
H-Mat Overview: Polymers

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Overall Objectives

- Quantify the hydrogen pressure-temperature-time-damage relationships of polymers with controlled structure and morphology (to inform models of hydrogen-induced degradation of polymers).
- Develop material damage models of process-structure-property-performance with the aim of motivating materials formulations that are less sensitive to hydrogen-induced damage.
- Discover modified and new materials systems that improve hydrogen compatibility that will increase the reliability of materials and components in hydrogen infrastructure.
- Develop and maintain tools for data management and dissemination.

Fiscal Year (FY) 2019 Objectives

- Establish quantitative metric(s) for comparison of damage in model elastomers (nitrile butadiene rubber [NBR] and ethylene propylene diene monomer [EPDM] rubber) pressure cycled for more than 100 cycles.
- Complete the evaluation of one baseline model material using the dynamic mechanical analyzer under 4,000 psi helium pressure at ambient conditions.
- Complete the development of mesoscale damage models and correlate rapid

decompression data of the NBR model material set.

Technical Barriers

The Hydrogen Materials Compatibility Consortium (H-Mat) crosscuts multiple subprograms. It addresses the following technical barriers from the Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Safety Data and Information: Limited Access and Availability
- Insufficient Technical Data to Revise Standards
- Limited Participation of Business in the Code Development Process
- No Consistent Codification Plan and Process for Synchronization of R&D and Code Development.

In addition, the consortium addresses barriers associated with system cost, system weight and volume, and materials durability, as well as a lack of materials performance data and understanding of failure mechanisms associated with materials used in hydrogen delivery and hydrogen storage infrastructure.

Technical Targets

Most Safety, Codes and Standards subprogram activities do not have quantifiable technical targets. Targets for hydrogen delivery and storage generally focus on uninstalled or installed capital cost or system lifetime (10+ years). The H-Mat polymers project focuses on reducing the frequency of replacement for the many components in hydrogen infrastructure such as tanks, hoses, valve internals, seals, and gaskets that are made of rubber or plastic and are degraded by repeated exposure to hydrogen. Hence, H-Mat addresses maintenance cost technical targets established by the program for these systems (e.g., limiting those costs to 2% of installed capital cost per year or less).

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

FY 2019 Accomplishments

- Conducted pressure cycling tests (simulating service conditions) on model polymer systems (NBR and EPDM) and in situ dynamic mechanical analysis (DMA) to provide data on structural, morphological, and thermal behavior.
- Conducted advanced ex situ imaging of materials after hydrogen exposure to elucidate damage mechanisms.
- Discovered that:
 - Compression set in NBR material compounds is significant, with nearly a 40% increase after high-pressure hydrogen exposure, while in EPDM it is insignificant.
 - High-pressure hydrogen exposure can increase plasticizer mobility.
 - Zinc oxide or zinc sulfide particles appear to nucleate nano to micro voids after high-pressure hydrogen exposure.
- Developed a mesoscale model for investigating gas bubble expansion and polymer volume change during rapid decompression and made significant progress in developing the molecular dynamics model.

INTRODUCTION

H-Mat, composed of Sandia National Laboratories (SNL, metals lead), Pacific Northwest National Laboratory (PNNL, polymers lead), Oak Ridge National Laboratory (ORNL), Savannah River National Laboratory, and Argonne National Laboratory, is a framework for cross-cutting early-stage research and development on hydrogen materials compatibility. Working in collaboration with partners in industry and academia, H-Mat R&D focuses on the effects of hydrogen on performance of polymers and metals used in hydrogen infrastructure and storage. H-Mat's ultimate goals are to improve the reliability of materials, reduce the costs of materials, and inform codes and standards that guide development and use of hydrogen technologies. H-Mat was launched in 2018 by the Fuel Cell Technologies Office in support of the H2@Scale initiative.

APPROACH

Leveraging the advanced computational capabilities, unique experimental facilities, and expertise at the national laboratories, H-Mat is establishing scientific frameworks to improve materials reliability by elucidating the mechanisms of hydrogen-materials interactions. The hydrogen pressure-temperature-time-damage relationships of polymers with controlled structure and morphology are measured experimentally and used for developing and validating computational models. Computational materials science is exploited to improve materials design and to provide the basis for predictive materials performance tools. State-of-the-art characterization techniques are integrated with these computational studies to bridge length scales from the quantum to the continuum.

With this approach, H-Mat will provide science-based strategies that enable (1) the microstructural design of metallic materials for enhanced resistance to hydrogen-assisted fatigue and fracture; and (2) the development of polymeric materials with improved resistance to hydrogen-induced degradation.

RESULTS

Task P1: Mechanisms of Hydrogen-Induced Degradation of Polymers

PNNL developed an in situ DMA capability by integrating a commercial DMA machine with a high-pressure autoclave. Appropriate designs and modifications were implemented to ensure both accuracy and safety. This system enables the measurement of mechanical properties in end-use conditions while simultaneously monitoring materials change during pressure cycling. PNNL successfully tested one model rubber (EPDM #1) with helium up to 4,000 psi using in situ DMA. Figure 1 shows that the material continued to swell after completion of pressurization due to limited gas diffusion; it also expanded dramatically after rapid gas decompression, followed by a slow shape recovery. Frequency sweep testing results suggest that high-pressure environments reduce storage modulus (deformation resistance) of the material, likely due to pseudo-plasticization effects.

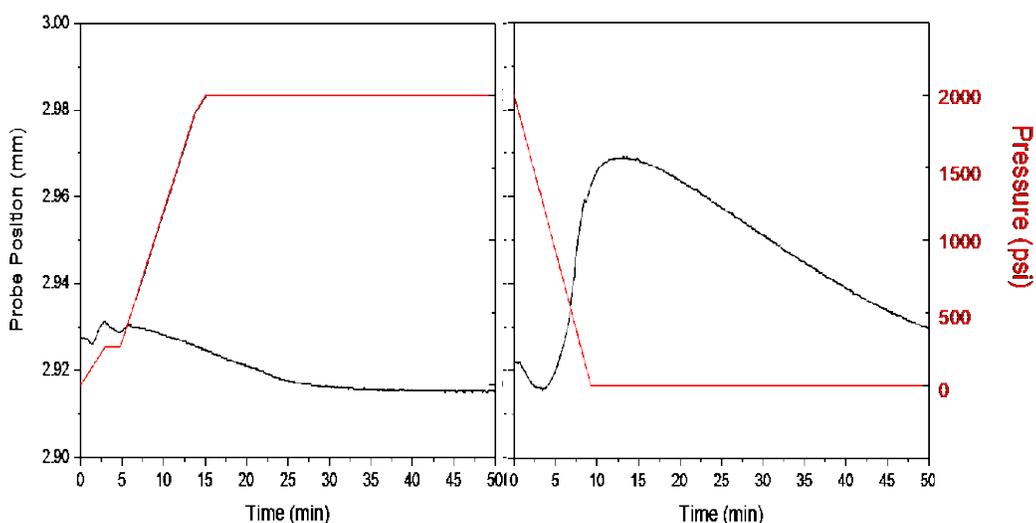


Figure 1. Tested material continued swelling after completion of pressurization due to limited gas diffusion (left) and expanded dramatically after rapid gas decompression, followed by a slow shape recovery (right)

PNNL studied both surface morphology and cryo-fracture morphology of model rubber compounds, pre and post high-pressure hydrogen exposure, using helium ion microscopy (HeIM), which provides better resolution and materials contrast than conventional scanning electron microscopy. NBR #5 demonstrated phase separation of plasticizer after being soaked in 27.6 MPa hydrogen for 20 hours to saturation, as evidenced in corresponding time-of-flight secondary ion mass spectroscopy studies (see Figure 2a). More importantly, EPDM #2 showed plasticizer phase separation from the rubber matrix only in the presence of hydrogen; no such behavior was observed in helium exposure. Figure 2b also reveals that surface cracks primarily formed around the plasticizer-enriched regions and extended further out after the sample was pressurized under 27.6 MPa of either helium or hydrogen gas for 20 h. Cracks were found on the cryo-fractured cross sections at the micrometer level, and, interestingly, large voids (30–50 μm) crossed by ligaments were found to form in hydrogen exposure.

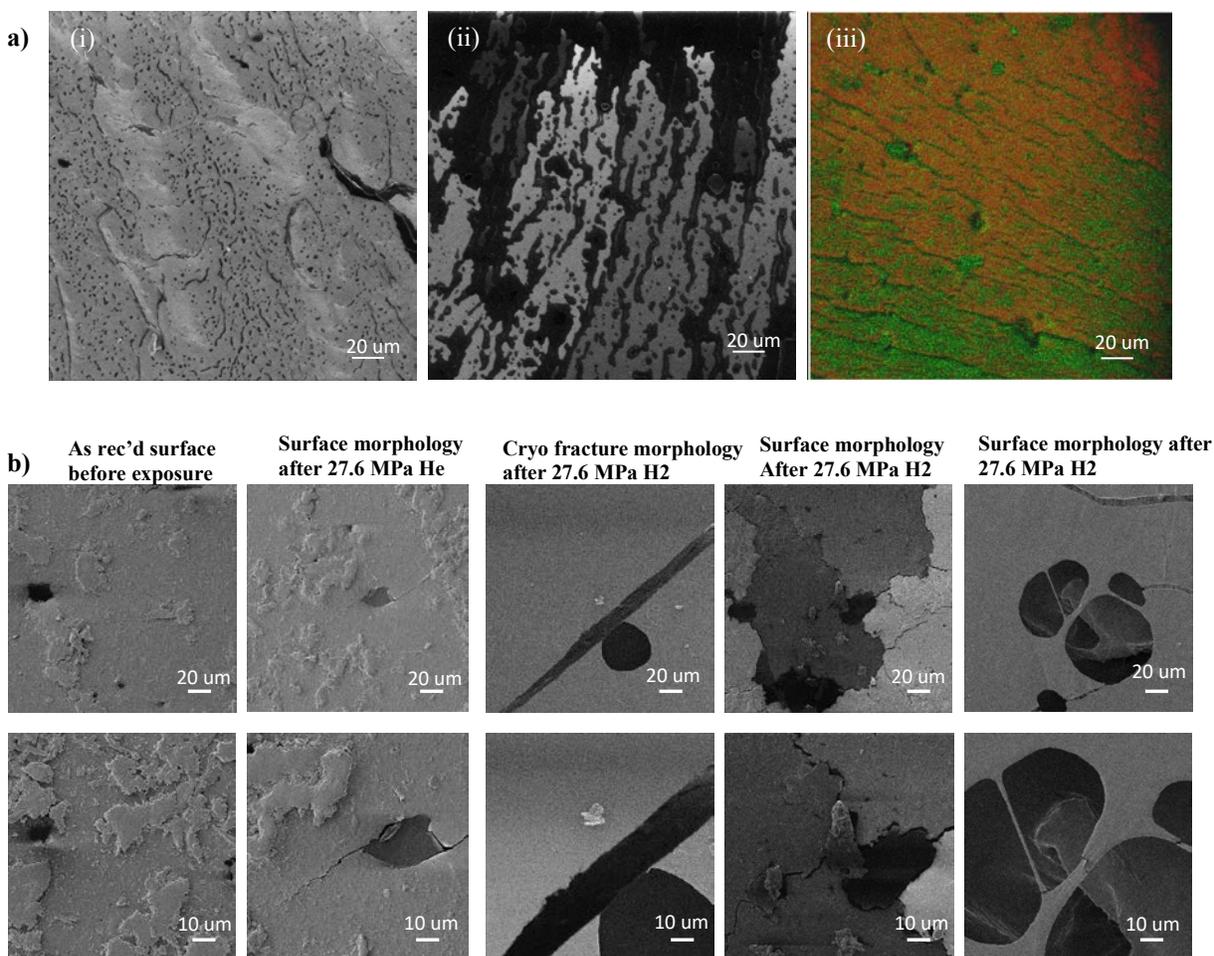


Figure 2. (a) HeIM images of NBR #5 (i) pre and (ii) post hydrogen (27.6 MPa for 20 h) with (iii) time-of-flight secondary ion mass spectroscopy analysis. Phase separation of plasticizer was observed under high hydrogen pressure. **(b)** HeIM images of EPDM #2 pre and post exposure to different gases. Hydrogen exposure resulted in severe surface cracking and phase separation of plasticizer; helium did not. Investigation on internal morphology showed formation of large bubbles/voids only after hydrogen exposure.

PNNL and SNL also evaluated morphological characteristics of NBR and EPDM in ambient air and high-pressure helium and hydrogen (under static and cycling conditions) using a combination of helium ion microscopy, transmission electron microscopy, scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy, and with micro-computed tomography. In hydrogen, a grey “halo” structure formed around zinc-based particles with a “tail” extending out further at one direction. This behavior was not seen in helium. In addition, elemental analysis found zinc sulfide distributed around the particles and heavily in the tail. The halo and tail may be gaps and voids developed during high-pressure hydrogen treatment.

Unique solid-state nuclear magnetic resonance capabilities for in situ analysis under pressure up to 10 MPa were used to understand polymer-hydrogen interactions at the molecular level. This technology enables the study of pore and void formation in the material by comparing the amount of hydrogen condensed in pores or voids within the material to the amount of free hydrogen outside the material. It also allows calculation of the diffusion coefficient of hydrogen within the pores and voids as well as the distance between adjacent pores/voids.

In addition, ORNL is using neutron scattering experiments to quantify the hydrogen pressure-temperature-time-damage relationships of polymers with controlled structure and morphology. In situ experiments with

polymer and elastomer samples immersed in high-pressure hydrogen were done at the ultra-small angle neutron scattering beam line at the Spallation Neutron Source at ORNL. Samples of un-pressure-cycled polytetrafluoroethylene polymer and EPDM elastomer exhibited changes in porosity while immersed in 69 MPa hydrogen. Ex situ experiments with moderate-pressure-cycled polymer samples were done using the small angle neutron scattering and ultra-small angle neutron scattering beam lines at the National Institute for Science and Technology Center for Neutron Research. The polymers were subjected to 22 pressure cycles of hydrogen with maximum pressures of 24 MPa followed by depressurization to atmospheric pressure. Neutron scattering measurements of the samples were done in air at atmospheric pressure. The polyether ether ketone sample exhibited distinct changes in internal structure while the other samples did not. More extensive measurements of hydrogen-induced changes in morphology in polymers and elastomers will be done in the next project year, with a focus on samples that have been pressure-cycled to maximum pressures ≤ 1 GPa in the ex situ measurements and samples subjected to higher pressures (~ 1 GPa) in the in situ measurements. We also expect to analyze the pressure-cycled samples for additional morphological changes using small-angle X-ray scattering.

Task P2: Computational Multiscale Modeling

Computational multiscale modeling efforts for both PNNL and SNL are unraveling the mechanisms of damage in EPDM under pressurized hydrogen environments. The FY 2019 focus was on model development and validation.

- SNL produced a nanoscale (\sim nm), all-atom molecular dynamic simulation to study the role of pressurized gas during the onset of cavitation. Capabilities were developed to identify and characterize cavitation along with dynamic structural changes. Results indicate two regimes of cavitation growth rate, where the transition is associated with mechanical yield of the material.
- PNNL produced a mesoscale ($\sim\mu$ m) phase field model to elucidate the pressure dependence of gas bubble dynamics. Simulations focused on the time and pressure dependence of volume, concentration, and mass. Results show bubbles rapidly expand immediately following pressure release due to an oversaturation of hydrogen gas, then slowly shrink in size, exhibiting a nonlinear trend in time.

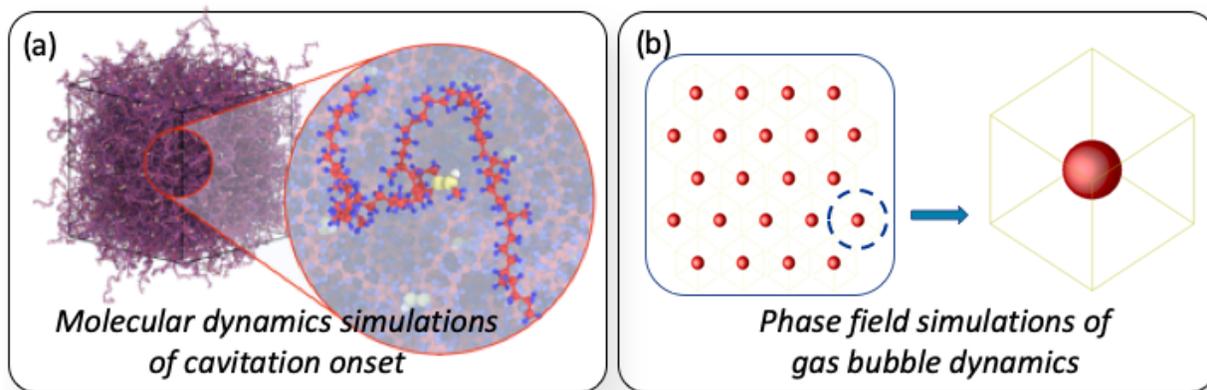


Figure 3. Depictions of the representative modeling length scales: (a) all-atom molecular dynamics simulations model cavitation at the nanoscale, and (b) phase field simulations model the pressure dependence of gas bubble dynamics at mesoscales.

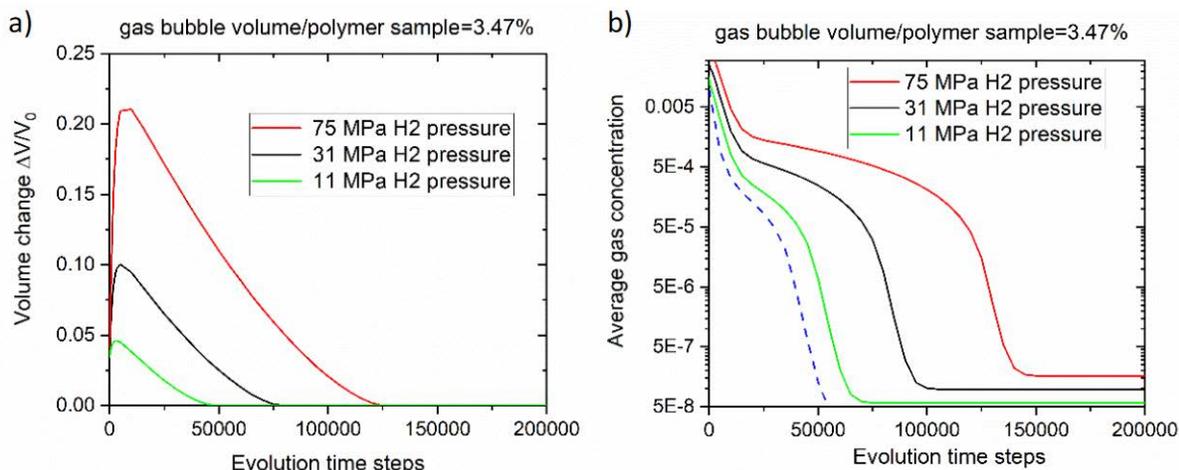


Figure 4. (a) Volume change and (b) hydrogen concentration decrease with decompression time. The time is proportional to the evolution time steps. The dashed blue line refers to the case without gas bubble. The results indicate that higher pressure causes larger volume change with slower recovery upon decompression and also that gas concentration evolving profiles depend on maximum pressure.

CONCLUSIONS AND UPCOMING ACTIVITIES

HeIM results distinguish hydrogen effects from high pressure effects as the phase separation of plasticizer occurred in hydrogen but not in helium. Transmission electron microscopy analysis shows that zinc-based particles changed morphologically after exposure to 27.6 MPa high-pressure helium or hydrogen. The larger particles, greater than 200 nm, in the rubber matrix were displaced and the rubber matrix material was torn along the displacing track. Scanning transmission electron microscopy with energy dispersive X-ray spectroscopy suggests formation of zinc sulfide at the surface of zinc oxide particles added as activators during compounding suggest possible hydrogen gas enrichment around the particles.

High-pressure helium and hydrogen exposure tests to 90 MPa with static and cyclic experiments also indicate hydrogen effects not seen with helium. Pressure cycling exceeding 10 cycles has additional effects on material property changes not previously observed with static and low cycling experiments.

A new partnership with a major rubber manufacturer is in progress for hydrogen-resistant formulations based on their cavitation-free commercial products used in natural gas exploration and production. The project will also partner with compounder Burke Industries to produce elastomer formulations with better hydrogen resistance.

In FY 2020, the addition of thermoplastics and thermosetting polymers will be studied in terms of hydrogen compatibility. Pressure cycling effects on materials' mechanical performance will be further investigated with in situ DMA. Fillers or particles will be added into the phase field model developed at PNNL to study their effects on gas bubble evolution during rapid decompression. The database will be available for internal testing between DOE and the H-Mat consortium.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

Members of the team were recognized at the Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, April 29 to May 2 in Washington, D.C., for excellent performance in the Safety, Codes and Standards program area.

FY 2019 PUBLICATIONS/ PRESENTATIONS

1. K.L. Simmons, W. Kuang, S.D. Burton, K. Han, B.W. Arey, N.C. Menon, and D.B. Smith, et al., “H-Mat Hydrogen Compatibility of Polymers and Elastomers,” Presented at International Conference on Hydrogen Safety, Adelaide, Australia, September 26, 2019.
2. K.L. Simmons, W. Kuang, Y. Shin, S. D. Burton, K. Han, Y. Li, and E.I. Barker, et al., “H-Mat Overview of Hydrogen Compatibility of Polymer Research,” Presentation at DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington D.C. April 30, 2019.
3. K.L. Simmons, “Hydrogen Compatibility of Polymers Program,” Presented at Kyushu University, 2019 HYDROGENIUS Research Symposium, Fukuoka, Japan, 2019.
4. K.L. Simmons, W. Kuang, S.D. Burton, Y. Shin, K. Han, A. Dohanlkova, and B.W. Arey, “Seminar on Science-based Advancement of Polymeric Materials for Hydrogen Technologies,” Presented by K.L. Simmons at Material Science Seminar, Pullman, Washington, March 8, 2019.
5. K.L. Simmons, W. Kuang, Y. Shin, S.D. Burton, K. Han, Y. Li, and E.I. Barker, et al., “H-Mat Overview of Hydrogen Compatibility of Polymers Research,” Presented at USCAR, Southfield, Michigan, March 12, 2019.