Screening Tests for Elastomers in the Hydrogen Economy

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A viable hydrogen delivery infrastructure will require that a wide variety of materials come in contact with high-pressure hydrogen as it is created, stored, transported, and used as fuel. Seals, gaskets, and non-metallic pipelines are prime examples of polymers that hydrogen will encounter throughout its life cycle. Hydrogen can quickly diffuse into polymer materials – up to their saturation level – and cause swelling. Then, when the pressure is released (e.g., hydrogen is consumed or transferred), the depressurization can cause supersaturation in the polymer. Bubble nucleation and growth can occur and cause irreversible damage to the polymer in the forms of micro-cracking, swelling, and embrittlement. This can lead to leaking out of sealed containment, which is not only inefficient but also a safety hazard due to its flammability.

Recently, EWI conducted a study to develop screening tests to detect material weaknesses that can develop within a hydrogen delivery system. The tests examined representative conditions during the development of new products to ensure that they could retain their integrity for their intended service life.

Seven different o-ring grades were exposed to hydrogen, experienced a fast depressurization, and were characterized for material property changes. O-rings (size -020) of different materials – nitrile butadiene rubber (NBR) with a hardness of 70A and 90A durometer, fluoroelastomer (FKM) with a hardness of 75A and 90A durometer, poly(tetrafluoroethylene) (PTFE) with a hardness of 55D durometer, silicone with a hardness of 70A durometer, and ethylene propylene diene monomer (EPDM) with a hardness of 70A durometer – were all purchased from McMaster Carr. Hydrogen (99.999%) was purchased from Delille Oxygen Company (Columbus, OH).

The pressure vessel used for this testing was a Jerguson gage (Jerguson Gage & Valve Co, Strongsville, OH) with a window on one side, see Figure 1. A schematic of the entire set-up is shown in Figure 2. For selected experiments, the Jerguson was submerged in a water bath to control temperature.

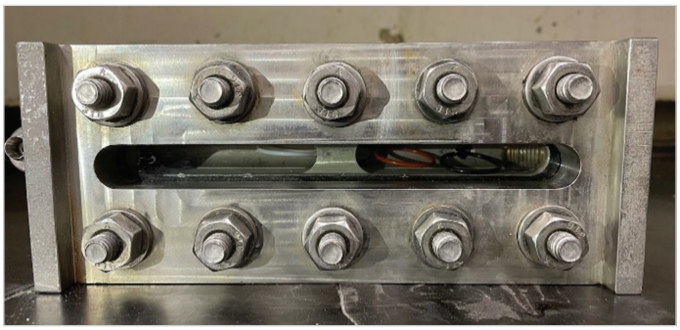

Figure 1. Jerguson gage for pressurized hydrogen soaking with two o-rings inside

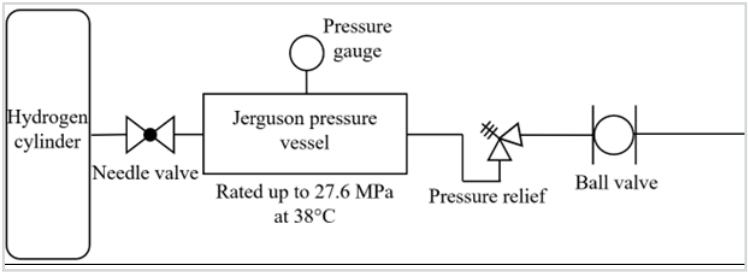

Figure 2. Pressurized hydrogen set-up

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Duplicate o-rings were placed in the Jerguson vessel, which was pressurized up to 16.5 MPa with hydrogen for 24 to 96 hours at temperatures between 22°C and 40°C. Then, the pressure was quickly released (< 1 second), and the o-rings were removed for characterization. Table 1 shows the details of the four trials. Characterization of the as-received o-rings was completed and used for the baseline values. Reported percent changes were calculated from these baseline values.

Table 1. Hydrogen Soak Trial Details

Trial	T (°C)	P (MPa)	Soak Time (h)	ΔP Time (s) Spacing (mm)
1	22	16.5	27	0.9
2	22	15.9	72	0.4
3	40	14.5	48	0.3
4	22	13.8	24 h x 4 releases = 96 h	0.3, 0.4, 0.3, 0.2

The following tests were performed:

- *Hardness was measured on the durometer A scale using a Rex Gauge Company gauge following ASTM D2240.*
- *Weight of each o-ring was measured on a Mettler Toledo 4 place balance, unless otherwise noted.*
- *The peak tensile strength and ultimate elongation were measured on a Chatillon with an 890 N load cell. The o-ring was strung between two oiled hooks and pulled apart until failure at a rate of 0.31 m/min. This test was based on ASTM D1414.*

Results

Resulting elastomer property differences after soaking in high pressure hydrogen and then releasing pressure quickly are documented and discussed in this section.

The results for the change in hardness showed generally showed no difference from the baseline measurements. All but one o-ring was within the error of the measurement. The outlier was the FKM 90A material at a 14% decrease, but the result was not duplicated as that sample did not show the same decrease.

The weight of each sample was measured before and immediately after (within 10 minutes of) depressurization, see Figure 3. Trial 3 data was not available due to balance unavailability during the proper time window for weighing the o-rings. All the measured values changed less than 0.25% following the hydrogen soak. In general, the NBR, silicone, and EPDM materials lost weight, which was likely due to hydrogen diffusion into the rubber and subsequent swelling, ultimately allowing the plasticizing oil to bloom to the surface and be removed from the rubber. FKM requires plasticizers that can withstand higher temperatures than the other materials. These molecules are less mobile than the others, thus the reason for less consistent weight loss. Also, some grades of PTFE do not contain plasticizers or lubricants, so weight loss would not have been expected and was not observed.

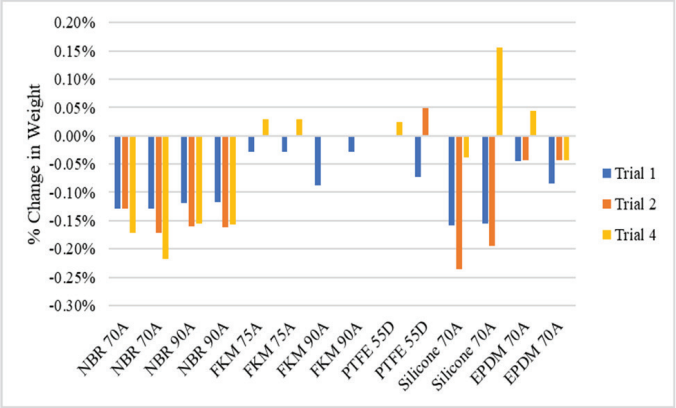

Figure 3. . Change in Weight after hydrogen soak and depressurization

The change in tensile strength was calculated by taking the average of five measurements on each of the as-received o-ring types and using it as the baseline strength. These data sets had standard deviations of 3% for NBR 70A, 10% for

NBR 90A, 3% for FKM 75A, 9% for FKM 90A, 3% for PTFE 55D, 5% for silicone 70A, and 5% for EPDM 70A.

The data in Figure 4 shows that most of the post-soak tensile values were within or near the as-received values. There were three clear outliers: FKM 75A Trial 2, FKM 90A Trial 2, and EPDM 70A Trial 1. All three of these had decreases in strength. This was likely due to an upset of the rubber microstructure due to fast depressurization. No complimentary tests have been performed yet to corroborate this hypothesis. Instead, this will be part of a future study using computed tomography (CT) scans.

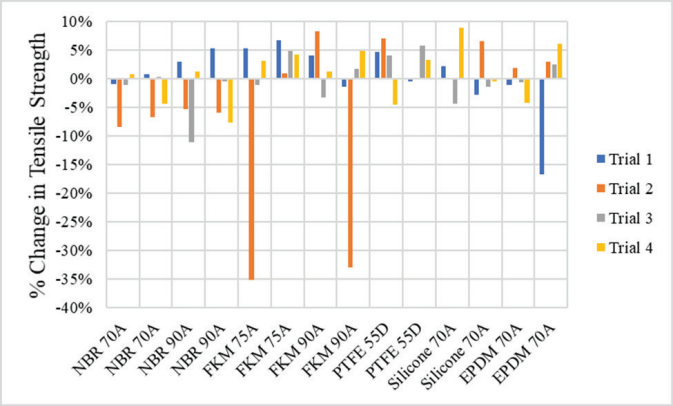

Figure 4. Change in tensile strength after hydrogen soak and depressurization

The change in ultimate elongation was calculated by taking the average of five measurements on each of the as received o-ring types and using it as the baseline strength. These data sets had standard deviations of 2% for NBR 70A, 10% for NBR 90A, 2% for FKM 75A, 10% for FKM 90A, 6% for PTFE 55D, 5% for silicone 70A, and 3% for EPDM 70A.

The data in Figure 5 shows that ultimate elongation decreased for NBR70A for all trials. This fits well with the weight loss data in that a loss of plasticizer in the rubber makes the material more brittle, resulting in a decrease in the ultimate elongation.

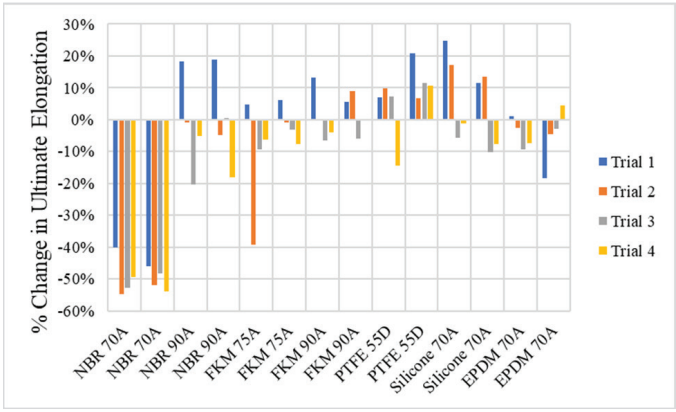

Figure 5. Change in ultimate elongation after hydrogen soak and depressurization

Summary

NBR, silicone, and EPDM all displayed a loss of weight, while FKM and PTFE did not. Furthermore, the NBR70 samples also displayed loss of ultimate elongation, suggesting that its plasticizer oil was removed through hydrogen diffusion. The changes are qualitatively shown in Table 2, where the yellow indicates a slight change, red indicates a large change and the arrows represent increase (up) or decrease (down). No significant changes were observed between trial runs, indicating that the materials responded in a similar fashion for the conditions tested.

Table 2. Qualitative Representation of Changes Observed after Hydrogen Soak and Depressurization

Material	Hardness	Weight	Strength	Elongation
NBR	▲	▼		▼
FKM	▼		▼	
PTFE				
Silicone		▼		
EPDM		▼	▼	

This work demonstrated an experimental process to quantitatively test the effects of pressurized hydrogen on polymeric materials. It was shown that some o-ring materials are susceptible to deleterious property changes. A high-pressure hydrogen testing system with a window was fabricated and was used to soak elastomeric o-rings in hydrogen at temperatures from 22 to 40°C and 13.8 to 16.5 MPa for up to 96 hours. Next, the o-rings were observed through the window during the depressurization. Finally, the o-rings were characterized before and after hydrogen exposure for hardness, weight, tensile strength, and ultimate elongation. The data showed the following four quantitative trends 1) durometer decreased up to 14%, 2) weight was mostly unchanged, 3) tensile strength decreased up to 35%, 4) ultimate elongation decreased up to 55%.

The screen tests were able to gather important data for design engineers to use for material selection or mechanical designs. Furthermore, this testing can mitigate future products from leaking and causing safety concerns when implemented as part of product design.

Future work will focus on accurately measuring axial thickness of the o-ring through the Jerguson gage window for an in-situ measurement. This measurement could be helpful in the design of o-ring gland size to ensure proper percent compression for continued hermetic sealing through different temperatures and pressures of hydrogen. This swelling measurement was attempted, but the error on the measurement was larger than the swelling of the o-ring. The setup had focus and shadow inconsistencies that caused erroneous results. To mitigate the error more consistent lighting and photographic methods need to be implemented.

To discuss further, contact Jeff Ellis at **jellis@ewi.org**.

Note: *Any reference to specific equipment and/or materials is for informational purposes only. Any reference made to a specific product does not constitute or imply an endorsement by EWI of the product or its producer or provider.*

Jeff Ellis *is a Senior Technology Leader in EWI's polymers group. He is responsible for steering EWI's plastics technology roadmap, developing strategies for external engagements, innovating new plastics technologies through internal research and development, and ensuring the quality of customer proposals and reports. Jeff's work has been implemented in all phases of his clients' product design cycle to increase product robustness and mitigate failures.*

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