H-Mat: Science-based Advancement of Polymeric Materials for Hydrogen Technologies

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Kevin L Simmons
H-Mat Co-Lead Polymers
Pacific Northwest National Laboratory

International Hydrogen Symposium, Fukuoka, JP

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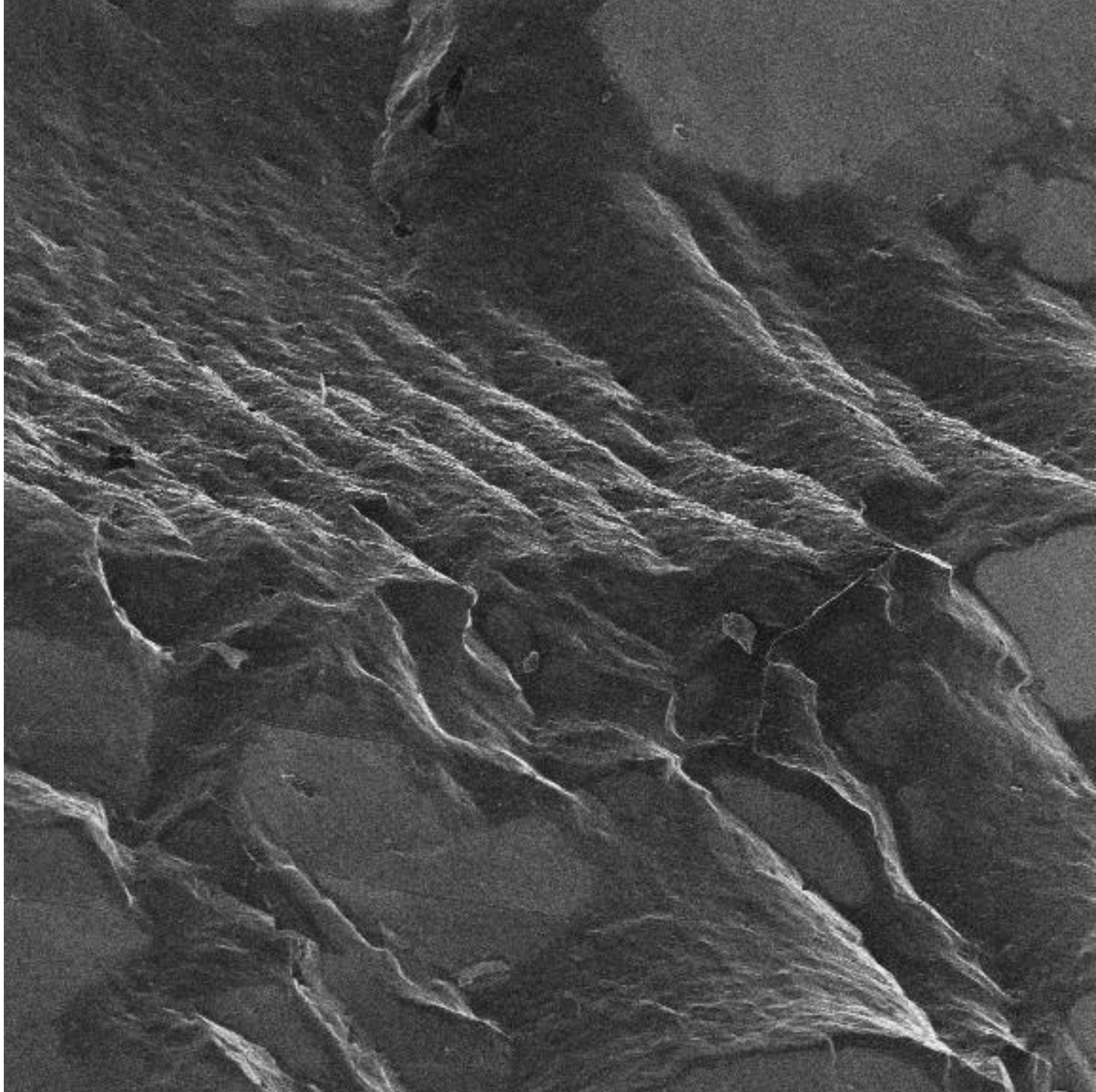
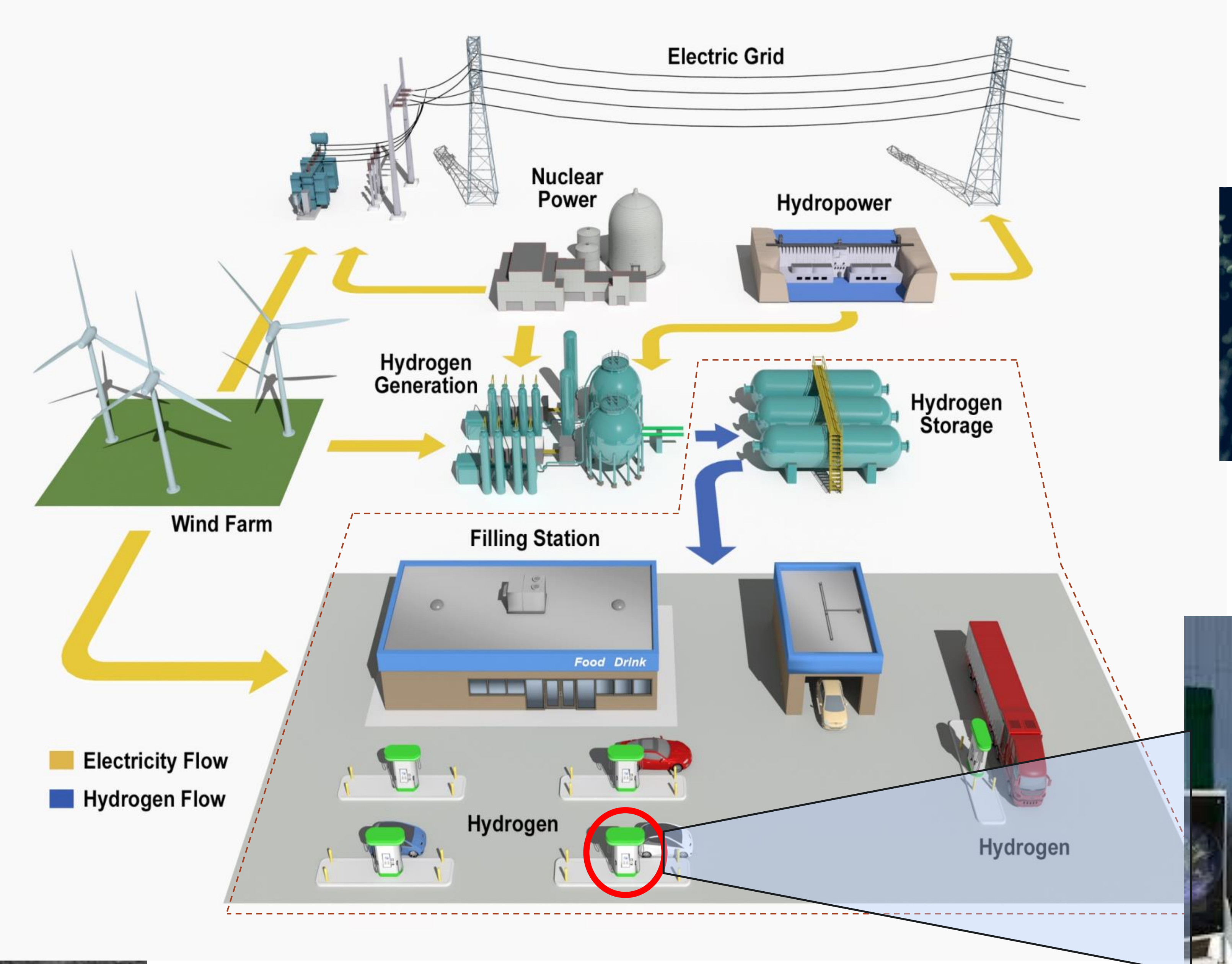


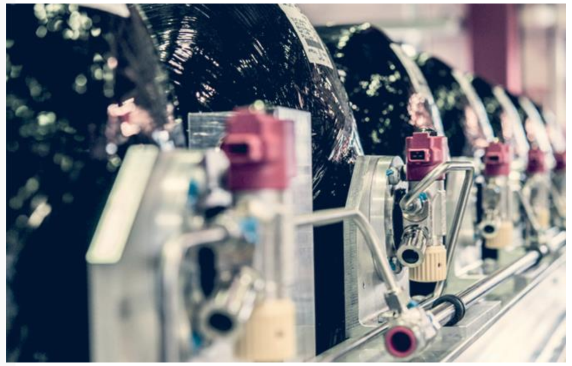
Outline

- H2@Scale
- H-Mat Consortium
- H-Mat Objectives
- Component Multi-scale Modeling and Experimental Validation
- Modeling
- Experimental
- Summary

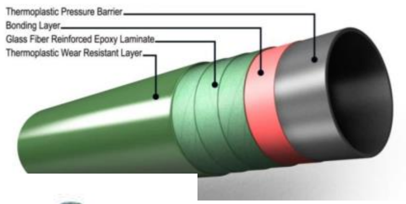
H2@Scale



Polymeric materials used in hydrogen infrastructure



H-Mat



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H-Mat Consortium Members

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

PNNL:
Wenbin Kuang
Yongsoon Shin
Sarah Burton
Kee Sung Han
Erin Barker
Yulan Li
Varun Gupta
Bruce Arey
Alice Dohnalkova

SNL:
Nalini Menon
Mark Wilson

ORNL:
Bart Smith
Amit Naskar

H-Mat Hydrogen Materials Compatibility Consortium SM
Pacific Northwest NATIONAL LABORATORY
OAK RIDGE National Laboratory
Sandia National Laboratories
SRNL TM
Argonne NATIONAL LABORATORY

H-Mat 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.

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, Polybutylene, Nylon, PEEK, PEKK, PET, PEI, PVDF, Teflon, PCTFE, POM

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

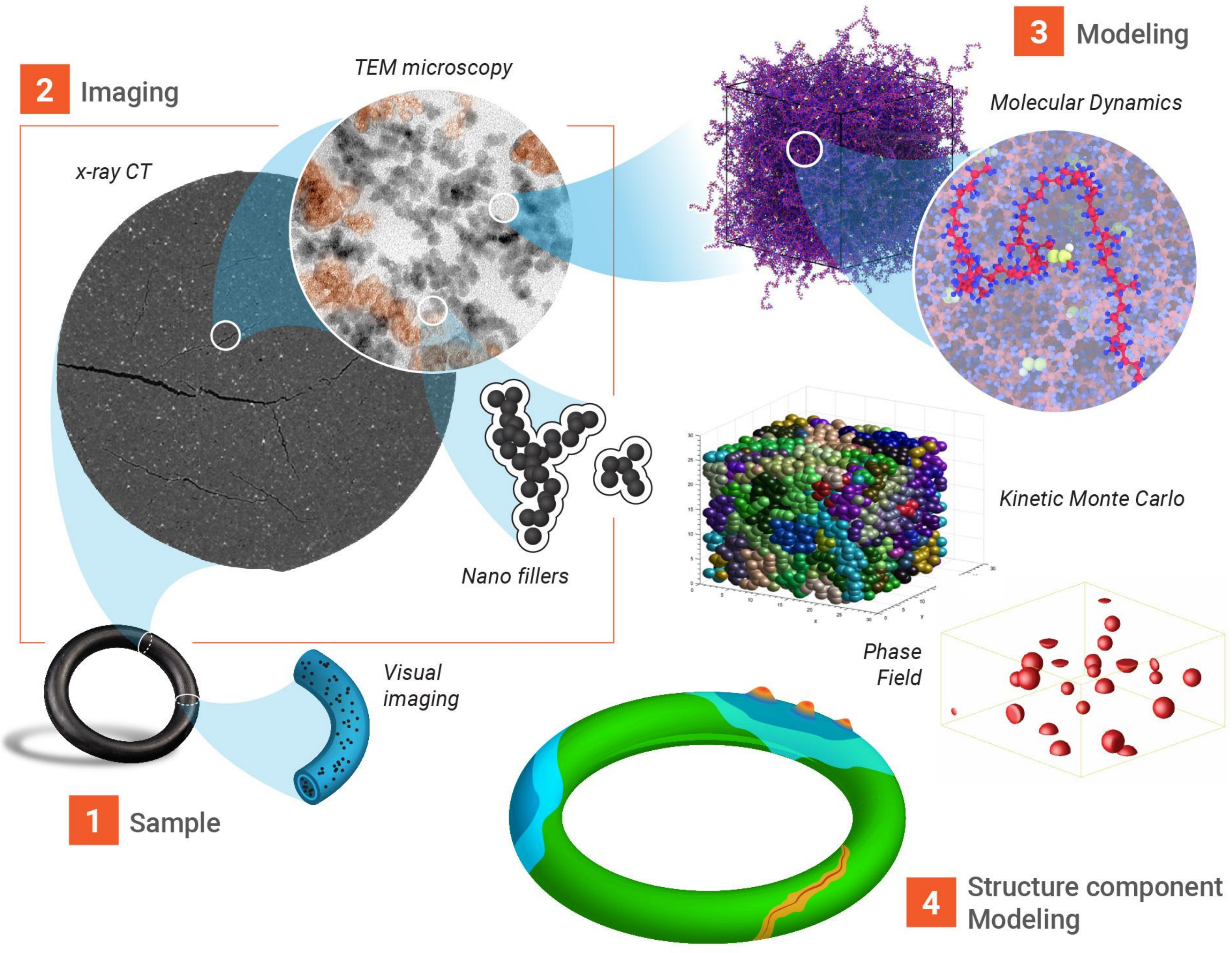
Thermosetting polymers
Epoxy, PI, Polyurethane

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

Component Challenges to Multi-scale Modeling and Experimental Validation

- Utilization of the National Lab capabilities in:
  - advanced computational capabilities
  - unique experimental facilities
  - scientific expertise
- Results will establish scientific frameworks to improve materials reliability in hydrogen infrastructure, and computational materials science will be exploited to improve the state-of-the-art of materials design of both metals and polymers, and to provide the scientific basis for predictive materials performance tools

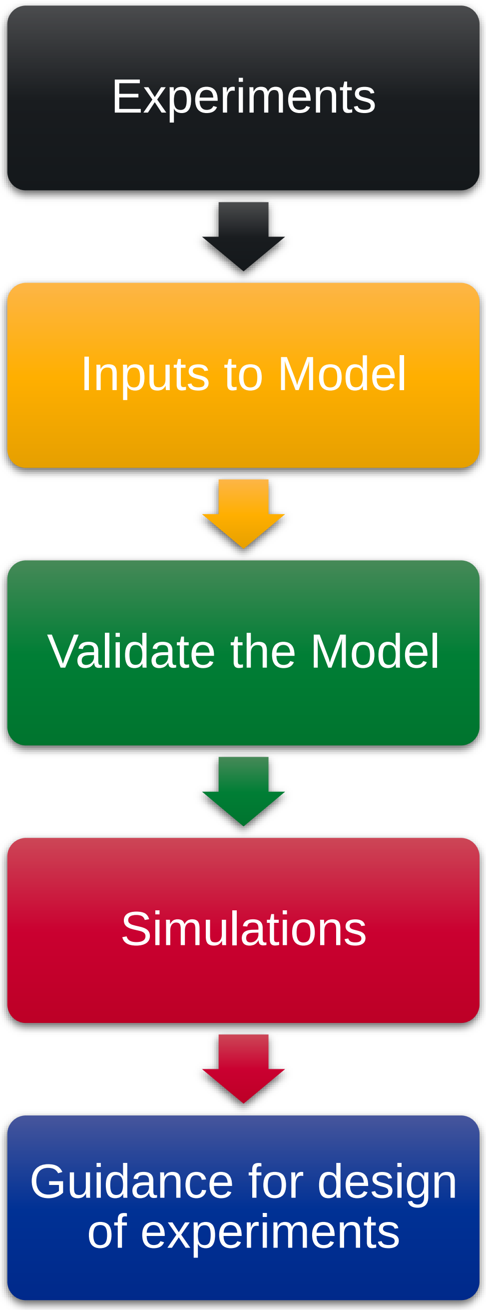
Experimental Studies **Multiscale modeling**



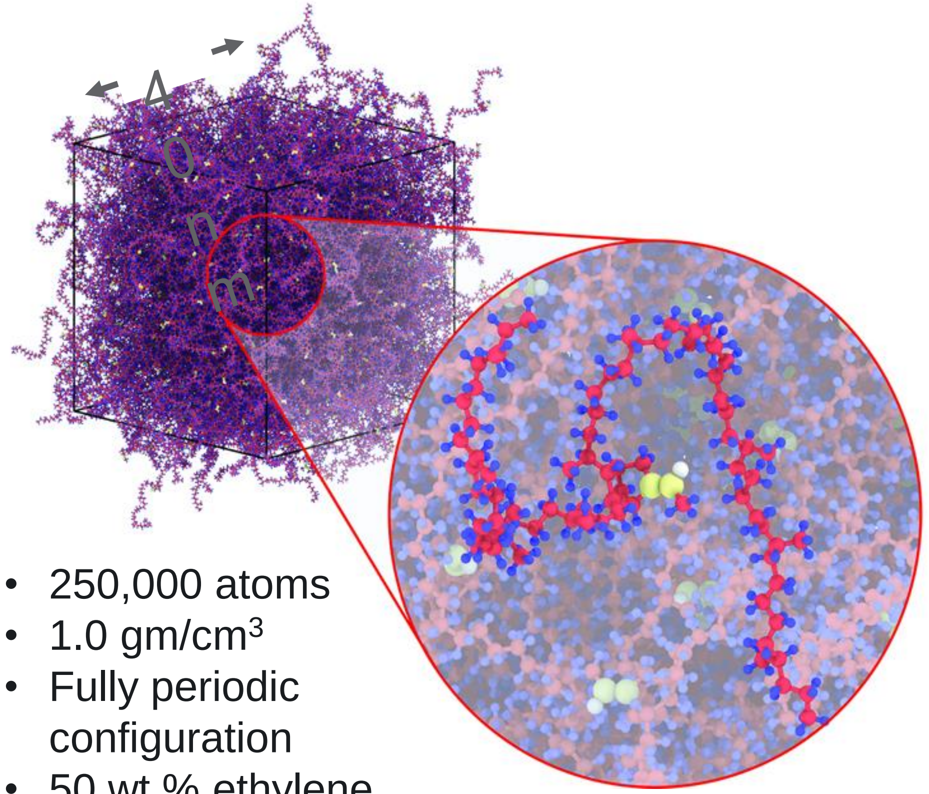
Modeling and Experiments: Workflow

- Experiments will provide following for the model:
  - Visual observations
  - Material properties
  - Topography of cavities and/or bubbles
  - Validation data

- Simulations will provide following for experiments:
  - Optimum parameters
  - Trends and what to expect.

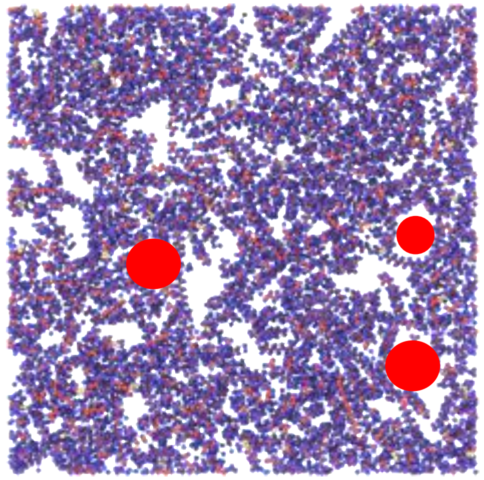


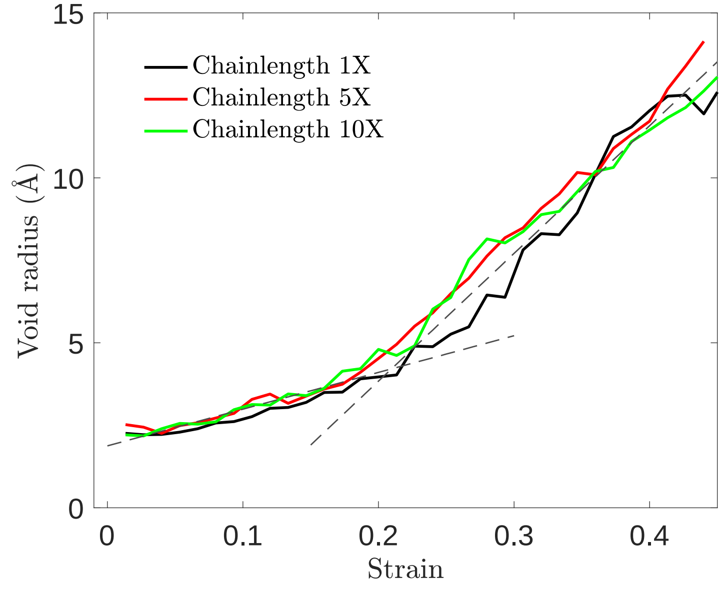
Molecular Dynamic Simulations of EPDM



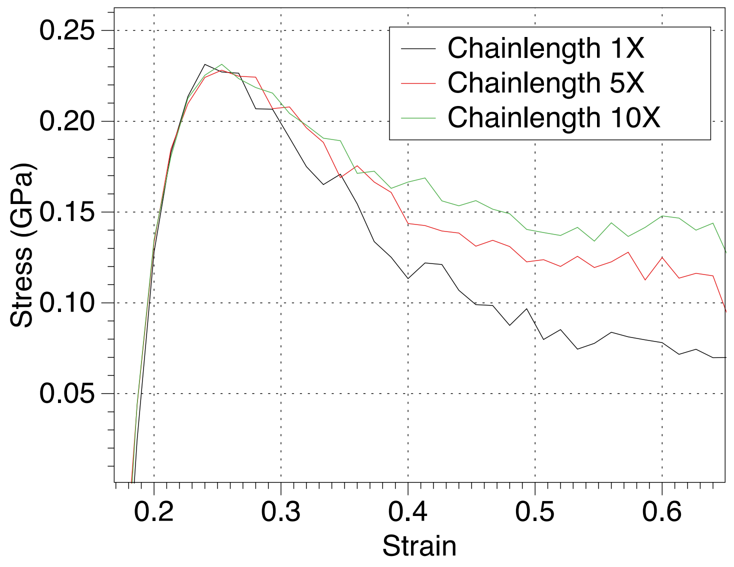
- 250,000 atoms
- 1.0 gm/cm^3
- Fully periodic configuration
- 50 wt.% ethylene
- 40 wt.% propylene
- 10 wt.% ENB

Postprocessing code to determine size and location of largest void region

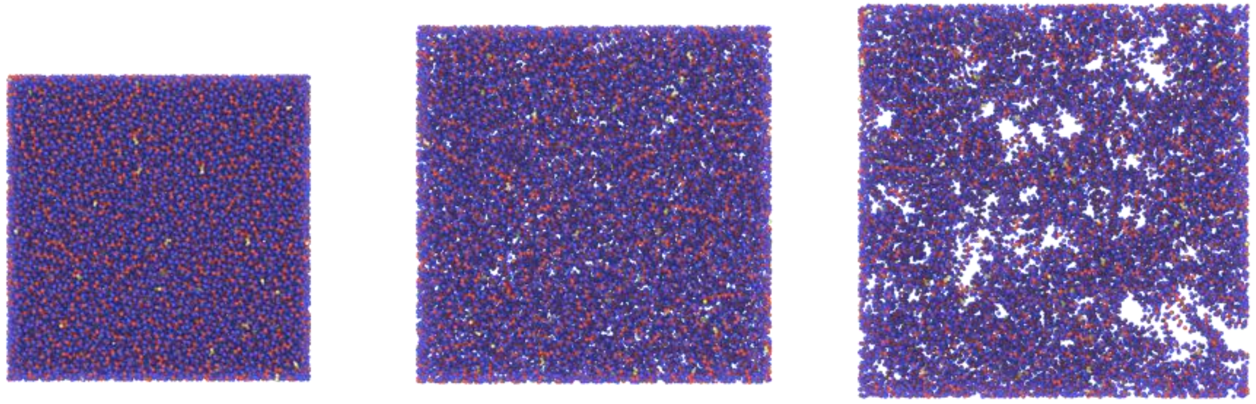




Result initially suggests that onset of cavitation precedes yield



Goal: quantify the onset of cavitation and the role of H2 in that process

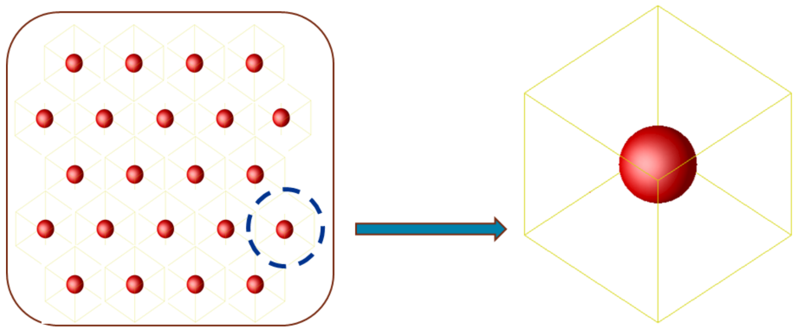


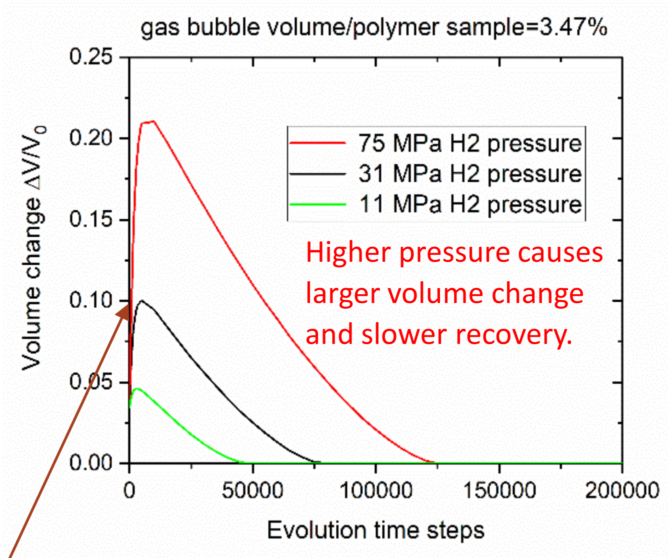
$\rho = 1.5\ g/cm^3$ ~20 nm length | $\varepsilon =$ 0.17 | $\varepsilon =$ 0.30

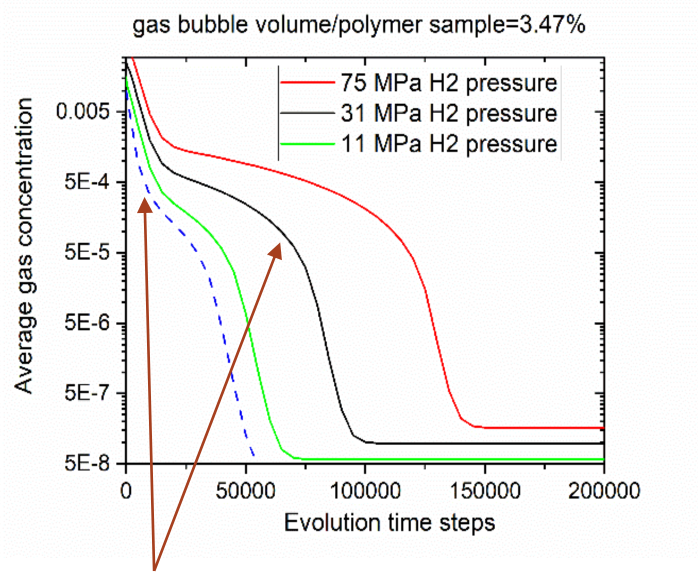
Phase Field Modeling

- Modeling H_2 gas bubble evolution in these soft polymeric materials under decompression
- Developed a phase-field model for simulating hydrogen diffusion and gas bubble evolution during high-pressured hydrogen decompression.
- Model is also integrated with linear elastic interaction between gas pressure and polymer deformation

Schematic illustration of H2 gas bubbles existed in the considered polymer block under H2 pressure. The red spheres represent H2 gas bubbles. The bubbles contained pressured H2 gas.





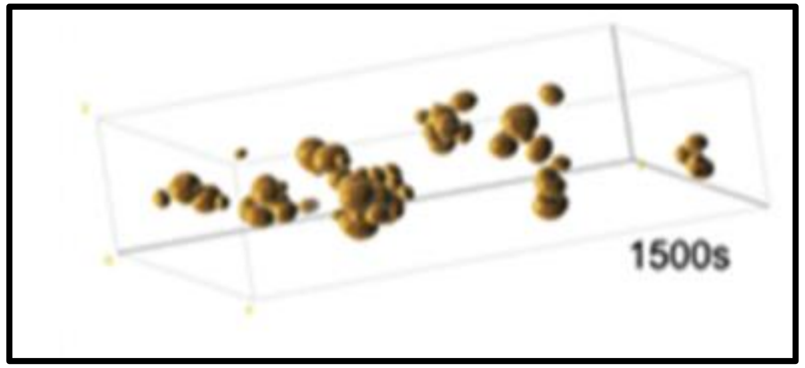


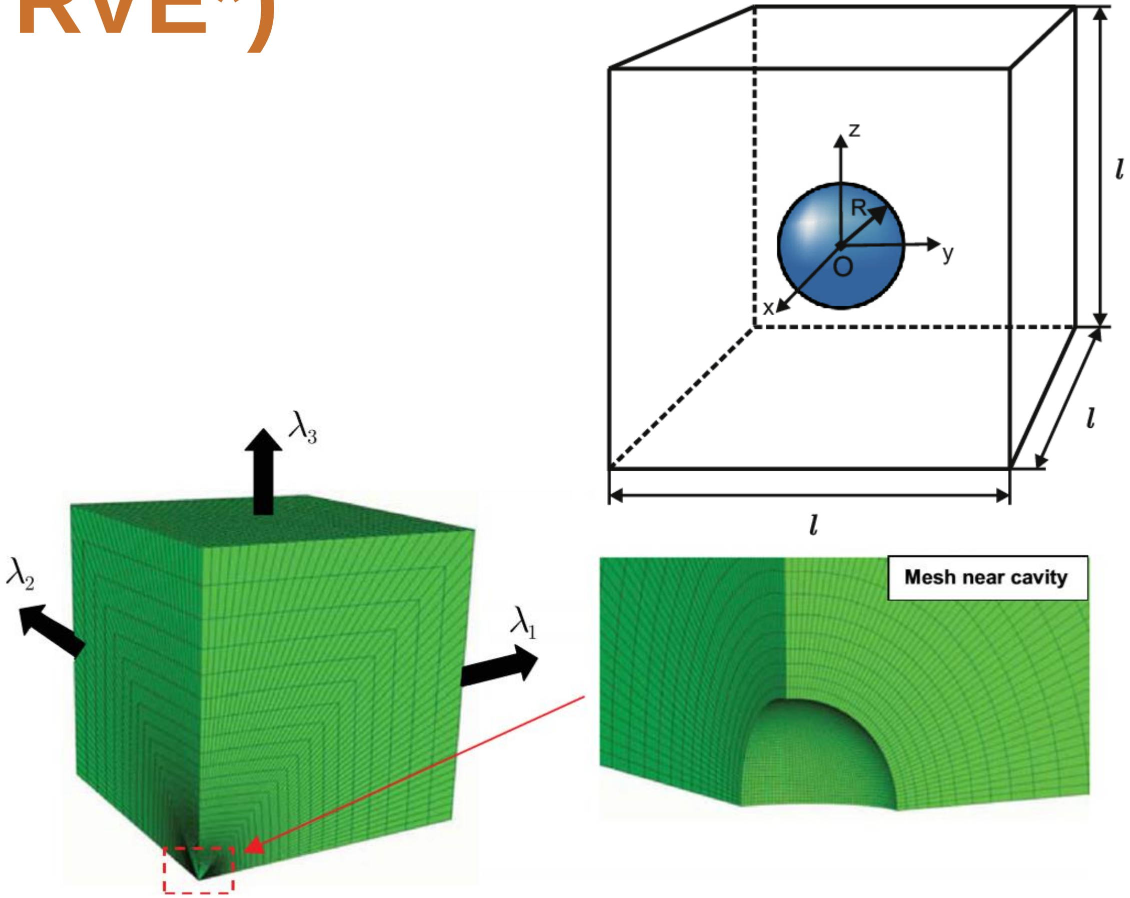
The gas bubble expands very quick just after pressure release then is followed by slowly shrinking

The gas content decreases during decompression and the decreasing dynamics are very different from homogeneous polymer which does not have any bubbles

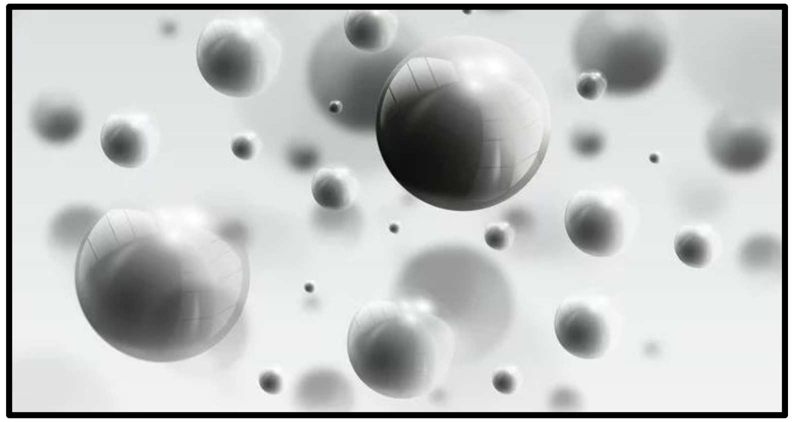
Finite Element Model for Coupled Diffusion-deformation (using RVE*)

- Modeling efforts can be subdivided into: (for pure polymer)
  - Cavity growth (with single cavity)
  - Interactions between cavities (cluster of cavities)





- Hyperelastic and/or viscoelastic material behavior
- Effect of filler particles (SiO_2 or Carbon)



*Representative Volume Element

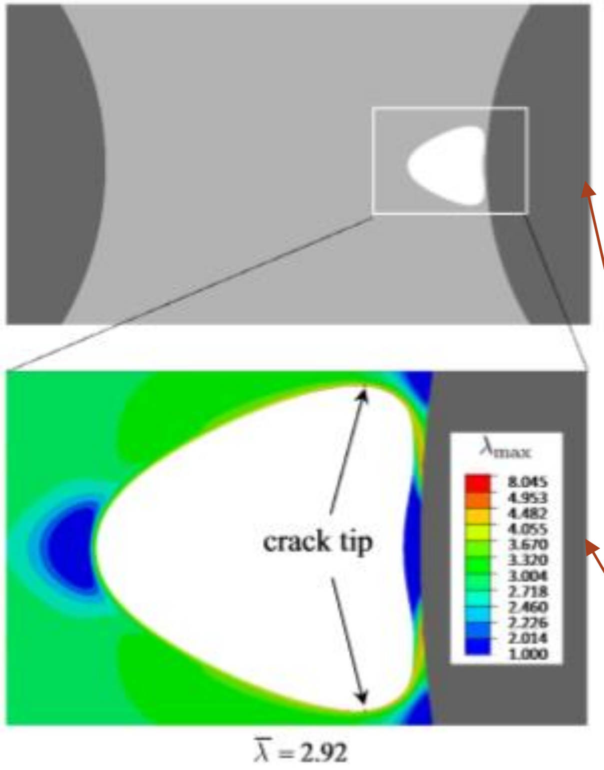
[1] Castagnet, Sylvie, et al. "In-situ X-ray computed tomography of decompression failure in a rubber exposed to high-pressure gas." *Polymer Testing* 70 (2018): 255-262.

Incorporation of Damage (using RVE)

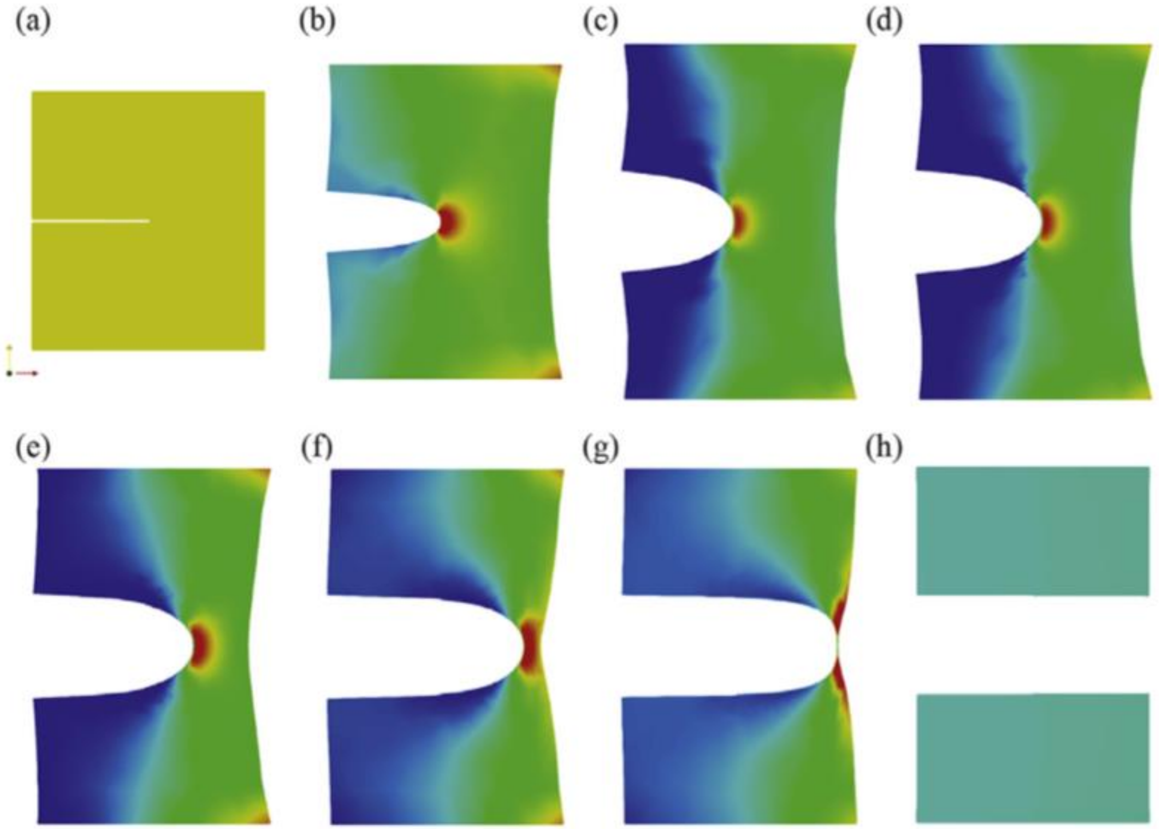
- Modelling efforts are subdivided into:

(for pure polymer)

  - Cavity creation in homogeneous material
  - Crack initiation and propagation



- Effect of filler particles (Si or Carbon)



Next Steps: Development of constitutive law which can be used to model large continuum structures

- Simulation of real life examples
- Predict the failure of polymer components exposed to high pressure H_2 environment

[1] Poulain, X., et al. "Damage in elastomers: nucleation and growth of cavities, micro-cracks, and macro-cracks." *International Journal of Fracture* 205.1 (2017): 1-21.
[2] Mao, Yunwei, and Lallit Anand. "A theory for fracture of polymeric gels." *Journal of the Mechanics and Physics of Solids* 115 (2018): 30-53.

Model Material Compounds for Experimental Studies

Composition (parts per hundred NBR)	Compound N2	Compound N5	Compound E2	Compound E5
EPDM (Esprene 505) [a]	**100**	**100**		
NBR (Nipol 1042) [b]			**100**	**100**
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
Sulfur	1.5	1.5	1.5	1.5
MBTS 2,2'-Benzothiazyl Disulfide [c]	1.5	1.5	1.5	1.5
TMTD Bis(dimethylthiocarbamoyl) Disulfide [c]	0.5	0.5	0.5	0.5
DOS	**10**	**10**	**10**	**10**
Carbon black (n330)		**23**		**21**
Silica (Nipsil VN3)		**28**		**25**
Density	1.015	1.182	0.919	1.073
Hardness (IRHD)	43.4	65.8	48.3	72

[a]Esprene505 (Sumitomo Chemical): ethylene 50%, propylene 40%, 5-ethylidene-2-norbornene (ENB) 10%

[b]Nipol 1042 (Zeon Corporation) :Medium High Nitrile Rubber, Acrylonitrile content 33.5%

[c]Accelerators: MBTS: 2,2'-benzothiazyl dfisulfide, TMTD: bis(dimethylthiocarbamoyl) disulfide

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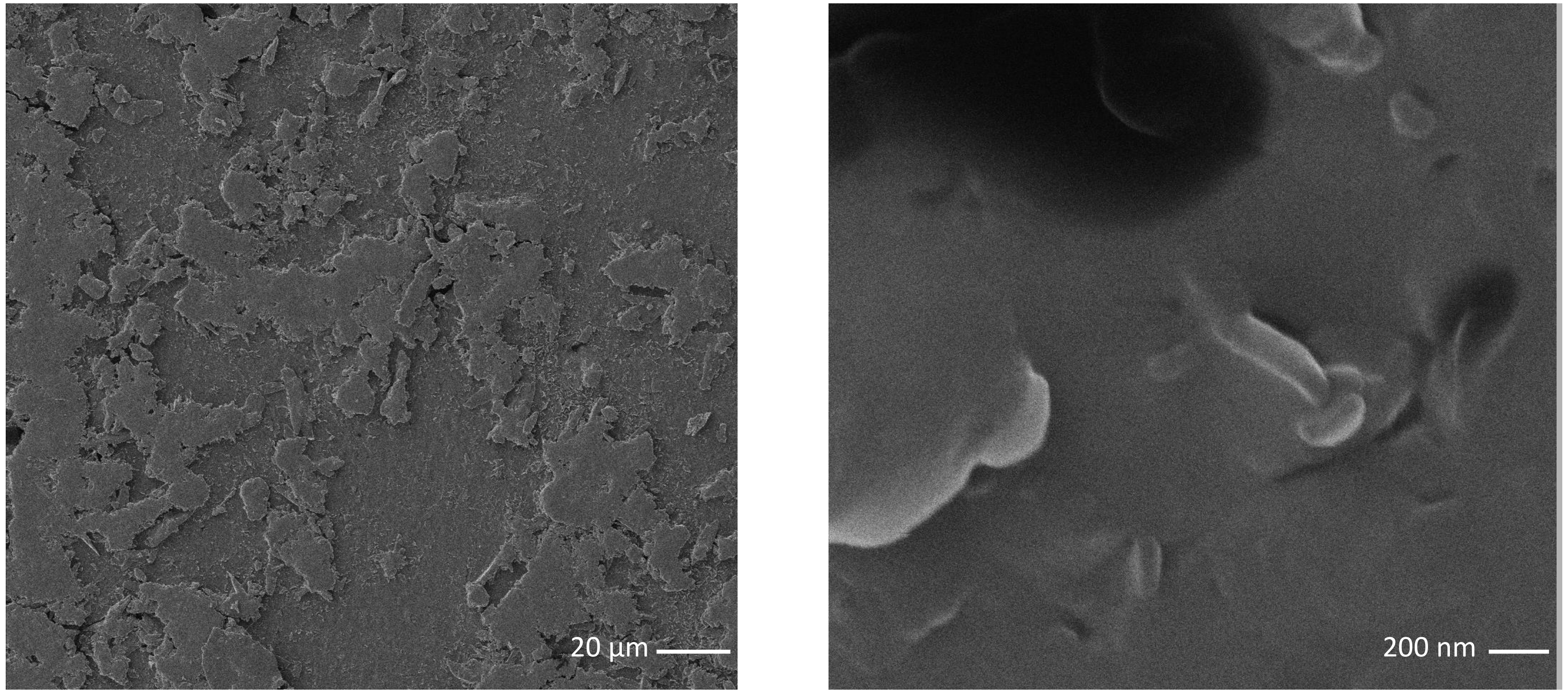
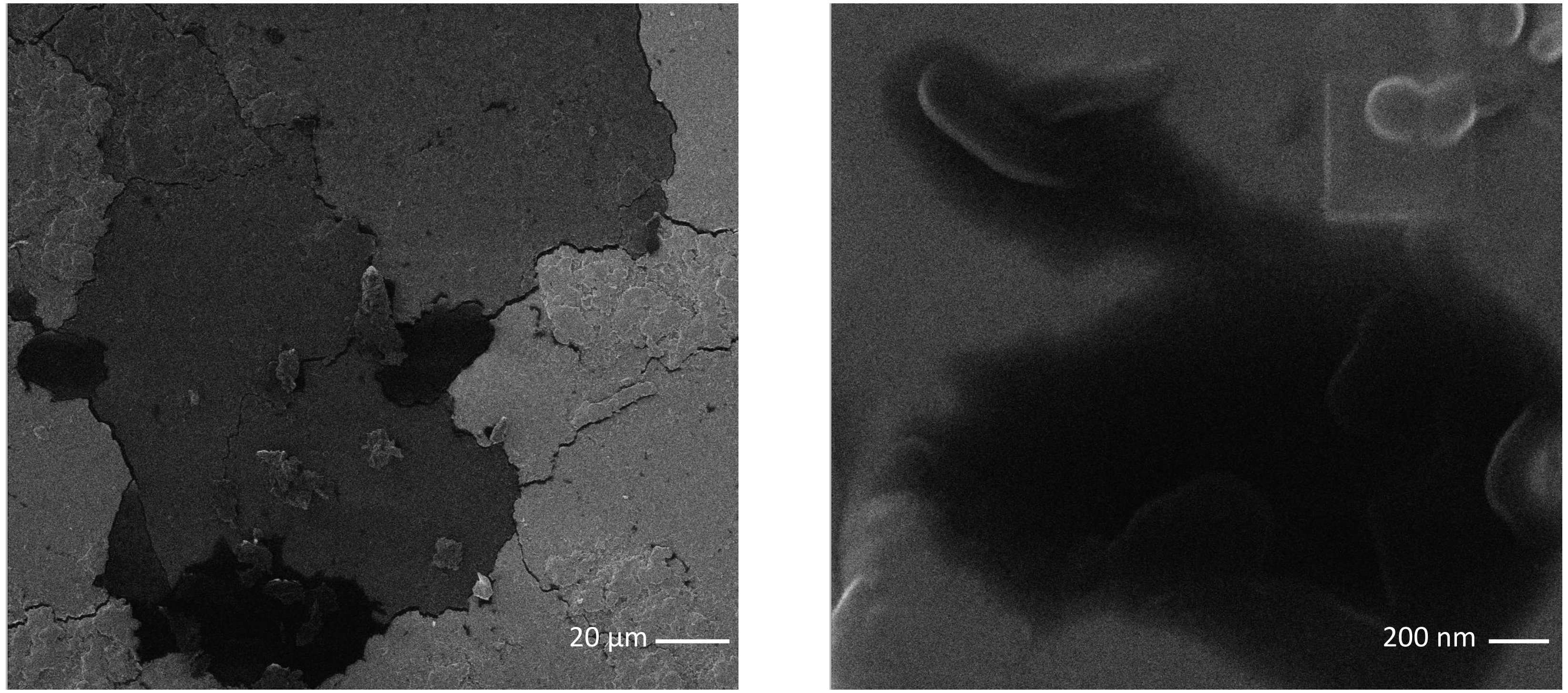
Helium Ion Microscopy of E2 Surface Morphology

- HeIM provides a nice contrast in polymer materials not found in traditional SEMs
- Surprised by the surface roughness in the as rec’d EPDM not seen in NBR
- Increase in surface blushing after H2 exposure at 28 MPa
- Dark material was speculated to be plasticizer
- Chemical analysis performance using TOF-SIMS to confirm

Pre Exposure



Post Exposure 28 MPa/24 hrs



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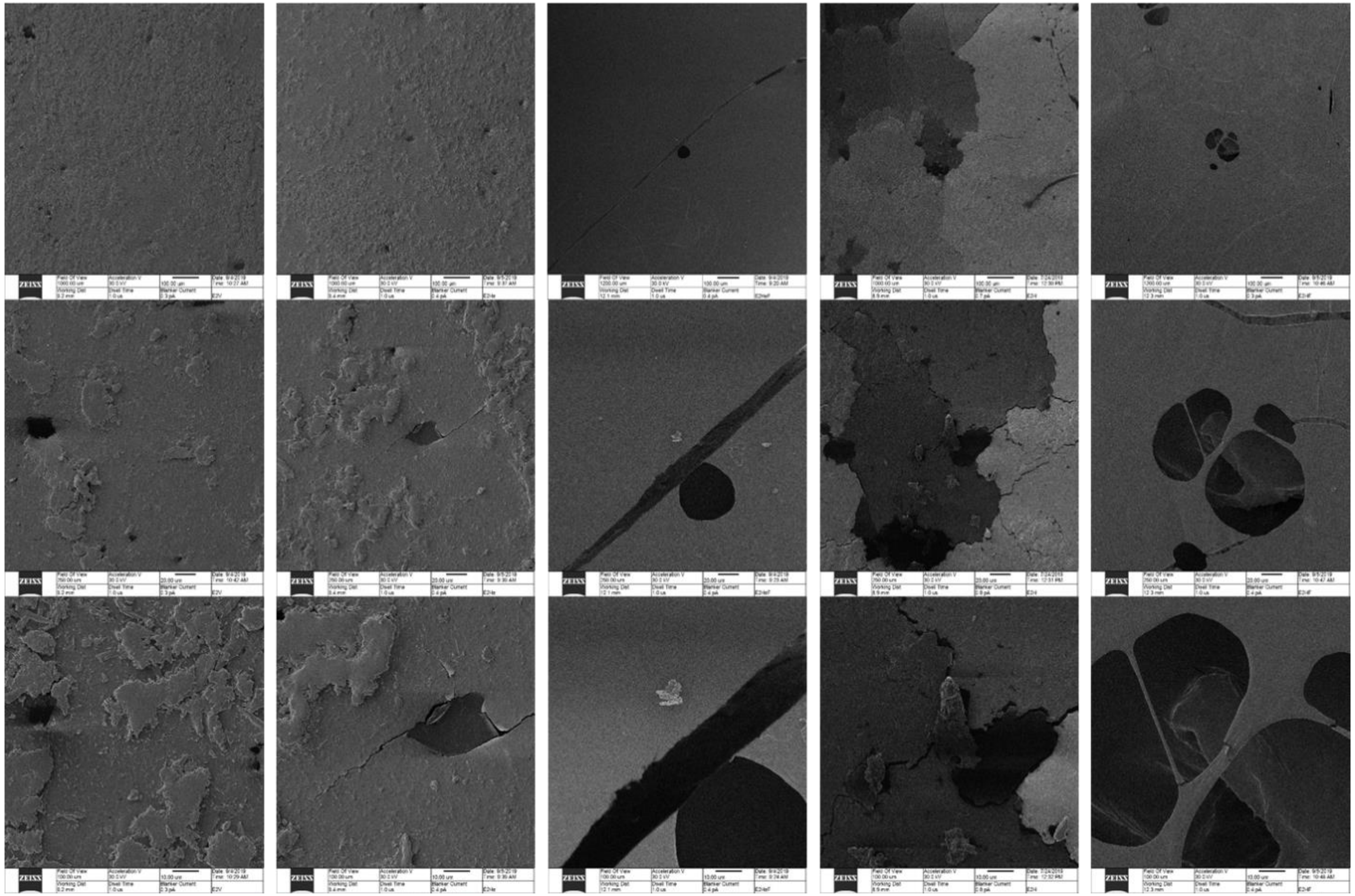
Helium Ion Microscopy of E2

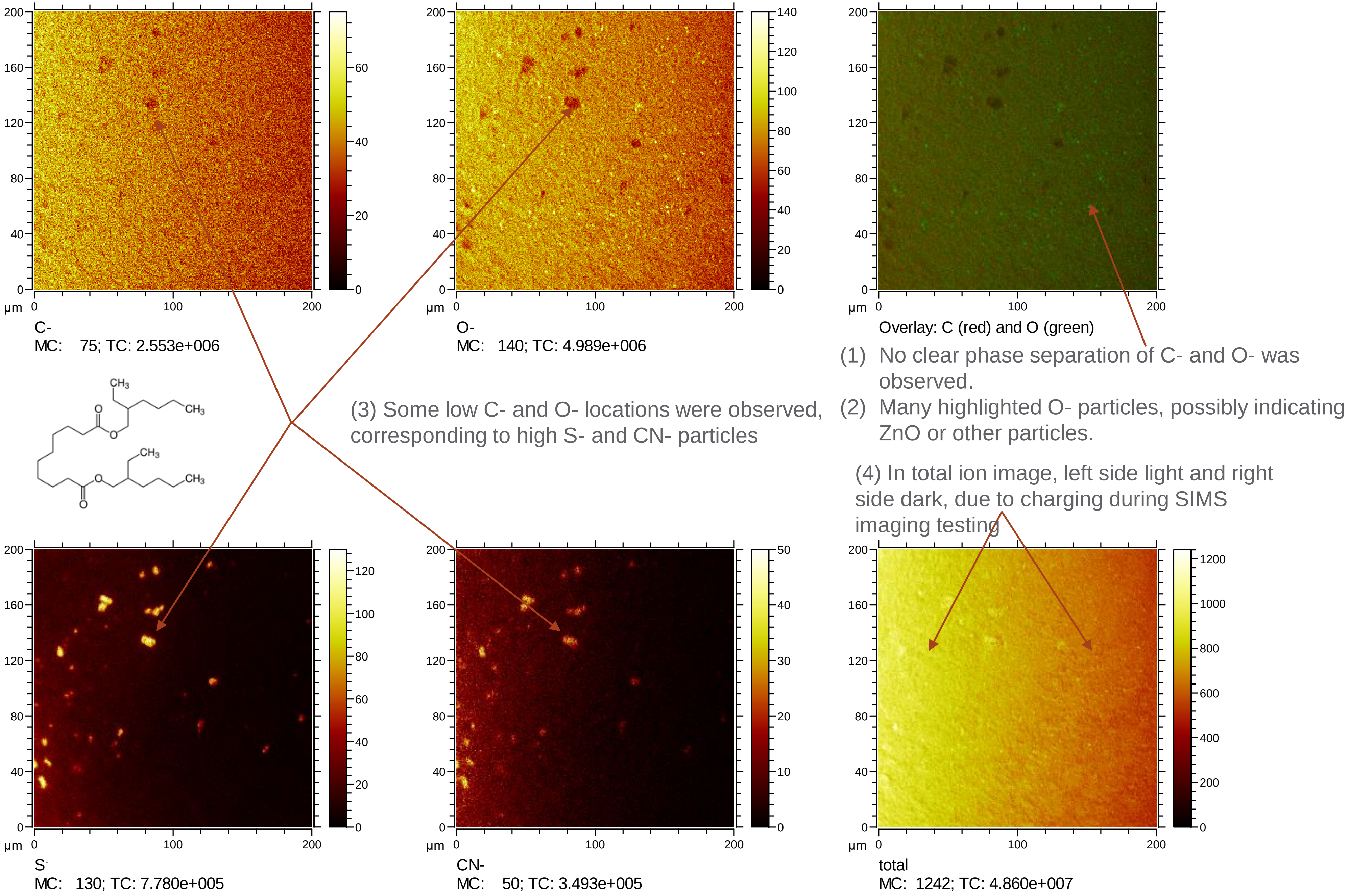
As rec'd surface before exposure	Surface morphology after 27.6 MPa He	Cryo fracture morphology after 27.6 MPa He	Surface morphology after 27.6 MPa H_2	Cryo fracture morphology after 27.6 MPa H_2



- Very little change between the as rec'd surface and the high pressure helium surface morphology
- Exposure to high-pressure hydrogen caused formation of micro-cracks and voids, and that phase separation of the plasticizer from the polymer
- Previous work with HeIM with ToF-SIMS show the dark regions to be plasticizer

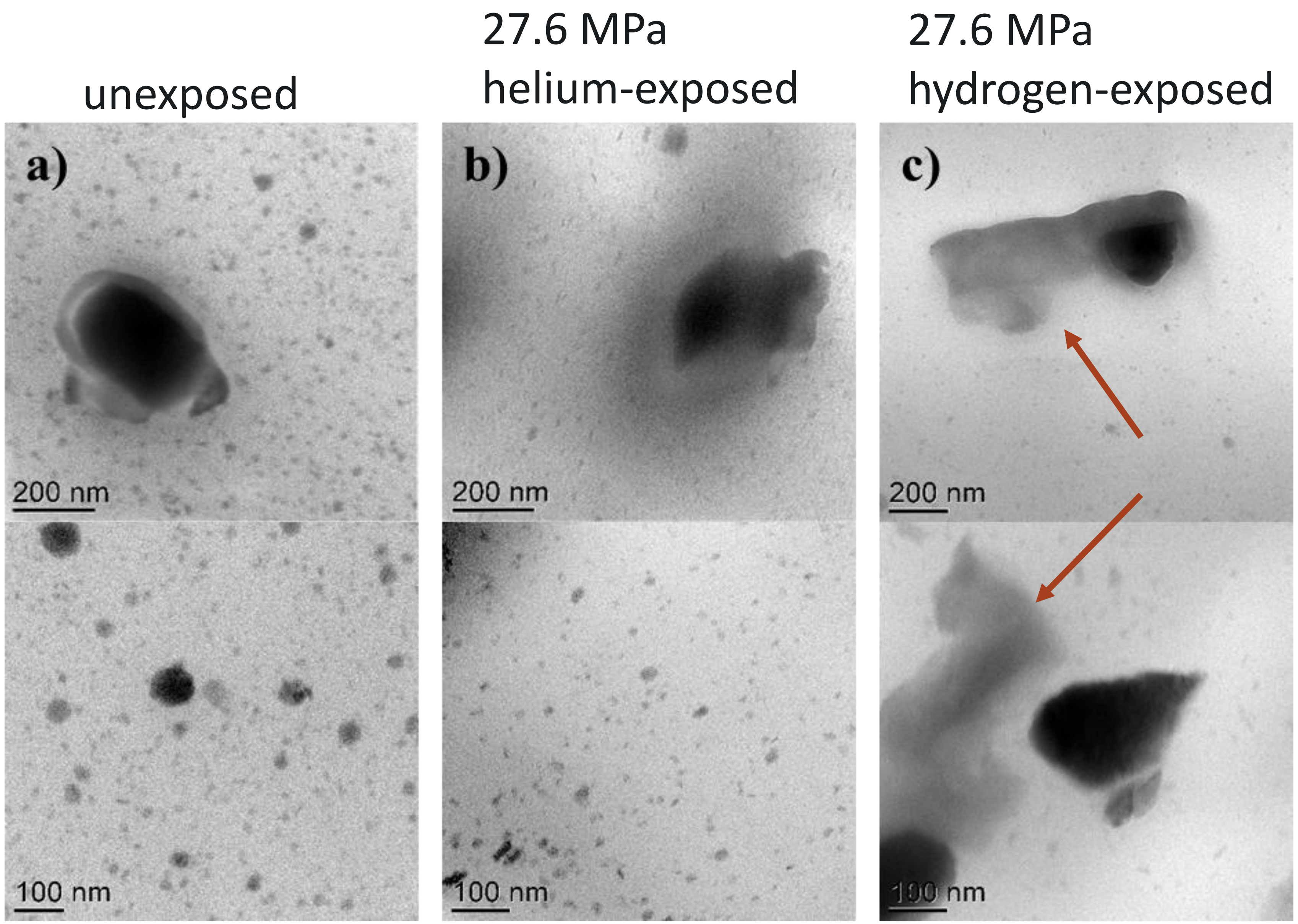
Cryo Fractured E2 HeIM and Time of Flight Secondary Ion Microscopy (TOF-SIMS) after H2

- Plasticizer appears to be well dispersed in these samples
- Difficult to separate EPDM from plasticizer
- Sulfur activators and accelerators are indicated by bright regions of spectra
- Sulfur and ZnO appear to form ZnS during processing



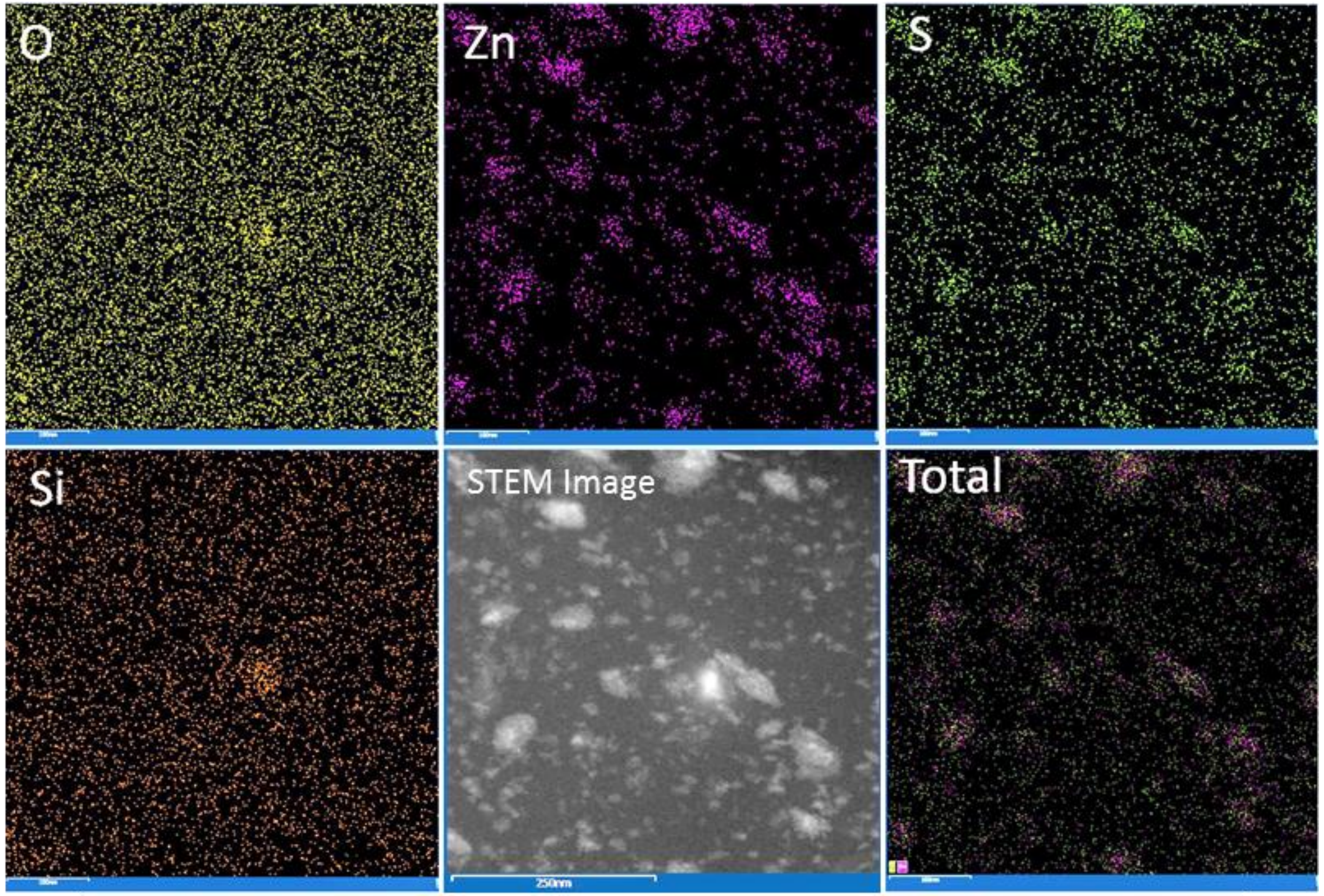
Transmission Electron Microscopy of E2 Samples

- The dark objects are zinc-based particles.
- Pre-exposed E2 specimen 5–10-nm size particles
- Grey “halo” structure was found around the large particles with about 200-nm diameters, speculated to be a void/gap between the particle or sulfur
- The hydrogen-exposed E2 shows potential signs of void formation and rubber deformation (arrow).

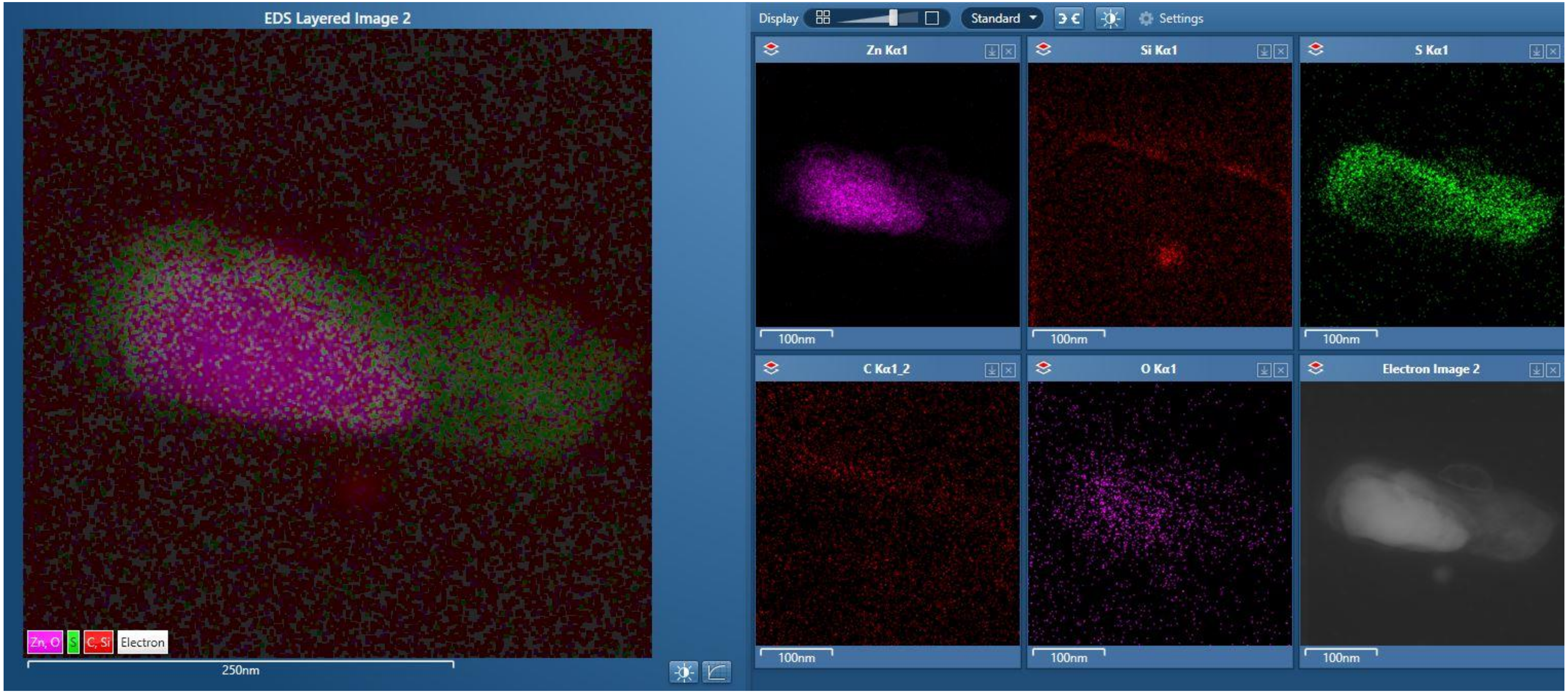


HAADF-STEM image with EDS analysis for unexposed E2

- HAADF-STEM image analysis of particles illustrate bright elements and the rubber matrix with dark elements due to their density differences
- The STEM image has a total of four elements analyzed by EDS, including oxygen (O), zinc (Zn), sulfur (S), and silicon (Si)
- The zinc element map showed high-intensity areas that matched up with the sulfur element distribution rather than high-intensity areas that overlapped with the intense signal regions of the oxygen element map, which would be expected since zinc oxide
- This suggested possible formation of zinc sulfide (ZnS), as reported in some literature

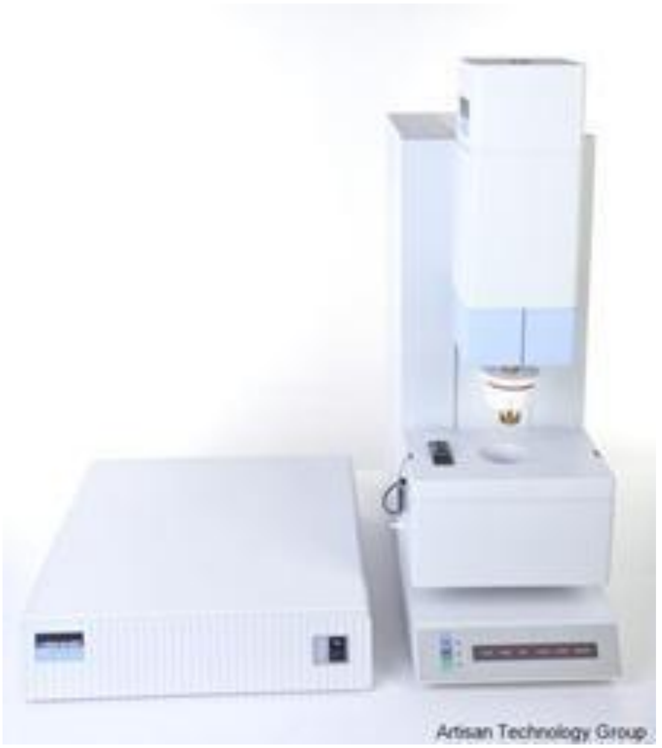


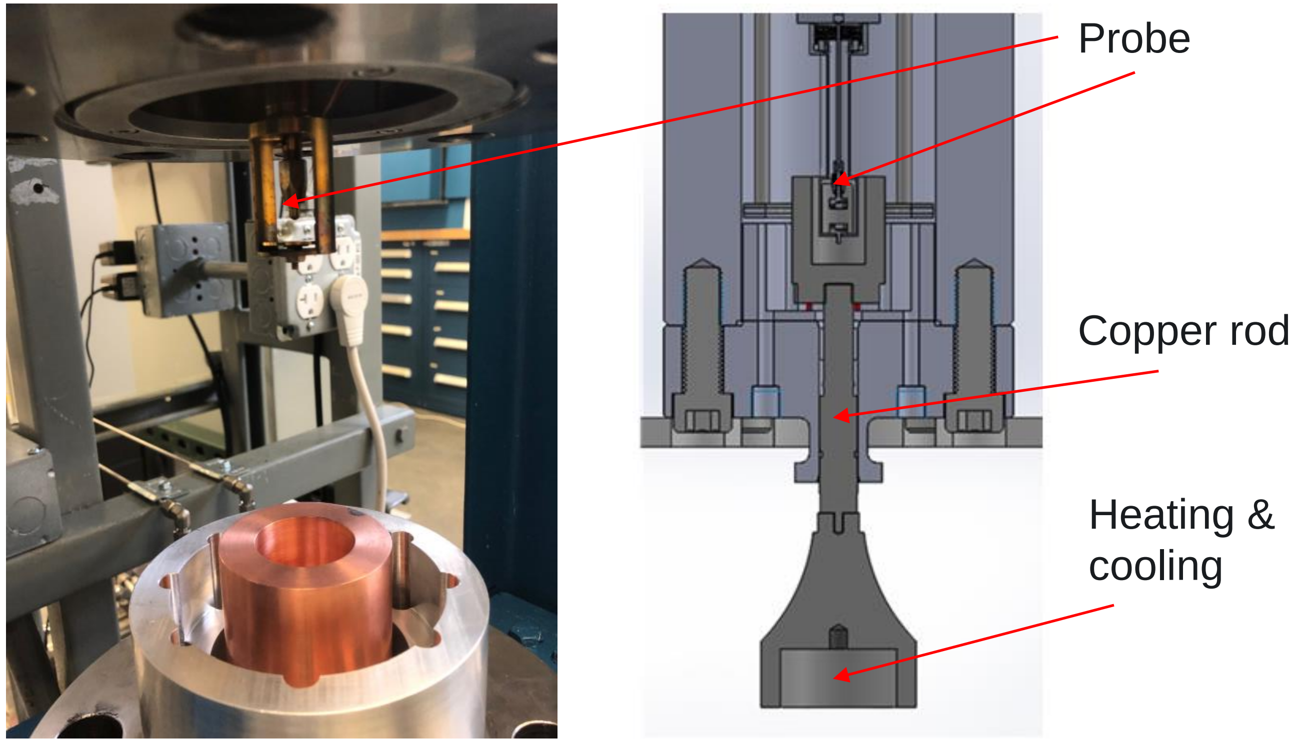
HAADF-STEM image with EDS analysis for High-Pressure Hydrogen Exposed E2



Sulfur in the grey areas around the particle, the ZnO formed ZnS through processing

In situ Dynamic Mechanical Analysis (*in situ* DMA)



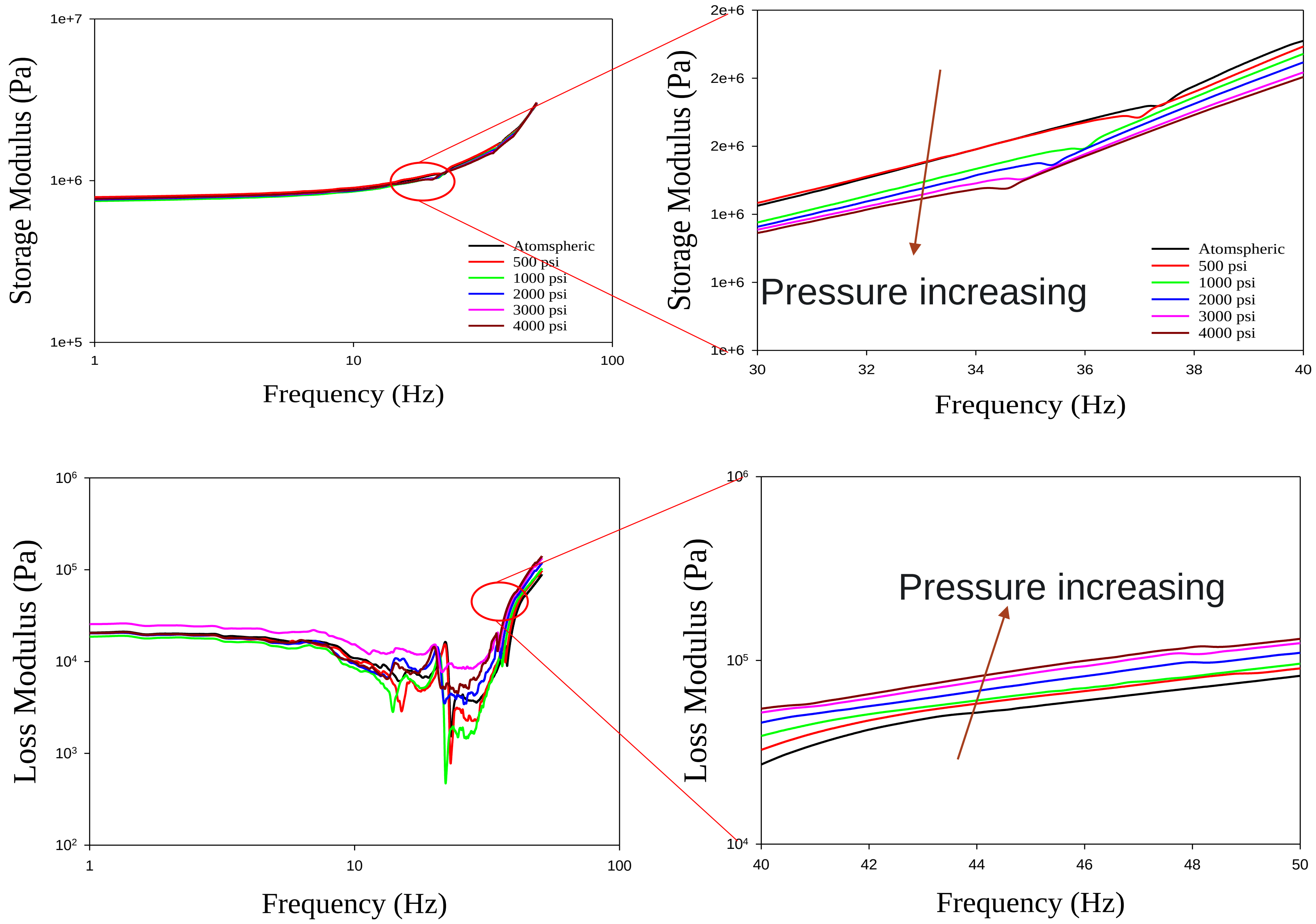


- Mechanical property values (e.g. storage modulus) in end-use conditions (pressure, gas, temperature, cycling, etc.)

- To understand how mechanical properties of model compounds vary during service cycles, yielding basic understanding of damage mechanism

Pressure Effect of Helium on E1

Frequency Sweep @RT



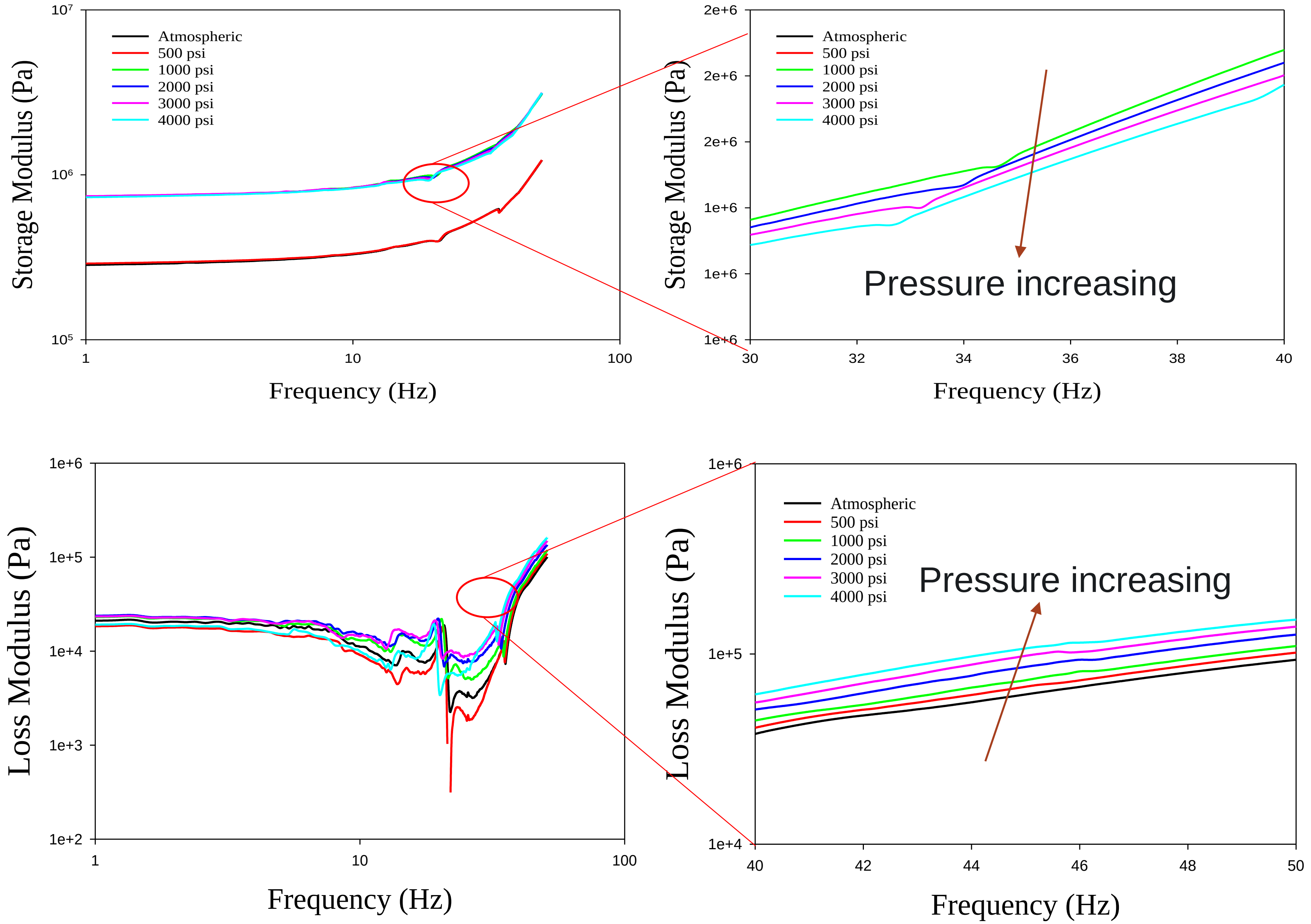
	E' at w=34	Δ (based on atmospheric condition)
Atmospheric	1.59 MPa	0%
500 psi	1.59 Mpa	0%
1000 psi	1.53 MPa	-3.8%
2000 psi	1.51 MPa	-5.0%
3000 psi	1.49 MPa	-6.3%
4000 psi	1.47 MPa	-7.5%

- Storage modulus (deformation resistance) reduces with pressure increasing due to pseudo-plasticization
- Pressure effect more significant at high frequencies
- Loss modulus (damping/irreversible deformation) increases with pressure increasing
- Combining storage and loss modulus data suggests that elastomer deteriorates in mechanical performance under pressure and level of deterioration depends on pressure (gas?)

- Step-pressurization (atmospheric, 500, 1000, 2000, 3000, 4000 psi)

Pressure Effect of Helium on E2

Frequency Sweep @RT



	E' at w=34	∆ (based on atmospheric condition)
Atmospheric	0.61 Mpa	0%
500 psi	0.61 Mpa	0%
1000 psi	1.51 Mpa	+147.5%
2000 psi	1.47 MPa	+141.0%
3000 psi	1.46 MPa	+139.3%
4000 psi	1.43 MPa	+134.4%

- Storage modulus (deformation resistance) reduces with pressure increasing from 1000 psi and up due to pseudo-plasticization
- Significant increase in storage modulus during pressure increasing from 500 psi to 1000 psi – were plasticizers affected by high pressure?
- Pressure effect more significant at high frequencies
- Loss modulus (damping/irreversible deformation) increases with pressure increasing – similar to E1

Helium Ion Microscopy of N2 Surface Morphology

- HeIM provides contrast in polymer materials not found in traditional SEMs
- Surprised by the surface cracks in the as rec'd NBR
- Increase in surface blushing after H2 exposure at 28 MPa
- Dark material was speculated to be plasticizer
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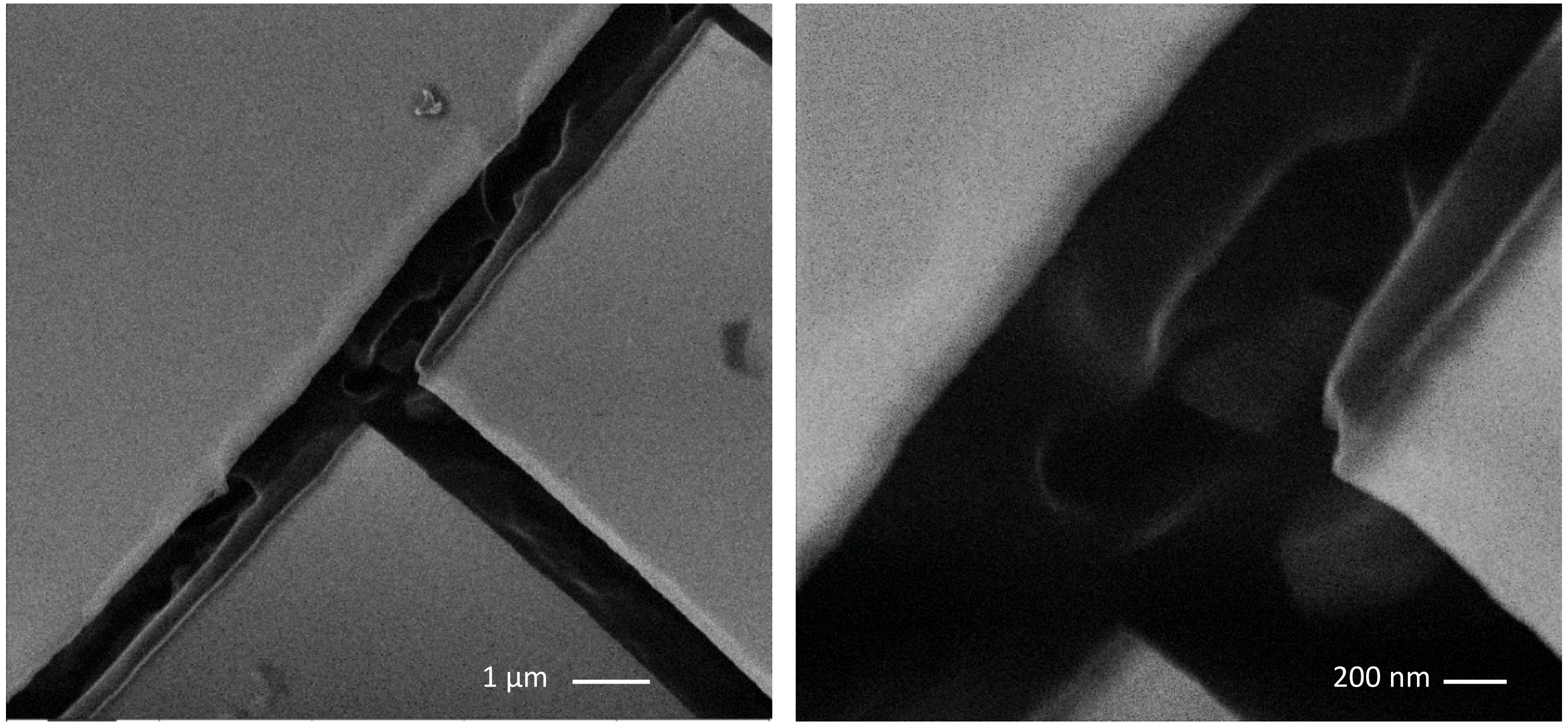
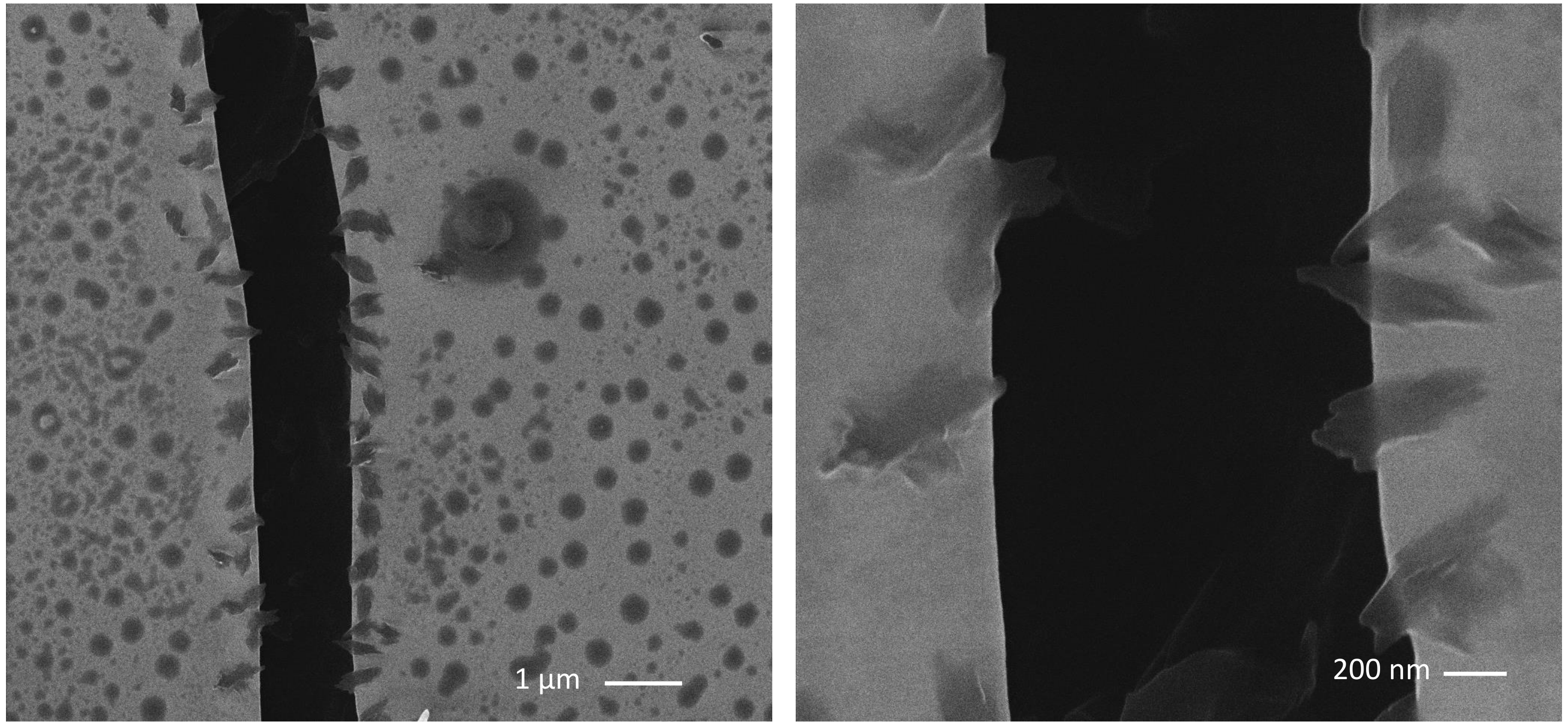
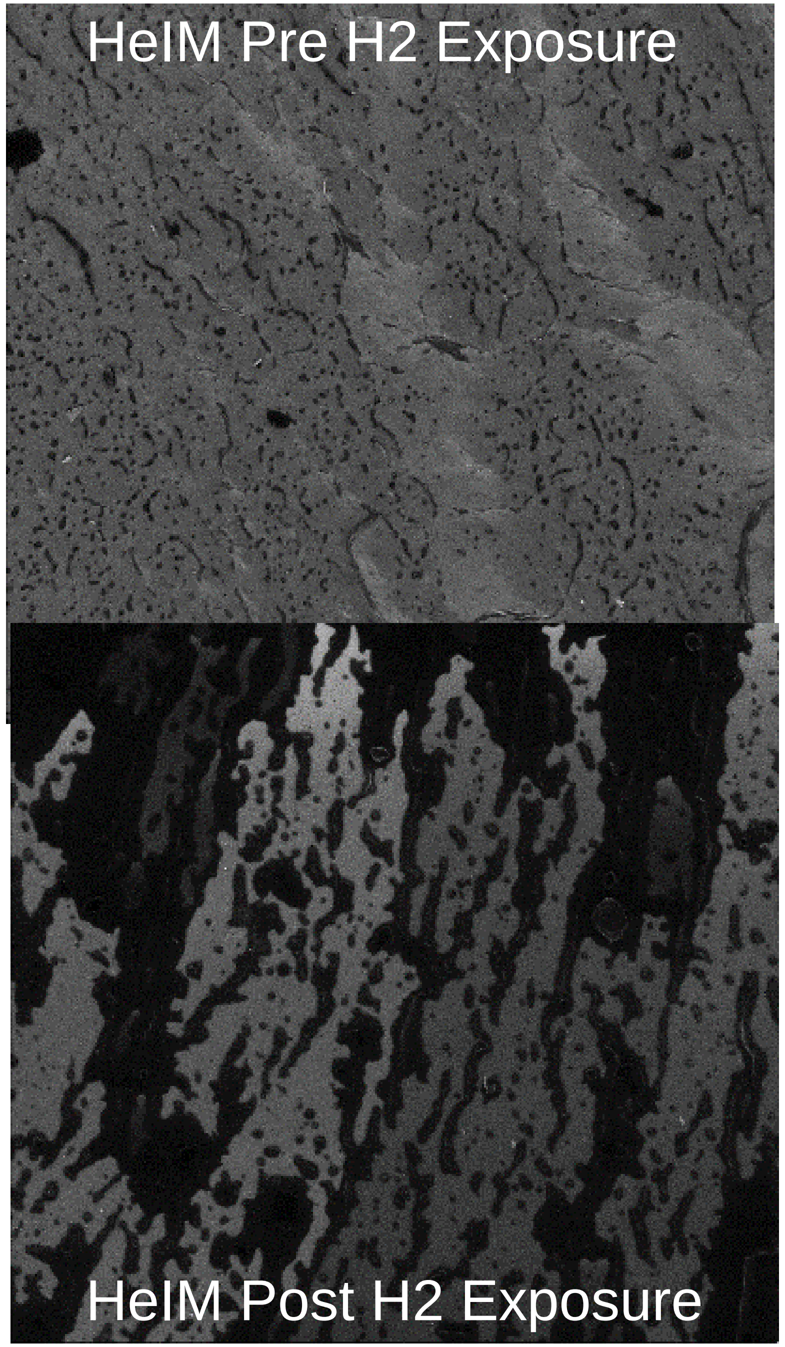
Pre Exposure

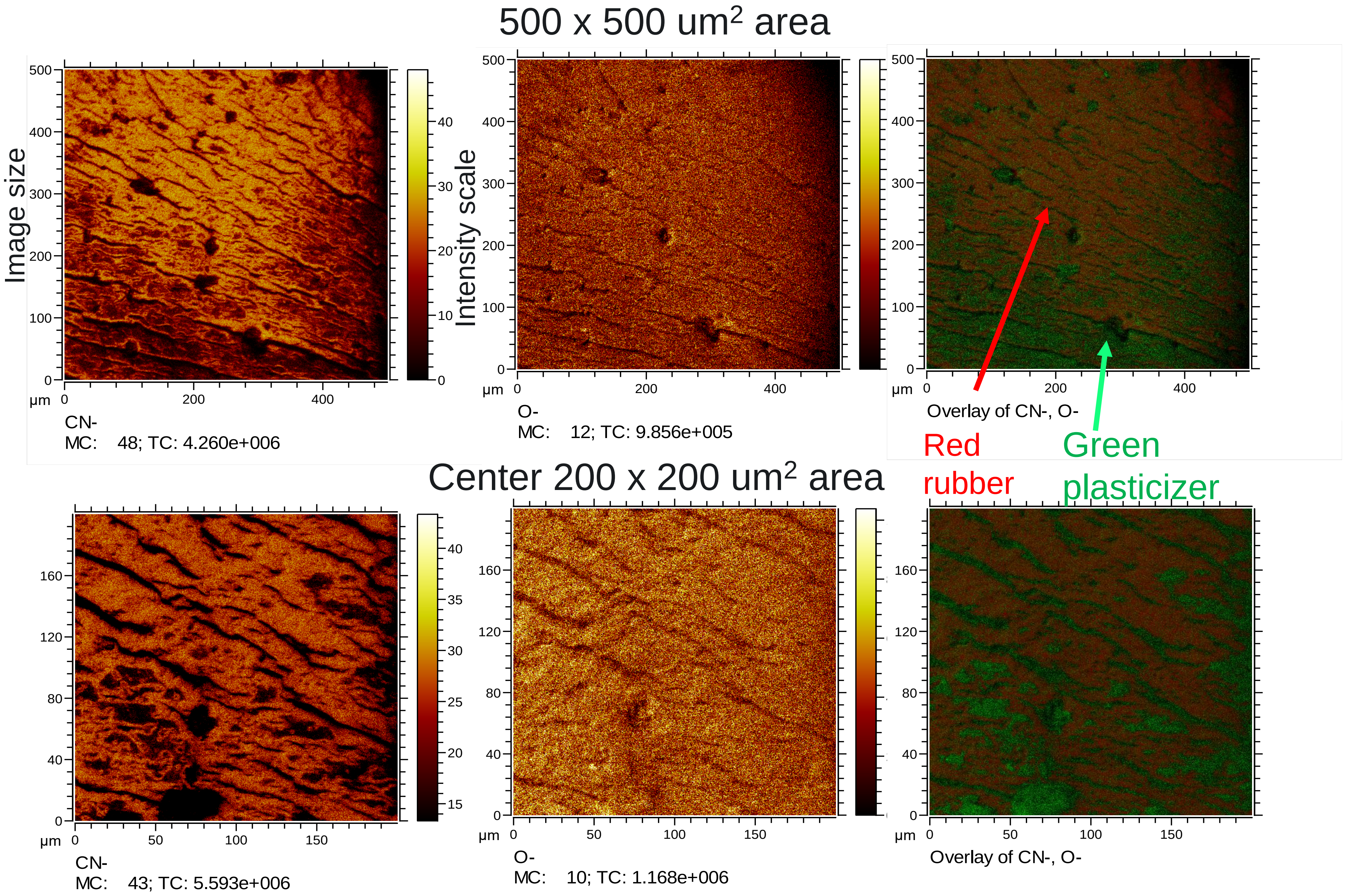


Post Exposure 28 MPa/24 hrs



Cryo Fractured N2 HeIM and Time of Flight Secondary Ion Microscopy (TOF-SIMS)

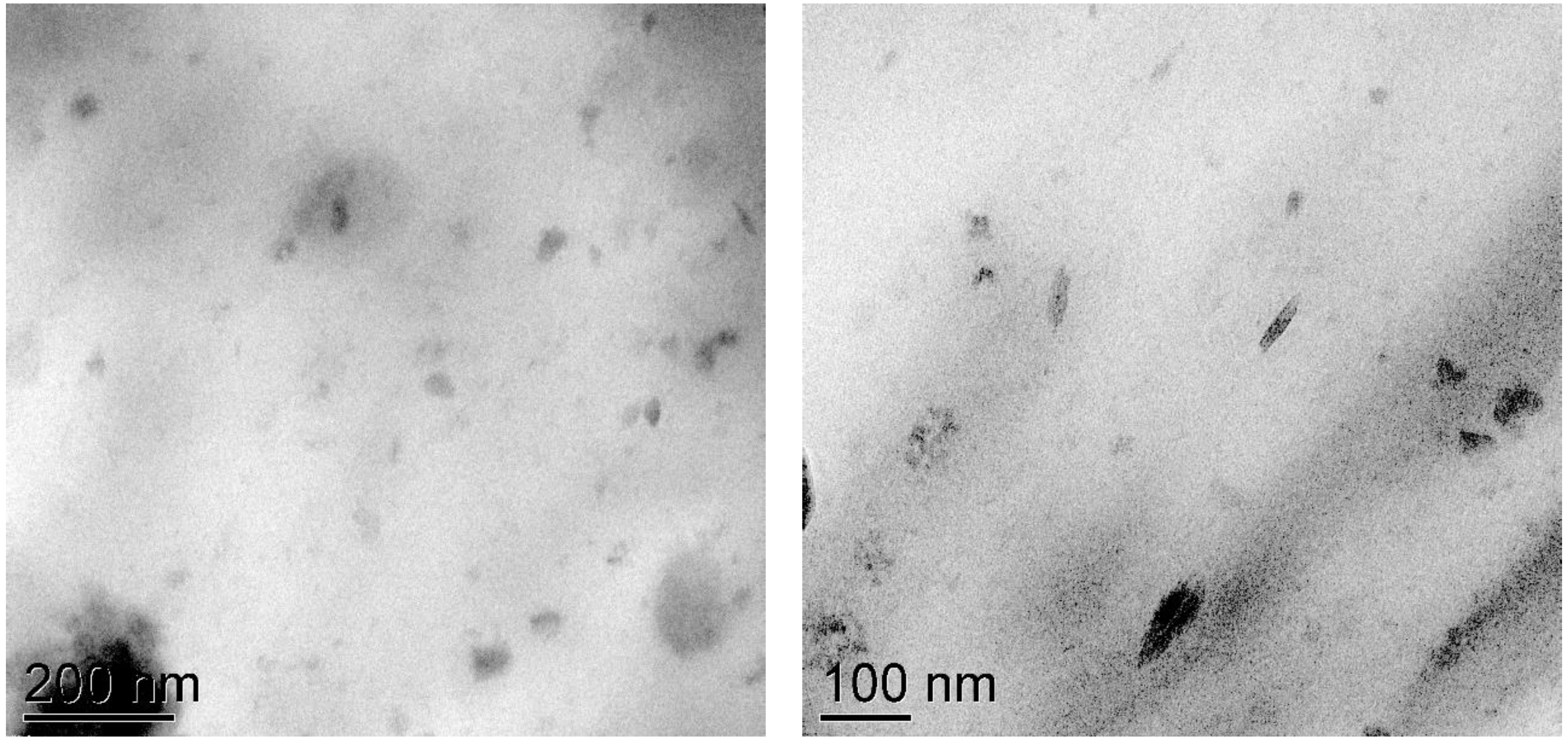




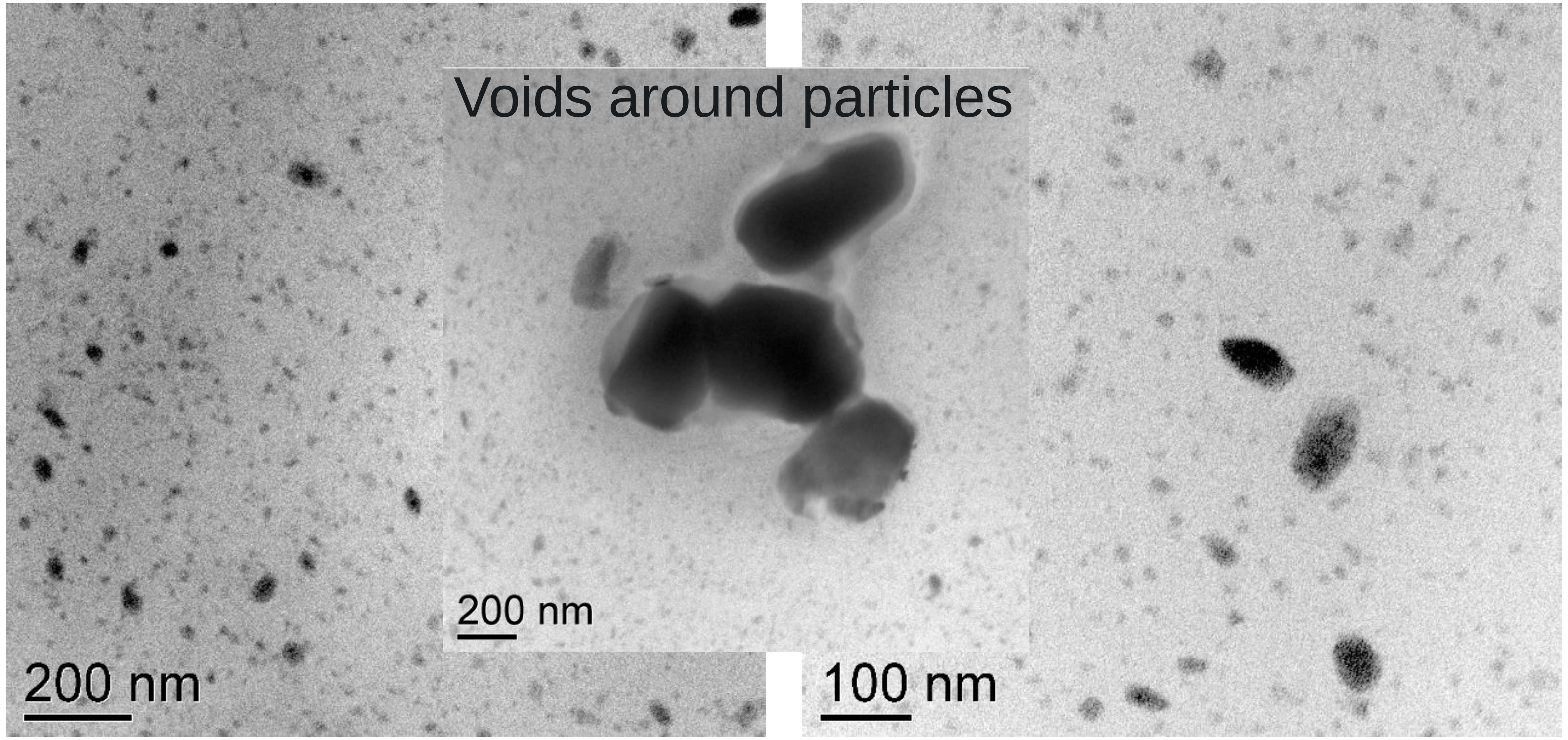
Transmission Electron Microscopy of N2 Rubber

- Significant change in morphology before and after one-time hydrogen exposure
- Zinc particles surrounded by extending "grey" halo after hydrogen exposure
- Small particles after hydrogen treatment averaged 20 nm to 25 nm in length and 15 nm in width.
- Small particles of ZnO with ZnS at the surface

Pre H2 Exposure

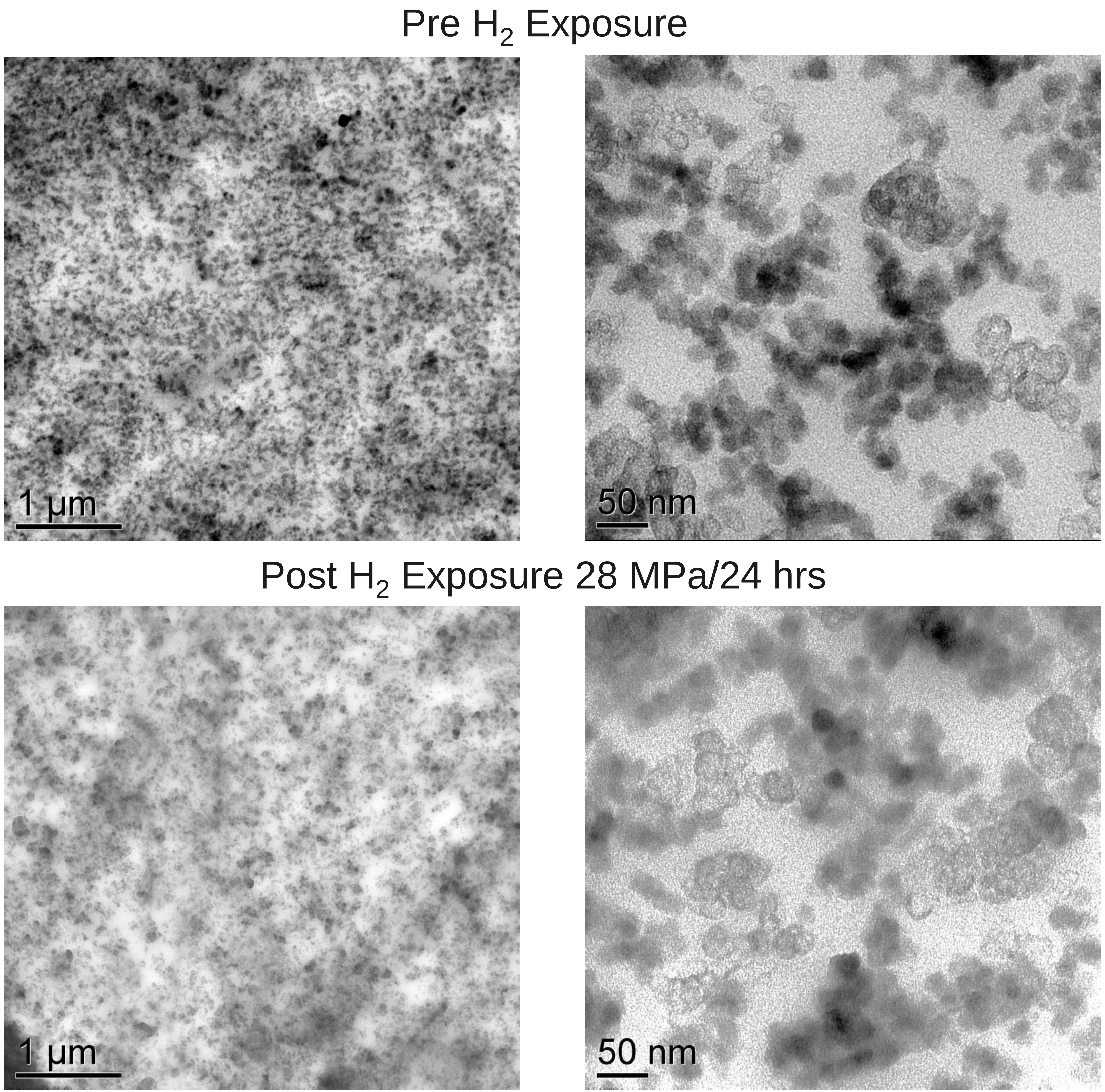


Post H2 Exposure 28 MPa/24 hrs



Transmission Electron Microscopy of N5 Rubber

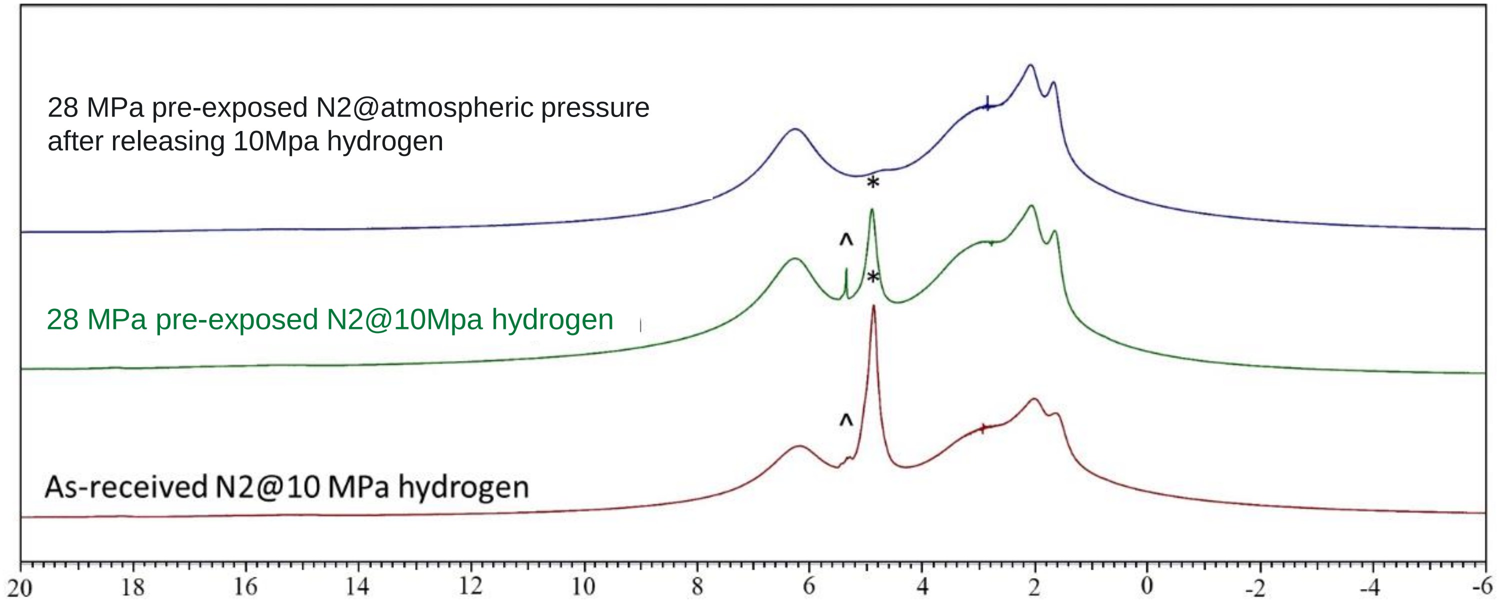
- Currently investigating void formation and particle delamination in filled NBR system
- Where does the cavitation want to initiate and how can we mitigate it?
- Current evidence is showing ZnO particle initiation



1H-NMR spectra of Sample N2 and N5

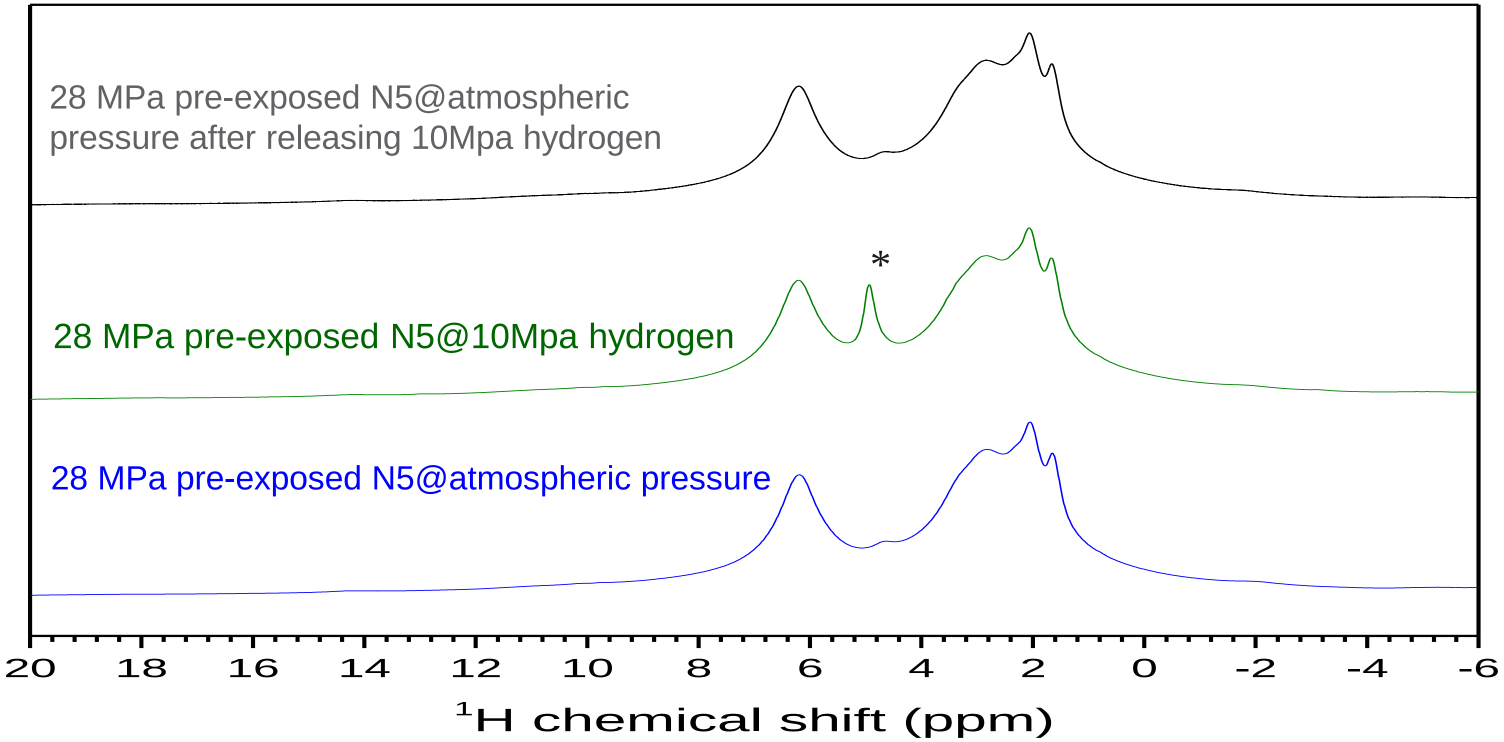
- Pre-exposure to 28 MPa hydrogen was done in a high-pressure vessel
- Unique experimental high-pressure gas rotor capable of 10 MPa hydrogen environment in-situ NMR tests
- Developing techniques for determining hydrogen diffusion and porosity spacing

N2 Samples



The peak (*) at 4.89 ppm represents the free hydrogen
The peak (^) at 5.3 ppm indicates the hydrogen condensed with the material.

N5 Samples

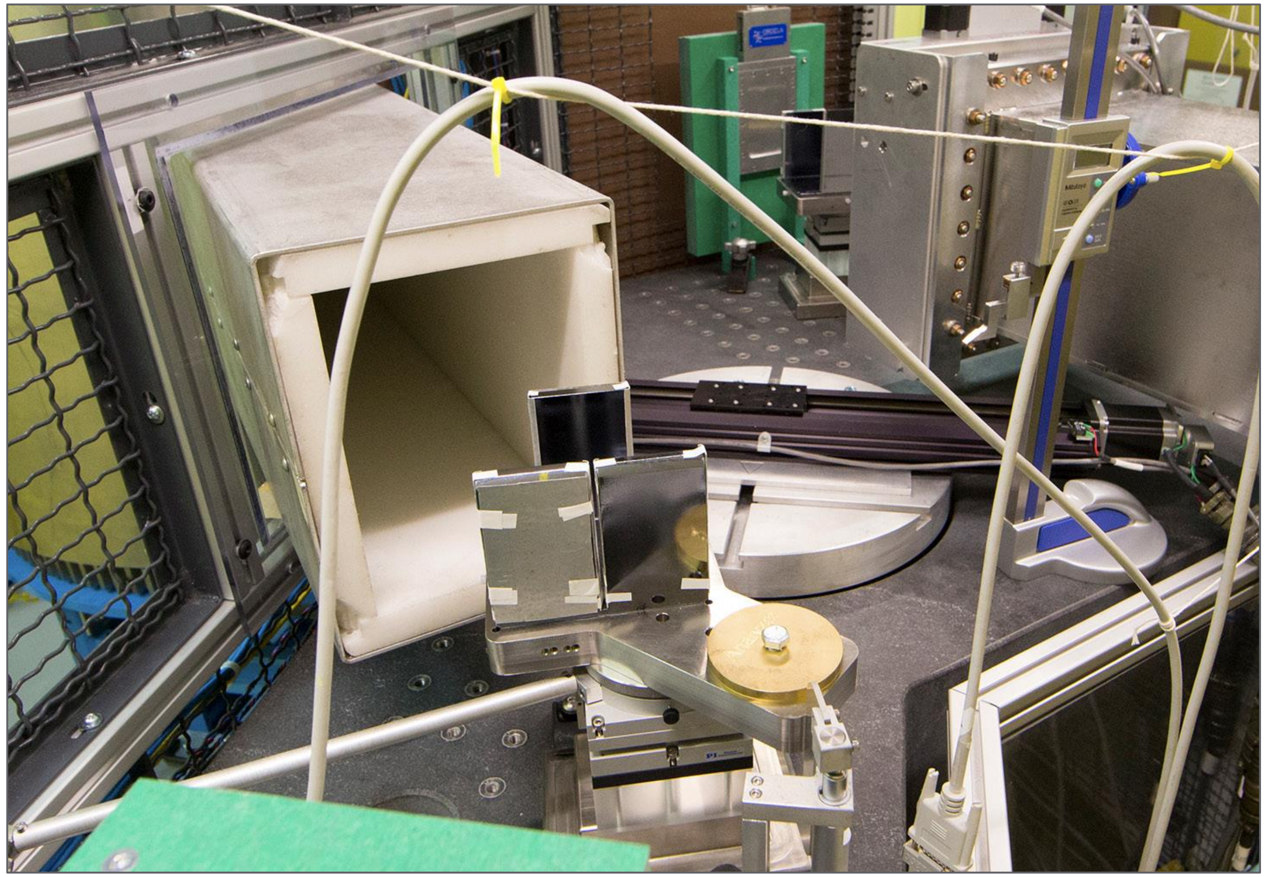


in situ Ultra Small Angle Neutron Scattering at ORNL Spallation Neutron Source (SNS)

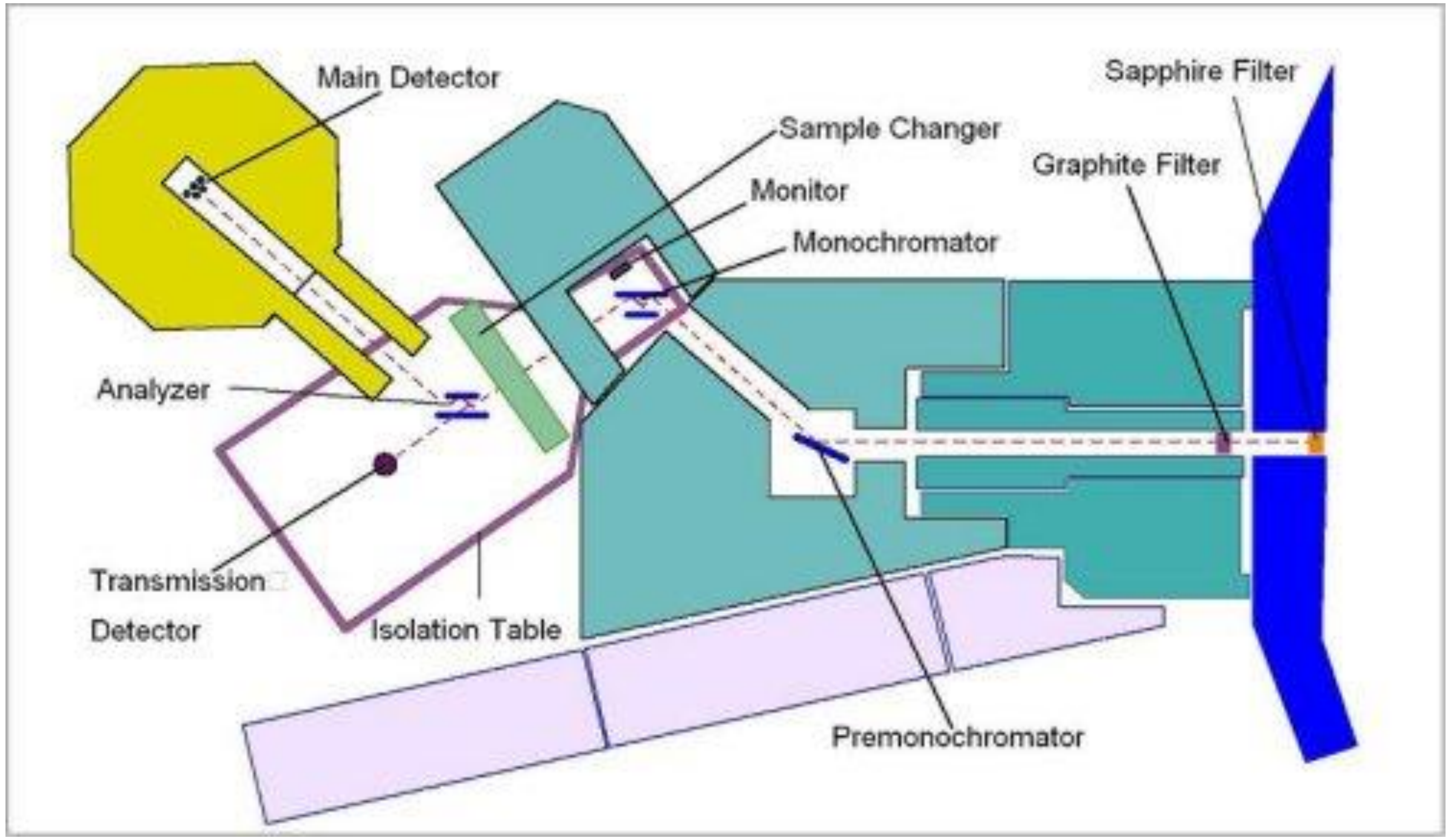
Polymer and elastomer samples: PEEK, POM, HDPE, PTFE, PA-6/6, NBR, EPDM

Q range: $1x10^{-5}$ Å^{-1} < Q < $5x10^{-3}$ Å^{-1}

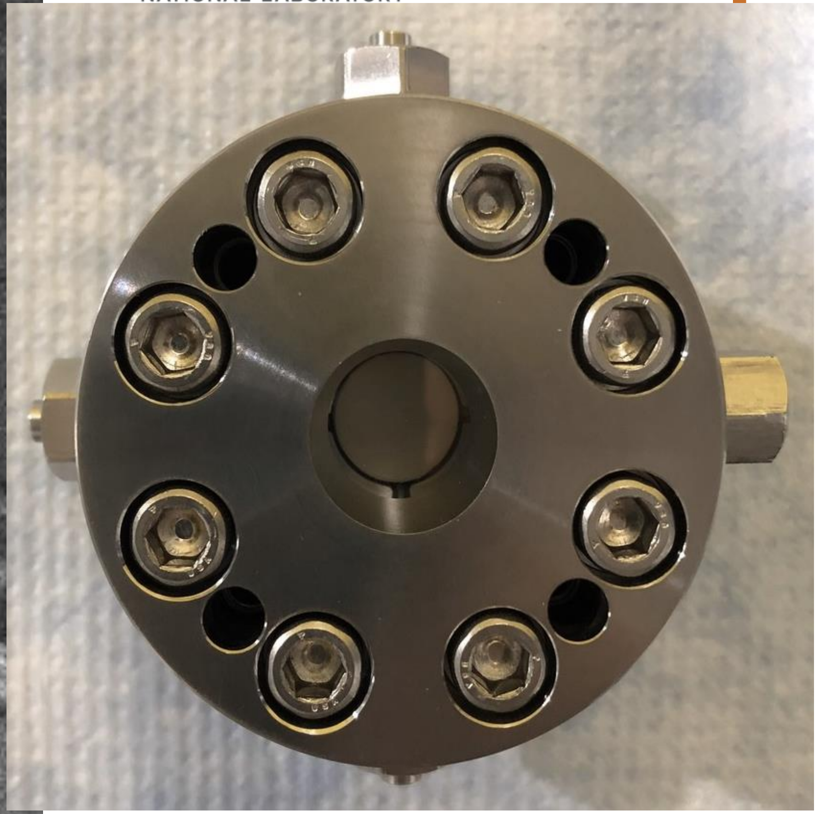
d = 125 nm - 60 µm



Bonse-Hart Double-Crystal Diffractometer at SNS USANS instrument with 4 Bragg reflections at 3.6, 1.8, 1.2, 0.9 Å . Pulsed neutron beam allows separation Bragg reflections using TOF



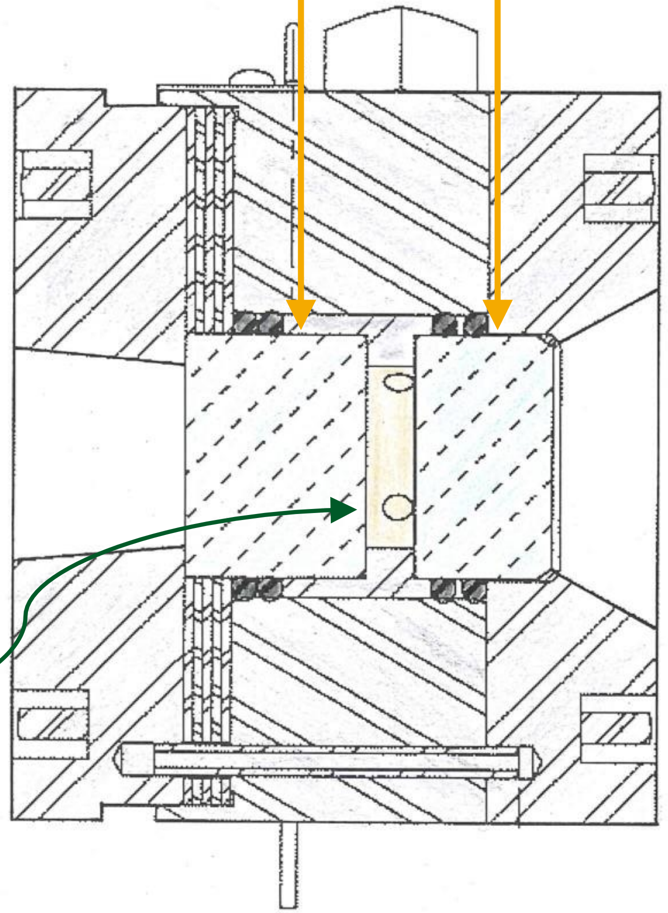
Process and Pressure Cell Schematic
Sample sizes: 18 mm diameter x 1-3 mm



9.5 cm

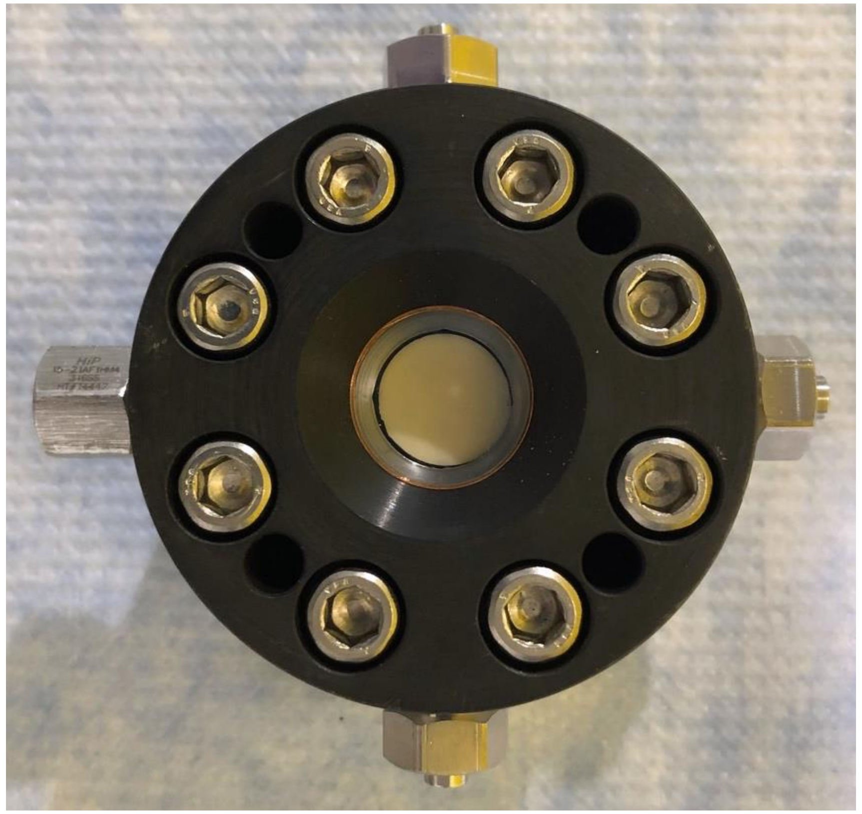
Incident beam

Sapphire windows



Sample thickness,
0.5-5.0 mm

Scattered beam

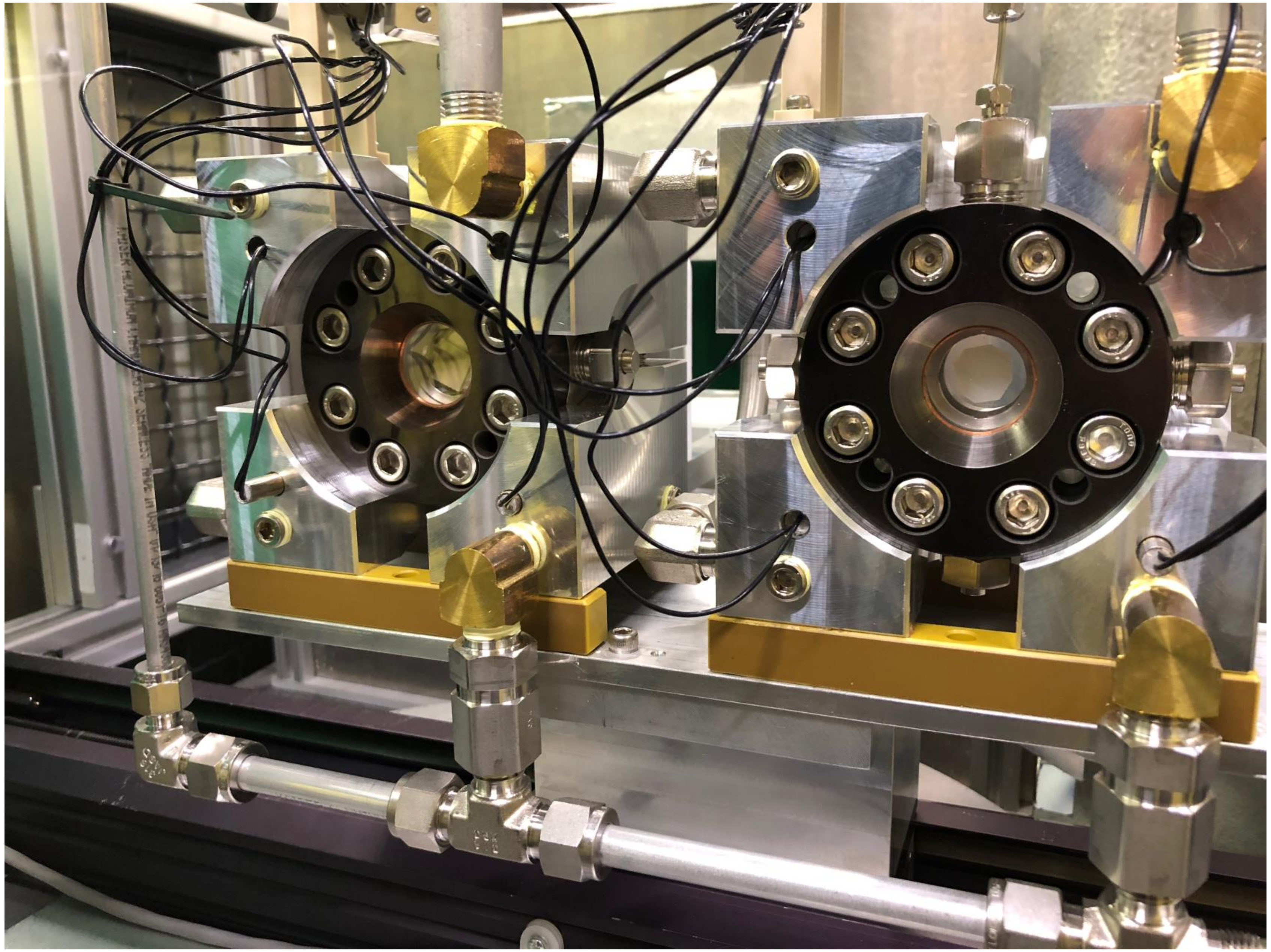


Samples were saturated while in queue for USANS

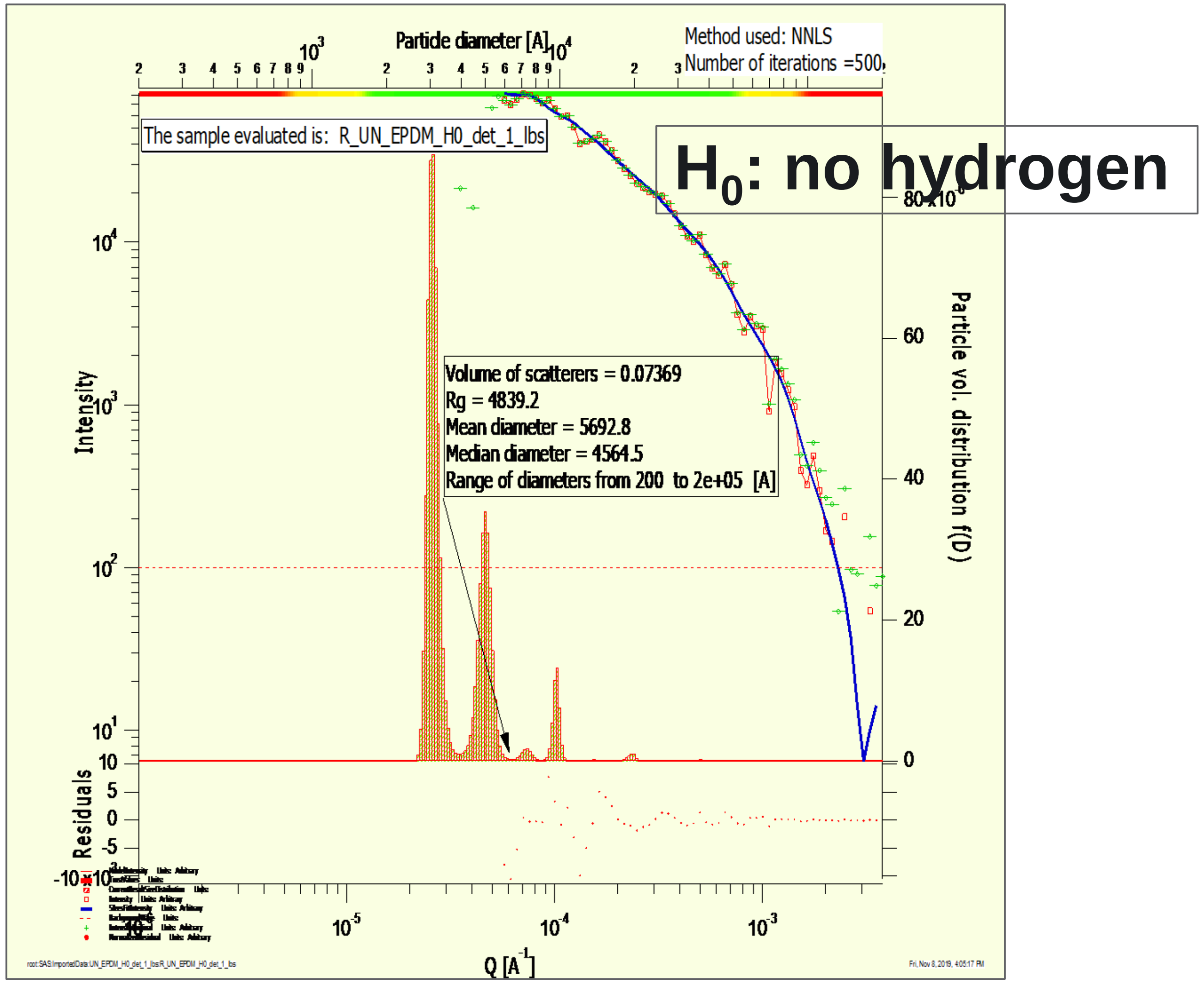
We have four pressure cells, but only two can be staged simultaneously

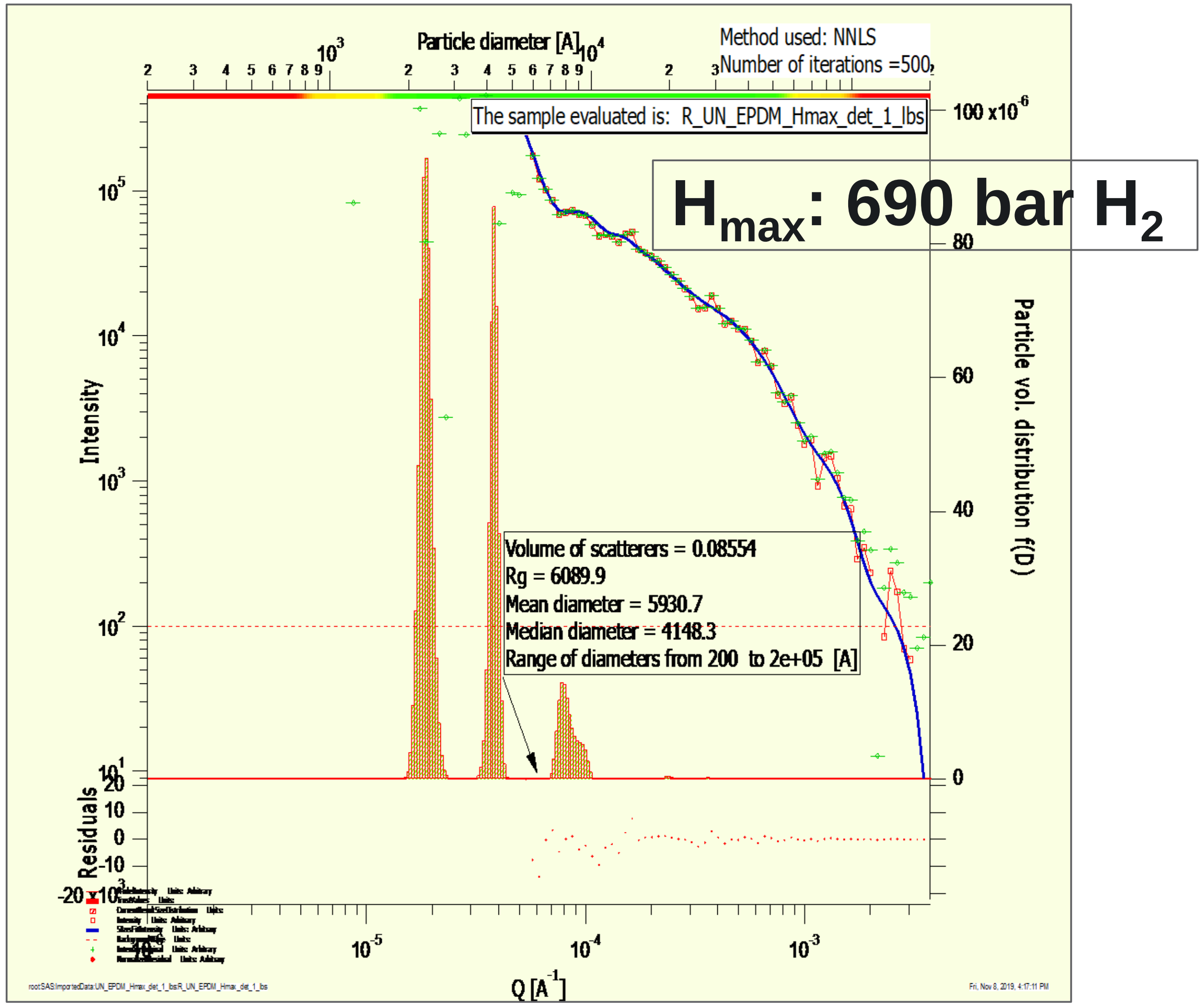
While one sample is in beam, other sample is soaking

USANS run times were ≥ 14 hours,
so **hydrogen soak times were ≥ 14 hours**



USANS results for EPDM – Scatterer number distribution



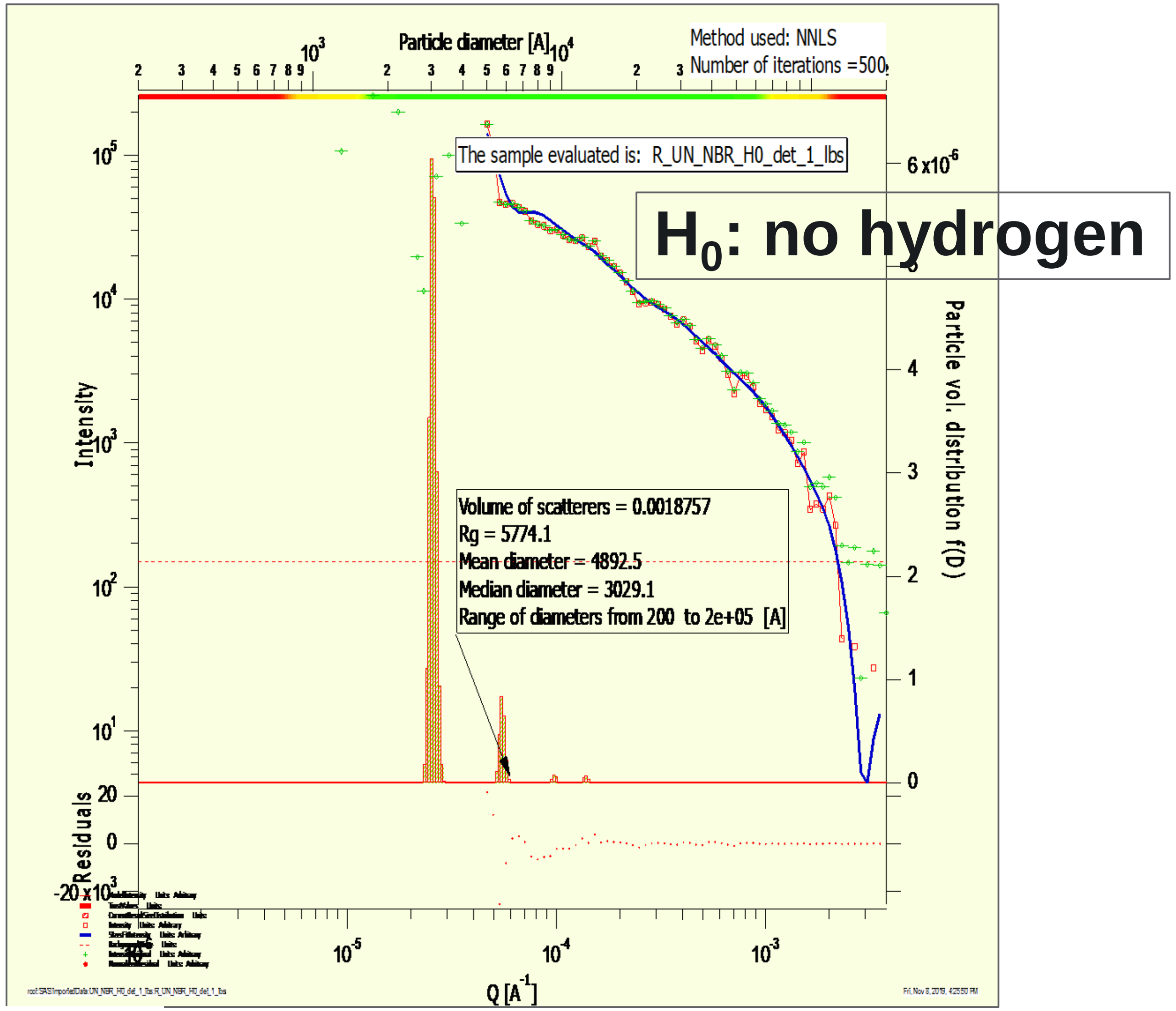


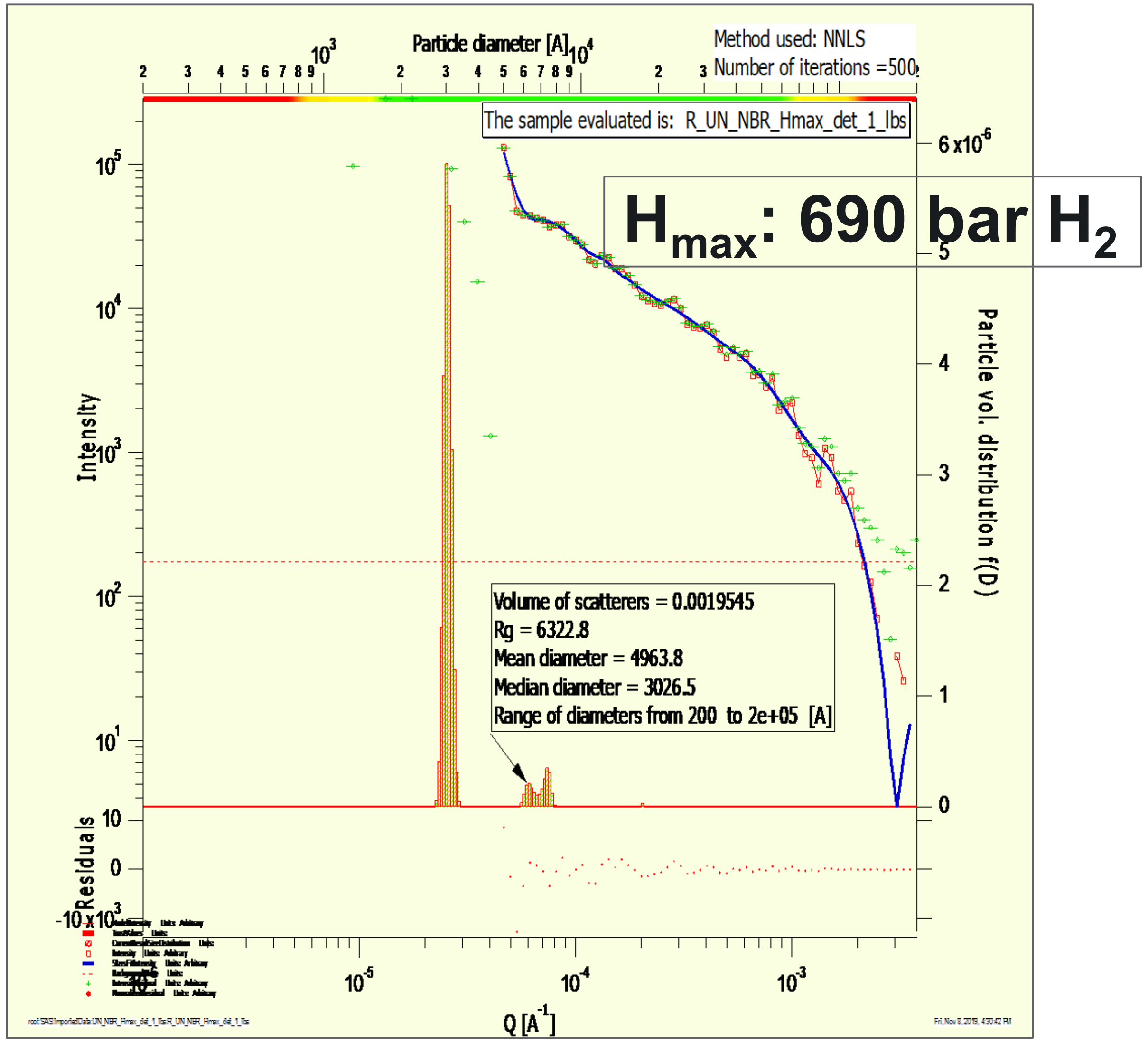
Significantly more scattering in EPDM than in polymers

More scattering centers, different sizes of scatterers

Some indication presence of H_2 increased number of scatterers by about 10%

USANS results for NBR - Scatterer number distribution





Weak indication that presence of H_2 produces small increase in number of scatterers

Summary

- Polymer materials play an important role in hydrogen infrastructure components by providing both static and dynamic sealing as well as high performance barrier
- High-pressure hydrogen gas interaction with polymers is not well understood in the hydrogen community
- Compression set in NBR material compounds is significant, with nearly a 40% increase after high-pressure hydrogen exposure while EPDM is insignificant
- High-pressure hydrogen exposure can increase plasticizer mobility
- ZnO/ZnS appears to nucleate nano to micro voids after high pressure H_2 exposure
- National labs experimental and analytical tools such as high pressure in-situ NMR and computer modeling are working to help understand the hydrogen influence in materials
- An increased understanding of the influence of high-pressure hydrogen will aid in future materials development to improve the reliability and performance of the polymer systems in hydrogen infrastructure

Acknowledgements

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Thank you