H-Mat Materials Overview: Polymers

Kevin Simmons, H-Mat Co-Lead
H-Mat Team

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FY19 Annual Merit Review

Crystal City, VA

PNNL is operated by Battelle for the U.S. Department of Energy

H-Mat Hydrogen Materials Compatibility Consortium

Overview

Timeline

- Project Start Date: September 2018
- Project End Date: September 2022
- % Completed: 7%
- FY18 Year Budget: $300K including lab partners and Ford subcontract
- Total FY19 Budget: $4500K
  - SNL:$ 2,390K
  - PNNL: $1,310K
  - ORNL: $550K
  - SRNL: $150K
  - ANL: $100K

Planned FY20 Funding: $3000K

Partners

- PNNL (H-Mat Polymer Lead)
- SNL
- ORNL
- Ford Motor Company

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

Collaborators

Swagelok, Arlanxeo
Kyushu University (Hydrogeniuous)

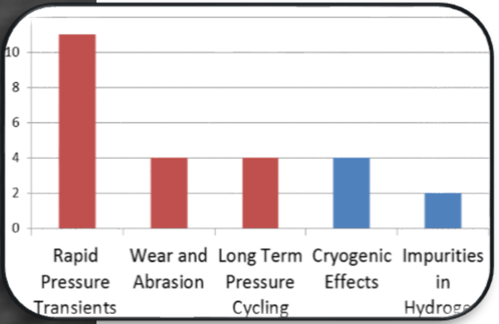
Relevance

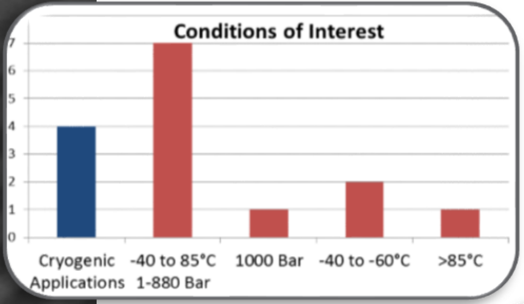
Objective: To address the challenges of hydrogen degradation by elucidating the mechanisms of hydrogen-materials interactions with the goal of providing science-based strategies to design materials (micro)structures and morphology with improved resistance to hydrogen degradation.

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

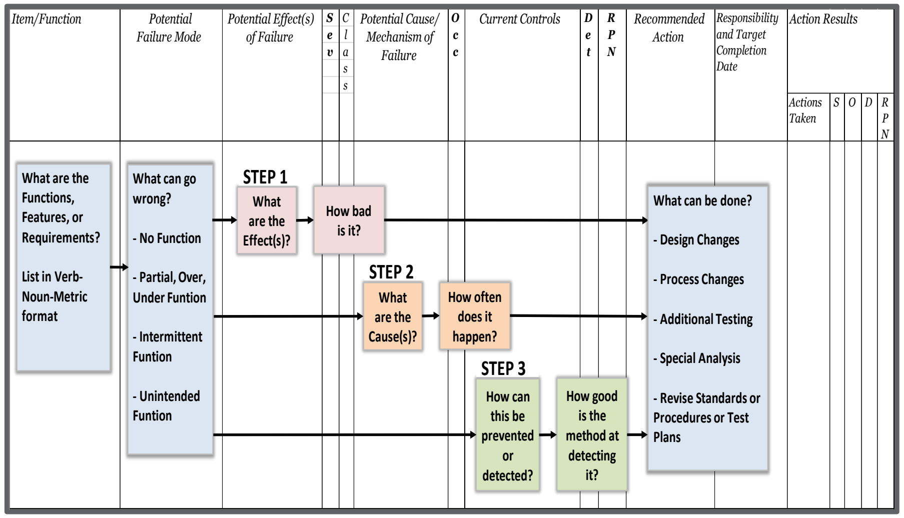
FY18 Approach

Identify the issues: Stakeholder Engagement





FMEA Prioritization of Critical Attributes



Item/Function	Potential Failure Mode	Potential Effect(s) of Failure	Sev	Class	Potential Cause/ Mechanism of Failure	Occ	Current Controls	Det	RPN	Recommended Action	Responsibility and Target Completion Date	Action Results: Actions Taken	S	O	D	RPN

What are the Functions, Features, or Requirements?

List in Verb-Noun-Metric format

What can go wrong?

- No Function
- Partial, Over, Under Funtion
- Intermittent Funtion
- Unintended Funtion

STEP 1

What are the Effect(s)? → How bad is it?

STEP 2

What are the Cause(s)? → How often does it happen?

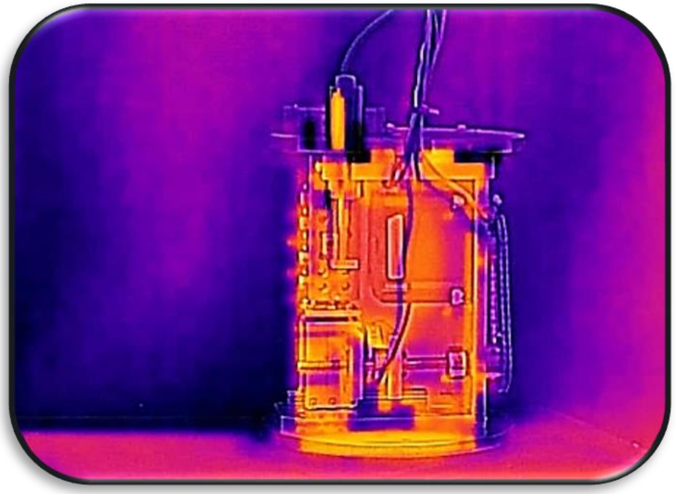
STEP 3

How can this be prevented or detected? → How good is the method at detecting it?

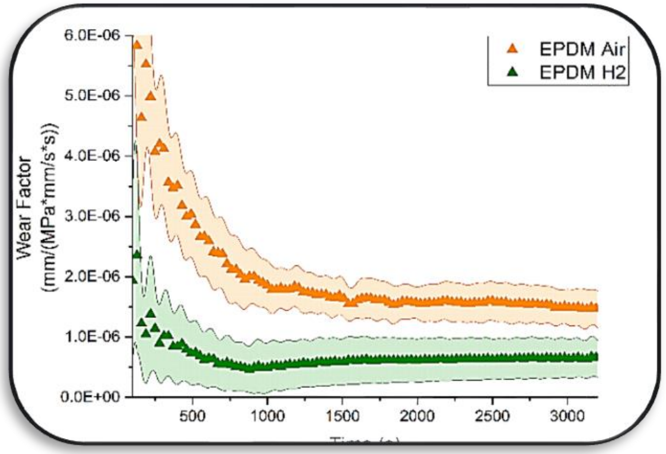
What can be done?

- Design Changes
- Process Changes
- Additional Testing
- Special Analysis
- Revise Standards or Procedures or Test Plans

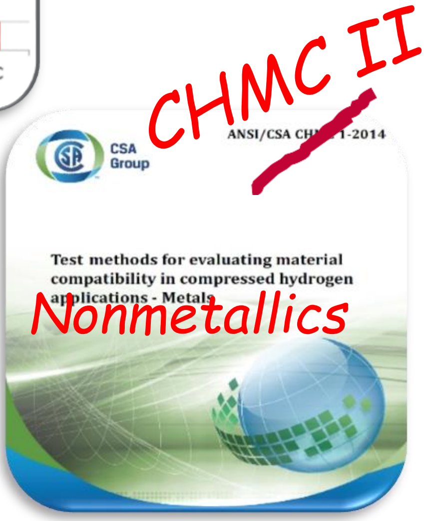
Test Method Development



Build the Database: Experimental Testing



Disseminate: Standards, Test Methods, Publications



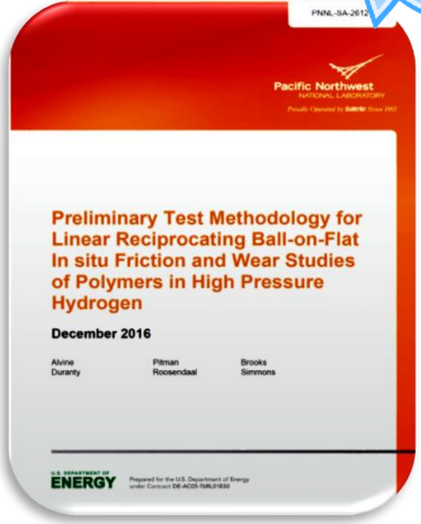
CSA Group

ANSI/CSA CH[illegible] 1-2014

CHMC II

Test methods for evaluating material compatibility in compressed hydrogen applications - Metals

Nonmetallics



PNNL-SA-2612

Pacific Northwest NATIONAL LABORATORY

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Preliminary Test Methodology for Linear Reciprocating Ball-on-Flat In situ Friction and Wear Studies of Polymers in High Pressure Hydrogen

December 2016

Alvine	Pitman	Brooks
Duranty	Roosendaal	Simmons

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

FY18 Accomplishment

Stakeholder Survey Feedback Summary

- Challenges Related to H_2 Compatibility
  - Rapid Pressure Transients (explosive decompression, blistering, liner collapse)
  - Long Term Pressure Cycling (fatigue, change in mechanical properties)
  - Wear and Abrasion changes from H_2 permeation in the material (o-ring and valve seat leakage)
  - Dimensional and Mechanical Properties changes (o-ring and valve seat leakage)
- Challenges Unrelated to H2 Compatibility
  - Temperature effects associated with sub-ambient and cryogenic temperatures
  - Impurities in the hydrogen impacting fuel cell use

FY18 Accomplishment

Stakeholder Survey Feedback Summary

- Take-away messages from stakeholder survey:
  - Wide range of suggested polymers of interest
  - Conditions of Interest:
    - ✓ Temperature -40 to +85 degrees C
    - ✓ 1(atm.) to 880 bar (13,000 psi)
    - ✓ Cryogenic applications
  - All agreed that more testing is required
- Materials of interest

Thermoplastics of Interest:
HDPE, PB-1, PA, PEEK, PP-R/PP-RCT, PEKK, PET, PEI, PVDF, PTFE, PCTFE

Elastomers of Interest:
EPDM, NBR, NBR/HNBR, Viton, Levapren

Thermosetting polymers of Interest:
Epoxy, Polyimide, Polyurethane

Polymers in components in hydrogen service selected for test methodology development:

- Elastomers: Viton A ,NBR, EPDM
- Low Temperature Seal: PTFE
- Tank liner Material: HDPE
- Hose Material: POM

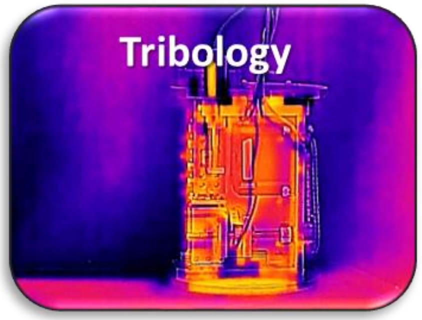
FY18 Accomplishments

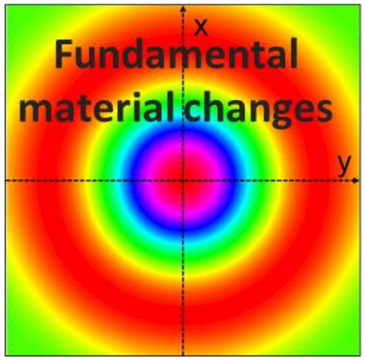
Industry Stakeholders and FMEA Influenced Test Methodology Development

- Industry survey confirmed knowledge on hydrogen compatibility of polymers is lacking and provided input regarding pressure and temperature priorities.
- The team completed a Failure Mode and Effects Analysis (FMEA) and identified the top failure causes:
  - Polymer seal (dynamic) material experiences a change in properties (strength, modulus, shear, hardness, etc.) due to hydrogen exposure
  - Polymer barrier material degrades from rapid high-pressure differentials (explosive decompression) due to hydrogen exposure
  - Polymer seal (static & dynamic) material selected exceeds hydrogen permeation rate
  - Polymer seal (static & dynamic) material geometry changes and volume swells or reduction due to hydrogen exposure

Project test methodology development directly aligns with industry stakeholder and FMEA input.

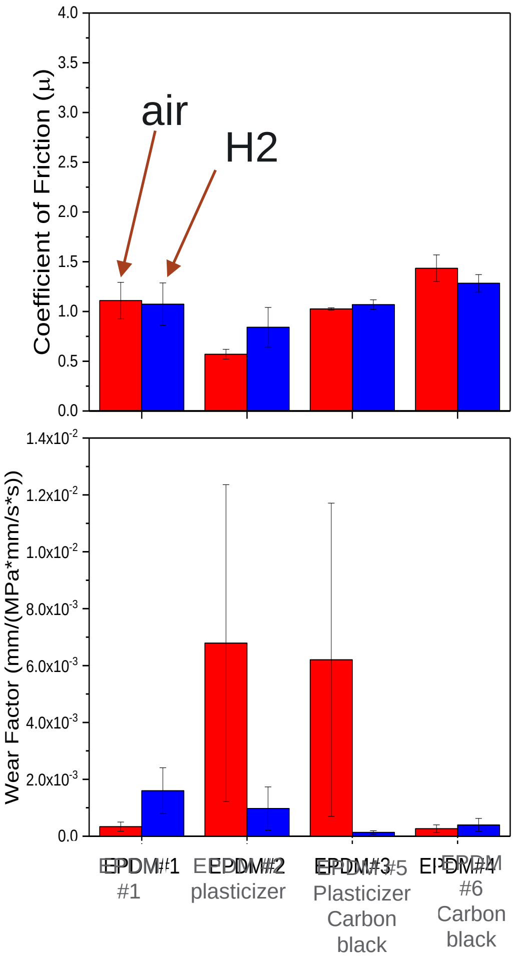
Project task approach:

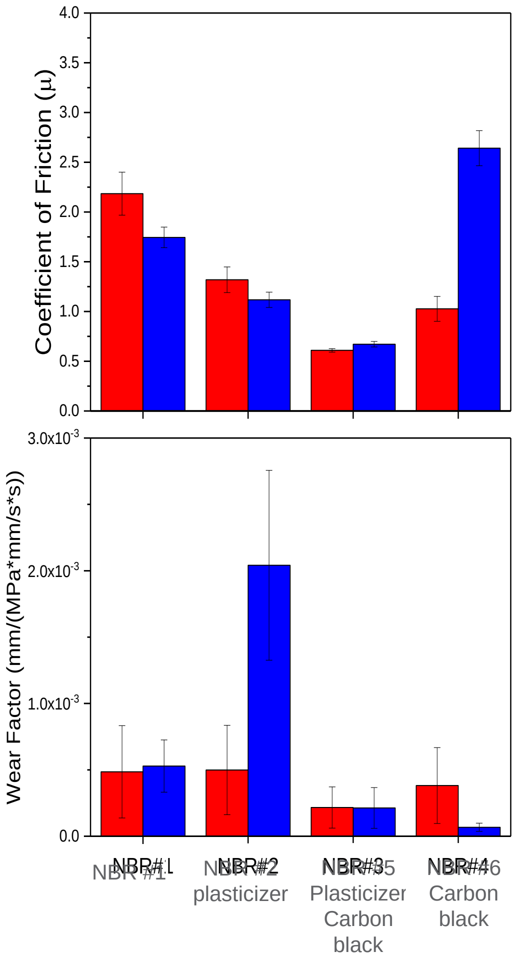


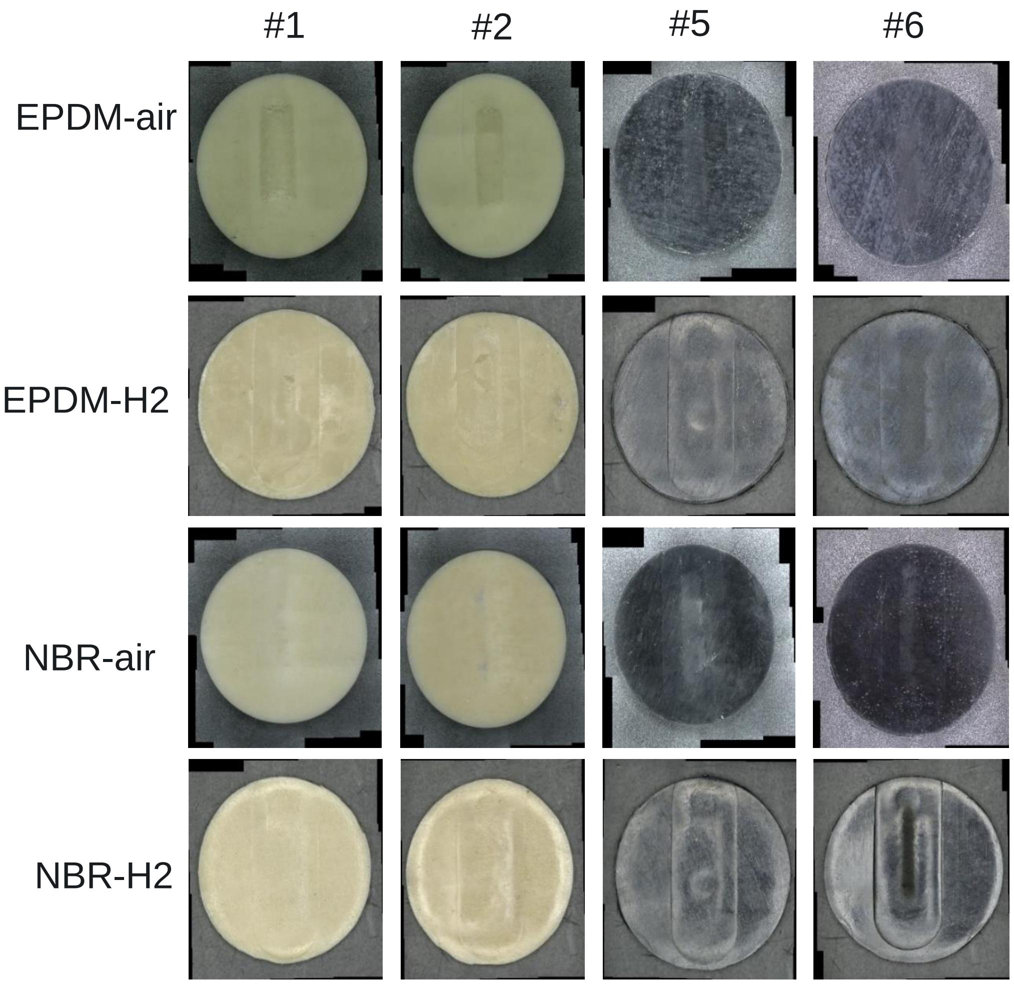


FY18 Accomplishments

Tribology Studies of NBR and EPDM







- High-pressure hydrogen affects tribological performance of EPDM and NBR in different ways based on plasticizer and filler influences
- Plasticizer and filler impact on wear and friction at various environments
- Draft publication in progress of hydrogen effects on friction and wear

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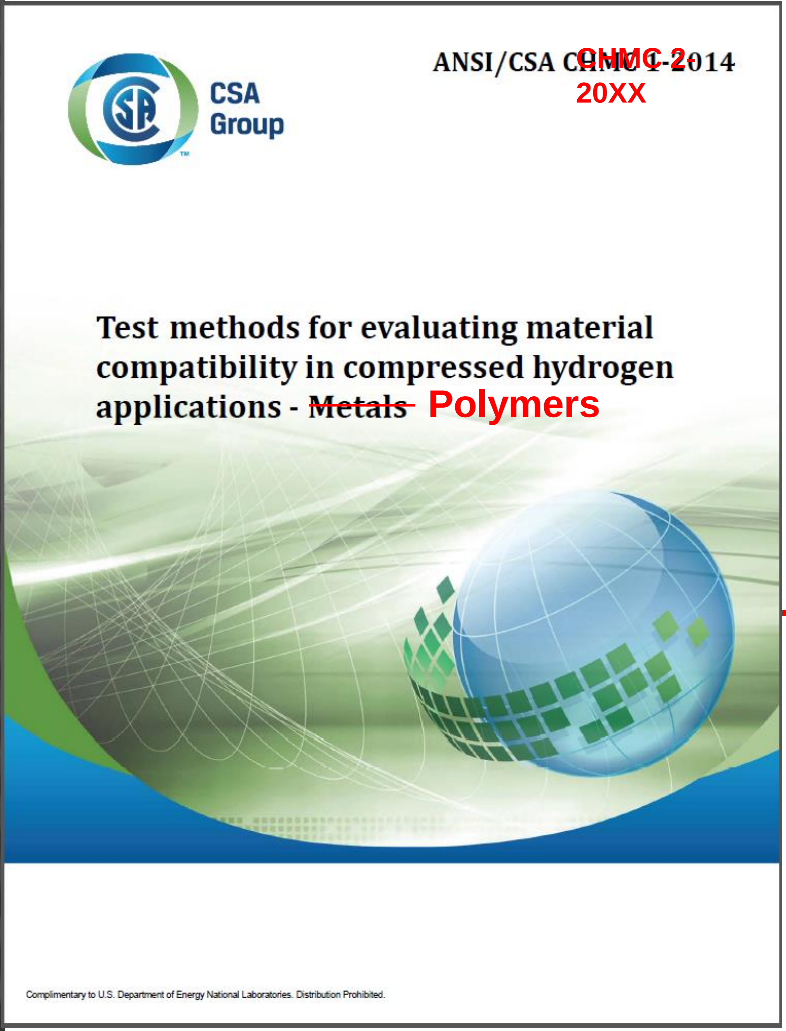
Accomplishments and Progress

CHMC 2 – Development of Test Method Document Sections



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Test methods for evaluating material compatibility in compressed hydrogen applications - ~~Metals~~ Polymers

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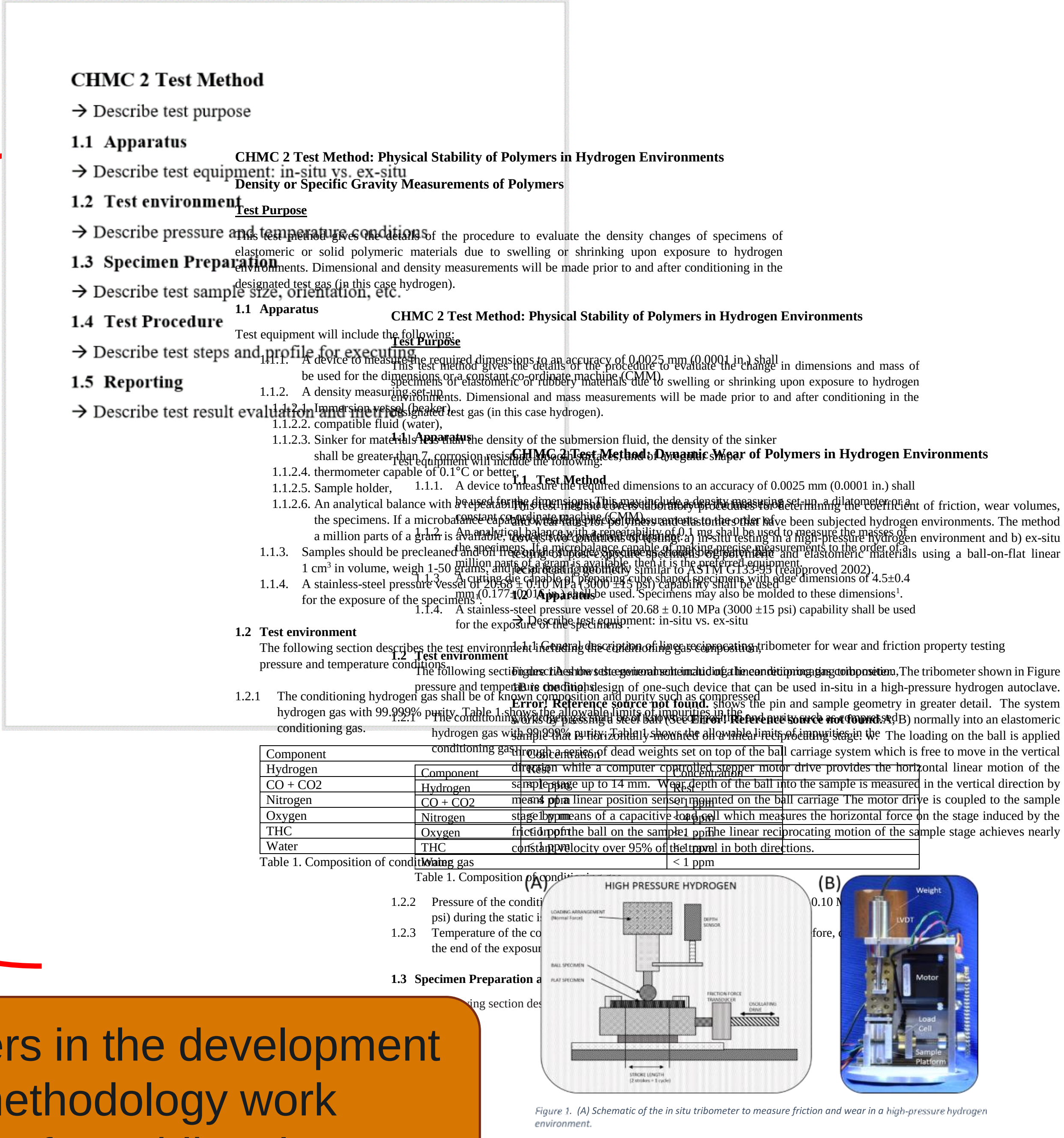

CHMC 2 Test Method

→ Describe test purpose

1.1 Apparatus

→ Describe test equipment: in-situ vs. ex-situ

1.2 Test environment

→ Describe pressure and temperature conditions

1.3 Specimen Preparation

→ Describe test sample size, orientation, etc.

1.4 Test Procedure

→ Describe test steps and profile for executing

1.5 Reporting

→ Describe test result evaluation and metrics

CHMC 2 Test Method: Physical Stability of Polymers in Hydrogen Environments

Density or Specific Gravity Measurements of Polymers

Test Purpose

This test method gives the details of the procedure to evaluate the density changes of specimens of elastomeric or solid polymeric materials due to swelling or shrinking upon exposure to hydrogen environments. Dimensional and density measurements will be made prior to and after conditioning in the designated test gas (in this case hydrogen).

1.1 Apparatus

Test equipment will include the following:

1.1.1. A device to measure the required dimensions to an accuracy of 0.0025 mm (0.0001 in.) shall be used for the dimensions or a constant co-ordinate machine (CMM).
1.1.2. A density measuring set-up
1.1.2.1. Immersion vessel (beaker),
1.1.2.2. compatible fluid (water),
1.1.2.3. Sinker for materials less than the density of the submersion fluid, the density of the sinker shall be greater than 7, corrosion resistant smooth surfaces, and of a regular shape.
1.1.2.4. thermometer capable of 0.1°C or better,
1.1.2.5. Sample holder,
1.1.2.6. An analytical balance with a repeatability of … the specimens. If a microbalance capable of making precise measurements to the order of a million parts of a gram is available, then it is the preferred equipment.
1.1.3. Samples should be precleaned and oil free … 1 cm³ in volume, weigh 1-50 grams, and …
1.1.4. A stainless-steel pressure vessel of 20.68 ± 0.10 MPa (3000 ±15 psi) capability shall be used for the exposure of the specimens[1].

1.2 Test environment

The following section describes the test environment including the conditioning gas composition, pressure and temperature conditions.

1.2.1 The conditioning hydrogen gas shall be of known composition and purity such as compressed hydrogen gas with 99.999% purity. Table 1 shows the allowable limits of impurities in the conditioning gas.

Component	Concentration
Hydrogen	Rest
CO + CO2	< 1 ppm
Nitrogen	< 4 ppm
Oxygen	< 1 ppm
THC	< 1 ppm
Water	

Table 1. Composition of conditioning gas

CHMC 2 Test Method: Physical Stability of Polymers in Hydrogen Environments

Test Purpose

This test method gives the details of the procedure to evaluate the change in dimensions and mass of specimens of elastomeric or rubbery materials due to swelling or shrinking upon exposure to hydrogen environments. Dimensional and mass measurements will be made prior to and after conditioning in the designated test gas (in this case hydrogen).

1.1 Apparatus

Test equipment will include the following:

1.1.1. A device to measure the required dimensions to an accuracy of 0.0025 mm (0.0001 in.) shall be used for the dimensions. This may include a density measuring set-up, a dilatometer or a constant co-ordinate machine (CMM).
1.1.2. An analytical balance with a repeatability of 0.1 mg shall be used to measure the masses of the specimens. If a microbalance capable of making precise measurements to the order of a million parts of a gram is available, then it is the preferred equipment.
1.1.3. A cutting die capable of preparing cube shaped specimens with edge dimensions of 4.5±0.4 mm (0.177±0.016 in.) shall be used. Specimens may also be molded to these dimensions[1].
1.1.4. A stainless-steel pressure vessel of 20.68 ± 0.10 MPa (3000 ±15 psi) capability shall be used for the exposure of the specimens[1].

1.2 Test environment

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Water	< 1 ppm

Table 1. Composition of conditioning gas

1.2.2 Pressure of the conditi… 0.10 M… psi) during the static i…
1.2.3 Temperature of the co… fore, … the end of the exposur…

1.3 Specimen Preparation a…

…ing section des…

CHMC 2 Test Method: Dynamic Wear of Polymers in Hydrogen Environments

1.1 Test Method

This test method covers laboratory procedures for determining the coefficient of friction, wear volumes, and wear rates for polymers and elastomers that have been subjected hydrogen environments. The method covers two conditions of testing: a) in-situ testing in a high-pressure hydrogen environment and b) ex-situ testing of post-exposure specimens of polymeric and elastomeric materials using a ball-on-flat linear reciprocating geometry similar to ASTM G133-95 (reapproved 2002).

1.2 Apparatus

→ Describe test equipment: in-situ vs. ex-situ

1.1.1 General description of liner reciprocating tribometer for wear and friction property testing

Figures 1A shows the general schematic of a linear reciprocating tribometer. The tribometer shown in Figure 1B is the final design of one-such device that can be used in-situ in a high-pressure hydrogen autoclave. **Error! Reference source not found.** shows the pin and sample geometry in greater detail. The system works by pressing a steel ball (See **Error! Reference source not found.**A, B) normally into an elastomeric sample that is horizontally mounted on a linear reciprocating stage. w. The loading on the ball is applied through a series of dead weights set on top of the ball carriage system which is free to move in the vertical direction while a computer controlled stepper motor drive provides the horizontal linear motion of the sample stage up to 14 mm. Wear depth of the ball into the sample is measured in the vertical direction by means of a linear position sensor mounted on the ball carriage The motor drive is coupled to the sample stage by means of a capacitive load cell which measures the horizontal force on the stage induced by the friction of the ball on the sample. The linear reciprocating motion of the sample stage achieves nearly constant velocity over 95% of the travel in both directions.

Figure 1. (A) Schematic of the in situ tribometer to measure friction and wear in a high-pressure hydrogen environment.

Team participation with stakeholders in the development of CSA document from test methodology work
Document currently under review for public release

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H-Mat Lab Collaborations

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Compatibility
Consortium

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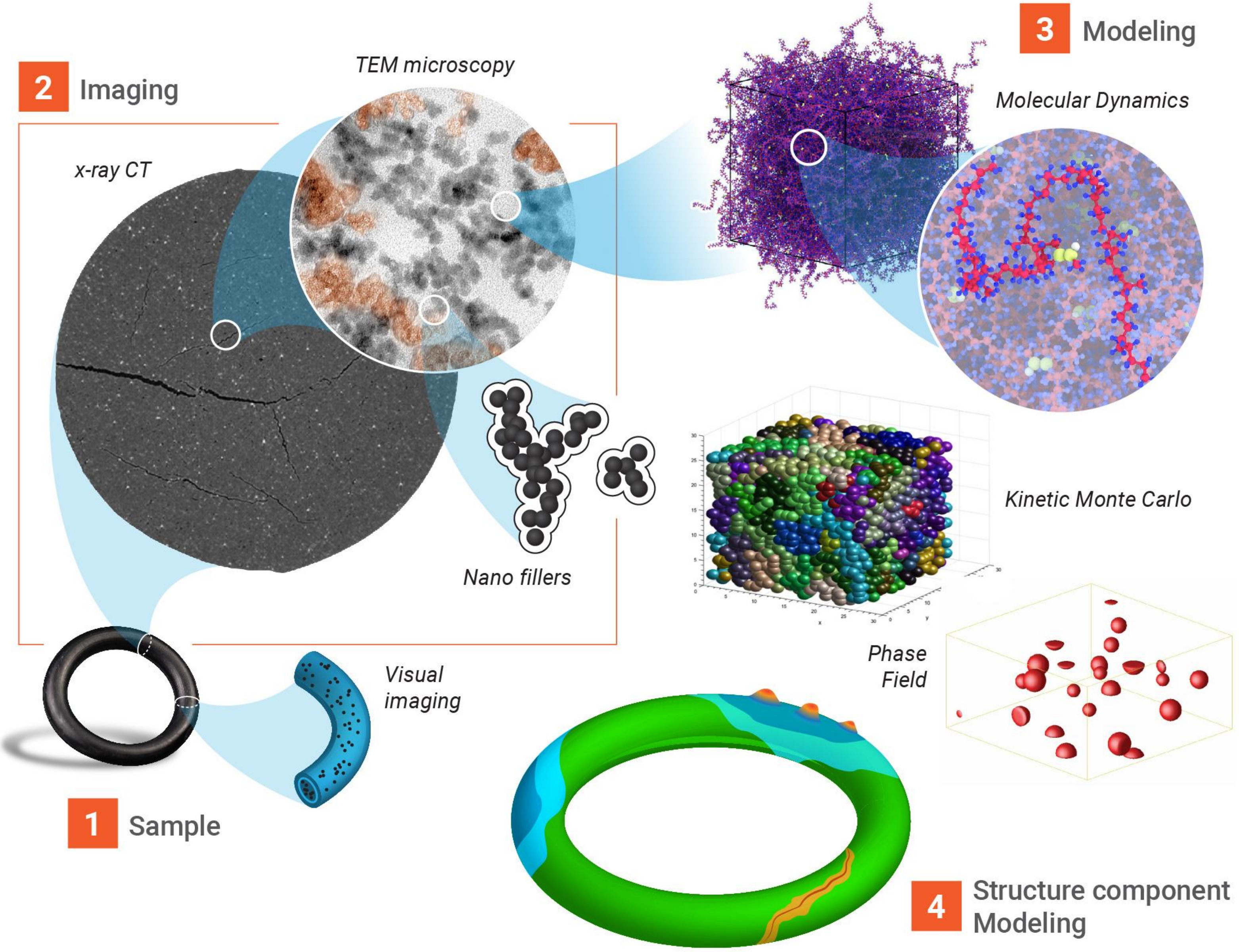
Accomplishments and Approach

Component Challenges to Multi-scale Modeling and Experimental Validation

Experimental Studies

Multiscale modeling



Accomplishments and Progress

Atomistic modeling of EPDM

NEED: Failure modes in elastomers, initiated through cavitation during H^{2} (de)compression, have origins in molecular rearrangement and degradation that are not fully understood.

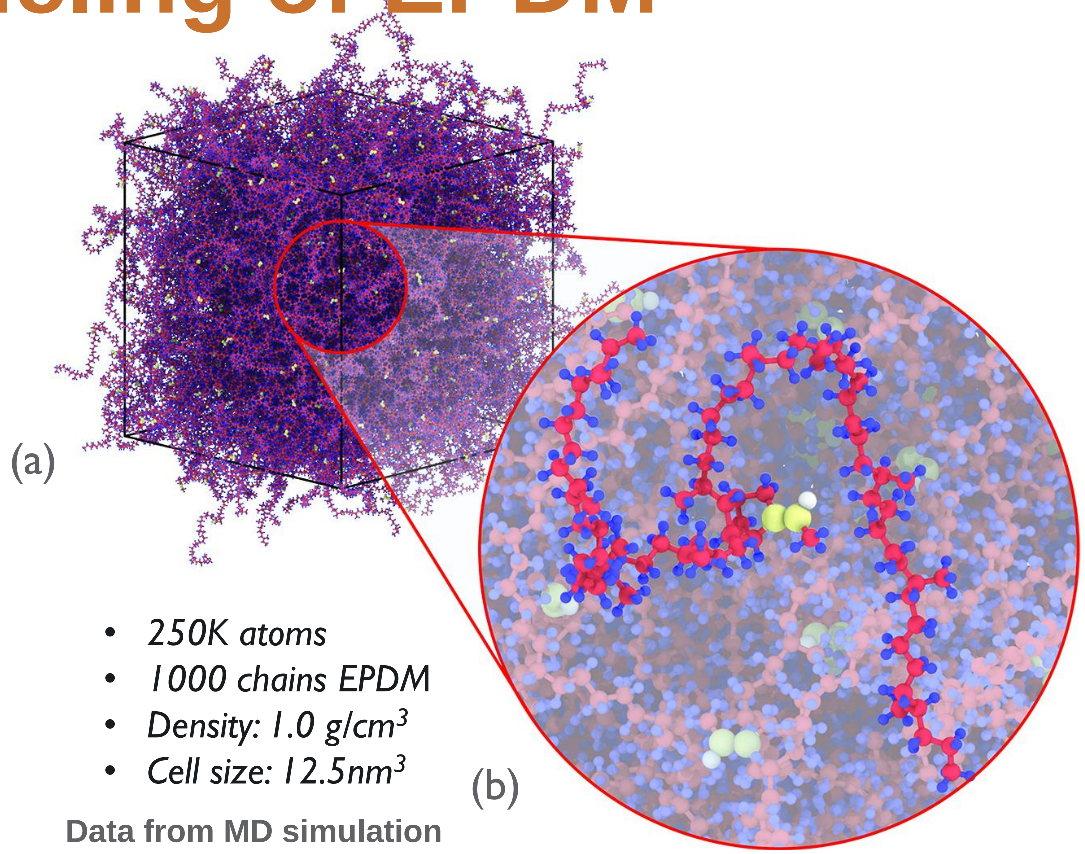
HYPOTHESIS: Atomistic modeling can provide insight as to these failure mechanisms with chemical specificity.

METHOD: Massively parallel molecular dynamics simulations are performed on all-atom representations of EPDM using LAMMPS (a).

Non-equilibrium simulations will be performed to assess microstructural processes and reactions that occur under pressurized H^{2} environments.

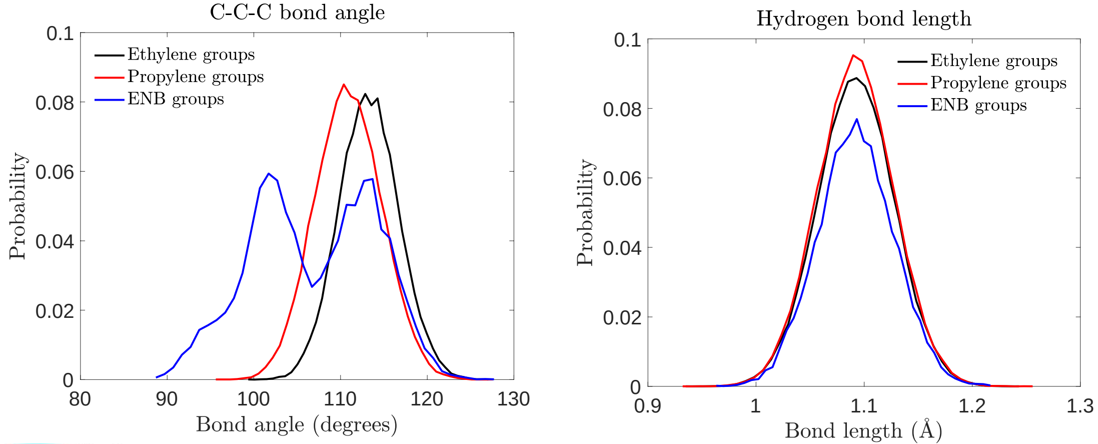
Equilibrated configurations, rates of dynamic processes, and associated energetics will be upscaled to higher length/time scale modeling efforts.

CURRENT: Validation of the model's non-equilibrium structural properties are currently being assessed (b) and later compared to experimental XRD and SANS diffraction data.



- *250K atoms*
- *1000 chains EPDM*
- *Density: 1.0 g/cm^{3}*
- *Cell size: 12.5nm^{3}*

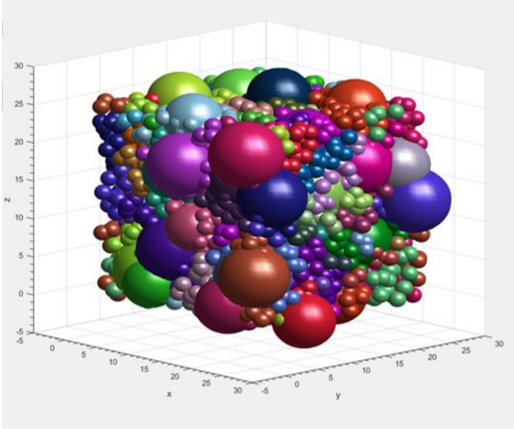
Data from MD simulation

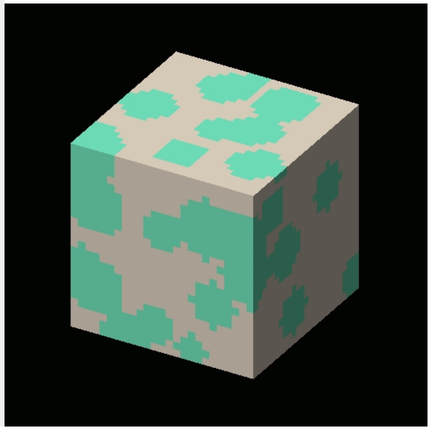


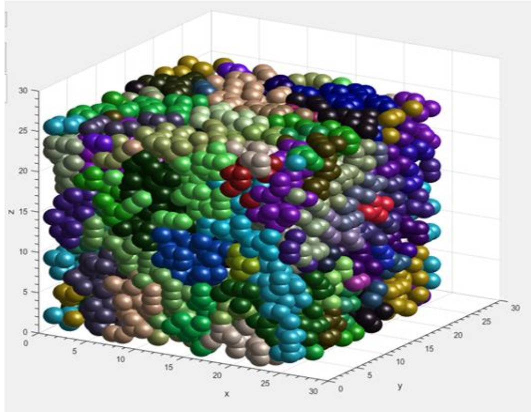
Accomplishments and Progress

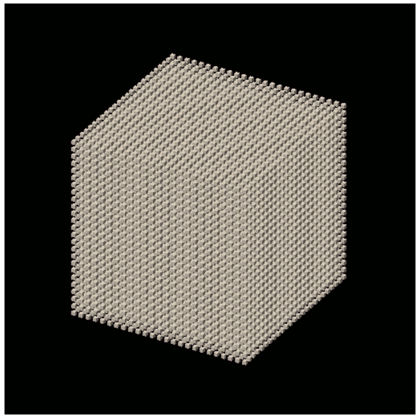
Material Integration into SPPARKS Code

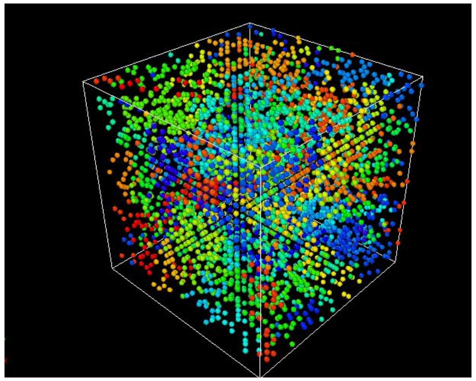
- **Progress**
  - SPPARKS code basic setup
  - Basic functionalities tested
- **Ongoing work**
  - Polymer chain representation for on-lattice application
    - ✓ Pseudo atom with bigger radius
    - ✓ Placement of monomers on lattice sites using techniques, such as self avoiding walk (SAW).
  - Pressure implementation to simulation medium.
- **Major tasks**
  - Identification of events and phenomena during pressurizing and depressurizing processes
  - Quantitative data for the likelihood or rates of identified competing events
- **Possible paths**
  - Findings from MD simulation
  - Theory and assumptions based on experimental observations







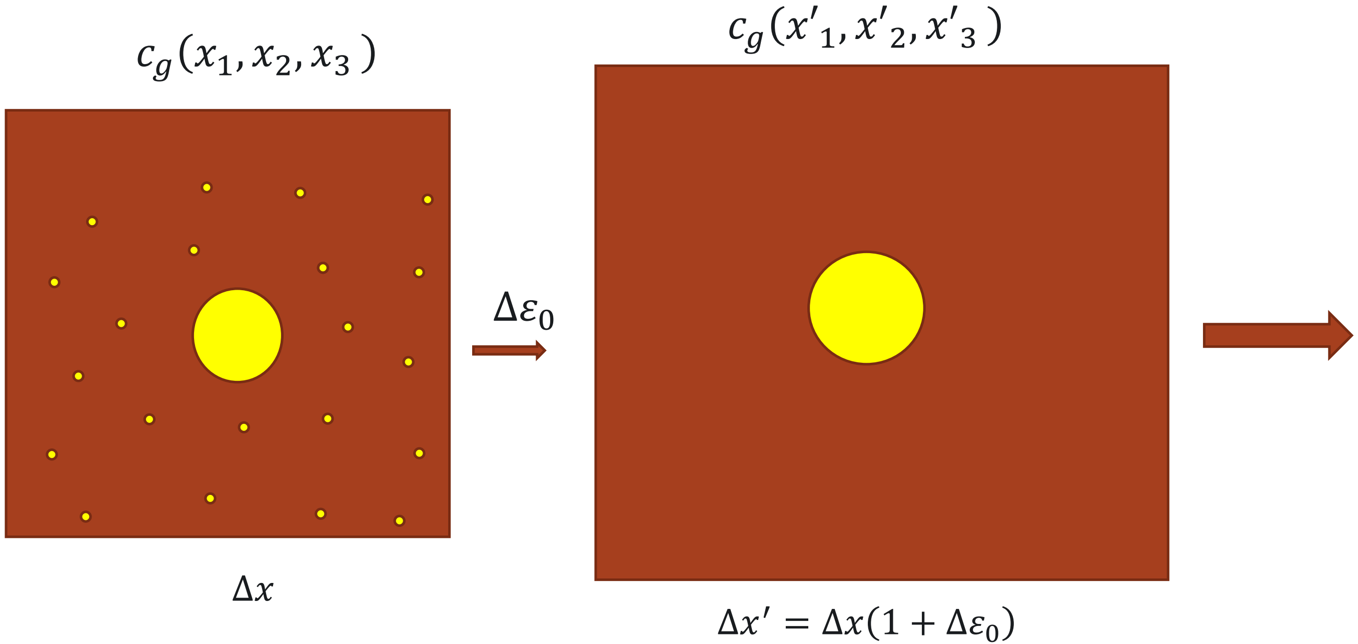




Accomplishments and Progress

Phase Field Model and Equations

- Code for one bubble case first!
- Stress distribution around gas bubble
- When to grow and when to shrink
  - (gas bubble size, solubility, pressure)
- 3D simulation!!



$c_g(x_1, x_2, x_3)$

$c_g(x'_1, x'_2, x'_3)$

$\Delta\varepsilon_0$

Δx

$\Delta x' = \Delta x(1 + \Delta\varepsilon_0)$

$$\frac{\partial c_g}{\partial t} = \nabla \cdot \left\{ M_{gg} \nabla \left(\frac{\partial (F + U^{def})}{\delta c_g} \right) \right\}$$

$$\frac{\partial \eta}{\partial t} = -L \left(\frac{\partial F}{\partial \eta} + \frac{\partial U^{def}}{\partial \eta} - \kappa^2 \nabla^2 \eta \right)$$

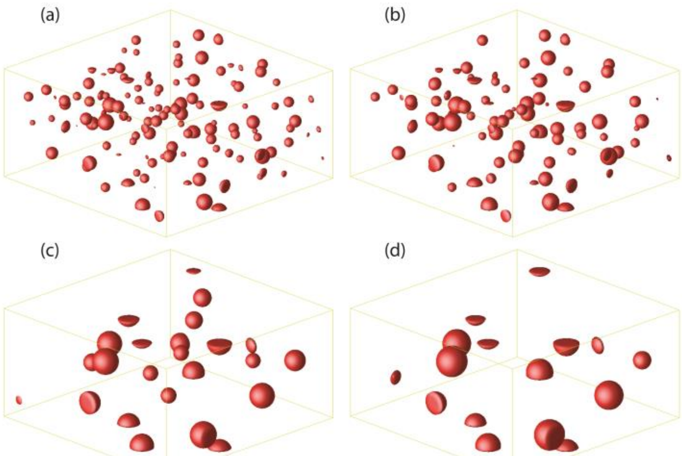
Mechanical equation

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0, \quad \sigma_{ij} = c_{ijkl}(\varepsilon_{kl} - \varepsilon^0_{ij})$$

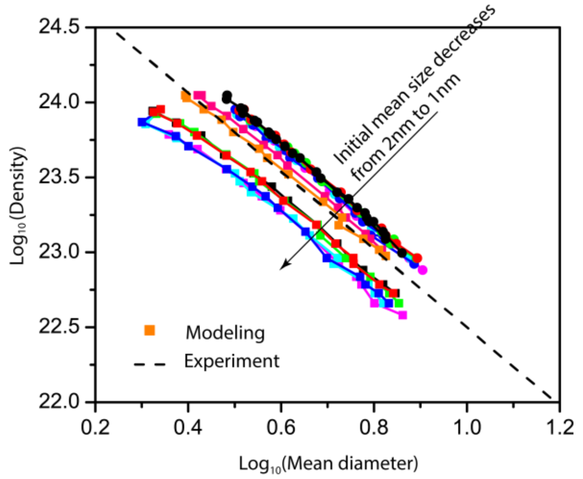
at boundary: $\varepsilon_{11} = \varepsilon_{33} = \varepsilon_0$

Hypothesis & validation: During decompression, gas molecules like to diffuse into gas bubble at first due to supersaturation and gas bubble growth

3d simulation



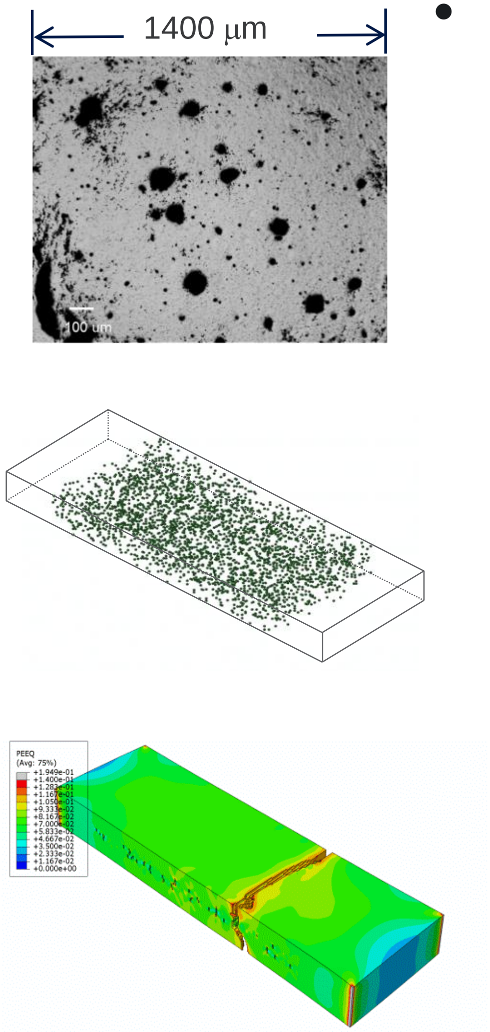
Gas bubble morphology evolution with time



Gas bubble density (per cubic meter volume) versus mean diameters (nm)

Accomplishments and Progress

Morphology to Component Scale Modeling



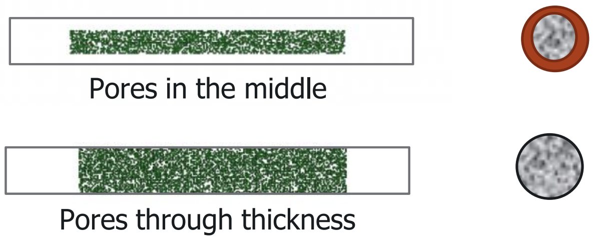
- Impact of porosity on the material properties for hydrogen applications
  - Morphological feature of interest – porosity
    - ✓ Experimentally observed or modeled using Phase Field
    - ✓ Extract feature information – spatial distribution, size and shape variation, and volume fraction
  - Approximation of porosity at component scale
    - ✓ Explicit representation of each pore becomes computational expensive
    - ✓ Approximate by varying density of individual finite elements
  - Constitutive model parameters
    - ✓ Extract material parameters for constitutive model from experimental measurements – Young's modulus, plastic behavior, temperature dependent properties, modified property values due to H_2 concentration, pressure dependent properties
  - Failure prediction at the component scale
    - ✓ Strain localization or other appropriate failure mechanism utilized to model failure of sample under tensile loading
    - ✓ Presence of pores and variation in material properties determines failure location

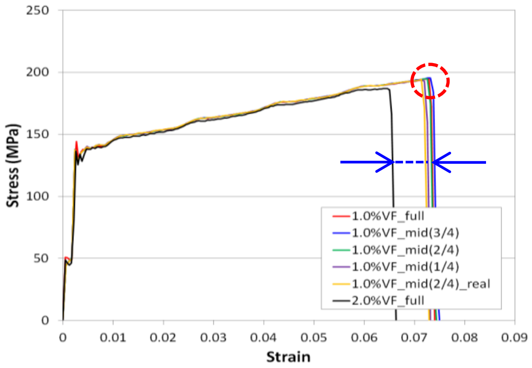
Accomplishments and Progress

Exploring Impact of Variation on Failure

- At the component scale, variations in properties can be created and investigated

Spatial variation in pore location barriers and seals

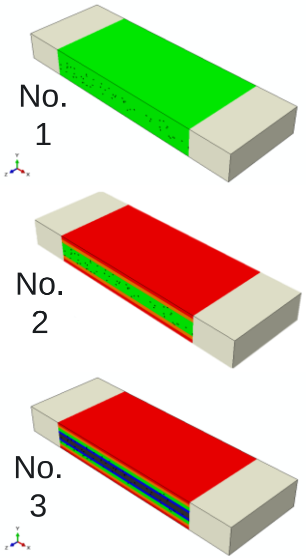


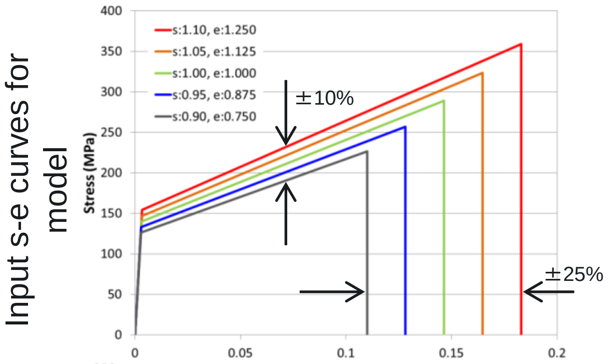


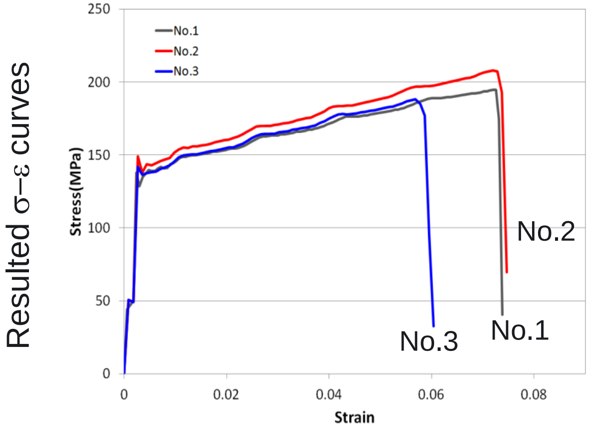
1.0% VF models

Choi et al. (2013) SAE Technical Paper #2013-01-0644

Spatial variation in matrix material properties due to grain size distribution

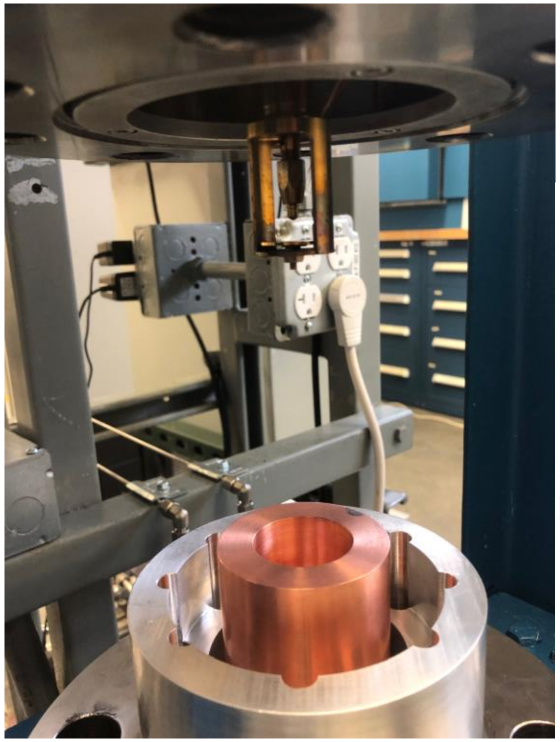




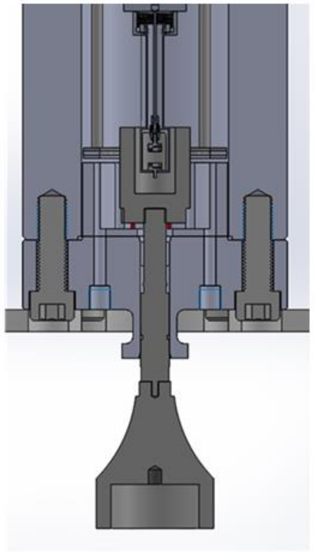


Accomplishments and Progress

In situ Dynamic Mechanical Analysis



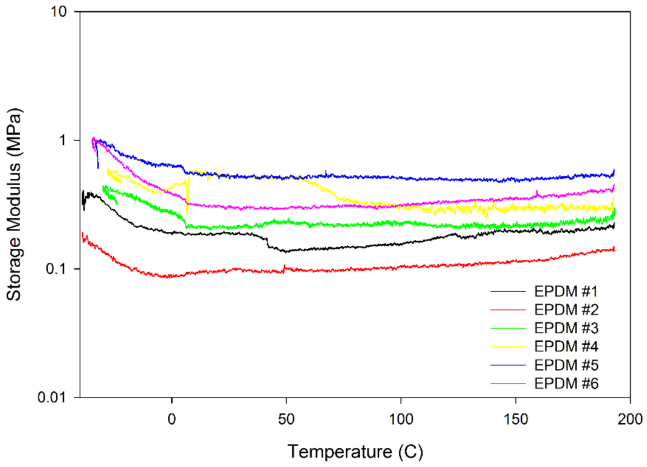
Internal fixture



- In situ DMA is complete & baseline experiments ongoing isothermally with high-pressure helium
- Capable of measuring various mechanical property values (e.g. storage modulus) in situ on account of high pressure, gas species, and temperature
- To understand effects of high pressure, hydrogen and a combination thereof on change in mechanical properties of example materials, which eventually leads to the basic understanding of the damage mechanism

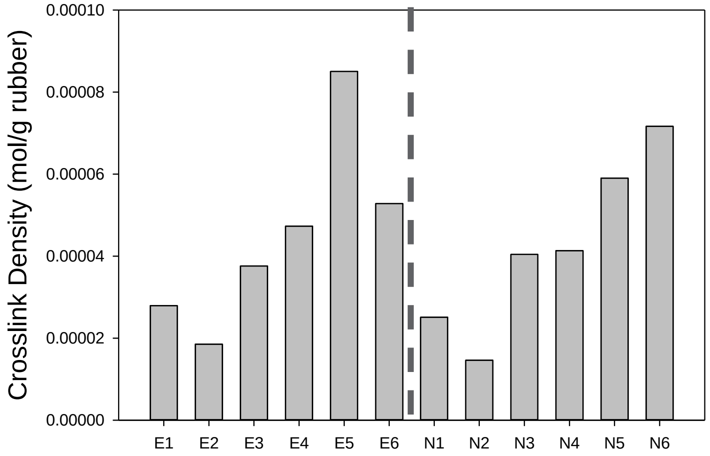
Accomplishment and Progress

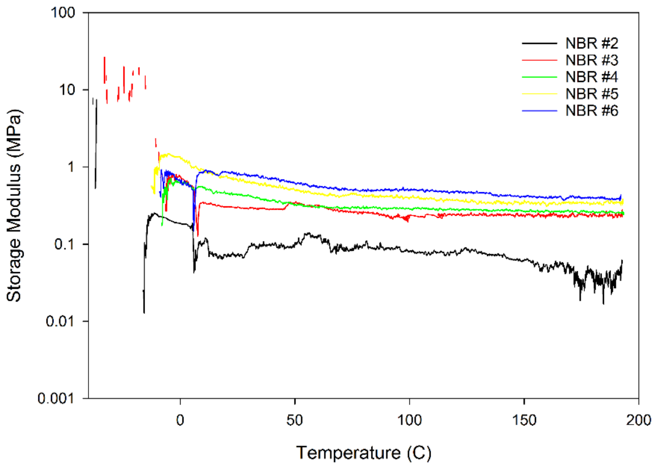
Mechanical Characterization (DMA)

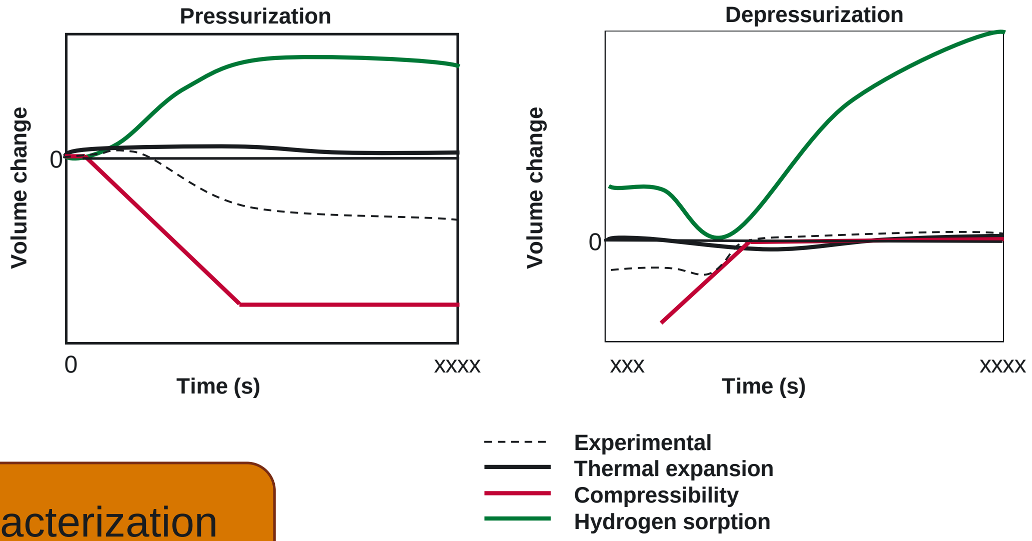


$$M_c = \frac{\rho R T}{G} \pi r^2$$

Estimation of crosslink density:





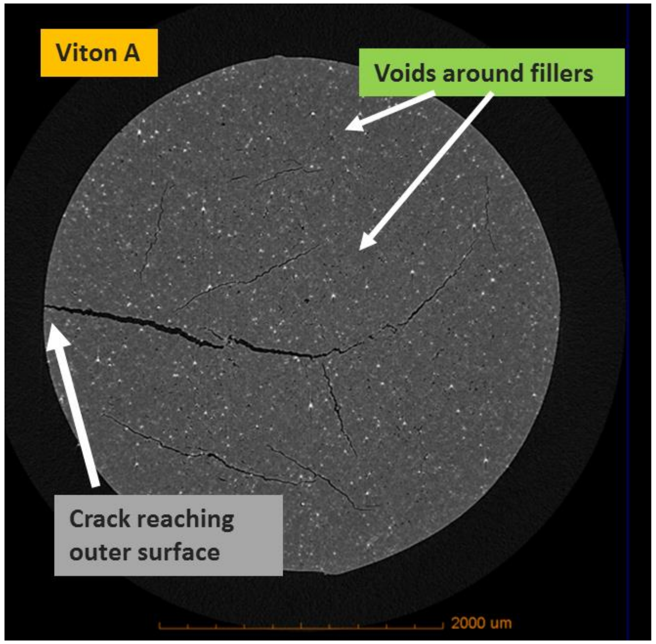


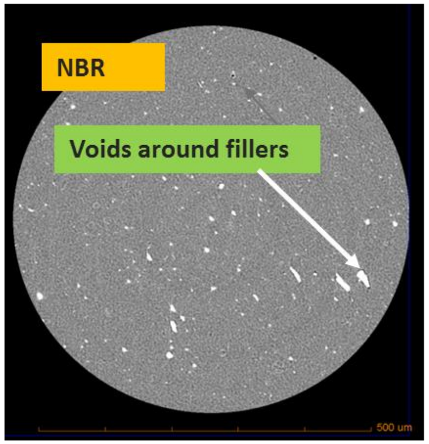
DMA is a valuable tool for polymer characterization now with novel in situ pressurization control

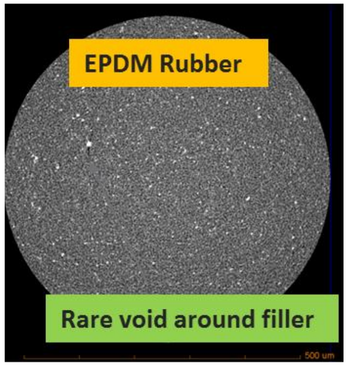
Accomplishments and Progress

Example of Validation Using Experimental Measurement

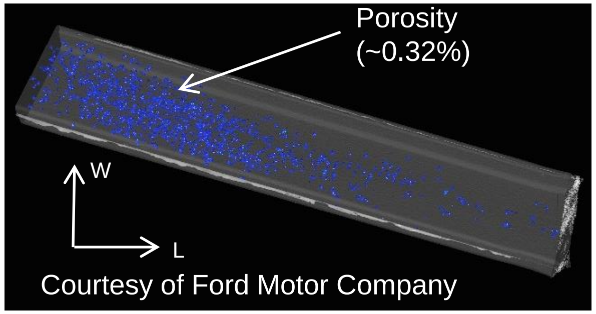
- CT images provided of the internal porosity of a tensile test specimen
- Digital sample created from CT images
- Matrix properties extracted from lower length scale simulations
- Analysis conducted using tensile test loading
- Able to replicate failure location of physical specimen



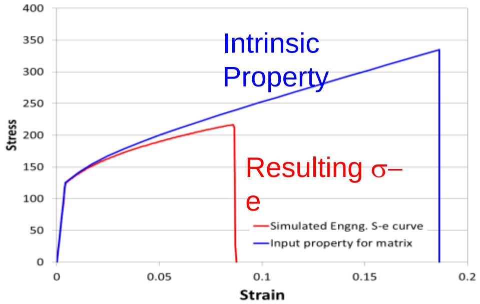




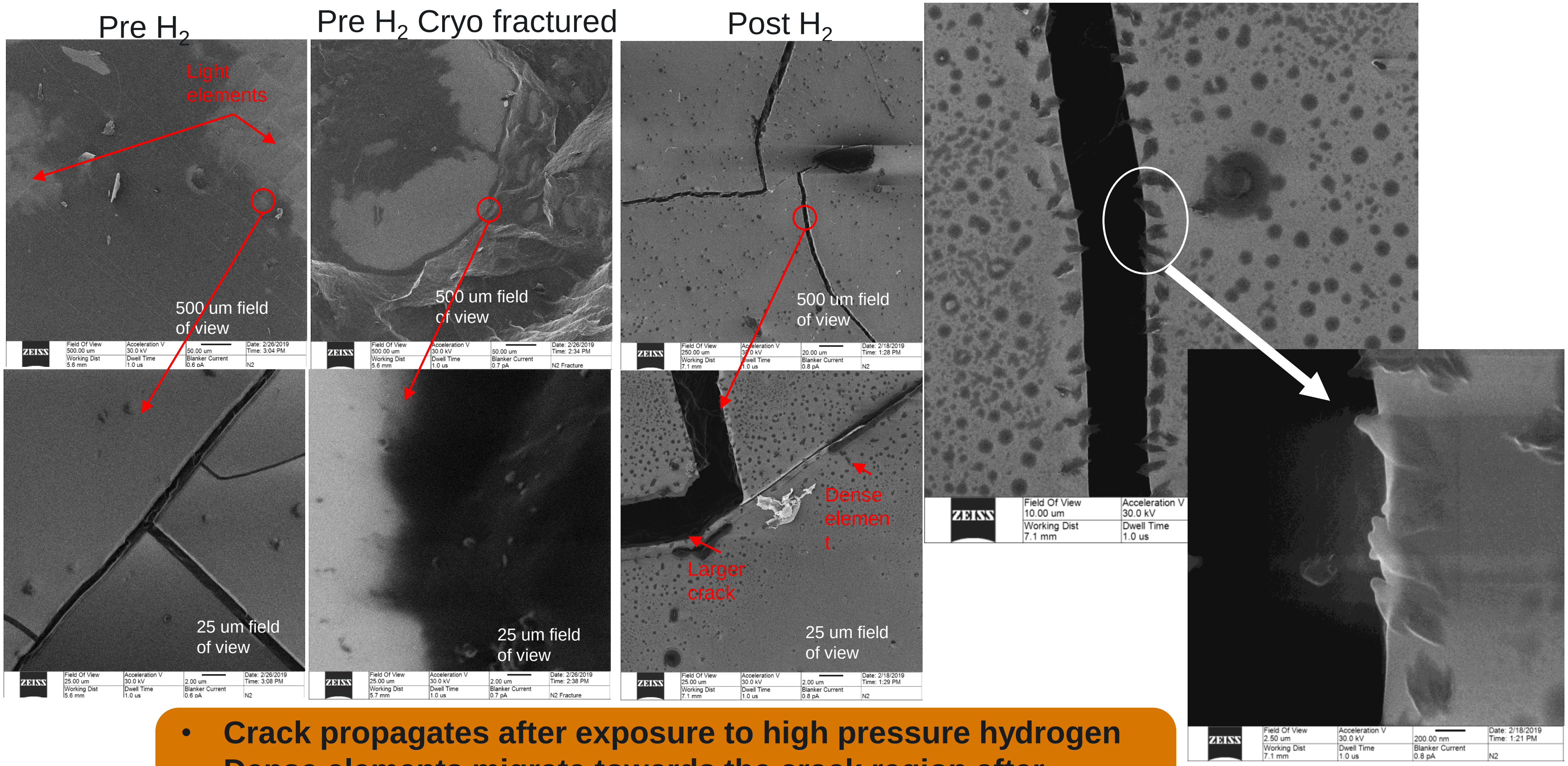
NBR and EPDM shown at 500 microns to magnify any voids or cracks



Courtesy of Ford Motor Company



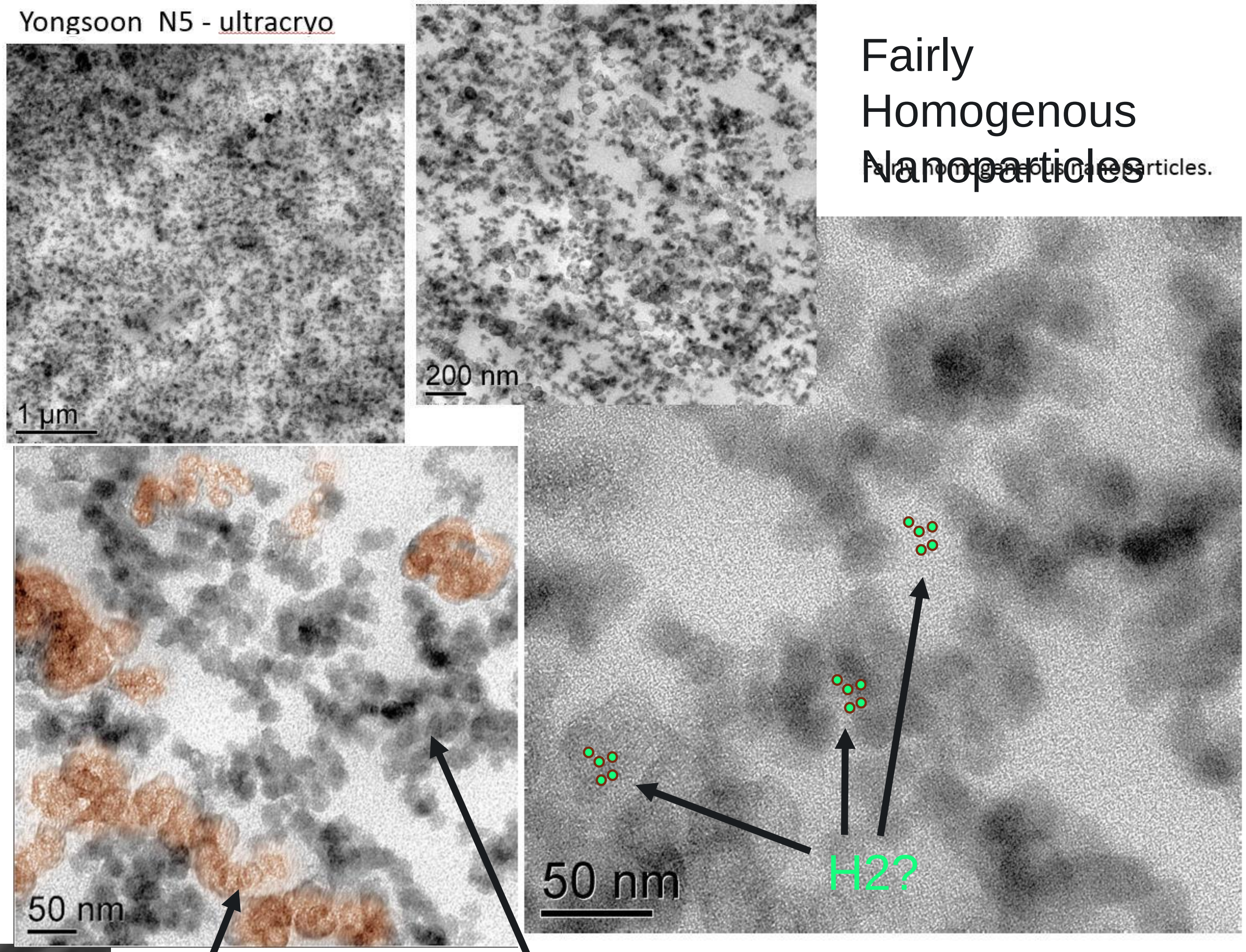
He Ion Microscopy Imaging of NBR #2 pre and post exposure



- **Crack propagates after exposure to high pressure hydrogen**
- **Dense elements migrate towards the crack region after exposure to hydrogen**

Accomplishments and Progress

Transmission Electron Microscopy NBR #5



Fairly Homogenous Nanoparticles

Fairly homogeneous nanoparticles.

Precipitated Silica nanoparticles

Carbon nanoparticles

NBR rubber compound with carbon filler only

Carbon black aggregates into amorphous regions of rubber which could be areas of increased regions of hydrogen

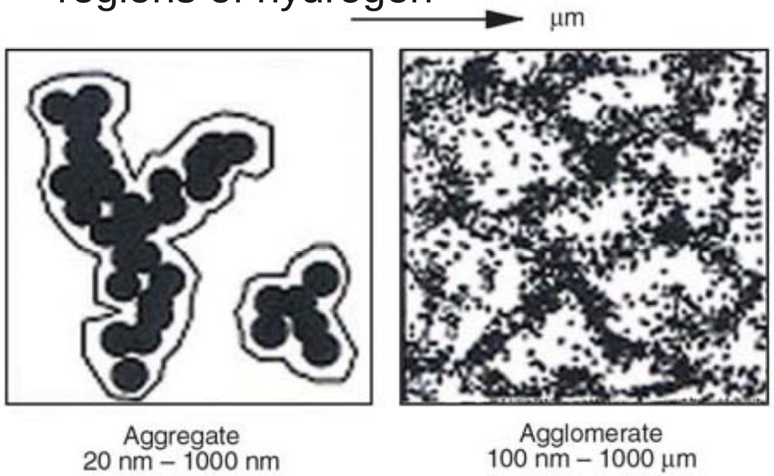
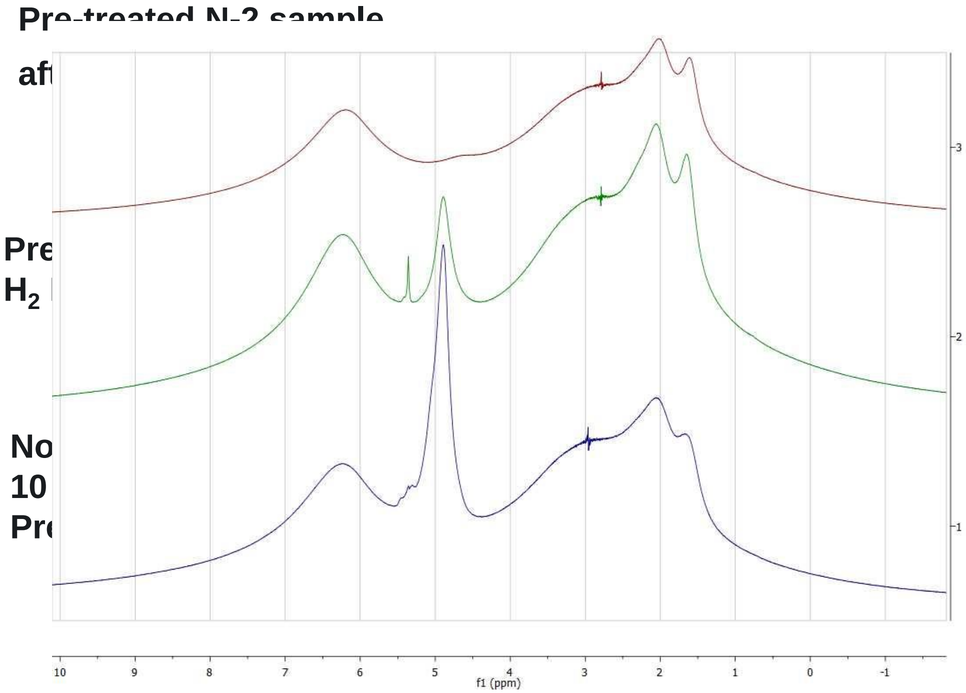


Figure 2. The aggregation and agglomeration of carbon black in rubber [9]

Lawandy et al Express Polymer Letters vol 3, no. 3, 2009, pp 152-158

Accomplishments and Progress

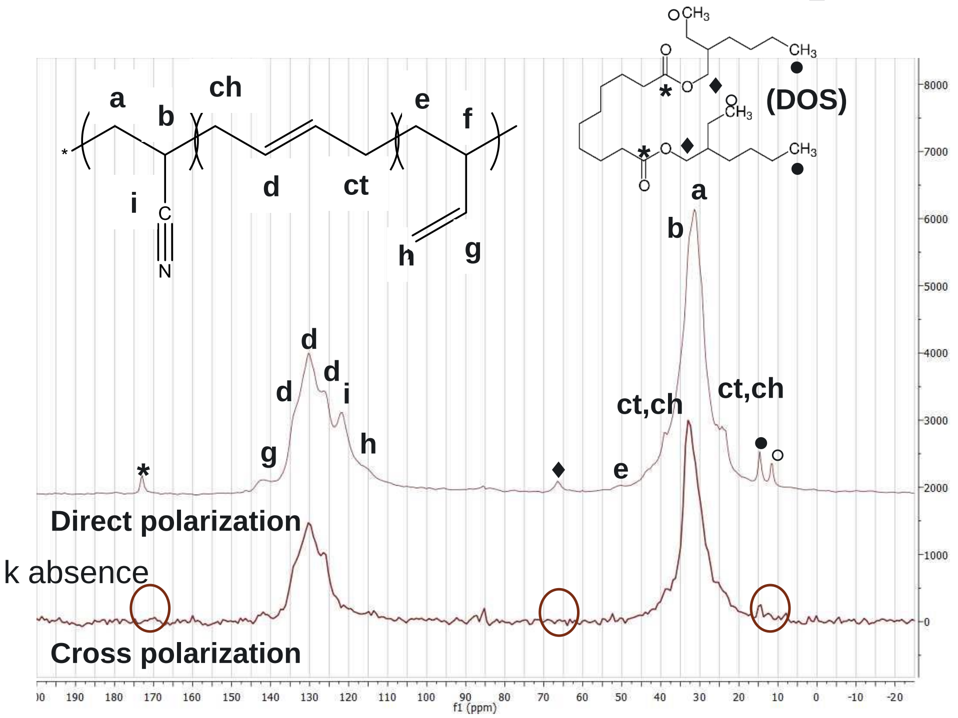
^{1}H and ^{13}C spectra with 10 MPa in situ H_2



5.3 ppm @ - Hydrogen condensed within sample pores/defects

4.89 ppm * - Free H2 peak

H_2 pretreated N-2 sample under 28MPa: NMR experiment under 10 MPa H_2



DP shows more quantitative than CP: observed plasticizer (DOS)

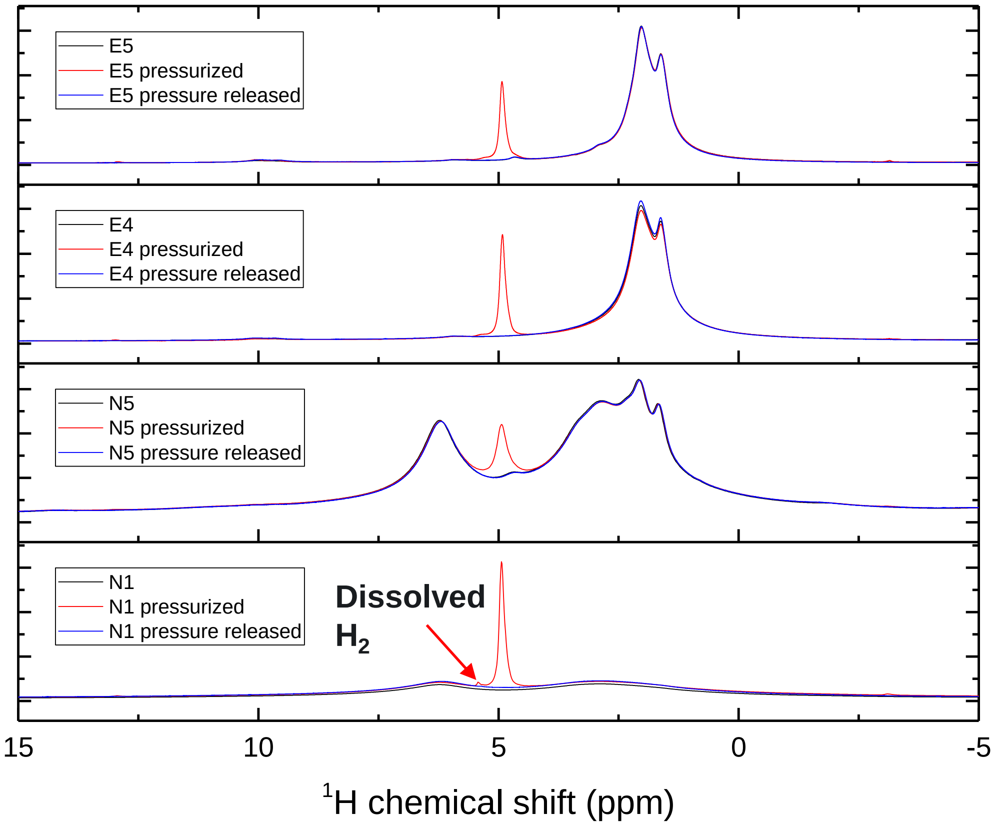
The DP is considered quantitative as long as the relaxation delay is set correctly.

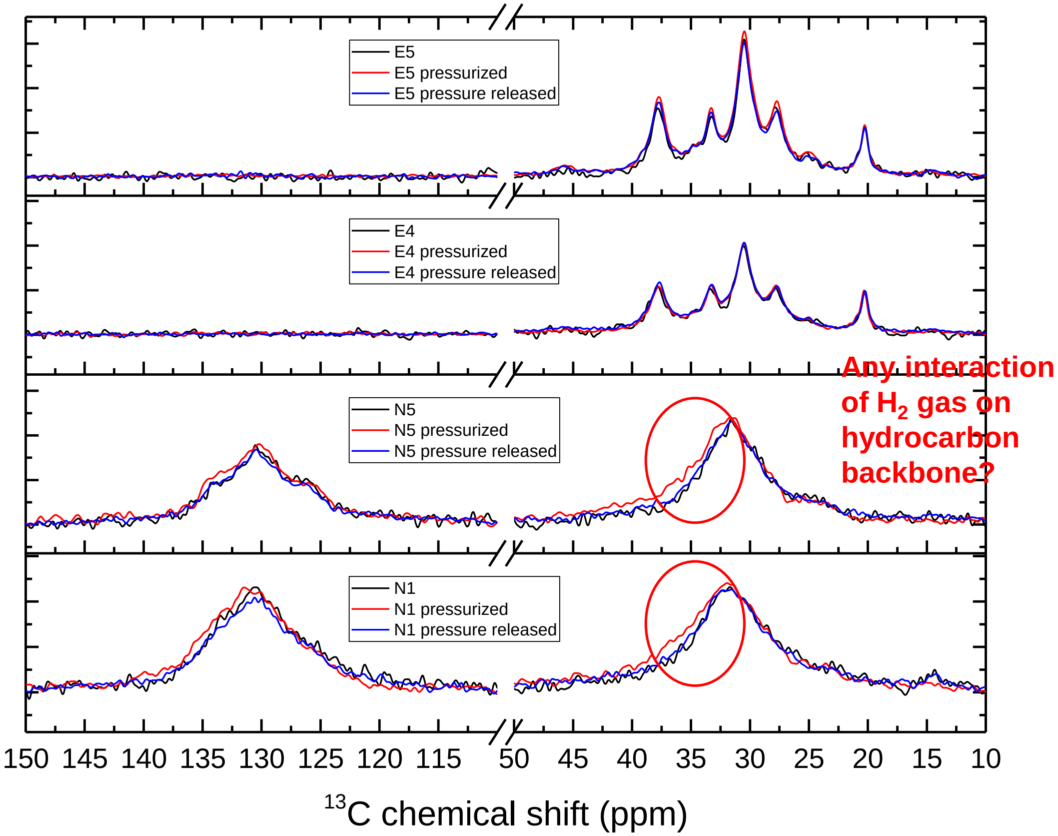
The cross- polarization experiment is usually quicker to record but is more efficient for rigid C-H species, and therefore results in qualitative spectra.

In these two spectra recorded using these two pulse sequences, the absences of peaks in the cp spectrum identify which regions must be less mobile.

Accomplishments and Progress

^1H and ^{13}C spectra with 10 MPa in situ H_2





Any interaction of H_2 gas on hydrocarbon backbone?

Possible interaction of H_2 gas on the NBR hydrocarbon backbone

Accomplishments Summary

- **H-Mat** is a consortium of national laboratories formulated to address the **materials science of hydrogen-induced degradation** of materials
    - *Motivation*: develop **science-based strategies** to design the morphology of materials for improved resistance to degradation in high-pressure hydrogen
- **H-Mat** integrates advanced **computational materials science** and innovative experimental capabilities across polymer morphology length scales
    - *Approach*: consideration of the intersection of **environmental, mechanics, and materials variables** associated with hydrogen effects in materials
- **H-Mat** tasks are formulated around **high-value materials and physical phenomena**
    - **Polymeric material systems:** multiscale modeling simulations in EPDM, NBR, and thermoplastic material system will inform morphology development and materials evaluation in high-pressure H2
    - **Modeling of different length scales:** new understanding evolving from MD, KMC, and Phase Field simulations to input component level modeling effects of hydrogen uptake and rapid gas expansion
    - **Material performance:** understanding the fundamentals of material performance from experimental high pressure hydrogen effects that support multiscale modeling efforts and provide future guidance in material design for degradation mitigation strategy understanding fundamental behavior of hydrogen effects on deformation and fracture
- **H-Mat** seeks to provide the foundational knowledge necessary to **design materials microstructures** for resistance to hydrogen-assisted fracture

Collaborative Activities

Partner		Project Roles
U.S. DEPARTMENT OF ENERGY	DOE	Sponsorship, Steering
Pacific Northwest NATIONAL LABORATORY	PNNL	Project Co-lead for Polymers, Polymer Characterization, Wear and Tribological Studies, Mechanical Properties and Moderate Pressure, Multiscale Modeling, Polymer Database Development
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, Polymer Outgassing

Additionally, collaborations being developed with industry and universities. Kyushu University, Swagelok and Arlanxeo have given support and offered resources to our project

Acknowledgements

Task	Lead	Principal Contributors
Mechanisms of hydrogen induced degradation of polymers	Nalini Menon (SNL) Kevin Simmons (PNNL)	• Bart Smith (SAXS, SANS) (ORNL) • Amit Naskar (SAXS, SANS) (ORNL) • Wenbin Kuang (DMA) (PNNL)
Computational multiscale modeling	Erin Barker (PNNL) Mark Wilson (SNL)	• Wond Menegesha (KMC) (SNL) • Yulan Li (Phase Field)(PNNL)
Hydrogen resistant polymeric formulations	Kevin Simmons (PNNL)	• Nalini Menon (SNL) • Wenbin Kuang (PNNL)
Materials for cryogenic hydrogen service	Kevin Simmons (PNNL)	• Daniel Merkel (experimental) (PNNL) • Aashish Rohatgi (materials) (PNNL) • Chris San Marchi (materials) (SNL) • Hee Seok Roh (computational) (ANL) • Nghiep Nguyen (computational) (PNNL) • Amit Naskar (Materials) (ORNL) • Chris Bowland (Materials) (ORNL)
Database Development	Chitra Sivaraman (PNNL) Rick Karnesky (SNL)	• Matt Macduff (database development) • Corina Lansing (database development)
Project Management	Kevin Simmons (PNNL) Chris San Marchi (SNL)	

Remaining Challenges and Barriers

Challenges and Barriers	Mitigation
Large amount of polymers and elastomers to test	Experimental and modeling efforts to understand degradation mechanisms in polymer systems for future mitigation developments in polymer systems
Low temperature material performance in high pressure hydrogen with thermal and pressure cycling environments not well understood to long term performance	Experimental data and modeling efforts to correlate material performance in extreme conditions to understand and develop new mitigation strategies for improved performance
Testing time is long	When appropriate double up on sample soaking
Dissemination of data is a broad audience	Engagement with stakeholders, implementation of h2tools.org with database and guide
Cannot see impact of hydrogen during long term cycling or frictional wear in a short test (Impact may not exist)	Experimental studies to understand the long term aging effects in high pressure hydrogen cycling environment

Proposed Future Work

- **Remainder of FY19**
  - Continued develop material models and run various scenarios
  - Continue in developing material data in NMR, TEM, SANS, SAXS, and X-ray CT for multiscale modeling support
  - Experimental development with in situ DMA for material property performance under high pressure hydrogen environments and rapid gas expansion
  - Pressure cycling experiments to support material degradation mechanisms and experiments with SANS and SAXS
  - Establishment of Datahub for data dissemination
- **FY20 (project continuation and direction determined by DOE annually)**
  - Demonstrate quantitative permeation measurement of elastomer in o-ring configuration to assess hydrogen transport in polymers under complex loading conditions
  - Begin experimental studies with temperature and pressure effects
  - Begin thermoplastic material experimental studies, possible materials are hose liner systems
  - Develop modeling tool for stakeholder use
  - New material development to begin
  - Complete Datahub development and begin using

Response to previous year's reviewers' comments

- H-Mat is a new project and was not reviewed last year
- FY18 project responses are below
- The approach of this project is well focused and excellent. It does not score as outstanding since the engagements with stakeholders are not so clear, which, according to the presentation, seem to be mainly within the U.S. Department of Energy (DOE) and its national laboratories, except for Ford.
  - *The project team was engaged with more than 20 stakeholders who were participating in the CSA CHMC-2 Polymers document. The project team presented information at the committee level that the team was working on and there was great dialogue in the subcommittees on information that wasn't learned through the stakeholder survey.*
- The project is on track and will eventually fill an important knowledge gap. Basic materials behavior differences have been demonstrated and quantified. At this moment of project development, however, it is not clear from the presentation which of the variations in behavior effects will really play a role in safety or lifetime performance of the up-scaled system.
  - *Rapid gas decompression and volume changes within the material are the most obvious issues that the team has found to be challenging to date. Pressure cycling would be the next test once the test system is operational and will be used to evaluate damage accumulation in the material as a function of pressure cycling*

Thank you

Backup Slides

Project ID# SCS026

FY 18 Accomplishment Summary

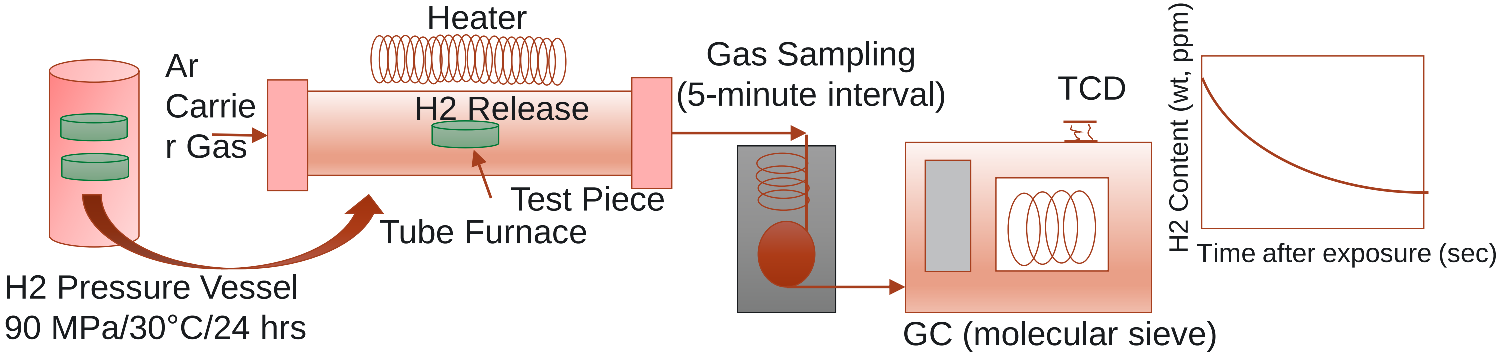
- Stakeholder Engagement & Dissemination
  - Completed CHMC 2 Polymers Standard based on test methodologies developed and industry input with over 20 active member participants
  - H2tools.org website for Hydrogen Compatibility of Polymers capabilities
- Technical Accomplishments
  - PNNL designed and built new novel in situ dynamic mechanical analyzer for high pressure hydrogen
  - Hydrogen permeability is influenced material morphology and additives
  - High-pressure hydrogen affects tribological performance of EPDM and NBR in different ways
  - Plasticizer and filler influence wear and friction differently at various environments
- Static high-pressure hydrogen gas material effects on EPDM and NBR additives
  - Both EPDM and NBR show an increase in compression set after H2 exposure; NBR shows a higher increase
  - Both EPDM and NBR show a decrease in storage modulus upon H2 exposure
  - Swelling upon H2 exposure is less with filler than without
  - Addition of fillers changes damage seen in NBR due to H2 exposure from linear microcracks to pinpoint voids
  - Addition of fillers helps EPDM with respect to H2 resistance – fewer cracks

Model Elastomer Material Compounds

- Transitioned from purchased commercial materials to controlled material compounds for research
- Developed model EPDM and NBR compounds with Kyushu University and Takaishi Industries
- Controlled compound additives in six different formulations for each material
  - No filler, crosslinked elastomer
  - Crosslinked elastomer with plasticizer only
  - Crosslinked elastomer with carbon black only
  - Crosslinked elastomer with silica filler only
  - Crosslinked elastomer with plasticizer, carbon black, and silica filler
  - Crosslinked elastomer with carbon black and silica filler

Used to evaluate the effects of hydrogen on polymers and known additives

Model Elastomer Compounds Hydrogen Content


Heater

Ar Carrier Gas

H2 Release

Test Piece

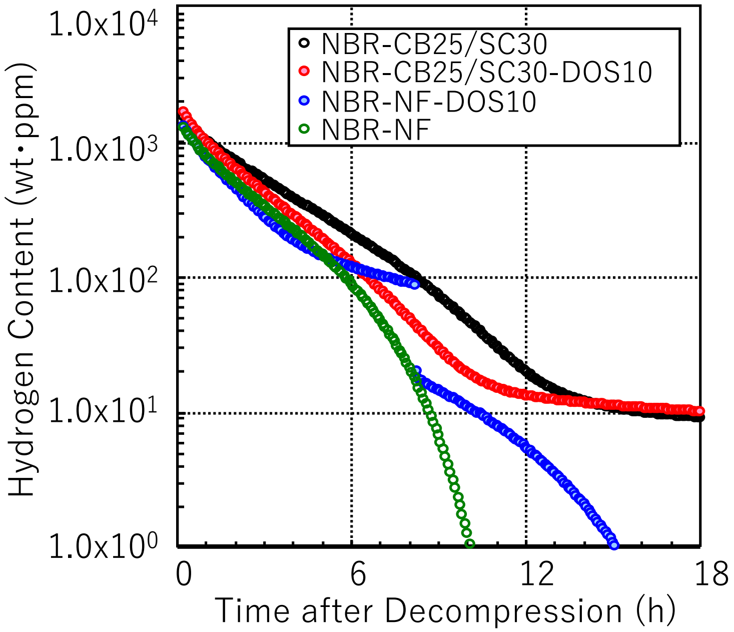
Tube Furnace

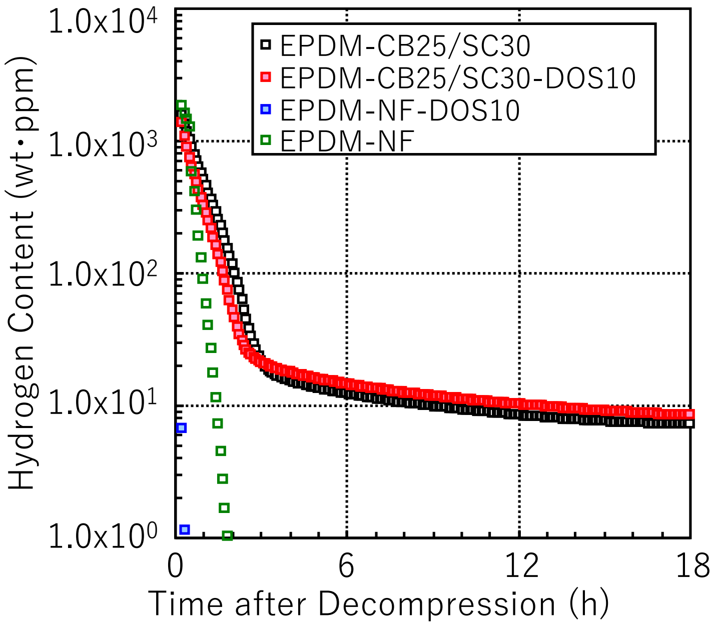
H2 Pressure Vessel
90 MPa/30°C/24 hrs

Gas Sampling
(5-minute interval)

TCD

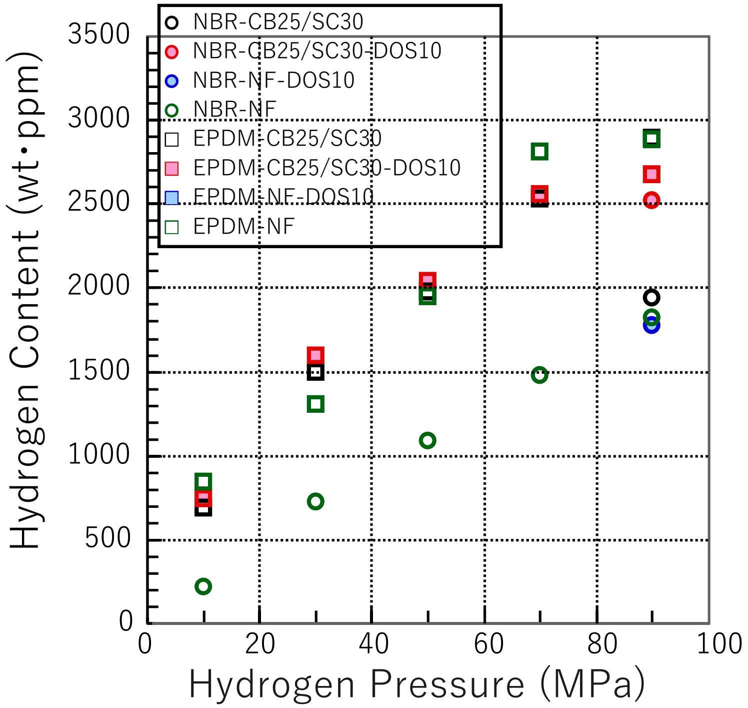
GC (molecular sieve)

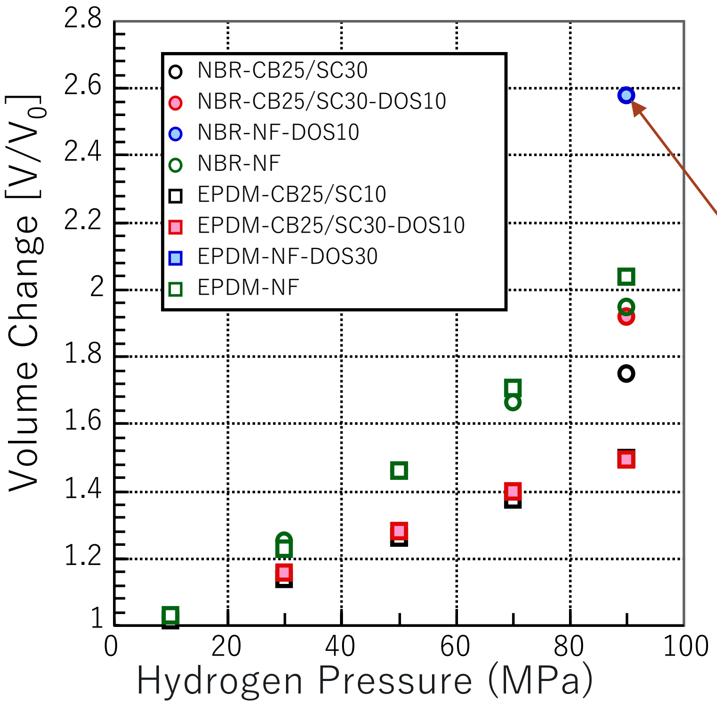




- **Polymer chemistry and morphology influence the H_2 content weight loss rate**
- **Filler influences hydrogen weight loss**

Hydrogen Content and Volume Change Related to Pressure

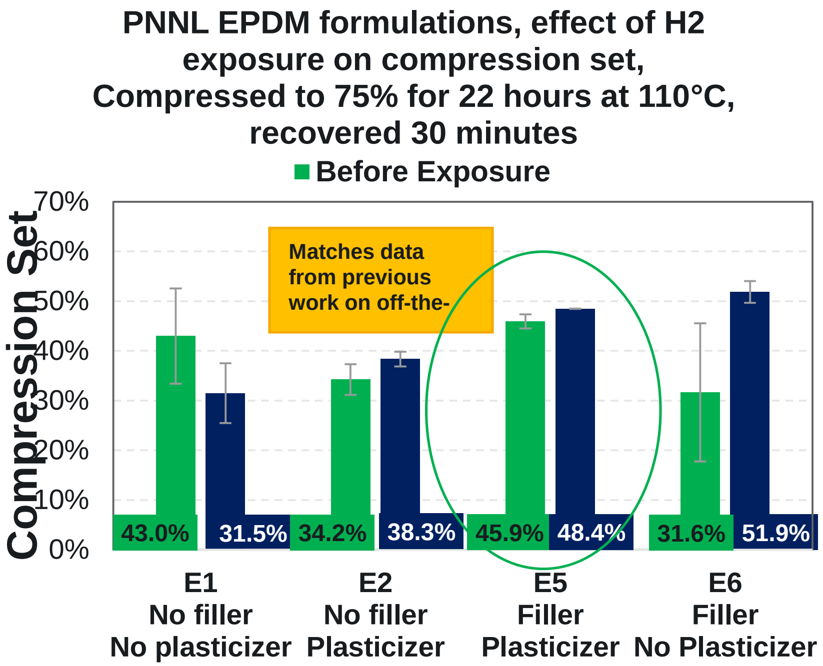




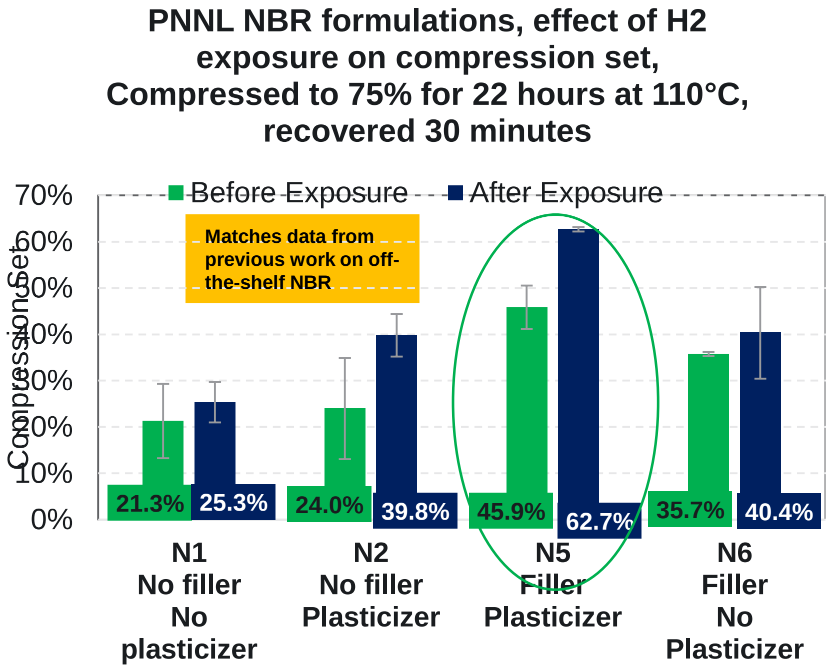
40% volume change with plasticizer additive in NBR

The filler material used in these model material compounds show a decrease in volume change for NBR by 10% and 30% in EPDM from unfilled baseline compound

Compression Set changes for EPDM and NBR with H2 Exposure



PNNL EPDM formulations, effect of H2 exposure on compression set, Compressed to 75% for 22 hours at 110°C, recovered 30 minutes

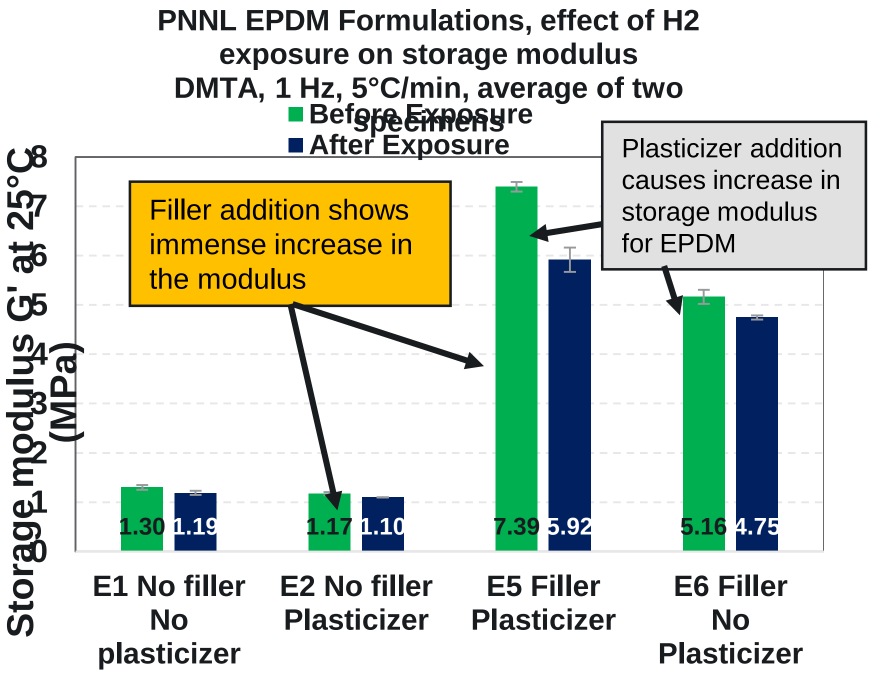


PNNL NBR formulations, effect of H2 exposure on compression set, Compressed to 75% for 22 hours at 110°C, recovered 30 minutes

Compression set change due to H2 exposure for a filled, plasticized EPDM system is insignificant

Compression set increase by ~37% due to H2 exposure for a filled plasticized NBR system

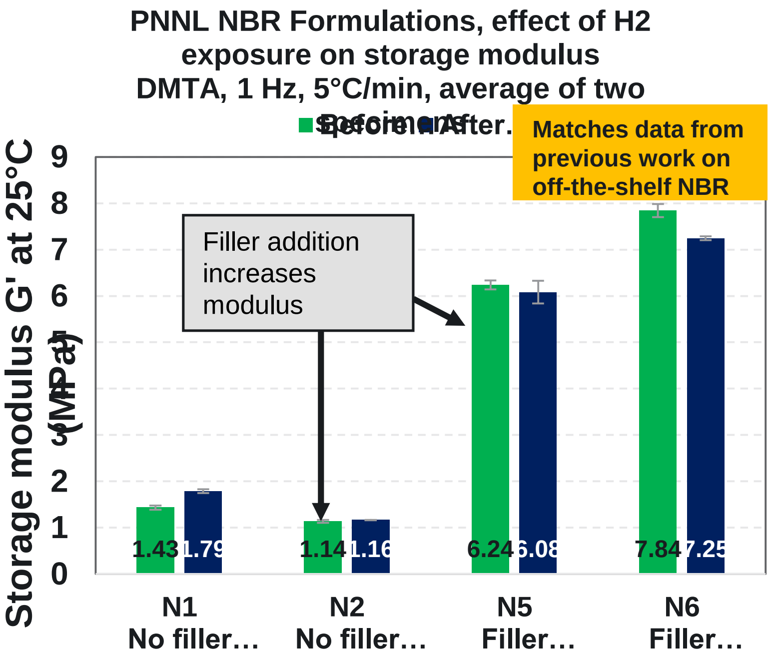
Storage Modulus changes for EPDM with H2 Exposure



PNNL EPDM Formulations, effect of H2 exposure on storage modulus DMTA, 1 Hz, 5°C/min, average of two specimens

Filler addition shows immense increase in the modulus

Plasticizer addition causes increase in storage modulus for EPDM



PNNL NBR Formulations, effect of H2 exposure on storage modulus DMTA, 1 Hz, 5°C/min, average of two specimens

Matches data from previous work on off-the-shelf NBR

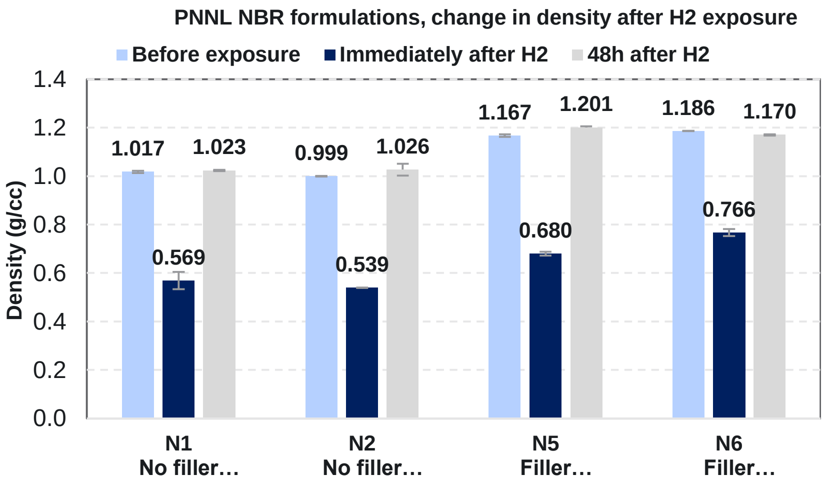
Filler addition increases modulus

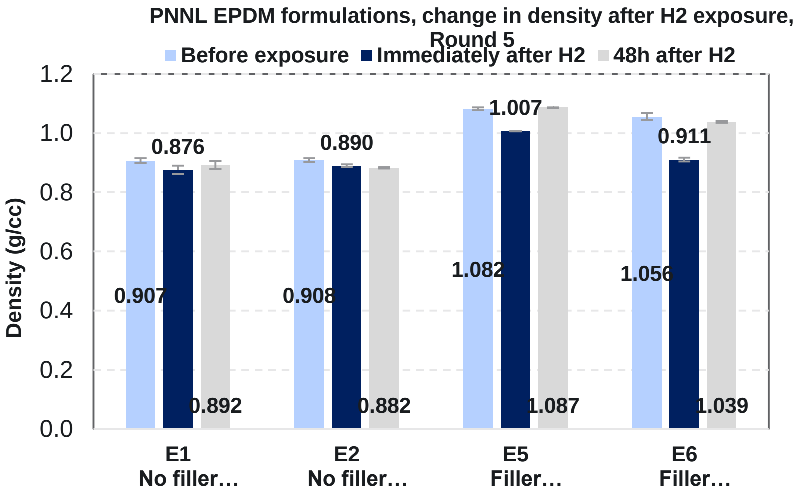
New finding

A 20% decrease in modulus is seen in filled plasticized EPDM after H2 exposure

Modulus decrease due to H2 exposure for filled plasticized NBR is insignificant

Density changes for NBR and EPDM with H2 exposure





#	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%

#	Filler	Plasticizer	Percent increase in volume	Recovery in volume
E1	No	No	4%	102%
E2	No	Yes	2%	103%
E5	Yes	Yes	8%	100%
E6	Yes	No	16%	102%

Significant swelling after H2 exposure

NBR N2 sample 1

Picture showing the evolution of H2 from NBR N2 over 48 hours

EPDM swells much less upon H2 exposure compared to NBR, which matches previous work on off-the-shelf materials