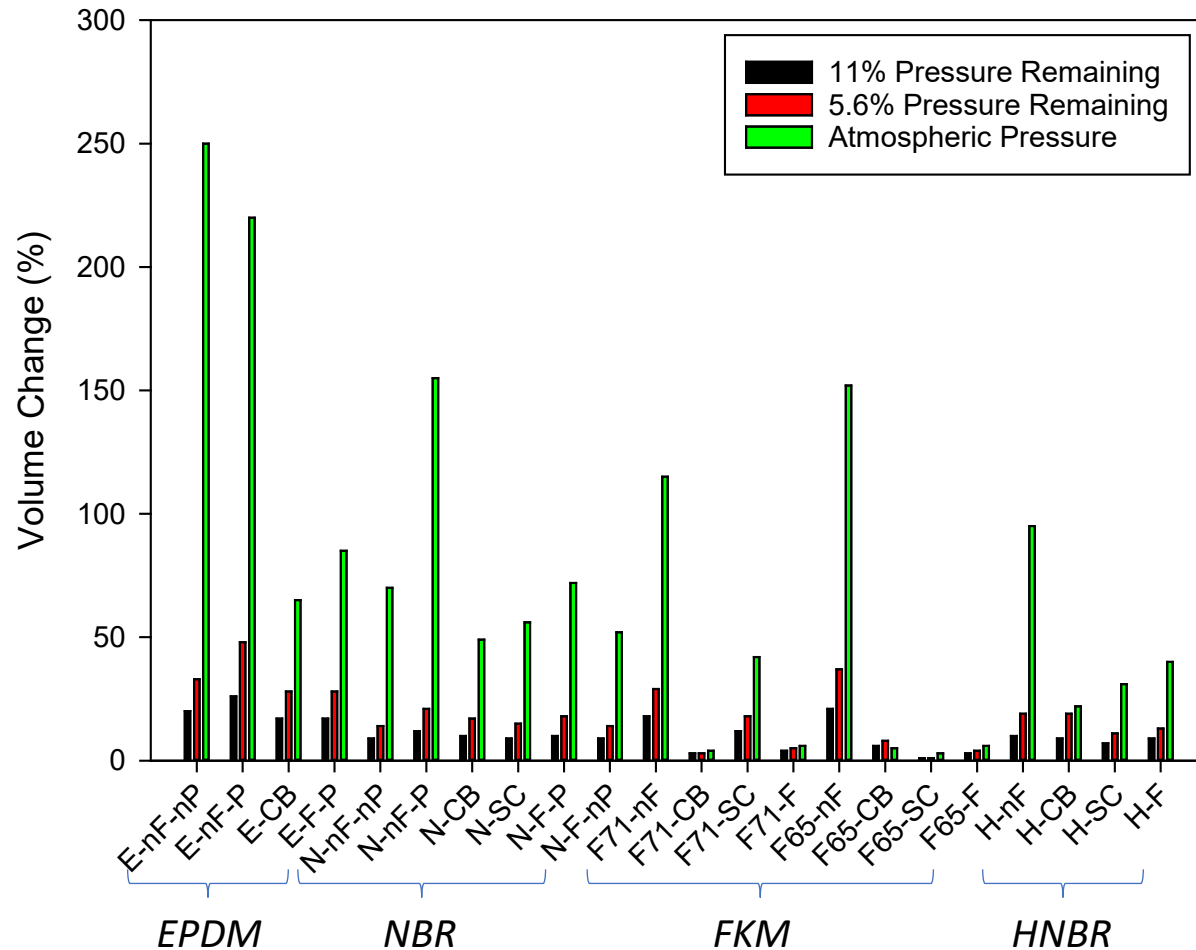
# FY23 Accomplishments

## Correlates Experimental Work with Diffusion-Deformation-Damage Mechanism



- Expand multiscale modeling to predict mechanical behaviors at the component level and validate the model using the high-pressure view cell system
- Effects of strain rate as the rate of volume expansion changes over time even at constant hydrogen decompression rate

# View Cell Work Finds Elastomers with High Resistance to Volume Swell During Rapid Decompression of High Pressure Hydrogen



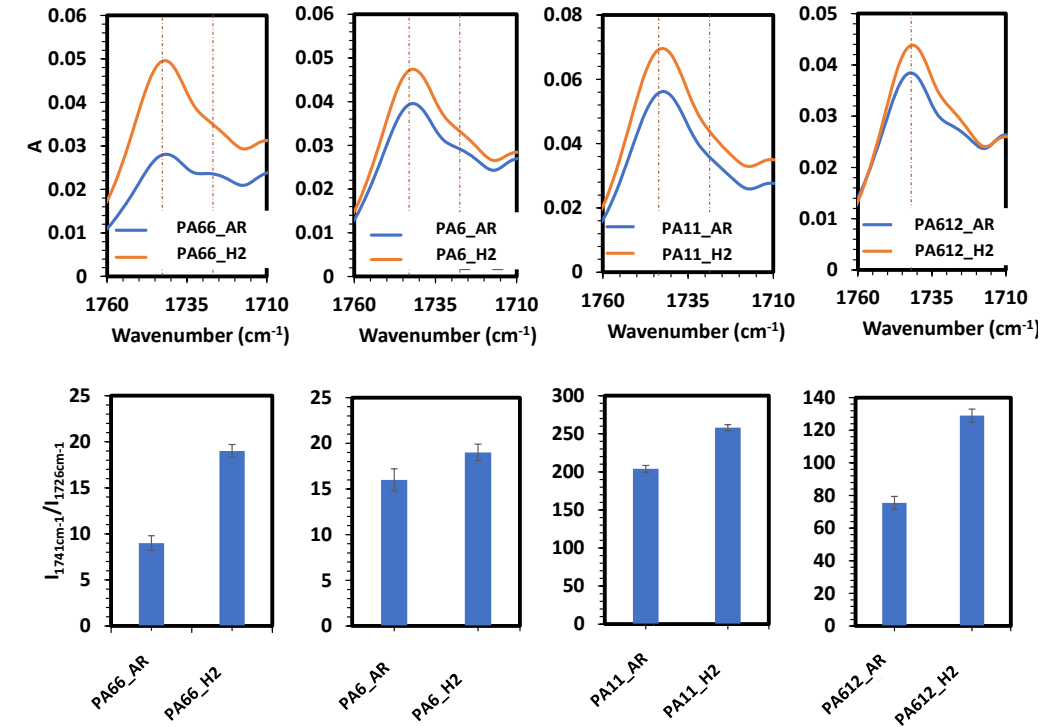
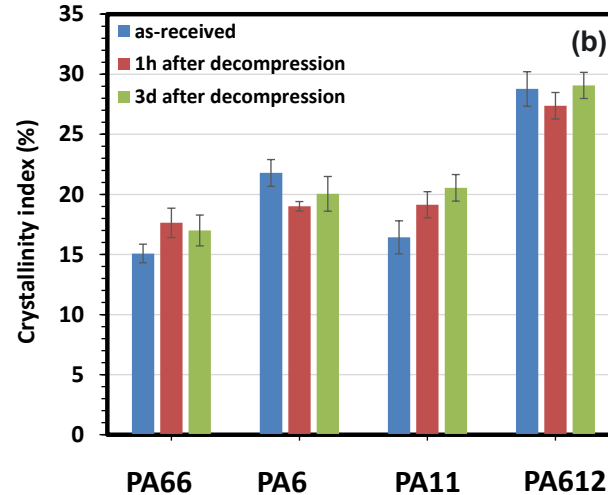
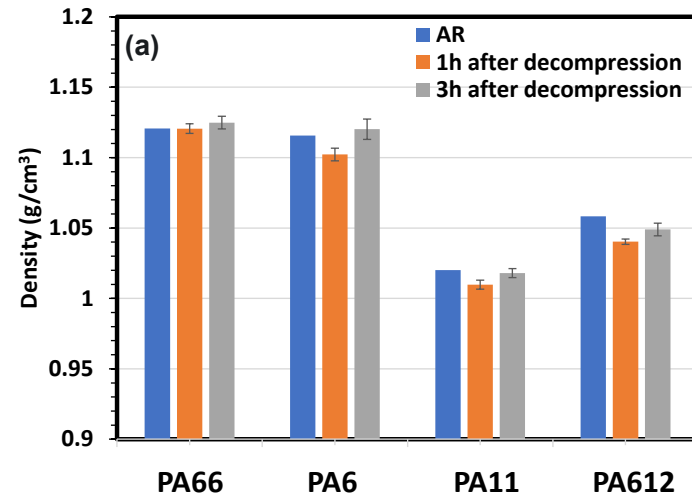
- Filled HNBR and FKM outperform EPDM and NBR
- Raising lower operating pressure by only 4% could mean 20-50% improvement over swelling resistance

# FY23 Accomplishments

## Initial Evaluation of Commercial Polyamides in High Pressure Hydrogen Environments

Transport Properties

|       | $C_0$ (wt ppm) | $D$ ( $m^2/sec$ )      | Hydrogen Condition  |
|-------|----------------|------------------------|---------------------|
| PA66  | 72.0           | $8.38 \times 10^{-10}$ | 90 MPa for 24 hours |
| PA6   | 78.3           | $7.88 \times 10^{-10}$ | 90 MPa for 24 hours |
| PA11  | 78.2           | $7.23 \times 10^{-10}$ | 90 MPa for 24 hours |
| PA612 | 81.0           | $7.47 \times 10^{-10}$ | 90 MPa for 24 hours |

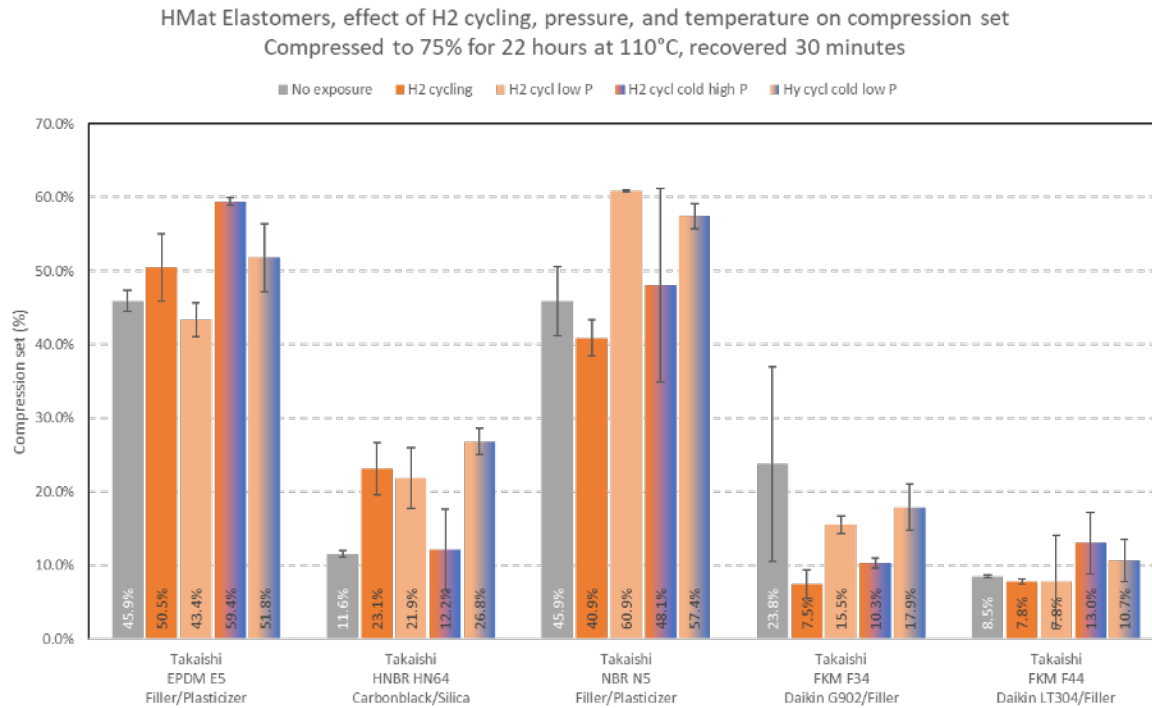


- Density and crystallinity decrease initially after removal from high pressure hydrogen but recover within 72 hours

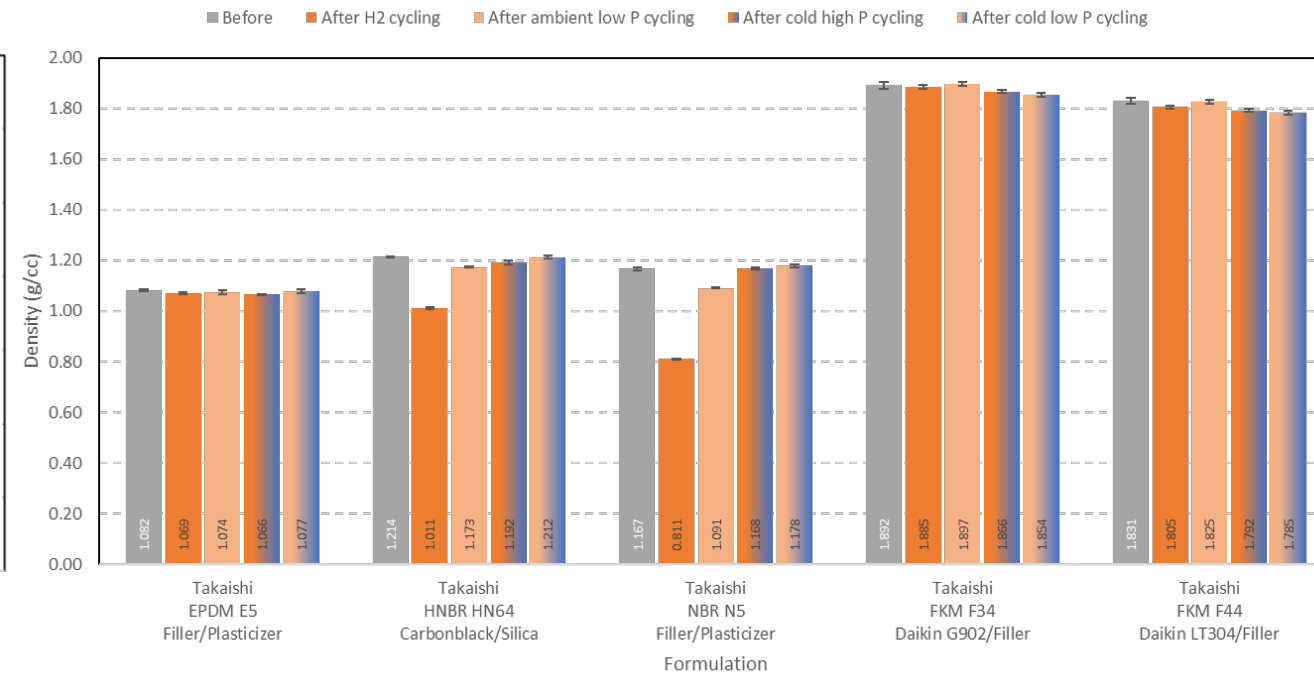
# FY23 Accomplishments

## Influence of High Pressure (12500-2500 psi) and Low Pressure (4500-1500 psi) Cycling in Cold Hydrogen Environments

- Filled and unfilled Takaishi EPDM, FKM 44, FKM 34, HNBR, NBR tested at depressurization rate of 2.29 MPa/min at -40°C

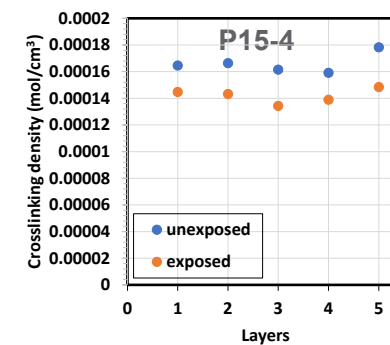
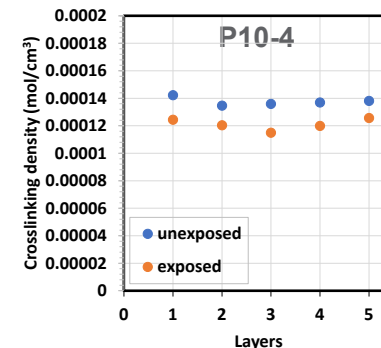
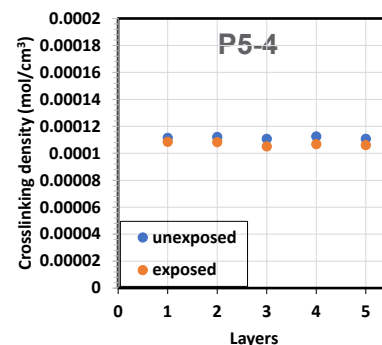
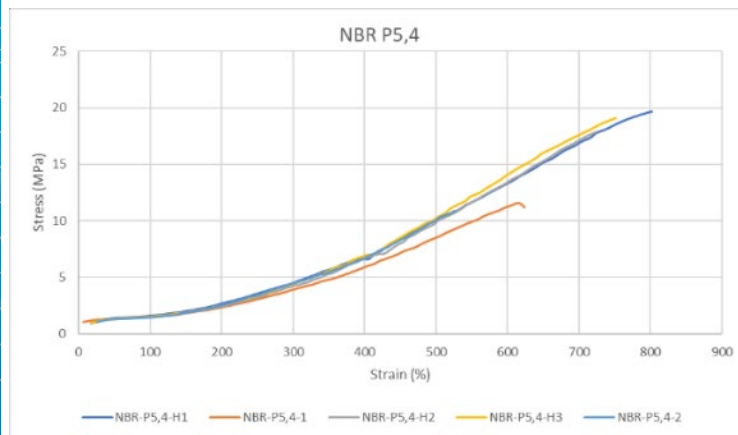


Assorted Takaishi rubber formulations, change in density before and after H2 cycling at ambient, cycling at low P (Rnd 42), cycling cold at high P (Rnd 45), and cycling cold at low P (Rnd 46)  
average of 2 specimens



- In cold environments, low pressure cycling results in higher compression set than high pressure cycling
- HNBR and NBR show more swelling for high pressure ambient compared to cold conditions

# PNNL's Self-Formulated, Peroxide-Cured NBR Compounds



|       | Exterior layer |         |                | Middle layer |         |                |
|-------|----------------|---------|----------------|--------------|---------|----------------|
|       | Unexposed      | Exposed | -ΔXL           | Unexposed    | Exposed | -ΔXL           |
| P5-4  | 0.1112         | 0.1102  | 0.0010 (0.9%)  | 0.1107       | 0.1051  | 0.0056 (5.1%)  |
| P10-4 | 0.1402         | 0.1251  | 0.0151 (10.8%) | 0.1359       | 0.1153  | 0.0206 (15.2%) |
| P15-4 | 0.1714         | 0.1466  | 0.0248 (14.5%) | 0.1615       | 0.1343  | 0.0272 (16.8%) |

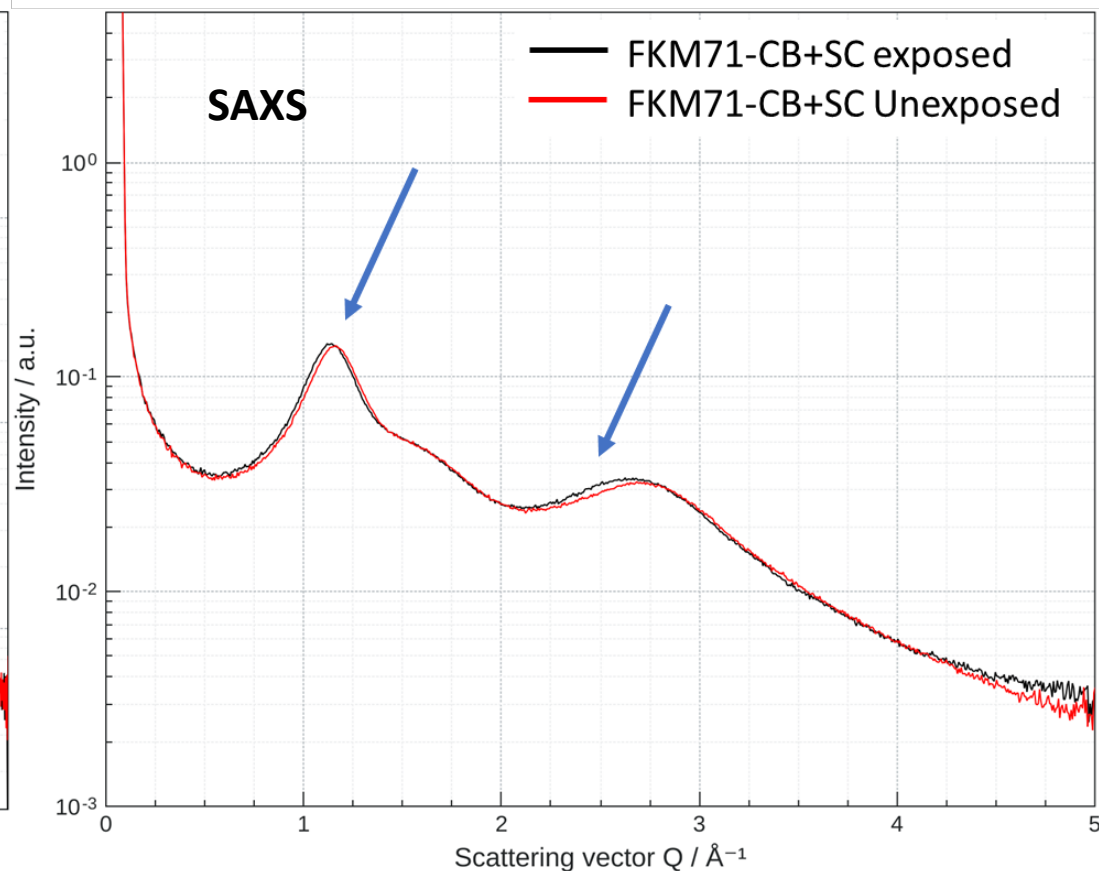
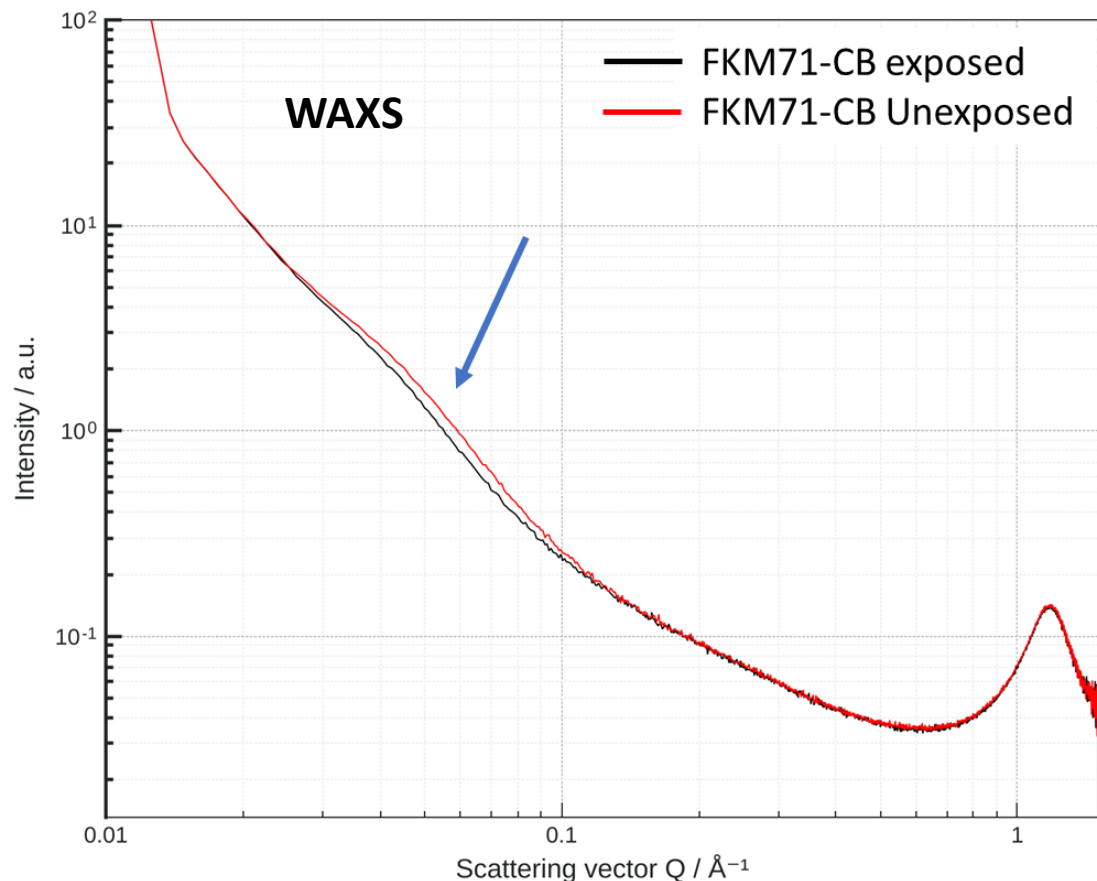
|                              | P5-4  | P10-4 | P15-4 |
|------------------------------|-------|-------|-------|
| NBR (Nipol 1042)             | 100   | 100   | 100   |
| ZnO                          | 3     | 3     | 3     |
| Stearic acid                 | 1     | 1     | 1     |
| DOS                          | 10    | 10    | 10    |
| Carbon black (N330)          | 23    | 23    | 23    |
| Silica (Nipsil VN3)          | 28    | 28    | 28    |
| Peroxide                     | 4     | 4     | 4     |
| TAIC                         | 5     | 10    | 15    |
| Total                        | 174   | 179   | 184   |
| Density (g/cm <sup>3</sup> ) | 1.123 | 1.142 | 1.142 |

| Compounds | Thickness (mm) | Radius (mm) | $C_0$ (wt ppm) | $C_0$ (wt ppm/mm <sup>3</sup> ) | $D$ (m <sup>2</sup> /sec) |
|-----------|----------------|-------------|----------------|---------------------------------|---------------------------|
| P5-4      | 4.64           | 2.41        | 376.5          | 4.45                            | $1.86 \times 10^{-10}$    |
| P10-4     | 4.64           | 2.50        | 414.6          | 4.55                            | $2.00 \times 10^{-10}$    |
| P15-4     | 4.64           | 2.40        | 443.2          | 5.28                            | $2.00 \times 10^{-10}$    |

- No significant change in tensile properties before and after static exposure to 28 MPa hydrogen
- Comparable transport properties to Takaishi model NBR compounds
- Crosslinking density found to decrease after static exposure to 90 MPa – more decrease seen towards core than outer surface

# Hydrogen Effects on Crystalline Structure of Fluoroelastomer

## Ultra SAXS/WAXS of peroxide-cured FKM



- WAXS - The reduction of the excess scattering is unusual
- Voids in the sample may collapse after pressurization

- SAXS - Changes indicated by blue arrows:
  - No changes in SAXS pattern (larger scale, long range effects)
  - ~ 3% increase in F-F bond distance upon exposure

# FY23 Accomplishments

## Information Dissemination & Industry Impact

- The H-Mat website and the DataHUB are complete. The website will now feature publications and presentations from the H-Mat project
- Memorandum of Understanding with Kyushu University for information sharing and active collaborations
- Member of the ISO TC197/WG31 O-rings working group for hydrogen materials selection
  - ISO-3601 Fluid Power Systems - O-rings
  - ISO-19880 Gaseous Hydrogen – Fuelling Stations – Part 7 : Rubber O-rings
- Completed workshop report on Hydrogen Materials Compatibility of Polymers in August with over 60 attendees participating in breakout sessions following three panel discussions
- AIChE Webinar on hydrogen materials compatibility with over 330 attendees

- The H-Mat team has been collaborating with 25+ companies from various subsector
  - Electrolyzer manufacturers
  - Pressure vessels
  - Balance of plant component manufacturers
  - Compressor manufacturers
  - Refueling components
  - Raw materials suppliers
  - Materials compounders and part manufacturer to understand the application of their products
- The H-Mat team material evaluations and recommendations to industry
- Assistance and performing material testing and evaluations



Accomplishments

# Reviewers Comments

**Comments: None**

# Collaborations

## Partner:

## Project Roles:



Project lead, management and coordination; micro- and macro-scale modeling; device and capability development; materials testing and characterization; cryogenic materials testing, pressure vessel material models and simulations, new formulation compounding; H-Mat website and DataHUB



Atomistic modeling; high pressure hydrogen cycling; testing and characterization



Neutron/X-ray scattering testing and characterization



High pressure differential scanning calorimetry; self-heal membrane development



Pressure vessel modeling and simulation

# Progress Toward DOE Targets & Milestones

| Milestone Name/Description                                                                                                                                 | Due Date   | Status                       |
|------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|------------------------------|
| PNNL: Develop EPDM and FKM technical reference reports on hydrogen compatibility for H-Mat website (Task PM1)                                              | 12/31/2022 | Complete on January 31, 2022 |
| PNNL: Complete evaluation of HNBR and FKM model compounds, and one PNNL formulation in high pressure hydrogen environments with PNNL view cell test system | 3/30/2023  | Complete                     |
| PNNL: Complete correlation of finite element models of void formation (Modeling tasks (P2))                                                                | 6/30/2023  | On track                     |
| PNNL: Complete permeation measurements on all model elastomers and select industrial grade thermoplastic formulations (Task P1)                            | 9/30/2023  |                              |

# Remaining Challenges & Barriers

- **Definition of material compatibility in applications is not consistent across industries, H-Mat is working to provide consistency**
- **Working to develop evaluation methods to measure material property performance in terms of specific environmental use cases, including in-service pressure, pressure cycling profiles, and temperature**
- **Essentially all applications suffer from a lack of understanding of material behavior in hydrogen service. Manufacturers have been searching for data on material properties in hydrogen to help them select appropriate materials for their applications, but this data is sparse and is dependent on environmental conditions. As a result, industry tends to opt for materials used in other gas-based systems and then evaluates their performance. Hydrogen does not behave the same as other gases. All material options are being considered**
- **References, standards, or codes developed specifically for polymers in hydrogen service are limited or non-existent**
- **The largest hurdles to materials selection for hydrogen service are material references, standards, and codes to help evaluate performance, reliability, and material limitations**



# Proposed Future Work

## Remainder of FY23

- Expand on partnerships with industry (H-Mat affiliation)
- Continue developing and testing new formations
- Complete report on forward recommendations and submit internally to DOE

Any proposed future work is subject to change based on funding levels.

## Experimental activities

- Relate common application conditions (low, medium, and high-pressure ranges) to material testing
- Work with industry to develop hydrogen resistant polymeric formulations or identify appropriate formulations for intended application
- Acquire material configuration tests (such as constrained O-ring test)
- Material wear performance at the component level for hydrogen compressors
- Hydrogen effects on coatings used on metal for corrosion mitigation
- Investigate combined cryogenic and hydrogen material effects and material off-gassing
- Lifetime material performance in hydrogen, life cycle replacement
- Understand the long-term damage accumulation. Destructive and non-destruct (aging)
- Transport properties at high pressures

## Computational

- Introduce AI/ML to assist with data analysis and trend analysis
- Develop website tool to provide material performance based on pressure, temperature, cycling, and time output
- Apply ML to predict results based on the simulations, material predictions based on lower pressure data, new material development
- Develop models to evaluate probability of damage to start
- Expand MD simulations on other material sets potentially (elastomers or thermoplastics, PE and PA), scattering data to simulations

## Consortium Impact

- Industry collaboration H-Mat open CRADA call for industry collaboration
- Standards, codes, and test methods development

# Summary

## Computational

- Molecular dynamic simulations predicted linear decrease in adhesive strength with gas concentration – a potential source for cavitation damage. Hydrogen diffusion in EPDM occurs via a hopping mechanism through free volume; large volume regions are connected by small “channels” with high gas mobility
- Finite element simulations concludes that higher coefficient of diffusion lowers risk of causing damage, filler mitigates swelling, and cavities away from free surface are more susceptible to failure due to longer path for hydrogen to diffuse out

## Information Dissemination

- H-Mat website is available to the public, and DataHUB is being populated and working toward public release
- Workshop with over 60 attendees and report submitted to DOE for review
- One-on-one discussions with over 25 companies on material testing and performance improvements
- ISO/TC197 WG 31 standards developments for o-rings
- 11 journal publications
- Three technical references on elastomeric materials
- AIChE Webinar on hydrogen materials compatibility with over 330 attendees

## Experimental

- Effects of strain rate as the rate of volume expansion changes over time even at constant hydrogen decompression rate
- Filled HNBR and FKM outperform EPDM and NBR
- Raising lower operating pressure by only 4% could mean 20-50% improvement over swelling resistance
- Density and crystallinity of commercial polyamides decrease initially after removal from high pressure hydrogen but recover within 72 hours
- Sandia...
- PNNL's peroxide-cured NBR sees crosslinking density decrease after hydrogen exposure
- WAXS of FKM shows unusual reduction of excess scattering, indicative of voids in the sample may collapse after pressurization
- SAXS of FKM finds ~ 3% increase in F-F bond distance upon exposure

## New Formulation

- Tested over 20 materials from industry and provided feedback on performance
- Support in testing new self-healing copolymer membrane developed by Clemson

# Acknowledgements

This work was fully supported by the U.S. Department of Energy (USDOE), Office of Energy Efficiency and Renewable Energy (EERE), Fuel Cell Technologies Office (FCTO) under Contract Number DE-AC05-76RL01830. We also acknowledge support from the Environmental Molecular Sciences Laboratory (EMSL). EMSL is a national scientific user facility sponsored by the Department of Energy's Office of Science, Biological and Environmental Research program that is located at Pacific Northwest National Laboratory.

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# Thank You!

