

POLYMER BEHAVIOR IN HIGH PRESSURE HYDROGEN, HELIUM, AND ARGON ENVIRONMENTS AS APPLICABLE TO THE HYDROGEN INFRASTRUCTURE

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ABSTRACT

Polymers for O-rings, valve seats, gaskets, and other sealing applications in the hydrogen infrastructure face extreme conditions of high-pressure H₂ (0.1 to 100 MPa) during normal operation. To fill current knowledge gaps and to establish standard test methods for polymers in H₂ environments, these materials can be tested in laboratory-scale H₂ manifolds mimicking end use pressure and temperature conditions. Beyond the influence of high pressure H₂, the selection of gases used for leak detection in the H₂ test manifold, their pressures and times of exposure, gas types, relative diffusion and permeation rates are all important influences on the polymers being tested. These effects can be studied ex-situ with post-exposure characterization. In a previous study, four polymers (Viton A, Buna N, High Density Polyethylene (HDPE) and Polytetrafluoroethylene (PTFE)), commonly used in the H₂ infrastructure, were exposed to high-pressure H₂ (100 MPa). The observed effects of H₂ were consistent with typical polymer property-structure relationships; in particular, H₂ affected elastomers more than thermoplastics. However, since high pressure He was used for purging and leak detection prior to filling with H₂, a study of the influence of the purge gas on these polymers was considered necessary to isolate the effects of H₂ from those of the purge gas. Therefore, in this study, Viton A, Buna N, and PTFE were exposed to the He purge procedure without the subsequent H₂ exposure. Additionally, six polymers, Viton A, Buna N, PTFE, Polyoxymethylene (POM), Polyamide 11 (Nylon), and Ethylenepropylenediene monomer rubber (EPDM), were subjected to high pressure Ar (100 MPa) followed by high pressure H₂ (100 MPa) under the same static, isothermal conditions to identify the effect of a purge gas with a significantly larger molecular size than He. Viton A and Buna N elastomers are more prone to irreversible changes as a result of H₂ exposure from both Ar and He leak tests as indicated by influences on storage modulus, extent of swelling, and increased compression set. EPDM, even though it is an elastomer, is not as prone to high-pressure gas influences. The thermoplastics are generally less influenced by high pressure regardless of the gas type. Conclusions from these experiments will provide insight into the influence of purging processes and purge gases on the subsequent testing in high pressure gaseous H₂. Control for the influence of purging on testing results is essential for the development of robust test methods for evaluating the effects of H₂ and other high-pressure gases on the properties of polymers.

1.0 INTRODUCTION

Polymers, used in the H₂ infrastructure, supporting activities in distribution and delivery of H₂, H₂ refueling stations, fuel systems for on-board fuel cell electric vehicle (FCEVs) and other H₂ technologies, are often subject to extreme conditions during H₂ fueling/dispensing operations including rapid transients of pressures (10 to 100 MPa in minutes) accompanied by drastic changes in temperatures (e.g. in the FCEV refueling application, the H₂ can be pre-chilled before refueling to temperatures of -40°C while the gas in the fuel tank heats up to +85°C during refueling). Elastomers such as Viton A and Buna N find extensive use as seals (e.g. o-rings, gaskets as well as other flange and threaded connections for both low pressure and high pressure service including manual, actuated, and check valves). EPDM rubber is often used in valve seals and gaskets. POM and Nylon, both thermoplastics, are used as liners for pipelines, while PTFE is used as valve seats, o-rings, seals, gaskets, and various kinds of fittings [1].

There are significant gaps in the knowledge of polymer performances in H₂ pertaining to wear and tribology, permeability, long term aging effects, damage induced from cycling and rapid decompression, and contamination of H₂ by leaching of impurities from polymers [2-4]. Though studies focusing on elastomers such as Viton A, Buna N, and EPDM have provided valuable information about the response of this class of materials to high pressure H₂ and to different temperatures [5-9], there is still a significant lack of understanding about rapid pressure decompression of elastomers with combined effects of temperature and pressure cycling and related metrics for damage assessment with elastomers. Thermoplastics such as HDPE and thermoset epoxy-glass composites (GFRP) have been studied for barrier properties with H₂ gas and are used in many liner applications for H₂ pipelines and pressure vessels [10] (e.g. the performance of HDPE in this application is well reasonably well understood). Permeation mechanisms [1,15,17] and factors influencing the transport of H₂ (such as diffusivity and solubility of gases, pressure and temperature effects [20], polymer microstructure-related influences [18, 20]) through polymers have been investigated and documented. However, specific effects relating to H₂ transport such

as of plasticization due to H₂ permeation in polymers and its influence on mechanical properties for both low-pressure and high-pressure H₂ need to be studied. Another area of interest in the investigation of polymer properties during H₂-transport is extricating influences of gases different from H₂ (e.g. Ar, He) on polymers at high pressures with respect to development of test methods and characterization techniques.

Towards this purpose, we have designed laboratory-based experiments mimicking operating conditions in the H₂ infrastructure, all of which involve a purge and a leak detection step with a gas other than H₂. Leak detection tests usually involve filling the pressure vessel containing the polymers to the same high-pressure as the test gas of interest. The purge gas stays at this pressure for a significant dwell time (e.g. 2-3 days) with the purpose of detecting leaks. This process can affect the polymers and alter their properties even before exposure with the test gas of interest. Polymers may be subject to multiple gases in the same experiment, for e.g., He may be used as purge gas prior to H₂ exposure. Therefore, it was thought important to isolate the influences of different purge gases on polymers from that due to H₂. In our current study, the influence of He exposure on select polymers (Viton A, Buna N, and PTFE) is compared to previous work where He exposure was followed immediately by high pressure H₂ exposure [previous work, 13]. In an additional experiment, the influence of using a heavier inert gas, Ar, as purge gas followed by high pressure H₂ exposure is considered for these and other polymers and compared to the He/H₂ exposure. All the exposures were followed by ex-situ characterization of the exposed polymers for changes in glass transition temperatures, modulus, densities/volumes, compression set (elastomers only), and mass loss. Conclusions from these experiments will provide insight into the influence of purging processes and purge gases on the subsequent testing in high pressure gaseous H₂. Control for the influence of purging on testing results is essential for the development of robust test methods for evaluating the effects of H₂ and other high-pressure gases on the properties of polymers.

2.0 EXPERIMENTAL PROCEDURES

2.1 Materials

Commercial off-the-shelf grades of the tested polymers were purchased from US-based material suppliers for these studies. O-rings made from elastomers Viton A, Buna N (Nitrile Rubber), and EPDM from the same lots were used in all the exposure experiments. In addition to the elastomers, o-rings made from PTFE and specimens cut from cast sheets of POM and Nylon-11 were used as representative of thermoplastic materials in this study. PTFE specimens were annealed by heating from room temperature to 273°C at 1°C/minute, held at that temperature for 23 minutes, and then cooled at the rate of 0.5°C/minute. This annealing process was performed to maintain consistency with the processing of the PTFE in previous work. POM and Nylon 11 were not annealed prior to exposure to any of the test environments as these materials are normally used as supplied by H₂ FCEVs manufacturers.

2.2 Test Methods

2.2.1 High-Pressure He, Ar and Hydrogen exposure

Basic diffusion calculations predict saturation of 3mm thick sections of the studied polymer types with H₂ within a period of one week, following calculations from our previous work for similar exposure conditions [8]. Specimens were cut from O-rings with a cross-sectional diameter of 0.32 cm or cast sheets with a thickness of 0.32 cm. The various polymer specimens were placed in aluminum sample holders (8 cm long and 4.4 cm diameter, with cylindrical specimen slots 6.7 cm long and either 1 cm or 1.7 cm in diameter) (Figure 1). The sample holders containing the specimens were arranged in a cylindrical pressure vessel (27.9 cm long, 5.08 cm diameter) for high pressure exposure. All pressure vessel parts, including the holder, were thoroughly wiped down with isopropyl alcohol prior to filling them with samples.

For the He exposure test, the pressure vessel was first evacuated, flushed with He gas at 21 MPa, vented to atmospheric pressure, and then filled with He (purity 99.9999%) at the test pressure of 103 MPa. The test gas was held in the pressure vessel for approximately 40 hours at an ambient temperature of 20°C. These He exposure conditions were selected to simulate a typical leak check procedure. For example, in previous H₂ exposure work [8], test specimens were exposed to He purge followed by He at pressure 103 MPa for 40 hours to ensure that the pressure vessel was not leaking. Immediately after the He exposure, the vessel was vented and filled with H₂ gas (purity 99.9999%) to a pressure of 103 MPa for a full week (168 hours) at 20°C. This previous H₂ exposure is referred to as He/H₂ throughout this report. To explore the effect of the purge gas, a separate set of test specimens were exposed to high-pressure H₂ using Ar as purge gas. In these Ar/H₂ exposure, the pressure vessel was pressurized with Ar gas (purity 99.9999%) purge at 103 MPa for 108 hours followed immediately by H₂ gas

(purity 99.9999%) to 103 MPa and the pressure was maintained for 168 hours at 20°C. In all cases, gases were vented (depressurized) at an uncontrolled fast rate for each experiment (venting time = 1-2 minutes). After complete venting of the gas at the end of the prescribed time, specimens were removed, examined for visible transformation of any kind, and then sealed in special vapor-seal bags until characterization.



Figure 1: Sample holder and O ring specimens of polymers used in tests

2.2.2 Characterization Methods

Characterization tests were performed with a minimum of three specimens per exposure condition for each tested polymer. Thermogravimetric analysis (TGA) and density measurements were performed on specimens before exposure, immediately after removal from the pressure vessel, and 48 hours after exposure to capture any transient changes in the samples. Dynamic mechanical thermal analysis (DMTA) and compression set tests were performed before gas exposure and within 2-4 days after removal from the pressure vessel. Microstructural damage (such as tears, shredding, cracks and blisters) was explored by micro computed tomography (micro CT) and optical microscopy techniques.

Details of the individual characterization tests are as described below. Polymer properties such as storage modulus and glass transition temperature (T_g), density, mass loss, and compression set were evaluated for both elastomers and thermoplastics. Visible effects of gas diffusion in these materials were monitored by imaging techniques. Details of the individual characterization tests are as described below.

2.2.2.1. Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA, TA instruments DHR-2 Hybrid Rheometer) was used to examine the viscoelastic properties of the polymers before and after each exposure. Thermoplastic (PTFE, POM, Nylon) and elastomer O-ring specimens (Viton A, EPDM, and Buna N) were examined using the Rectangular Torsion geometry under strains ranging from 0.03% to 0.5% depending on material, 1 Hz frequency, with heating at a rate of 5°C/minute over the temperature range -100°C to 150°C, except for PTFE (0°C to 250°C) and nylon (0°C to 180°C). Glass transition temperature data was determined from measurements of storage modulus (G'), loss modulus (G''), and Tan delta (G''/G') as a function of temperature. Changes in storage modulus and loss modulus of polymers are representative of changes in their viscoelastic state which in turn is reflective of microstructural changes within the polymer due to exposure to different environments. In our study, changes in storage modulus (20°C) due to high-pressure gas exposure are reported for all polymers.

2.2.2.2 Compression Set

Compression set provides information on the permanent deformation in elastomeric polymers on the application of a compressive force at a given temperature, % compression, and duration of compression. Figure 2 shows the compression test set-up used for elastomers.

Three specimens of each polymer type were tested before and after gas exposure. After the dimensions of the specimens were measured with a laser micrometer, they were placed on the bottom plate of the compression set-up. A constant deflection of 25% was exerted on the samples at a temperature of 110°C with a steel spacer bar of 2.35 mm height over a period of 22 hours (ASTM D 395 Method B). After removal from the compression jig, the specimens were allowed to recover for 30 minutes at room temperature. The dimensions of the specimens were measured again with the laser micrometer. Compression set is expressed as a percentage of the original deflection:

$C_B = [(t_o - t_1) / (t_o - t_n)] \times 100$ where

C_B = Compression set (%)

t_o = original thickness of the specimen

t_1 = final thickness of the specimen

t_n = thickness of the spacer bar (2.35 mm)

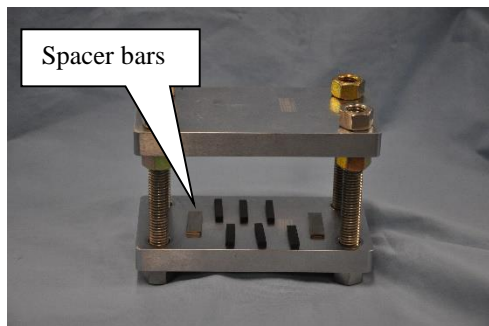


Figure 2: Compression set test set-up for elastomers

2.2.2.3 Density Measurements

The density was measured (ASTM D792-13) before exposure, immediately after exposure, and 48 hours after removal from the pressure vessel for all polymers. The weight of the specimens was determined in air using a Mettler Toledo XS403S balance (Figure 3) with a Mettler Toledo density determination kit with a repeatability of 0.5 mg+0.0008% of the gross weight of the specimen. Each specimen was then immersed in water, and the apparent mass in water was determined using the density determination kit. The measured masses of the specimens and the densities of water and air at 21°C were used to calculate the densities of the specimens.

Density (21°C/21°C) = [((($W_{air} / (W_{air} - W_{water})$) * ($D_{water} - D_{air}$))) + D_{air}] where

W_{air} and W_{water} are the weights of specimen in air and water respectively at 21°C and D_{water} and D_{air} are the densities of water and air respectively.

The difference between polymer density before and after exposure to H₂ was calculated in each case and is reported as the specific volume of the polymer (i.e. volume per mass).

2.2.2.4. Thermogravimetric Analysis (TGA) for Mass Loss

Thermogravimetric analysis is used to determine mass loss of polymers upon heating with time or temperature. Mass loss can provide insight into structural changes in the polymers due to high-pressure H₂. Mass loss from polymer specimens heated in 100µL aluminium crucibles from 30°C to 200°C at 2°C/minute under Ar purge at 40 mL/min (Mettler Toledo TGA/DSC 1) was carefully monitored. Any significant change immediately after exposure and 48 hours later was compared to data from non-exposed specimens to determine the possibilities of H₂ retention in these polymers.

2.2.2.5 Microstructural damage

Internal microstructural damage in the elastomers was characterized by optical microscopy and microcomputed tomography (micro-CT). Microstructural damage was not explored in the thermoplastics because, unlike the elastomers, there was no evidence of damage upon surface examination. For this work a Zeiss Xradia 520 Versa was used, which has a potential resolution of better than 1 micron. Each elastomer sample was imaged at ~4.6 mm field of view and a pixel size of ~4.6 micron to see the entire width of the O ring. The interior was imaged with a pixel size of ~0.7 micron and a field of view of ~0.7 mm. From the 3D data sets movies of a series of ~1000 2D slices and 3D rendering movies can be produced. Typical 2D images from some of the experiments are presented in section 3.4. These images provide a tremendous amount of information on the state of the polymers after gas exposures and enable discerning the source of voids, cracks and other anomalies in the sample due to gas diffusion.

3.0 RESULTS AND DISCUSSION

The effects observed with measurable properties common polymers exposed to high-pressure (100 MPa) He, He/H₂ and Ar/H₂ gas environments at 20°C for a maximum of a week (168 hours) are described in the following sections.

3.1 Thermomechanical properties

Overall, elastomers exhibited a significant decrease and thermoplastics, an increase in storage modulus. For Buna N, there was no change in storage modulus with /H₂, but about a 5% decrease with He alone (not shown) and a 20% decrease with He/H₂ (Figure 3).

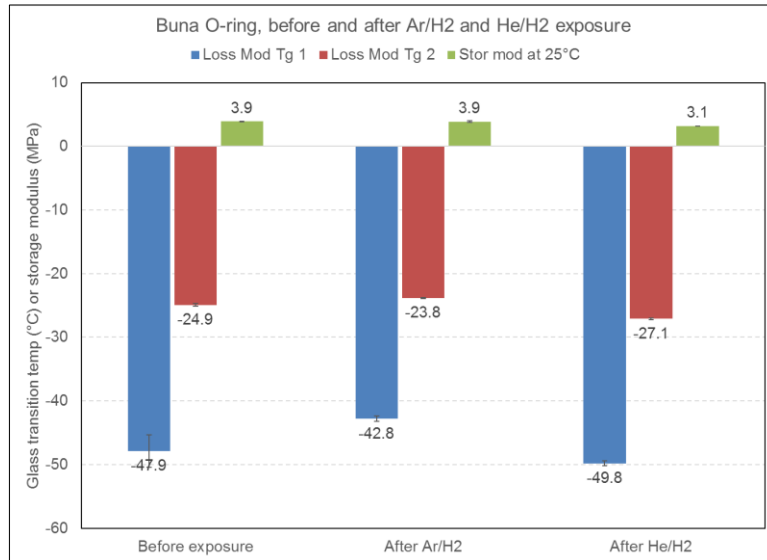


Figure 3. Glass transition temperature (from loss modulus) and storage modulus of Buna N before and after exposure to Ar/H₂ and He/H₂ (test conditions: 0.1% strain, 1 Hz, 5°C/minute)

For Viton A, the decrease in storage modulus in the Ar/H₂ environment was 41%, decrease in He/H₂ was 28% and the storage modulus was unaffected in He. (Figure 4). For EPDM rubber in Ar/H₂, the storage modulus decreased by 10% (Figure 5). This polymer was not tested in He or He/H₂ environments.

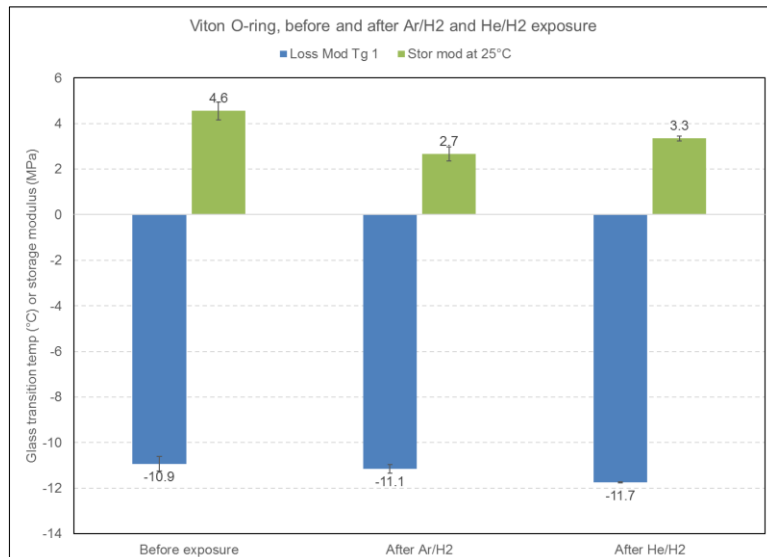


Figure 4. Glass transition temperature (from loss modulus) and storage modulus of Viton A before exposure and after exposure to Ar/H₂ and He/H₂ (test conditions: 0.1% strain, 1 Hz, 5°C/minute)

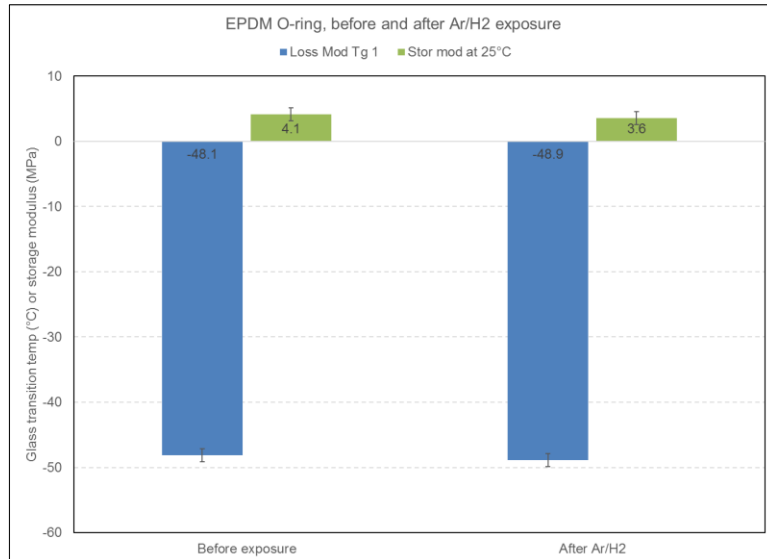


Figure 5. Glass transition temperature (from loss modulus) and storage modulus of EPDM before exposure and after exposure to Ar/H₂ (test conditions: 0.1% strain, 1 Hz, 5°C/minute)

Thermoplastic materials Nylon-11 showed a 6% increase and POM showed no change in storage modulus in Ar/H₂. Nylon and POM were not tested in He and He/H₂. PTFE showed a large increase in storage modulus (18%) in Ar/H₂ and small increases in He (6%) and He/H₂ (4%) (Figure 6).

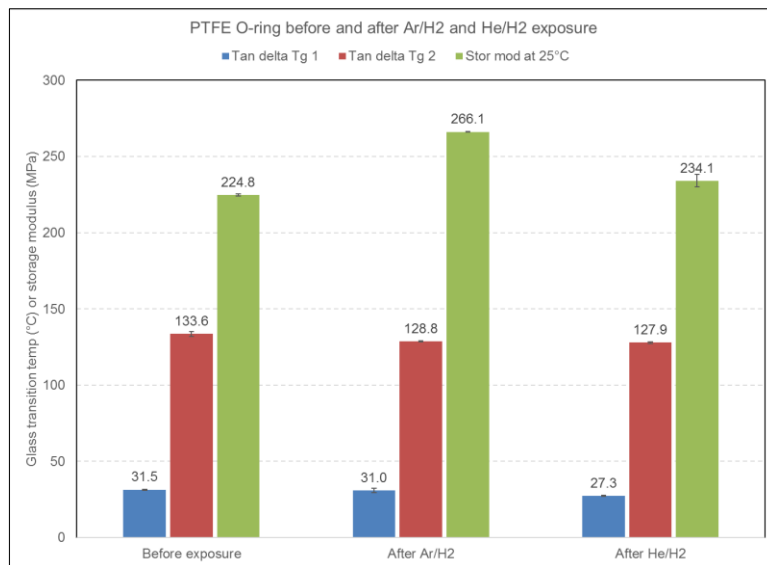


Figure 6. Glass transition temperature (from Tan delta) and storage modulus of PTFE before exposure and after exposure to Ar/H₂ and He/H₂ (test conditions: 0.1% strain, 1 Hz, 5°C/minute)

The decrease in storage modulus seen with the elastomers tested in the different gases may be explained on the basis of the crosslink density of the elastomers, the gas molecular sizes and permeability of the gases [21]. Ar has a larger mean kinetic diameter (0.40 nm) compared to He (0.26 nm) and H₂ (0.29 nm) [19] making the diffusion of Ar through the polymers slower than He or H₂. Buna N and EPDM have a molecular structure with high crosslink density and decreased free volume compared to Viton A. The permeability, diffusivity and the solubility coefficients for these polymers are shown in Table 1 [1]. Viton A has the lowest permeability to H₂ compared to the other elastomers. EPDM is five times more permeable to H₂ as Viton A and three times as permeable to H₂ as Buna N.

A combination of large gas molecular size for Ar (0.40 nm) and high crosslink density for Buna N and EPDM suggests that Buna N and EPDM may not promote Ar gas diffusion as much as He or H₂ gases [21]. This may manifest in Buna N and EPDM being relatively unaffected by Ar in the purge step compared to Viton A. In Ar /H₂ environments, Buna N retains its storage modulus pointing to this polymer being unaffected by H₂

after a Ar purge step. EPDM, however shows a 10% decrease in storage modulus after Ar/H₂ indicating that there is a certain degree of influence by H₂. In He/H₂ environments, Buna N shows a greater decrease in storage modulus indicating that the He purge step may have affected the polymer slightly more than the Ar purge step. We have not tested EPDM in He or He/H₂ yet. Viton A's severe drop in storage modulus after Ar/H₂ and He/H₂ and no drop with He exposure shows that it is highly affected by H₂ exposure. Viton A has large free volumes and can, theoretically, facilitate faster diffusion of all gases [1, 22] than the other elastomers in this study. The thermoplastics (Nylon and PTFE, permeability coefficient 0.4 and 3.2 mol.H₂/m.s.MPa respectively) seem to show an opposite effect with increases in storage modulus in some cases. This effect is more pronounced for PTFE in Ar/H₂ (18%) compared to storage modulus changes in He/H₂ (4%). Nylon shows a 6% increase in storage modulus in Ar/H₂ and has not been tested in any other environments. Previous work at Oak Ridge National Labs (unpublished at this time) with HDPE that had been exposed to high-pressure H₂ and then examined for microstructural changes with small angle neutron scattering (SANS) has proved that the high-pressure can exert extreme hydrostatic pressure to align molecular chains such that there is tighter packing of polymer chains within the thermoplastic microstructure. The HDPE from this exposure study showed an increase in storage modulus similar to the increased storage modulus seen with the PTFE in our study, enhancing the possibility of a similar effect in the latter. In spite of an increase or decrease in storage modulus after exposure, none of the polymers, however, showed a significant change in glass transition temperature.

Polymer	Permeability coefficient, 10 ⁻⁹ , mol. H ₂ /m.s.MPa	Diffusivity coefficient, 10 ⁻¹⁰ , m ² /s	Solubility coefficient, 10 ⁻⁹ , mol. H ₂ /m ³ . MPa
Perbunan (Buna N)	5.1	4.2	12
FKM (Viton A)	3.5	1.9	19
EPDM	17	5.0	33

Table1. Permeability, diffusivity and solubility coefficients (at ~20°C) for Buna A, Viton A and EPDM [1]

3.2 Swelling

The elastomers show significant swelling after exposure to high-pressure gases as determined from the measured specific volume after exposure. Depressurization and swelling are time-sensitive events and therefore, needed to be measured immediately after and a minimum of 48 hours later. Figure 7 compares the specific volume of Buna N after He exposure (this study) with the specific volume after He/H₂ exposure (previous study [13]) and after Ar/H₂ exposure (this study). Buna N swells in an Ar/H₂ environment more than the others (74% compared to 14% for He and 23% for He/H₂). In all three cases, this polymer shows 100% recovery in 48 hours' time. Swelling of Viton A (Figure 8), is significantly less than Buna N. The specific volume change is about 36% after both He/H₂ and Ar/H₂ exposures and near 10% for He exposure (slightly less than that seen for Buna N).

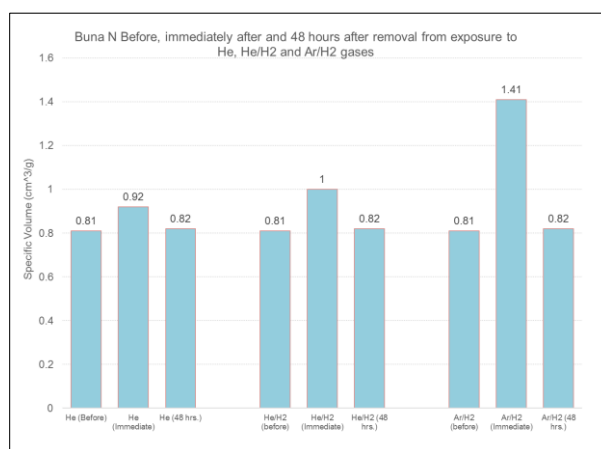


Figure 7. Specific volume (cm³/g) of Buna N before, immediately after and 48 hours after exposure to He, He/H₂ and Ar/H₂

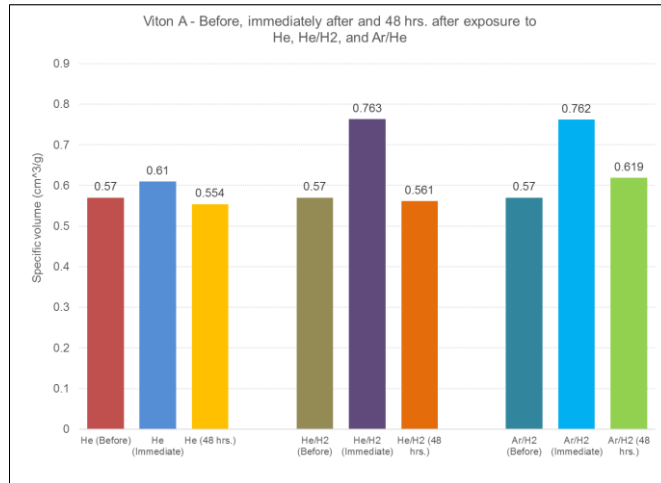


Figure 8. Volume changes per gram of Viton A immediately after and 48 hours after exposure to He, He/H₂ and Ar/H₂

Viton A does not return to original volume within 48 hours, maintaining a specific volume about 10% greater than the original volume. Figure 9 shows the response to Ar/H₂ for all polymers tested in terms of volume change or swell. As expected, the thermoplastics do not show much swell whereas with the exception of EPDM, elastomers show a considerable change.

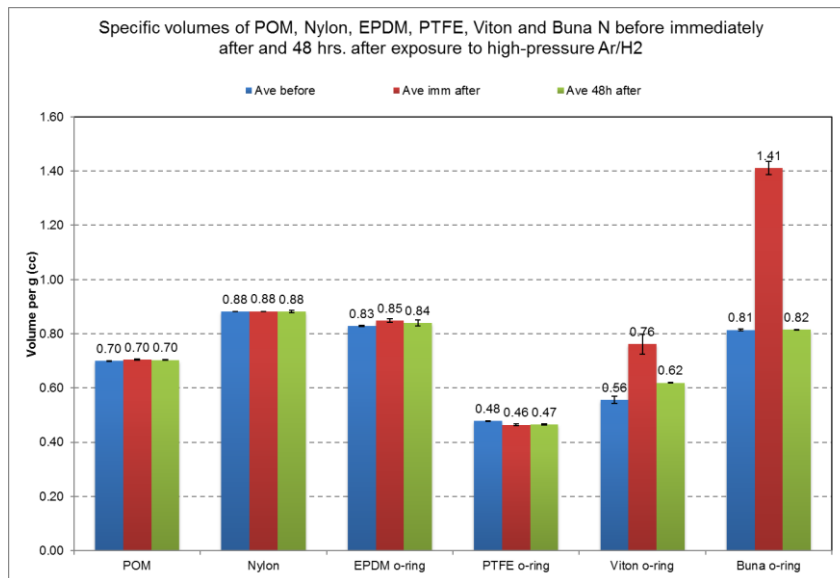


Figure 9. Specific volume changes seen with thermoplastics and elastomers after exposure to Ar/H₂

The swelling seen in Ar/H₂ is three times greater than He/H₂ indicating that Ar has a strong effect on Buna N compared to H₂ and may not be a desirable purge gas. On the other hand, He seems to be a good choice of purge gas for Buna N for the reason that the influence is much lesser than Ar and H₂. It is important to note that the effects seen with Buna N in this test are not permanent. Viton A shows the same severe swelling in both Ar/H₂ and He/H₂ indicating that both Ar and He have strong effects on Viton A. However, with Ar, the effects are semi-permanent compared to He because after He/H₂ exposure, the polymer completely recovers and after Ar/H₂ it does not. This could indicate permanent change in the microstructure in the form of voids or retention of residual gas in Viton A. Therefore, He may be a good choice of purge gas for Viton A also. Unlike Buna N and Viton A, the unique chemical nature of EPDM (45-85% ethylene and propylene, 2.5-12% diene) can be compared to polyolefins such as PE and PP to a great extent and therefore, changes seen after exposure to Ar/H₂ is minimal pointing to the fact that Ar can be used as purge gas with EPDM. For thermoplastics, the change in volume was minimal with exposures of Ar/H₂, He/H₂ and He and both Ar and He can be used as purge gases in experiments.

3.3 Compression Set

Compression set is highest in Ar/H₂ for all of the tested elastomers (Figure 10). Buna N shows an increase in compression set of 60% with Ar/H₂, an increase of 46% in He/H₂ and an increase of 9% with He/H₂. Helium is a better purge gas choice over Ar for Buna N with respect to compression set. On the other hand, Viton A (a material known for its low compression properties under ambient conditions), exhibits a dramatic increase in the compression set for Ar/H₂ exposure: 428% increase for the Ar/H₂ vs. 60% for the He/H₂ and 92% for the He gas exposures. It seems that Ar has a strong effect on Viton A as far as compression set properties are concerned. He seems like a good choice for purge gas for Viton A. EPDM shows a 20% increase in compression set in Ar/H₂. He/Ar and He exposure studies with EPDM were not part of this study. All data is shown in Table 2 for comparison.

Polymer	Before exposure	After exposure to He	After exposure to He/H ₂	After exposure to Ar/H ₂
Buna N	14.0%	20.5%	15.2%	22.4%
Viton A	5.3%	10.2%	8.5%	28%
EPDM	7.0%	NA	NA	8.4%

Table 2. Comparison of compression set properties for Buna N, Viton A, and EPDM before and after exposure to He, He/H₂ and Ar/H₂

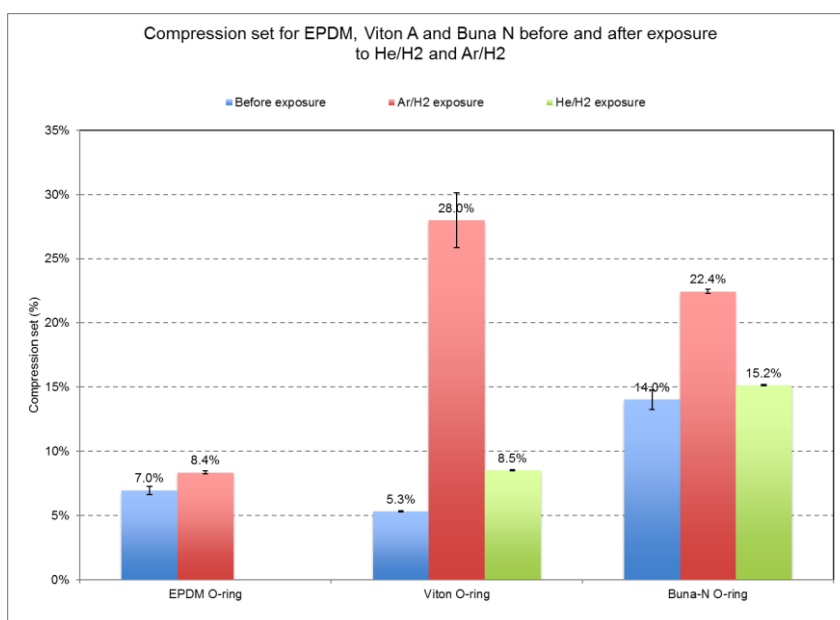


Figure 10. Compression set of elastomers before and after exposure to He, He/H₂ and Ar/H₂.

3.4 Mass loss

Though mass loss was studied with the goal of exploring the effect of the different gas environments on these polymers, it seemed to reflect more on the chemical nature of the polymers over gas influences. For both Ar/H₂ and He/H₂ exposures, mass loss was greater after 48 hours compared to immediately after removal from the test. Also, Ar/H₂ exposure seemed to show much higher mass loss for most polymers compared to He/H₂ exposure (Figure 11). This could be due to the higher mass of Ar (39.9 amu) vs. He (4.0 amu) and H₂ (1.0 amu) [9] and may indicate absorption of Ar by the polymers upon Ar/H₂ exposure. Buna N, overall shows a greater mass loss over Viton for both He/H₂ and Ar/H₂ exposures. Mass loss seen with EPDM is comparable to Viton A before and after Ar/H₂ and He/H₂ exposure. Nylon shows significant mass loss compared to all the other polymers. POM shows much lower mass loss tendencies compared to nylon. Buna N compounding involves significant amounts of plasticizers, processing aids, anti-oxidants and other volatile additives compared to Viton A. The outgassing of some of these volatile species could be a major contributor to the overall high mass loss seen with Buna N in both He/H₂ and Ar/H₂ exposures. EPDM does not seem as susceptible to Ar/H₂ and He/H₂ as Buna N. Nylon's hygroscopic nature causes it to absorb large amounts of moisture in manufacture and storage and this could be the reason for the large mass loss seen.

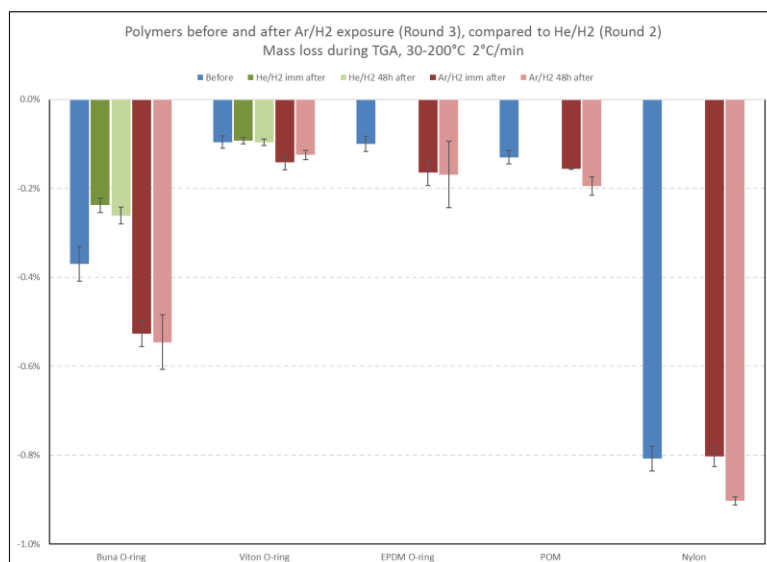


Figure 11. Mass loss measured in polymers before, immediately after, and 48 hours after exposure to He/H₂ and Ar/H₂ (TGA, 30-200°C, 2°C/minute)

3.5 Microstructural damage

In this study, none of the elastomers showed massive changes or damage with He exposure. With He/H₂ exposure, Viton A showed many voids around specific high density fillers [previous work, 13] whereas Buna N was unaffected and showed no visible degradation. With Ar/H₂ exposure, Buna N did not show micro-cracking; instead there were voids around filler particles, voids in the matrix and blister areas (Figure 12) which were absent in the control. With EPDM exposed to Ar/H₂, voids/cracks or blister damage were not observed (not shown here).

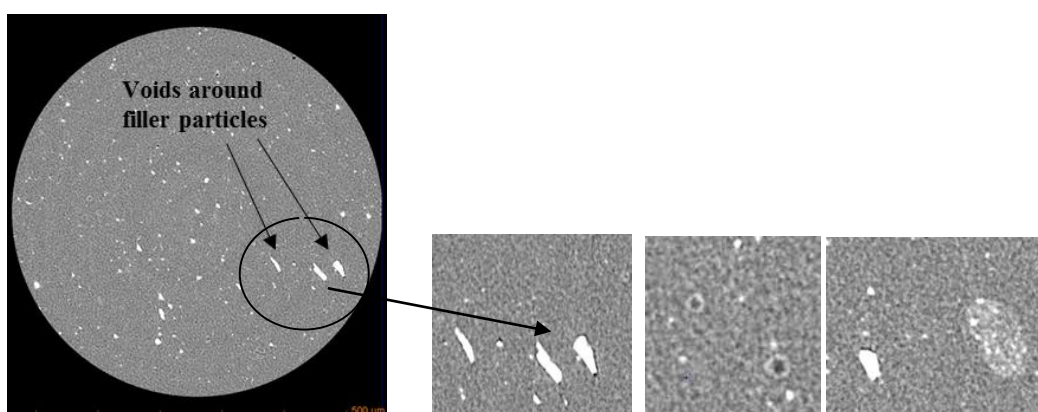


Figure 12. Micro CT imaging reveals microstructure damage in Buna N after Ar/H₂ exposure seen as (a) voids around filler particles, (b) voids in the matrix and (c) blister areas

Microstructural damage, after Ar/H₂ exposure, was the most severe in Viton A. Optical microscopy showed that the surface of the Viton A o-rings had cracks (300-1500 microns long) which were parallel to the o-ring axis (Figure 13). Micro-CT analysis suggests that surface cracks originated from the internal structure of the O-ring. High Z fillers in the polymer had developed voids around them from exposure. When voids around adjoining individual filler particles coalesce under high pressure (Figure 14), localized mini-cracks develop in all planes of the O-ring. Large crack formation and growth is speculated to be due to the coalescing of these smaller cracks (Figure 15). Buna N and Viton A, under high-pressure Ar/H₂, showed that even minimal exposure to high-pressure gases (even as part of a purge or leak detection test with pressurizing and depressurizing steps), the formation of voids and cracks can happen leading to possible failure in cycling further. Buna N and EPDM, with high crosslinking, seem to be resistant to this internal cracking under high-pressure gases. Viton A, much less crosslinked and with large free volumes, seems more prone to attack by high-pressure Ar, He and H₂ resulting in early internal damage and micro-cracking leading to surface damage.

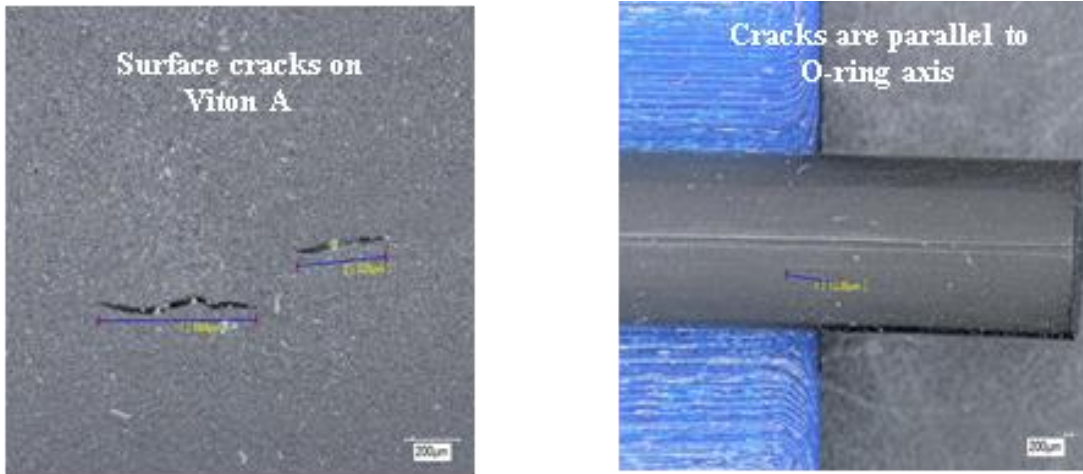


Figure 13. Optical micrographs showing (a) cracks on the surface of Viton A o-rings after Ar/H₂ exposure and (b) orientation of cracks parallel to o-ring axis

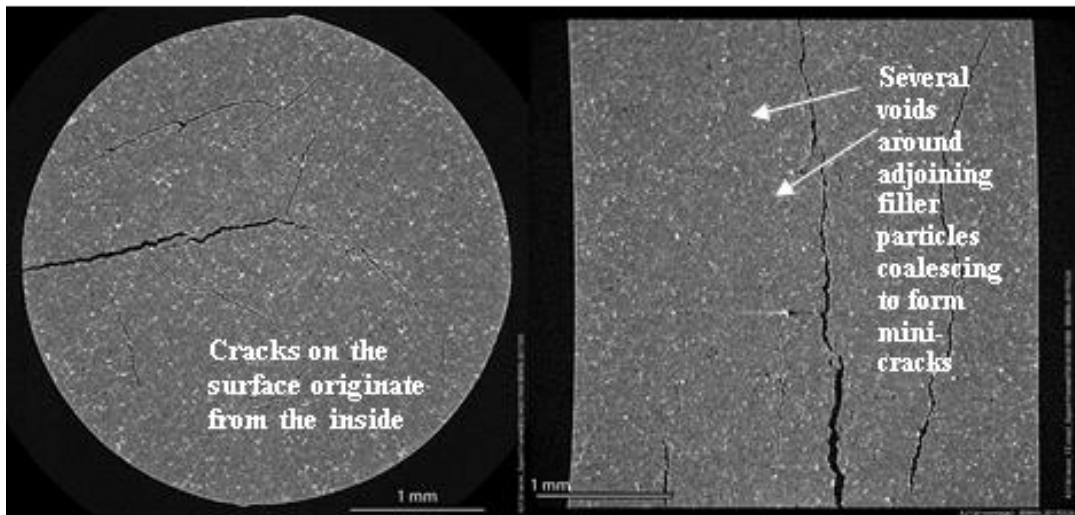


Figure 14. Micro-CT cross sections show (a) cracks seem to originate from the internal microstructure (b) voids appear to nucleate around filler particles and coalesce to form microcracks

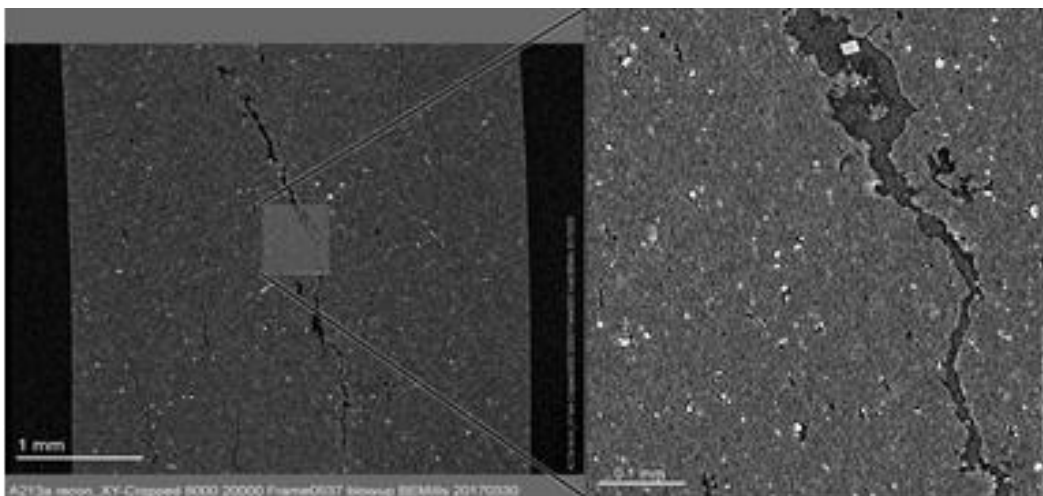


Figure 15. Micro-CT cross sections show large cracks in Viton A that appear to develop by coalescing of smaller cracks

4.0 CONCLUSIONS

Polymers commonly used in the Hydrogen Infrastructure were exposed to different gas environments (such as Ar/H₂, He and He/H₂) under static isothermal high-pressure conditions with the purpose of separating effects due to gases other than hydrogen during leak detection and purging steps in a typical high-pressure exposure. The influences of these gases on the polymers were investigated ex-situ using polymer characterization techniques that measured T_g and storage modulus, compression set, mass loss, density /specific volume changes, and micro-CT properties of the polymers. Both unexposed and exposed polymers were analyzed for gas influences and the following conclusions were drawn:

1. Leak detection and purge operations with Ar/H₂, He/H₂ and He are important for investigating polymers in high pressure hydrogen exposure experiments. Control for the influence of purging on polymer testing results is essential for the development of robust test methods for evaluating the effects of H₂ and other high-pressure gases on the properties of polymers
2. Elastomers showed more hydrogen, argon and helium effects compared to thermoplastics.
3. Data from Buna N and Viton A testing in different gas environments show that helium gas purging is suitable for testing these polymers. EPDM testing can be done with Ar as purge and leak detection gas.
4. Thermoplastics POM and nylon do not show any major effects in any of the gas environments. PTFE showed major influences with the different gas environments; but, is compatible with helium as a purging and leak detection gas.

In future steps, these polymers will be tested in a high pressure hydrogen cycling environment for investigation of effects of hydrogen at different temperature conditions. The results from this study should help with isolating purging and leak detection gas effects from those of hydrogen.

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References

1. Barth, R., Simmons, K. and San Marchi C., Polymers for H₂ Infrastructure and Vehicle Fuel Systems: Applications, Properties, and Gap Analysis No. Sandia 2013-8904, October 2013.
2. Marchi, C.S. and Somerday, B., Technical reference on H₂ Compatibility of Materials (2008).
3. Polymer and Composite Materials Meeting, Fuel Cell Technologies Office, US Department of Energy (DOE), Washington D.C., October 17-18, 2012, Meetings Proceedings: Polymer and Composite Materials used in H₂ service
4. 2013 Annual Merit Review and Peer Evaluation Report, US Department of Energy H₂ and Fuel Cells Program, May 13-17, 2013, Arlington, VA, Polymer and Composite Performance in H₂
5. Yamabe, J., and S. Nishimura, Influence of fillers on H₂ penetration properties and blister fracture of rubber composites for O-ring exposed to high pressure H₂ gas. *Int. J. H₂ Energy*, 2009, 34: pp. 1977-1989.
6. Rutherford, S.W., Limmer, D.T., Smith, M.G., Honnell, K.G., Gas Transport in ethylene-propylene-diene (EPDM) elastomer: Molecular simulation and experimental study, *Polymer*, 48, 2007, pp. 6719-6727
7. Pae, K.D., and D. R. Mears, The effect of hydrostatic pressure on mechanical behavior and properties of polytetrafluoroethylene and polyethylene. *Polym. Lett.*, 1968, pp. 269-273.
8. Phil Embury, High pressure gas testing of elastomer seals and a practical approach to designing for explosive decompression service, *Sealing Tech.*, 6, June 2004, pp 6-11.
9. Davis, L.A., and C.A. Pampillo, Kinetics and deformation of PTFE at high pressure, *J. Mater. Sci.*, 1983. 18, pp. 3063-3071.
10. Smith, D. B., Frame, B.J., Anovitz L.M., Makselon, C., Feasibility of using glass-fiber-reinforced polymer pipelines for H₂ delivery, 2016 Proceedings of the ASME 2016 Pressure Vessels and Piping Conference (PVP 2016), 6B, paper no. PVP2016-63683, pp. V06BT06A036 8 pages ISBN: 978-0-7918-5043-5
11. Flaconneche, B., et.al., Transport Properties of Gases in Polymers: Experimental Methods, *Oil & Gas Science and Technology – Rev. IFP*, 56 (2001), No.3, pp 245-259

12. www.Hescarcity.com, author: Ghani Adriaan Hammoutene
13. Menon, N.C., Kruizenga, A.M., Alvine, K.J., San Marchi, C., Nissen, A., Brooks, K., Behaviour of polymers in high pressure environments as applicable to the H2 infrastructure, 2016 Proceedings of the ASME 2016 Pressure Vessels and Piping Conference (PVP 2016), 6B, paper no. PVP2016-63713, pp. V06BT06A037 16 pages ISBN: 978-0-7918-5043-5
14. Van Amerongen G.J., The permeability of different rubbers to gases and its relation to diffusivity and solubility, *Journal of Applied Physics*, 1946, 17, pp. 972-985.
15. Zeman, S., and Kubik, L., Permeability of polymeric packaging materials, *Technical Sciences*, 2007, 10, pp. 26-34
16. Zhang, H., and Cloud, A., The permeability characteristics of silicone rubber, Proceedings of 2006 SAMPE Fall Technical conference, Coatings and Sealant section, November 2-6, 2006, Dallas TX. ISBN 978-0-938994-72-5.
17. Yashutoshi Naito, Keishin Mizoguch, Katushiko Terada and Yoshinori Kamiya, The effect of pressure on gas permeation through semi crystalline polymers above the glass transition temperatures, *Journal of Polymer Science: Part B Polymer Physics*, 1991, 29, pp. 457-462.
18. George, S.C., Sabu Thomas, Transport Phenomena through polymeric systems. *Prog. Polym. Sci.*, 2001, 26, pp. 985-1017.
19. Tan, Z. Basic concepts to Engineering application for Air emission control, Chapter 2: Basic properties of gases, Springer, 2014, XXVIII, 481 p, 128 illus. ISBN 978-981-287-211-1.
20. Van Amerongen G.J., Influence of structure of elastomers on their permeability to gases, *Journal of Polymer Science*, 1950, Volume V #3, pp. 307-332.
21. Kane, M.C., Permeability, Solubility and Interactions of Polymers – An Assessment of Materials for H2 Transport, Savannah River Laboratory internal report WSRC-STI-2008-00009-Rev0