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BEHAVIOUR OF POLYMERS IN HIGH PRESSURE ENVIRONMENTS AS APPLICABLE TO THE HYDROGEN INFRASTRUCTURE

Nalini C. Menon
Sandia National Laboratories
Dept. of Materials Chemistry
Livermore, CA 94550
Email: ncmenon@sandia.gov

Dr. Alan M. Kruizenga
Sandia National Laboratories
Dept. of Materials Chemistry
Livermore, CA 94550
Email: amkruiz@sandia.gov

Dr. Kyle J. Alvine
Pacific Northwest National Laboratory
Richland, WA
Email: kyle.alvine@pnnl.gov

Dr. C. San Marchi
Sandia National Laboratories
Hydrogen and Materials Science
Livermore, CA 94550
Email: cwsanma@sandia.gov

April Nissen
Sandia National Laboratories
Dept. of Materials Chemistry
Livermore, CA 94550
Email: anissen@sandia.gov

Kriston Brooks
Pacific Northwest National Laboratory
Richland, WA
Email: kriston.brooks@pnnl.gov

ABSTRACT

Polymeric materials have played a significant role in the adoption of a multi-materials approach towards the development of a safe and cost-effective solution for hydrogen fuel storage in Fuel Cell Vehicles (FCVs). Numerous studies exist with regards to the exposure of polymeric materials to gaseous hydrogen as applicable to the hydrogen infrastructure and related compression, storage, delivery and dispensing operations of hydrogen at fueling stations. However, the behavior of these soft materials under high pressure hydrogen environments has not been well understood. This study involves exposure of select thermoplastic and elastomeric polymers to high pressure hydrogen (70-100 MPa) under static, isothermal, and isobaric conditions followed by characterization of physical properties and mechanical performance. Efforts have also been focused on deriving suitable conditions of static testing in high pressure hydrogen environments as a valuable part of developing a suitable test methodology for such systems. Also, one of the primary challenges associated with polymer materials in hydrogen fuel cell vehicles is their exposure to large pressure gradients during fuel consumption and refueling operations. Therefore, the performance of these select polymers under the influence of a dynamic environment such as in high pressure cycling of hydrogen (35 MPa to 100 MPa to 35 MPa) was evaluated in a follow-up to this study. The goal of the high pressure cycling tests was to enable better understanding of the relationship between pressure gradients and polymer failure modes and also contribute significantly to test methodology development for polymeric materials.

Key Words: Polymers, high pressure hydrogen environment, hydrogen infrastructure, FCVs, pressure gradients, test methodologies, polymer properties

1. INTRODUCTION

Hydrogen as a transportation fuel in Fuel Cell Vehicles (FCVs) has found tremendous value in recent times with its potential as a source of clean energy with zero pollution and is poised to play an integral role in our energy future. With major advancements such as (a) reduced cost, improved durability and performance of fuel cells, (b) efficient methods of producing hydrogen from renewable sources such as natural gas, (c) reduced cost of delivery of hydrogen to the end user and (d) the development of advanced materials-based hydrogen storage technology, it is clear that the use of hydrogen as an energy carrier is becoming more and more a reality[1]. Therefore, it is very critical that the effect of hydrogen on materials used in all aspects of the hydrogen economy such as production, storage, delivery, and conversion be well understood.

Non-polymeric materials (metals) such as steels, stainless-steels, aluminum and alloys have been well studied for hydrogen exposure with respect to effects such as embrittlement for the past 100 years and continue to be active areas of research today [2,3]. On the same token, several polymers are used commonly in components used for hydrogen service E.g.: High Density Poly Ethylene (HDPE) is used as liners for hydrogen storage tanks, and along with PolyphenyleneSulphide (PPS) as pipeline liners in high pressure hydrogen distribution systems, Polytetrafluoroethylene (PTFE) is used for seals in mechanical compressors, Viton A and Nitrile Butadiene (NBR) rubbers as seals and gaskets in valves etc. [4, 5]. While in service as part of the hydrogen infrastructure, these polymers may be exposed to a wide range of varying pressures (10-100 MPa) and temperatures (-70°C - +85°C) and often, as in fuel dispensing operations, can be subject to hydrogen pressure cycles in addition to temperature cycles. Transport properties in polymers, under different pressure and temperature conditions, have been well investigated with the goal of understanding gas-polymer interactions after sorption by many researchers in this field[6-9]. Permeability, diffusivity and solubility data with regards to hydrogen transport is available on a number of polymers at different temperatures. This information has supported numerous works attempting to understand the relationship of polymer micro-structure to permeability of hydrogen[10]. For example, it is now known that hydrogen diffusivity in glass polymers appears to be an order of magnitude lower than elastomers; whereas the solubility is not very different for the two classes. This would lead to the general trend that the permeability is also an order of magnitude lower for thermoplastics over elastomers, given that permeability is a product of diffusivity and solubility. Polymer properties such as degree of crystallinity, presence of bulky side groups, crosslinking, presence of additives such as fillers and plasticizers etc. can change permeability of hydrogen dramatically from polymer to polymer or within the same class of polymer. Relaxation effects and time scales in elastomers are much faster compared to glassy polymers and this can cause penetrant gas molecules to quickly establish equilibrium in the former as compared to the latter.

Most studies have focused on defining the behavior of polymers in hydrogen with respect to measuring mass/volume changes, structural integrity changes such as with blistering and mechanical properties such as tensile static properties, long term creep deformation, and ductile fracture[11-12]. The influence of hydrogen penetration on the blister fracture properties of carbon particle and silica-filled Ethylepropylenedienemonomer (EPDM) and NBR composites was studied by Yamabe and Nishimura at a maximum pressure of 10 MPa. Pressurized hydrogen and nitrogen at 30 MPa pressure was used to study gas sorption and tensile behavior of semi-crystalline Polyethylene (PE) and Polyamide (PA11) and compared to experiments in atmospheric pressure by Castagnet et.al. Similar work with polymers in hydrogen environments was focused on hydrogen pressures ranging from 3-70 MPa. The investigation of polymers in very high pressure hydrogen environments (closer to 100MPa) is not that prevalent at this time, probably due to the tremendous capital investment requirements of such a set-up.

In this study, a select group of two elastomers (NBR and Viton A®) and two thermoplastics (HDPE and PTFE), of known grades, were exposed to static conditions of 100MPa at ambient temperature for one week. Selection of the polymers was based on the criteria that they be used in the manufacture of multiple components (eg. NBR and Viton A are used in seals, gaskets, dispensing hoses etc.) for application in the hydrogen infrastructure. Both non-molded and molded parts made from these polymers were examined to differentiate the effect of residual thermal stresses that can be present in molded specimens and potentially influence performance in a real-life hydrogen application. The time of exposure of one week was based on diffusion calculations for the elastomers and the thermoplastics. The influence of hydrogen exposure on polymer properties such as the modulus, glass transition temperature (T_g), compression set properties, density, outgassing characteristics and tensile strength was investigated. One of the primary challenges associated with polymer materials in hydrogen fuel cell vehicles is their exposure to large pressure gradients during fuel consumption and refueling operations. Therefore, investigating the performance of polymers under the influence of a dynamic environment such as in high pressure cycling of hydrogen (35 MPa to 100 MPa to 35 MPa) with and without temperature cycling (-40°C to 85°C) was considered crucial as part of a follow-up study to be presented in a subsequent publication. High pressure cycling tests will enable better understanding of the relationship between pressure gradients and polymer failure modes due to processes such as rapid gas decompression. An underlying goal of these experiments was also deriving suitable conditions of static and dynamic testing for polymers in a high pressure hydrogen environment towards the valuable effort of developing suitable test methodologies for such systems.

2. EXPERIMENTAL

2.1 MATERIALS

Four polymers of known grades were selected to be part of the static and dynamic hydrogen exposure tests. The material properties of the polymers are shown in Table1. Viton A Type A (66% Fluorine), is a 75 Durometer low compression set premium grade of Viton A rubber with high chemical resistance and a wide service temperature range (-23°C to 200°C). The Buna-N (NBR) is a high acrylonitrile content grade rubber with superior resistance and medium-low flexibility. The HDPE grade is not known at this time; but has a high possibility of being a PE80/PE100 grade, normally used in long term high strength piping applications. In the high pressure cycling experiment, a virgin grade of HDPE was tested (denoted HDPE-V) along with the PE80/PE100 grade for comparison. The PTFE is a premium virgin Type I Grade 1 polymer, which is an unfilled virgin grade sintered after molding or during extrusion, with dimensional stability up to 230°C, and normally used for seals and O-rings in Aerospace applications. Thermoplastic materials of the same chemistry from different producers can vary in residual thermal stresses depending on their processing during manufacture. Therefore, it was viewed necessary to subject them to an annealing process to possibly relieve stresses before exposure to a high pressure hydrogen environment. To enable this, all HDPE specimens were heated at 1°C/minute from room temperature to 93°C, held at that temperature for 28 minutes and then cooled to room temperature at the rate of 0.5°C/minute. All PTFE specimens were heated 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. Conditions for annealing were determined based on T_g and softening points for the two thermoplastics.

2.2 TEST METHODS

2.2.1 High pressure Hydrogen Exposure

Samples of HDPE, PTFE, Buna N and Viton A received from various vendors were used to prepare specimens for characterization tests before and after exposure to hydrogen. Specimen sizes depended on the test and varied in dimensions, except for the thickness of all specimens in all tests being kept constant at 3 mm. This was adopted based on diffusion calculations that specified 3 mm in thickness for complete penetration over a period of a week for all polymer types and specimen shapes. The Sandia National Laboratories code DIFFUSE was used to determine exposure time (Baskes, Michael I. DIFFUSE 83, SAND83-8231, 1983). This program numerically determines the diffusion rate of hydrogen through a given material. A planar geometry using Sievert's Law as the boundary condition was employed. The lowest diffusion coefficient of the four polymers was chosen (1.9e-6 cm^2/s for HDPE) as all materials were simultaneously exposed. Time for the hydrogen concentration to increase from effectively zero to equilibrium was determined for a 20ksi external pressure, at 25°C. Calculations showed that 13 hours are sufficient to achieve complete saturation in all polymers, but to be conservative samples were exposed for 7 days (13 times more).

After the various polymer specimens were readied, they were introduced into sample holders that are containers (about 5.08 am long and 2.54 cm diameter) made of aluminum (Figure 1). The sample holders containing the specimens were arranged in the cylindrical pressure vessel (27.9 cm long, 5.08 cm diameter). All pressure vessel parts, including the holder, were thoroughly wiped down with IPA prior to filling them with samples. The test chamber was connected to the pressure system (Figure 2) and was purged with helium gas three times starting with the test pressure of 15,000 psig and the second and third trial at 3000 psig. This was done to purge residual oxygen, to prevent the formation of an explosive hydrogen-oxygen mixture and also to test the pressure set-up for leaks and other problems. Each purge involved a fill (pressures described above) followed by reasonably complete venting of the purge gas at room temperature.

Helium purging was followed by hydrogen purging which involved filling and venting the test chamber three times at 3000 psig of 99.9999% hydrogen each time. At the end of the purge cycles, the test chamber was filled with 99.9999% hydrogen gas at 15,000 psig at room temperature.

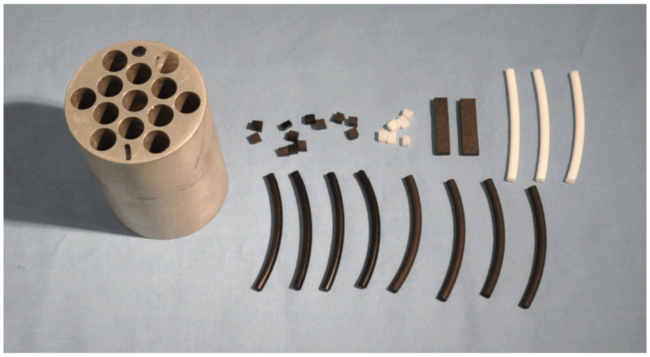

Figure 1. PRESSURE VESSEL SAMPLE HOLDER AND POLYMER SPECIMENS TESTED

The exposure test was run for a week's period at the end of which the vessel was depressurized at a very fast rate (< 1 minute) and specimens were removed for characterization tests. Specimens were stored in special bags with very low permeability immediately after removal from the pressure vessel to prevent contamination as well as to retain the hydrogen absorbed in the polymer to the maximum extent.

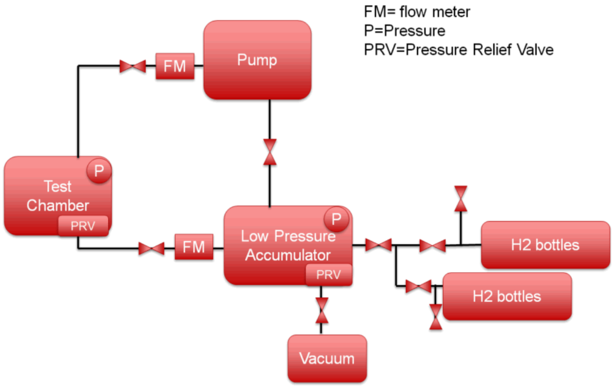

Figure 2. SIMPLIFIED DIAGRAM OF PRESSURE MANIFOLD FOR TESTING POLYMER PREFORMANCE UPON EXPOSURE TO HYDROGEN

2.2.2 Characterization Tests

Characterization tests were performed with a minimum of three specimens per exposure condition for all polymers. Two out of the four characterization tests (Thermogravimetric Analysis (TGA) and density) were performed before, immediately after removal from the pressure vessel and also 48 hours after exposure to capture any possible differences in the sample morphology.

The other characterization studies (DMTA and Compression set) were performed before and within 2-4 days after hydrogen exposure. Properties such as modulus, glass transition temperature Tg, compression set for the elastomers, change in density/volume and tensile strength before and after hydrogen were measured and recorded. Details of the individual characterization tests are as described below.

2.2.2.1. Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (TA instruments DHR-2 Hybrid Rheometer) was used to examine the viscoelastic properties of the polymers before and after hydrogen exposure. Thermoplastics (HDPE and PTFE) were examined under torsion with Rectangular Torsion geometry 0.005% strain, 1 Hz frequency, and 0.05N static force, with heating from -125°C to 85°C for HDPE and from 0°C to 250°C for PTFE at a rate of 5°C/minute. Elastomers, on the other hand, were examined under torsion with the rectangular Torsion geometry at 0.005% strain, 1 Hz frequency, with heating from -150°C to 250°C at a heating rate of 5°C/minute. Glass transition temperature data was collected from plots of storage modulus (G’), loss modulus (G”), and Tan delta (G”/G’) vs temperature. Changes in storage modulus (25°C) for all polymers, before and after exposure to hydrogen, were used to compare possible changes in molecular orientation, structural integrity and crystallinity of the polymers.

2.2.2.2 Compression Set (Elastomers)

Compression set provides information on the permanent deformation possible in elastomeric polymers on the application of a compressive force for a given temperature. When elastomers are exposed to hydrogen, there can be a change in the molecular orientation, and the free volume available can change. Elastomers can also weakly interact with hydrogen such that some of the hydrogen can be captured within the polymer upon depressurization. These behaviors can influence their compression set properties. Figure 3 shows the compression test set-up with Buna N and Viton A rubbers.

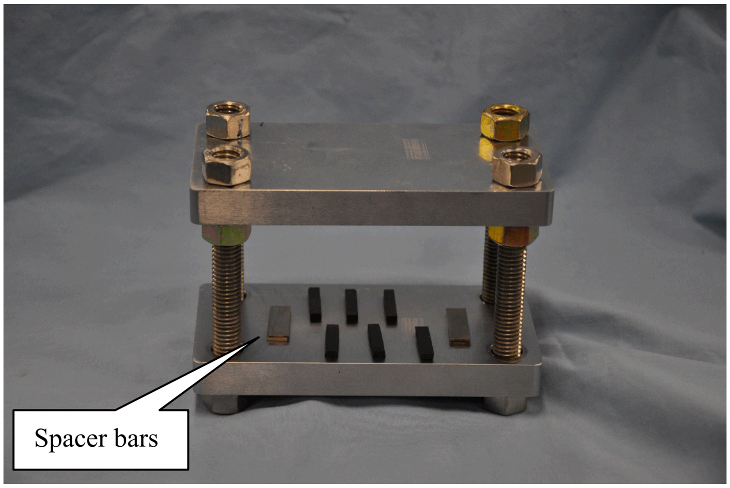

Figure 3. COMPRESSION SET TEST SET-UP FOR ELASTOMERS BEFORE AND AFTER HYDROGEN EXPOSURE

Three specimens of each polymer type were tested for before and after hydrogen exposure conditions. 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 with a spacer bar of 2.35 mm height at a temperature of 110°C over a period of 21.5 hours (ASTM D 395 Method B). The dimensions of the specimens were measured with the laser micrometer after removal from the compression jig and 38 minutes recovery at room temperature. 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 height of the specimen
t_1 = final thickness of the specimen
t_n = thickness of the spacer bar (2.35 mm)

A large change in compression set can point towards a permanent chemical change in the elastomer with retention of hydrogen and play a significant role in the use of these polymers in the hydrogen infrastructure. As can be noted, this test is relevant only for elastomeric polymers.

2.2.2.3 Density Measurements

Density measurements (ASTM D792-13) on the four types of polymers were performed before, immediately after exposure and 48 hours after removal from the test chamber. Weights were determined in air using a Mettler Toledo XS403S balance (Figure 4) with a Mettler Toledo Density Determination kit with a repeatability of 0.5 mg+0.0008% gross weight of the specimen. The specimens were then immersed in water using the designated set-up, and their apparent masses after immersion determined. The water temperature, water density and air density at 21°C (lab temperature) were used in the calculations.

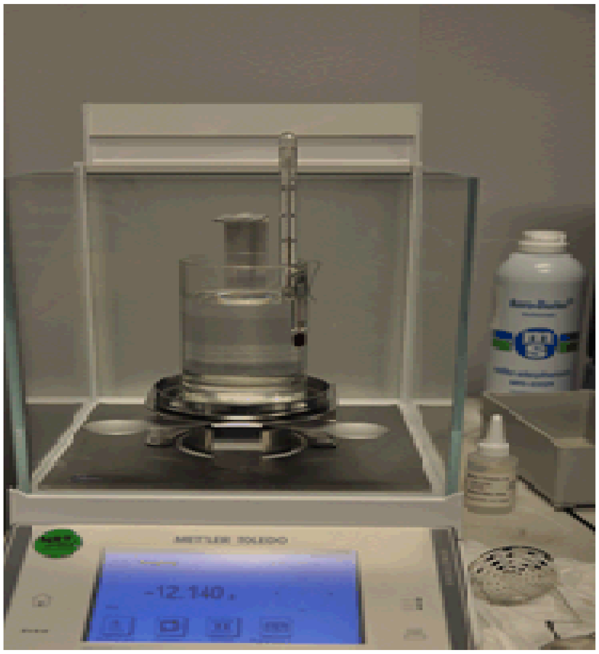

Figure 4. DENSITY MEASUREMENT SET-UP

Density of the specimens was calculated by:

Density (23°C/23°C) = $[(((W_{air} /(W_{air} - W_{water})) * (D_{water} - D_{air})) + D_{air}]$ where

W_{air} = Weight of specimen in air at 21°C
W_{water} = Weight of specimen in water at 21°C
D_{water} = Density of water at 21°C
D_{air} = Density of air at 21°C

The difference between polymer densities before and after exposure to hydrogen was calculated in each case and converted to change in volume for the polymers. Change in volume was related to polymer properties for each polymer type.

2.2.2.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is used to determine mass loss of polymers upon heating with time or temperature and can provide important information on hydrogen exposure effects on the polymers. Polymer specimens were heated from room temperature to 200°C (Mettler Toledo TGA/DSC 1) and mass loss carefully monitored. Any significant change in mass immediately after exposure and 48 hours later was compared to that prior to exposure for information on possibilities of hydrogen retention in the polymers and related effects.

2.2.3 Mechanical Testing

Tensile testing (ASTM D 638-14) of the thermoplastic polymers before and after exposure to hydrogen was conducted to assess the influence of the permeation of hydrogen into polymers on their mechanical strength. Dog-bone specimens, (overall length 34.80±0.508 mm, overall width of 9.652±0.0508 mm, a gage length of 14.732±0.508 mm with a narrow section width of 2.54±0.508 mm) were laser cut from sheets of HDPE (PE80/PE100 grade) and PTFE (Type I Grade 1) (Fig. 5) and tested at speed of 0.0254 mm/s at room temperature. Five specimens each were tested for before and after hydrogen exposure conditions for each thermoplastic. Tensile strength data was used to determine whether hydrogen exposure had a permanent deleterious effect on the HDPE and PTFE polymers.

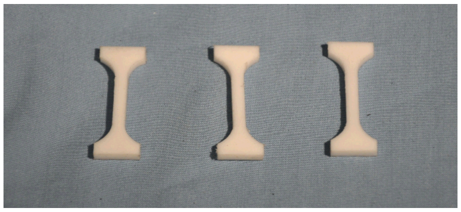

Figure 5. PTFE-BASED TENSILE SPECIMENS

3. RESULTS AND DISCUSSION

Polymer behavior in a hydrogen environment was studied with an assortment of four popular polymers used in hydrogen fuel cell vehicles and other applications of the hydrogen infrastructure. HDPE, PTFE, Buna N and Viton A are commonly used as liners, O rings, gaskets etc. and are very important to the proper functioning of the component in the final application. Hydrogen environments can be described as being of low (30 MPa) or high pressures (100 MPa) and can be static or dynamic while in operation. An attempt was made to study polymer behavior when exposed to a static high pressure (15,000 psig) isothermal (25°C) environment both in the form of molded and non-molded specimens. Both polymer characterization tests and mechanical performance tests were employed. After exposure, the materials were either characterized immediately or within a period of 48 hours of removal from the pressure vessel. Data collected from these tests was used to understand the response of these materials to high pressure hydrogen under static conditions and to utilize it in the future for test methodology development of cyclic hydrogen pressure tests.

Transport behavior for a given penetrant molecule varies from polymer to polymer and depends on the conditions of exposure. The free volume within the polymer and the segmental mobility of the polymer chains determine the transport properties of a gas through a polymer[10]. Elastomers with greater free volume will permit easy diffusion through the polymer chains compared to glassy polymers which semi-crystalline regions. Segmental mobility, on the other hand, is affected by the extent of unsaturation, the degree of crosslinking, degree of crystallinity and nature of substituents. For example: lower degree of unsaturation and crosslinking can allow easier permeation of the penetrant into the polymer.

In addition to segmental mobility and free volume, the glass transition temperature can have a profound effect on transport properties also. Higher Tg materials can be less affected by gas permeation, depending on the exposure conditions. Penetrant size can play a huge role in the rate of diffusion through polymers as well. In this case, the two penetrants were helium and hydrogen gases. It has been assumed here that with the prolonged exposure to hydrogen, most of the helium has been replaced by the hydrogen within the specimens. Also, the possibility of helium causing more than a surface contact angle change in non-aromatic polymers has been established[14].

In elastomers, after permeation and complete saturation, the rapid escape of absorbed gas from between the polymer chains upon release of external pressure can cause "explosive decompression". This rapid gas decompression can cause massive swelling and cracking of the rubbers, which can be a critical issue in application[15]. It is also important to note the permeability and diffusivity of polymers change with temperature; higher the temperature, higher the diffusivity and permeability. From literature, it is clear that between the two thermoplastics in this study, overall, HDPE has lower permeability to hydrogen than PTFE at room temperature and that the permeability coefficients for Viton A and Buna N are comparable at room temperature. (Table 1). For simplicity's sake, it is assumed that process of permeation takes place in three distinct steps: absorption or condensation on the surface of the polymer, diffusion through the polymer via gradients in concentration, and pressure, and finally desorption from the polymer into the atmosphere.

Polymer	Permeability Coefficient X 10^{-9} (mol.H2/m.s.MPa)	Diffusion Coefficient X 10^{-10} (m^2/s)	Solubility coefficient (mol.H2/m^3.MPa)
HDPE	0.82	1.9	4.3
PTFE	3.2	-	-
Buna N	5.0	4.3	11.4
Viton A	3.5	1.9	19

Table 1.HYDROGEN TRANSPORT PROPERTIES FOR HDPE, PTFE, BUNA N AND VITON A POLYMERS (Source: Sandia Report 2013-8904)

For the study presented in this paper, static isobaric isothermal conditions of high pressure (100 MPa) and room temperature (25°C) were adopted. This was done as a baseline study to examine and document the response of these select polymers to high pressure hydrogen. This study provided valuable insight into changes in polymer properties that result when specimens were subject to static conditions and that knowledge can be very useful to study the same polymers under cycling hydrogen pressures and varying exposure temperatures. The parameters adopted here will also help to better refine the test methodology for future dynamic cyclic pressure tests. Also, the rate of depressurization adopted in this study was uncontrolled and rapid (<1 min for complete release). This was done to provide information on their behavioral response towards a worse-case scenario of accidental rapid release that these polymers may be subject to under utility.

3.1 Elastomers in High pressure Hydrogen

Observations made immediately after removal of the specimens from the test chamber pointed to a visible change in dimensions (swelling) of the elastomers as opposed to virtually no change for the thermoplastics (Figure 6).

This can be attributed to the mechanism of transport phenomena in elastomers. Under the stress of high pressure, in elastomers, long polymer chains uncoil themselves and slide over one other and also accommodate free chain bond rotations that change the free volume within the polymer. Hydrogen, being a small molecule, can diffuse easily through the elastomer polymer chains. This easy permeation of the hydrogen gas through the polymer chains that present little barrier, results in the complete saturation of the polymer.

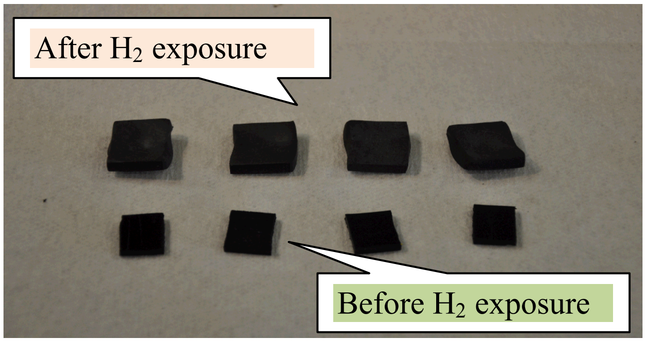

Figure 6: PICTURE SHOWING THE DIFFERENCE IN SWELLING FOR VITON A AND BUNA N ELASTOMERS AFTER HYDROGEN EXPOSURE

Upon removal of the external stress (depressurization), dissolved hydrogen gas can come out of solution and nucleate at microscopic voids or imperfections within the polymer. The gas expands and causes the polymer to swell. Dissolves gas escapes from the surface and causes bubbles to grow within the bulk of the polymer. When these diffusion-controlled processes are complete, irreversible damage can be caused within the polymer in the form of tearing. The non-molded elastomer samples exhibited massive swelling immediately after removal from the high pressure chamber, but, did not display shredding or tearing.

DMTA plots for Buna N and Viton A are shown below in Figures 7 and 8. Each plot shows the before and after exposure storage moduli and the tan delta peaks. It is clear from the plots that there is a decrease in storage and loss moduli after exposure to hydrogen for both the elastomers, with Viton A showing more of a decrease (54%) than the Buna N. (41%). The permeability coefficients for the two polymers (derived from literature) are similar and higher than the thermoplastics. The presence of unsaturation in Buna N rubber confers crosslinkability in the polymer. Crosslinking delays the slippage and sliding of the polymer chains and free rotation about the main chain can be significantly reduced. With reduced segmental mobility and the reinforcement by crosslinks, a lower free volume exists and therefore, only a slow hydrogen penetration is possible. Also, after sorption, the solubility of the hydrogen in Buna N rubber is less than that of Viton A, which means that the plasticizing effect of hydrogen gas transported through this elastomer is also less. This enables a higher storage modulus for Buna N over Viton A after exposure.

Whereas with Viton A, there is easy slippage between the polymer chains and this creates more free volume and therefore, more hydrogen penetration. As will be described later in this paper, it was also confirmed from density measurements that a higher amount of hydrogen is retained in Viton A from hydrogen exposure than the Buna N. This could be due to the presence of the relatively large fluorine atoms in the Viton A micro-structure that hinders easy escape of the adsorbed gas.

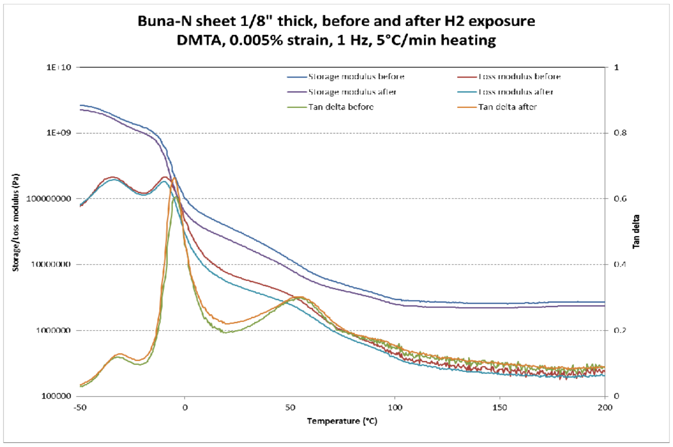

Figure 7. DMTA PLOT FOR BUNA N RUBBER BEFORE AND AFTER HIGH PRESSURE HYDROGEN EXPOSURE

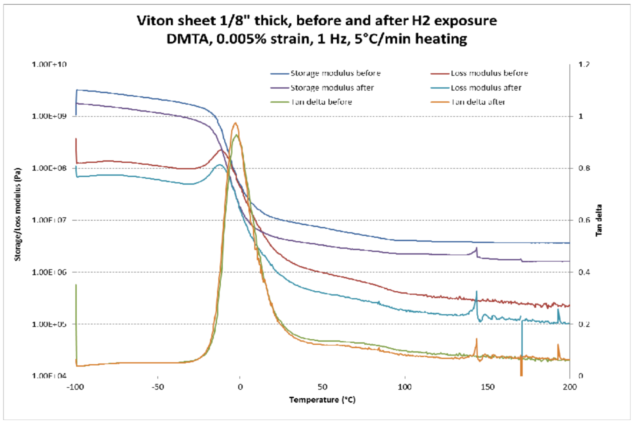

Figure 8. DMTA PLOT FOR VITON A RUBBER BEFORE AND AFTER HIGH PRESSURE HYDROGEN EXPOSURE

Solubility of hydrogen may result in plasticization in such a polymer[13] and therefore, storage modulus changes for Viton A are significantly larger than Buna N. Also for Buna N, the glass transition temperature (Tan delta peak in DMTA plots) does not show a significant change after hydrogen exposure. For Viton A there seems to be a shift in Tg to a lower number with hydrogen exposure. This could be the result of reduced crystallinity due to rearrangement of molecular chains in Viton A from hydrogen absorption and resulting plasticization. Data pertaining to both these plots is given in Table 2.

	Before Hydrogen exposure		After Hydrogen exposure	
Polymer properties	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)
Buna N	-32	34.0±2	-31	19.9±3.7
Viton A	-2	10.7±0.5	-3	5.4±1.4

Table 2. GLASS TRANSITION TEMPERATURE (TAN DELTA) AND STORAGE MODULI OF BUNA N AND VITON A BEFORE AND AFTER HYDROGEN EXPOSURE

Compression set properties of Buna N and Viton A after exposure to hydrogen for seven days are shown in Figure 9. The plots show the average of three specimens measured for each polymer type. In industry, Viton is known for its high temperature resistance and low compression set properties compared to Buna N and responded to the compression set test differently from Buna N. As expected, the highly crosslinked Buna N polymer shows a high compression set and the Viton A shows a significantly low compression set before hydrogen exposure. After hydrogen exposure, the compression set for Buna N did not change much. But the compression set for Viton A almost doubled. The solubility coefficient of hydrogen in Viton A at room temperature (19 mol.H_2 /m^3.MPa) is much higher than Buna N (11.4 mol.H_2 /m^3.MPa). It is possible that more hydrogen gas was retained in the Viton A polymer, increasing the compression set immensely.

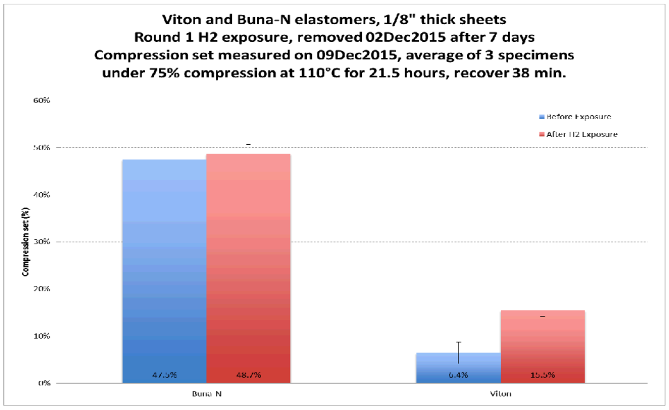

Figure 9. PLOT SHOWING THE COMPRESSION SET PROPERTIES OF BUNA N AND VITON A ELASTOMERS

The chemistries of the polymers in Viton A (a di-polymer of vinylidene fluoride and hexafluoropropylene), the presence of processing aids, the use of diamine crosslinkers (as opposed to crosslinking by vulcanization in Buna N) etc. can also influence the compression set properties of this polymer in hydrogen use. It should be noted that in spite of the increased compression set with hydrogen exposure, Viton A is still much superior to Buna N for this property.

Density changes are often used to determine the sorption properties of gases when transported through polymers. For elastomers, Buna N and Viton A, Table 3 shows the percent change in volume per gram of polymer after hydrogen exposure. Both the elastomers show a massive increase in volume upon hydrogen exposure. High solubility of hydrogen gas in these polymers results in swelling. The percent change in volume for Viton A is, however, much greater than that of Buna N. The diffusion of hydrogen through the Buna N rubber is fast and that coupled with a lower solubility of hydrogen in this polymer can mean a smaller increase in initial volume compared to Viton A. In the latter, the change in volume for Viton A is 21% greater than Buna N.

Polymer	Percent Change in Volume per gram upon Hydrogen exposure	
	Immediately after Removal	48 hours after Removal
Buna N	57.2%	3.9%
Viton A	69.0%	11.5%

Table 3. PERCENT CHANGE IN VOLUME SEEN IN BUNA N AND VITON A, IMMEDIATELY AFTER HYDROGEN EXPOSURE AND 48 HOURS LATER

Thermogravimetric analysis (TGA) of the elastomers proved to be quite interesting. All elastomers become brittle and degrade at high temperatures. Viton A has high temperature resistance and is stable until 204°C; whereas, Buna N is recommended for use up to 121°C. The percent mass loss seen with no exposure to hydrogen for the two elastomers was similar (Figure 10). However, upon exposure to hydrogen, the mass loss was lower than before exposure for both elastomers. This could be due to the dissolving of hydrogen in the polymers and the retention of the same. Viton A retains more hydrogen than Buna N rubber does immediately after exposure. Also, when samples were checked 48 hours after removal from the pressure vessel, it seemed that a significant amount had desorbed leaving residual amounts in the polymers.

The TGA data shown here agrees with the trend observed with the percent change in volume with these two elastomers in density measurement experiments before and after hydrogen exposure. Viton A retains 43% more hydrogen over Buna N immediately after exposure. After 48 hours, it seems that Viton A still holds 41% more hydrogen over Buna N. This capacity to hold hydrogen can be due to the greater amount of free volume in the Viton A polymer microstructure compared to Buna N and agrees with the fact that its solubility coefficient is higher than Buna N. This property of Viton A may be responsible for the drop in storage modulus, the increased percent change in volume, and the higher compression set seen with characterization tests described before.

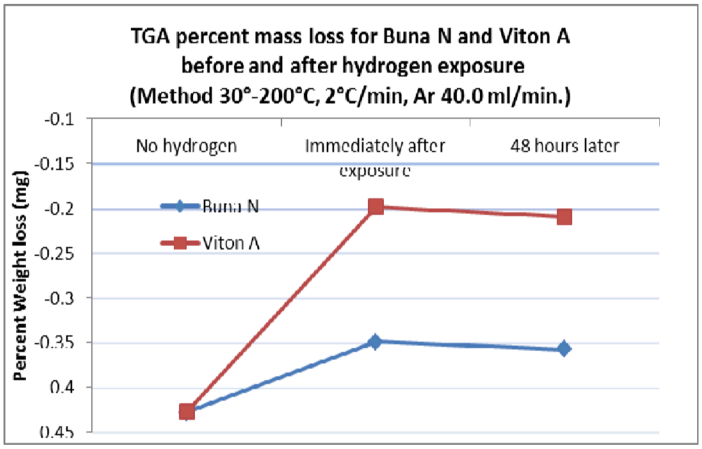

Figure 10. THERMOGRAVIMETRIC ANALYSIS (TGA) PLOT SHOWING THE PERCENT WEIGHT LOSS IN BUNA N AND VITON A BEFORE AND AFTER EXPOSURE TO HYDROGEN

Dissolution and high retention of hydrogen in this polymer can cause long term degradation and loss of mechanical performance. It could, therefore, be a material challenge to overcome to enable the better use of Viton A in the hydrogen infrastructure. It is also possible that one select other suitable grades from the same family for high pressure hydrogen use. A balance of compression set properties, and modulus coupled with the superior high temperature resistance and low temperature flexibility of fluoroelastomers is desirable for the end use application in the hydrogen infrastructure.

3.2 Thermoplastics in High pressure Hydrogen

It is clear that there is a difference between the response of thermoplastics and elastomers to hydrogen, judging from their appearance immediately after exposure. While the elastomers showed massive swelling, the thermoplastics did not exhibit any such change (Figure 11). Both the thermoplastics in this study, (HDPE and PTFE) are semi-crystalline and have ordered and amorphous regions within the polymer microstructure. The processing and therefore the thermal history of these polymers, prior to the test, strongly influence their response to high pressure hydrogen. To relieve any residual stresses due to prior processing, both polymers were annealed prior to use.

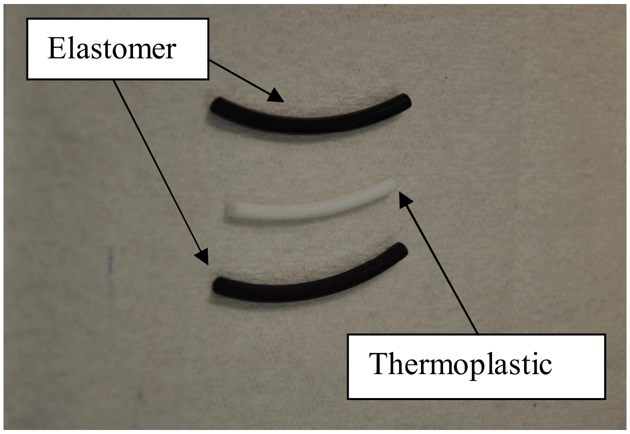

Figure 11. PICTURE SHOWING A COMPARISON OF THE DEGREE OF SWELLING SEEN IN ELASTOMERS, BUNA N AND VITON A, VERSUS THERMOPLASTIC, PTFE; THE ELASTOMERS WERE THE SAME SIZE AS THE THERMOPLASTIC PIECE BEFORE EXPOSURE

It is known that gas permeation properties depend on polymer crystallinity, chain orientation, presence of bulky side chain groups, presence of fillers and plasticizers, size of the permeant, polymer molecular weight, etc. For simplicity's sake, it is assumed that process of permeation takes place in three distinct steps: absorption or condensation on the surface of the polymer, diffusion through the polymer via gradients in concentration, and pressure, and finally desorption from the polymer into the atmosphere at the opposite side of the film. In thermoplastics, permeation will depend on the relative amounts of the two phases, crystalline and amorphous, and also on the size, distribution and shape of the secondary phase. Diffusion happens in the amorphous phases (above Tg) and the crystalline region acts as a barrier to permeation. Simplicity/complexity of chain structure, less or more side branching, chain regularity (isotactic vs syndiotactic) can all decide the crystallinity and therefore diffusion of hydrogen gas through these thermoplastics. In HDPE polymer manufacturing, HDPE made through different processes are often, blended together such that there is a large bi modal molecular mass distribution. There can be residual catalyst moieties and usually the degree of crystallinity is around 65%. In the manufacture of PTFE, particles of the polymer produced are fused together into molded sheets or rods, and the final properties are very dependent on the molecular weight, the degree of crystallinity, the degree of orientation plus on the macroscopic flaws (internal bubbles, foreign impurity etc.) and the micro-porosity generated from the imperfect pressing together of the particles, Particle size of PTFE produced dictates the voids in the finished product; whereas the processing dictates the crystallinity and the void content. The molecular weights control the crystallinity as well the final physical properties. Given the variables in thermoplastic manufacture, it is often difficult to predict permeation properties through HDPE and PTFE.

DMTA plots for HDPE and PTFE are shown in Figure 12 and 13. Each plot shows the before and after exposure storage moduli and the Tg from the tan delta peaks. It is evident from them that the storage moduli for the two polymers do not change significantly upon hydrogen exposure for the time and temperature conditions adopted in this study. This has to be directly tied to their molecular arrangement at this temperature. These thermoplastics are linear molecules with a planar zig-zag molecular orientation in the crystalline regions. They are tightly packed and polymer chains fit closely together.

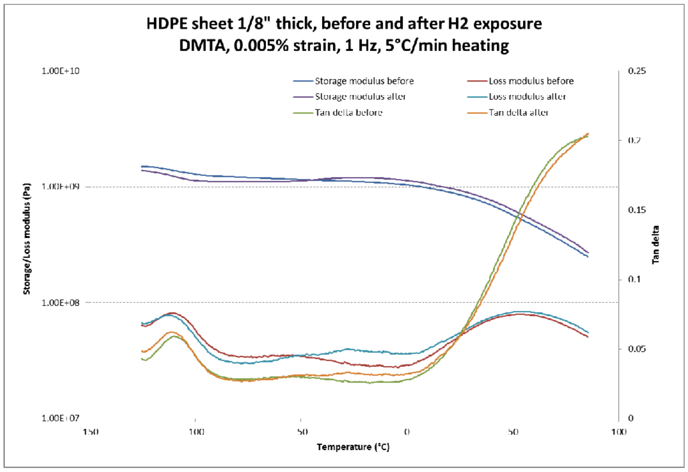

Figure 12. DMTA PLOT FOR HDPE BEFORE AND AFTER HIGH PRESSURE HYDROGEN EXPOSURE

The significant difference seen in their permeability coefficients (Table 1) is presented by the difference in the size of the hydrogen and fluorine atoms and the inability of the PTFE molecule to pack itself as tightly as the HDPE in the crystalline zones. Low permeability through polymers leads to less absorption of hydrogen and overall less degradation due to hydrogen attack.

For semi-crystalline polymers, such as HDPE and PTFE, the material behaves midway between a fully crystalline material and fully amorphous material. Below the Tg, the material behaves like a metal or ceramic. Around the Tg, the modulus drops and the mechanical behavior is termed "leathery" where the polymer can be extensively reformed and slowly returns to original shape upon removal of the stress. Just above the Tg, a rubbery plateau is observed. Here extensive deformation is possible with rapid spring back to the original shape upon removal of the stress. These trends are very clear in Fig. 13 for PTFE. The Tgs of the two polymers follow the same trend as the storage moduli where there is not much change seen after exposure to high pressure hydrogen. This means that there is possibly no fundamental change in molecular arrangement and the crystalline and amorphous regions remain more or less the same after hydrogen exposure. Data from the DMTA is as shown in Table 4.

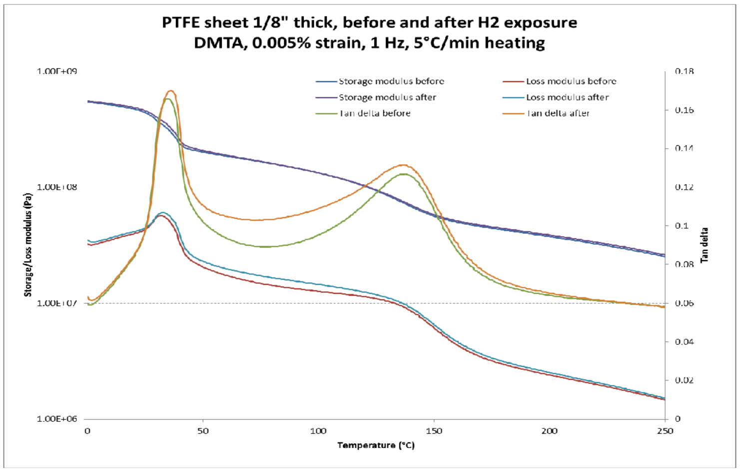

Figure 13. DMTA PLOT FOR PTFE BEFORE AND AFTER HIGH PRESSURE HYDROGEN EXPOSURE

	Before Hydrogen exposure		After Hydrogen exposure	
Polymer properties	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)	Tg (°C) (Tan Delta peak)	Storage Modulus (MPa)
HDPE	-110	848±7	-111	913±25
PTFE	34, 137*	431±12	36, 137*	441±14

*PTFE shows two Tgs because of possible separation of components

Table 4. GLASS TRANSITION TEMPERATURE (TAN DELTA) AND STORAGE MODULI OF HDPE AND PTFE BEFORE AND AFTER HYDROGEN EXPOSURE

Density measurements on the two thermoplastics before and after hydrogen exposure revealed interesting structure-property relationship. Figure 14 shows the comparison of the elastomers and thermoplastics with respect to percent change in volume after exposure to high pressure hydrogen.

Change in densities as a result of hydrogen exposure was not significant for HDPE and PTFE. Overall, HDPE has much lower density (0.95) compared to PTFE (2.1). Also, it is known that these semi-crystalline polymers have low permeability coefficients, HDPE (0.82 mol H2/m.s.MPa) much lower than that of PTFE (3.2 mol H2/m.s.MPa). Density is directly related to crystallinity for thermoplastics. The degree of crystallinity is dependent on the polymer micro-structure. As explained previously, HDPE has a much simpler tightly packed linear polymer structure (degree of crystallinity (lit.) = 71%) whereas PTFE tends to be slightly distorted due to the bulky fluorine atoms (degree of crystallinity (lit.) = 61%). The percent change in volume (a direct measure of the change in densities) before and after hydrogen exposure for the two thermoplastics is shown in Table 5. It is evident that the polymers have not changed considerably after exposure to hydrogen.

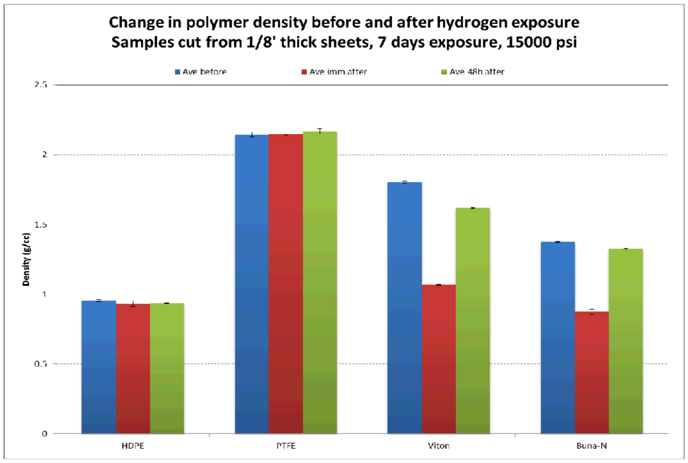

Figure 14. CHANGE IN DENSITY OF POLYMERS, HDPE, PTFE, VITON A AND BUNA N BEFORE, IMMEDIATELY AFTER AND 48 HOURS AFTER HYDROGEN EXPOSURE

Polymer	Percent Change in Volume per gram upon Hydrogen exposure	
	Immediately after Removal	48 hours after Removal
HDPE	2.5%	1.9%
PTFE	-0.3%	-1.0%

Table 5. PERCENT CHANGE IN VOLUME SEEN IN HDPE AND PTFE, IMMEDIATELY AFTER HYDROGEN EXPOSURE AND 48 HOURS LATER

Thermogravimetric analysis of the thermoplastics did not reveal mass loss of any volatiles upon heating from 30°C to 200°C. HDPE and PTFE polymers are very resistant to hydrogen attack and did not seem to have retained any hydrogen upon exposure.

Tensile testing was performed on HDPE and PTFE specimens before and after hydrogen exposure. In previous studies, it has been reported that for semi-crystalline polymers, both tensile strength and modulus of elasticity increase approximately linearly with pressure[16]. This increase has been attributed to the increase in Tg or increase in crystalline phase changes. Though an increase in Tg was not observed with hydrogen exposure per DMTA for either semi-crystalline polymer in this study, it is possible that there was a crystalline phase change or a stiffening of the material leading to an increase in tensile strength and more evidently, the modulus. Figure 15 shows the stress strain curve and Table 6 shows the tensile data for the same. All specimens were deformed homogeneously to failure.

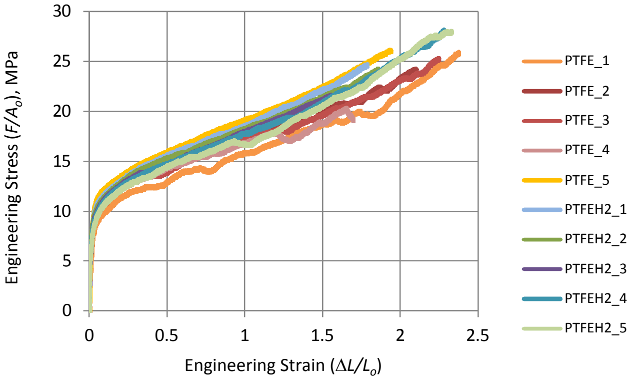

Figure 15. STRESS STRAIN CURVE FOR PTFE BEFORE AND AFTER HYDROGEN EXPOSURE

Sample	Young's Modulus MPa	Yield Stress MPa	Strength MPa
PTFE_1	379.43	7.71	25.93
PTFE_2	483.28	8.62	24.27
PTFE_3	479.28	9.12	25.32
PTFE_4	462.66	8.66	20.35
PTFE_5	659.77	9.94	26.16
Average	**492.88**	**8.81**	**24.41**
PTFEH2_1	641.54	9.66	24.73
PTFEH2_2	656.83	9.43	24.30
PTFEH2_3	679.29	8.97	21.64
PTFEH2_4	718.15	8.87	28.17
PTFEH2_5	639.92	8.45	28.05
Average	**667.15**	**9.08**	**25.38**

Table 6. TENSILE DATA FOR PTFE, BEFORE AND AFTER HYDROGEN EXPOSURE

For semi-crystalline polymers, the tensile modulus can be considered to be a combination of the modulus of the crystalline regions and amorphous regions. The increase in

Young’s modulus (~ 35%) for PTFE specimens has been attributed to stiffening of the material due to elastic deformations after hydrogen exposure. From the plot it is clear that there is no necking region and that failure occurred in the elastic region. Elastic deformations in thermoplastics are a result of polymer chains uncoiling and stretching and usually this process is reversible. This means that when the stress is removed, the material reverts to its original molecular conformation. Bulky side groups, such as the fluorine atoms on PTFE molecules, can restrict chain motion and make the material more rigid. This is reflected in the stress strain curve for PTFE.

In the case of HDPE, the stress strain curves are slightly different (Figure 16). The specimens exhibited a necking region and cold-drawing deformation behavior. The test was stopped in the necking region and did not fail at this stage. Plastic deformation, which comes from polymer chains moving past each other, is the reason for necking and cold-drawing. In this case, there are no bulky fluorine atoms on the polymer chains and this means the chains are able to uncoil and slide past one another freely. This leads to the necking region of the plastic. Under tensile stress, chains align parallel to each other such that the material stiffens and this is seen as an increase in the Young’s modulus. Tensile data for HDPE is shown in Table 7.

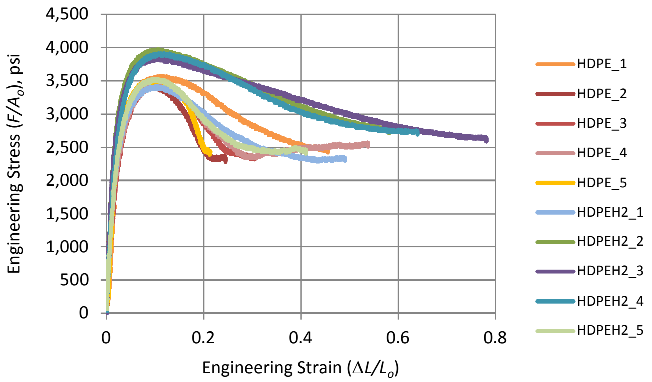

Figure 16. STRESS STRAIN CURVE FOR HDPE BEFORE AND AFTER HYDROGEN EXPOSURE

The test was stopped in the necking region and specimens did not exhibit failure at this stage. Plastic deformation, which comes from polymer chains moving past each other, is the reason for necking and cold-drawing. In this case, there are no bulky fluorine atoms on the polymer chains and this means the chains are able to uncoil and slide past one another freely. This leads to the necking region of the plastic. Under tensile stress, chains align parallel to each other such that the material stiffens and this is seen as a 15% increase in the Young’s modulus after hydrogen exposure. Tensile data for HDPE is shown in Table 7.

Sample	Young’s Modulus MPa	Yield Stress MPa	Strength MPa
HDPE_1	872.31	20.78	24.66
HDPE_2	1091.79	20.77	23.64
HDPE_3	638.47	19.60	23.84
HDPE_4	758.23	19.81	23.75
HDPE_5	955.36	21.01	24.31
Average	**863.23**	**20.39**	**24.04**
HDPEH2_1	831.49	20.26	23.60
HDPEH2_2	1160.27	24.17	27.39
HDPEH2_3	1255.82	23.47	26.51
HDPEH2_4	923.96	22.90	26.98
HDPEH2_5	779.73	20.62	24.33
Average	**990.25**	**22.28**	**25.76**

Table 7. TENSILE DATA FOR PTFE, BEFORE AND AFTER HYDROGEN EXPOSURE

In this study, both the thermoplastics (PTFE and HDPE) behaved similarly, showing an increase in Young’s modulus with hydrogen exposure. These polymers are not very permeable to hydrogen due to their tight microstructure and yet, upon hydrogen exposure, show a change in the stiffness. This means that hydrogen exposure is possibly changing the polymer chain alignments sufficiently in the timeframe (one week) and at room temperature, as were the conditions of the study.

4. CONCLUSIONS

In this study, a select group of two elastomers (NBR and Viton A®) and two thermoplastics (HDPE, PTFE), of known grades, were exposed to static conditions of 100MPa at ambient temperature for a week. Selection of the polymers was based on the criteria that they be used in the manufacture of multiple components (eg. Buna N and Viton A are used in seals, gaskets, dispensing hoses etc.) for application in the hydrogen infrastructure. Both non-molded and molded parts made from these polymers were examined. The influence of hydrogen exposure on polymer properties such as the modulus, glass transition temperature Tg, compression set properties, density, outgassing characteristics and the tensile strength was investigated for HDPE, PTFE, Buna N and Viton A in this study.

From this brief baseline study on select polymers, it is clear that there is an immense difference in the response of thermoplastics and elastomers to high pressure hydrogen exposure. The polymer microstructure and related characteristics are fundamentally different for each polymer and is the basis for their varying responses. The free volume within the polymer and the segmental mobility of the polymer chains determine the transport properties of a gas through a polymer. Elastomers with greater free volume will permit easy diffusion through the polymer chains compared to glassy polymers which semi-crystalline regions. Segmental mobility, on the other hand, is affected by the extent of unsaturation, the degree of crosslinking, degree of crystallinity and nature of substituents. For example: the high degree of crystallinity in thermoplastics can result in lower permeability of hydrogen compared to elastomers that do not possess crystalline zones in the microstructure. In addition to segmental mobility and free volume, the glass transition temperature can have a profound effect on transport properties also. Higher Tg materials can be less affected by gas permeation, depending on the exposure conditions. This study was successful in establishing the relationship of polymer response to hydrogen exposure to polymer microstructure.

Characterization of the polymers before and after exposure helped with establishing that relationship, with respect to high pressure exposure to hydrogen. The two thermoplastics investigated, have not shown any significant change in major physical properties such as Tg, modulus, and tensile strength. Amongst the elastomers, Viton A showed very significant variations in modulus, compression set, in the percent change in volume upon hydrogen exposure. Buna N rubber showed similar changes; but, not to the same extent. These behaviors can directly impact their application in the hydrogen infrastructure. Therefore, the qualification of polymer chemistries against applications in the high pressure hydrogen infrastructure is critical for their long term performance.

5. FUTURE WORK

One of the primary challenges associated with polymer materials in hydrogen fuel cell vehicles is their exposure to large pressure gradients during fuel consumption and refueling operations. Therefore, investigating the performance of polymers under the influence of a dynamic environment such as in high pressure cycling of hydrogen (35 MPa to 100 MPa to 35 MPa) with and without temperature cycling (-40°C to 85°C) was considered a crucial part of a follow-up study to be presented in a subsequent publication. The simple test conditions (static, isobaric, isothermal) chosen for this study, exposed the complexities that must be thoroughly planned before such a group of polymers, widely different in chemistries, can be evaluated together under high pressure cycling conditions coupled with temperature cycling. An attempt must be made towards suitable test methodology development prior to high pressure cycling experiments. For example: the inclusion of a discharge controlled regulator on the high pressure cycling pressure manifold to enable control on the rate of depressurization during venting (Figure 17)

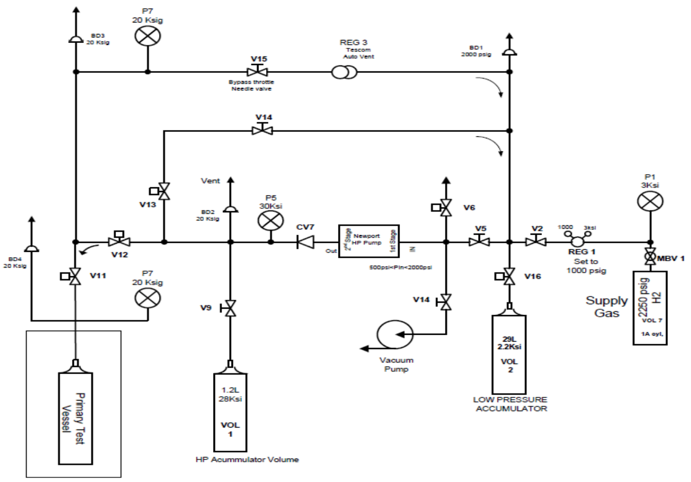

Figure 17. SIMPLIFIED DIAGRAM SHOWING THE PRESSURE MANIFOLD AND DETAILS FOR HIGH PRESSURE HYDROGEN CYCLING TESTS

Also penetrant size can play a huge role in the rate of diffusion through polymers as well. In this case, the two penetrants were helium and hydrogen gases. It has been assumed here that the purging with hydrogen after helium has removed all helium from the pressure vessel and the specimens. Although the possibility of helium causing more than a surface contact angle change in non-aromatic polymers has been established, purging with a different gas such as nitrogen or argon, whose molecular radii are much larger than helium can ensure prevention of permeation into the polymers while purging the vessel. This aspect needs to be carefully considered in future work prior to high pressure cycling of hydrogen and polymers.

Exposure of polymers to gases other than hydrogen at low pressures to study permeation through polymers and exposure of polymers to hydrogen at temperatures other than ambient are poised to be part of future investigation.

ACKNOWLEDGMENTS

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