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

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ABSTRACT
Polymers have played a significant role in the adoption of a multi-materials approach towards the development of solutions for Fuel Cell Vehicles (FCVs). Even though numerous studies exist with regards to the exposure of polymeric materials to gaseous hydrogen in relation to the hydrogen infrastructure, the behavior of these soft materials under high pressure hydrogen environments has not been fully understood. This limited study involves exposure of common 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. Attempts have been made to explain hydrogen effects on polymer functional properties using polymer structure-property relationships and also to understand role played by additives such as fillers.

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. Therefore, it is 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.[1] Non-polymeric materials (metals) such as steels, stainless-steels, aluminum, and alloys under hydrogen exposure have been well studied with respect to effects such as embrittlement over the past 100 years and continue to be active areas of research today [2,3]. Similarly, 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 Poly(phenylenesulphide) (PPS) and Poly(oxymethylene) (POM) as pipeline liners in high pressure hydrogen distribution systems;

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Polytetrafluoroethylene (PTFE) is used for seals in mechanical compressors; and Viton A and Nitrile Butadiene (Buna N or NBR) rubber as seals and gaskets in valves, etc.[4,5].

In service, these polymers may be exposed to a wide range of varying pressures (10-100 MPa) and temperatures (-70°C to 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 by many researchers in this field[6,7]. Permeability, diffusivity, and solubility data with regards to hydrogen transport on a number of polymers at different temperatures, has supported numerous works attempting to understand the relationship of polymer micro-structure to permeability of hydrogen and related effects[8]. Apart from a few prominent studies[9,10] on physical changes such as blistering and shredding, and mechanical properties changes such as with tensile static properties, long term creep deformation, and ductile fracture, the investigation of polymers in high pressure cycling hydrogen environments closer to 100 MPa is less pursued at this time. This may be due to the tremendous capital investment and associated safety requirements of such a set-up.

In this study, known grades of select elastomers (NBR and Viton A) and thermoplastics (HDPE and PTFE) were exposed to static conditions of 100 MPa at ambient temperature (25ºC) for one week. Selection of the polymers was based on stakeholder input as well as their hydrogen application (e.g. NBR and Viton A are used in seals, gaskets, and dispensing hoses, HDPE is used as tank liners, and PTFE is used as seals in compressors). Sheets, O-rings, and gaskets made from these polymers were examined to differentiate the effect of residual thermal stresses that can be present due to processing. Exposure to hydrogen for a week's time-period was based on diffusion calculations for these elastomers and 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. An attempt has been made to employ typical polymer structure-property relationships to explain the response of polymers to hydrogen exposure.

MATERIALS AND PROCEDURE

Samples of HDPE, PTFE, Buna N, and Viton A, were used to prepare specimens for characterization tests before and after exposure to hydrogen. Specimen sizes depended on the test and varied in dimensions. The thickness of all specimens in all tests was kept constant at 3 mm. This was adopted based on diffusion calculations for this thickness allowing complete saturation over a period of a week for all the polymer types and specimen shapes in this study. The Sandia National Laboratories code DIFFUSE was used to determine exposure time (Baskes, Michael I. DIFFUSE 83, SAND83-8231, 1983). A planar geometry using Sievert's Law as the boundary condition with the lowest diffusion coefficient of the four polymers chosen (1.9e-6 cm^2/s for HDPE) was used to calculate the time for the hydrogen concentration to increase from effectively zero to equilibrium was determined for a 138 MPa external pressure at 25°. Sample holders (Figure 1), about 5.08 cm long and 2.54 cm diameter, made of aluminum were used in the pressure vessels for the exposure.

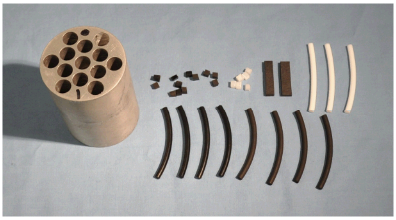

Figure 1: Polymer specimens and sample holder

The test chamber was connected to an existing pressure manifold and purged with helium gas three times starting with the test pressure of 103 MPa for the first purge and 21 MPa for the second and third purges. Each purge involved a fill (up to pressures described above) followed by reasonably complete venting of the purge gas at room temperature. At the end of the purge cycles, the test chamber was filled with 99.9999% hydrogen gas at 103 MPa at room temperature. At the end of the week's period of exposure, the vessel was depressurized at a very fast rate (< 1 minute) and specimens removed for characterization tests. Specimens were checked immediately for visible changes of any kind and observations noted. These were stored in special bags with very low permeability, immediately after removal from the pressure vessel to prevent contamination as well as to preserve hydrogen effects in polymers to the maximum extent prior to characterization.

CHARACTERIZATION TESTS

Characterization tests were performed with a minimum of three specimens per exposure condition for all polymers. Thermogravimetric Analysis (TGA) and density measurements were performed on specimens three times: before hydrogen exposure, immediately after removal from the pressure vessel, and also 48 hours after exposure, to capture any changes in sample out-gassing with time. Dynamic Mechanical Thermal Analysis (DMTA) and compression set tests were performed before hydrogen exposure and within 2-4 days after removal from the pressure vessel. **Dynamic Mechanical Thermal Analysis (DMTA):** Thermoplastic sheets (HDPE and PTFE) were examined under torsion using the Rectangular Torsion geometry, 0.005% strain, 1 Hz frequency, and 1 N axial tension, 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. Elastomer sheets were examined under torsion using the Rectangular Torsion geometry at 0.005% strain, 1 Hz frequency, and 1 N axial tension, with heating from -150°C to 250°C at a heating rate of 5°C/minute. For O-ring and gasket samples made from PTFE, Viton A, and Buna N, strains ranging from 0.05% to 0.5% were used depending on sample form factor. Heating rate was always kept constant at 5°C/minute. **Compression Set (Elastomers):** This test measures the permanent deformation possible in elastomeric polymers on the application of a compressive force at a given temperature. Dimensions of the specimens were measured with a laser micrometer, and 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 test and recovery to RT. Compression set is expressed as a percentage of the original deflection: $C_B = [(t_o - t_l)/(t_o - t_n)] \times 100$ where C_B = Compression set (%); t_o = original height of the specimen; t_l = final thickness of the specimen; t_n = thickness of the spacer bar (2.35 mm) **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. Masses were determined in air using a Mettler Toledo XS403S balance 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. 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 and; D_{air} = Density of air at 21°C **Thermogravimetric Analysis (TGA):** Polymer specimens were heated from room temperature to 200°C at 2°C/minute using 100 µL aluminum crucibles in a Mettler Toledo TGA/DSC 1 and changes in mass were measured. Mass loss was converted to changes in density and polymer volume. Any significant change 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. **Mechanical Testing:** Tensile testing (ASTM D638-14) 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) and tested at the speed of 0.0254 mm/s at room temperature. Five specimens each of the thermoplastics were tested for before and after exposure conditions. Tensile strength data was used to determine whether hydrogen exposure had any effect on the HDPE and PTFE polymers' strength and modulus.

RESULTS AND DISCUSSION

Elastomers' Behavior in Hydrogen: Observations made immediately after removal of the specimens from the test chamber pointed to a visible change in dimensions (swelling) of the elastomers (Figure 2). Swelling was seen with all specimens to the same extent but did not display shredding or tearing due to the minimal cycling in our study.

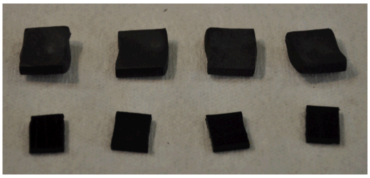

Figure 2: Picture showing the swelling seen in Buna N (two on right side) and Viton A (two on left side) after hydrogen exposure

DMTA plots for sheet Buna N and Viton A are shown below in Figure 3. 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%).

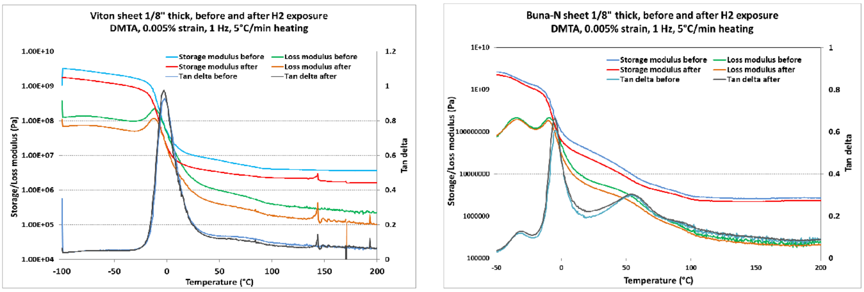

Figure 3. DMTA plots for Viton A (left) and Buna N (right) before and after hydrogen exposure

The presence of unsaturation in Buna N rubber confers crosslinkability, reduced segmental mobility and a lower free volume and therefore, only a slow hydrogen penetration is possible. This supports a higher storage modulus for Buna N over Viton A after hydrogen exposure. With the Viton A polymer, there is easy slippage between the polymer chains and this creates greater free volume and therefore more hydrogen penetration. However, it can be foreseen that the presence of the relatively large fluorine atoms in the Viton A micro-structure can also hinder easy escape of the gas. Solubility of hydrogen may result in plasticization in such a polymer[11] and therefore, storage modulus changes for Viton A are significantly larger than Buna N. For both Buna N and Viton-A, the glass transition temperature (Tan delta peak in DMTA plots) do not show significant changes after hydrogen exposure. Compression set properties of Buna N and Viton A after exposure to hydrogen for seven days are shown in Figure 4. 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 sheet did not change much; whereas that for Viton A almost doubled. The lower crosslinking in the latter can influence its compression set properties in hydrogen use.

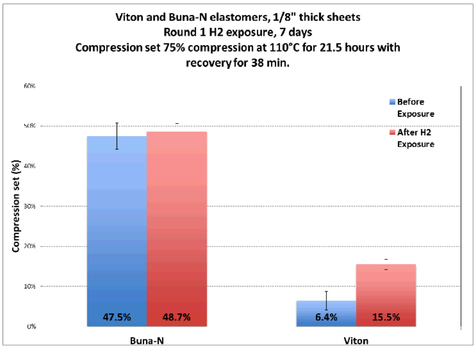

Figure 4. Compression set for Buna N and Viton A sheet materials before and after hydrogen exposure

Tied to a possibility of residual hydrogen in Viton A comes interaction of the gas with fillers in the polymer. To analyze if fillers can influence hydrogen effects in these elastomers, micro CT (Computerized Tomography) analysis of both Buna N and Viton A samples was done before and after hydrogen exposure (Figures 5). Micro CT images of Buna N show very little change with respect to hydrogen effects after exposure. A few voids were detected in the rubber matrix before and after exposure and therefore were not due to hydrogen. In the images for the Viton A, it is clear that voids have appeared around high density filler particles after hydrogen exposure. Further investigation to identify types of fillers in elastomers susceptible to hydrogen exposure is planned for the future.

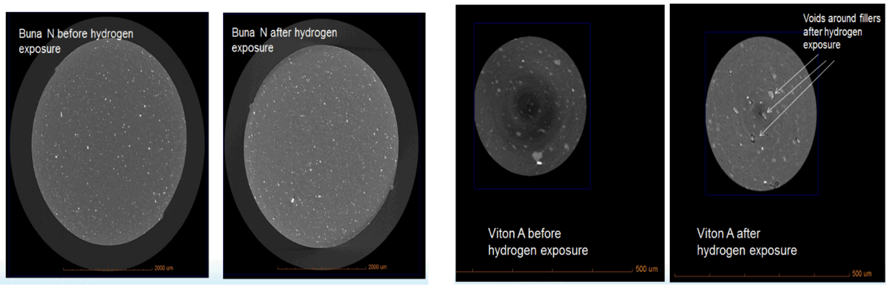

Figure 5. Micro CT images for Buna N and Viton-A before and after hydrogen

Polymer	Percent Change in Volume per gram upon Hydrogen exposure	
	Immediately after Removal	48 hours after Removal
Buna N Sheet	57.2%	3.9%
Buna N O-ring	22.6%	0.2%
Viton A Sheet	69.0%	11.5%
Viton A O-ring	37.1%	0.8%
Viton A gasket	114.3%	7.0%

Table 1. Percent change in volume for elastomers

Density changes, used to determine the effect of sorption properties of gases when transported through polymers, converted to percent change in volume per gram of polymers, Buna N and Viton A, are shown in Table 1. The percent change in volume for Viton A is therefore much greater than that of Buna N. The diffusion of hydrogen through the Buna N rubber is slower than in Viton A due to its crosslinked nature and that manifests itself as a smaller increase in initial volume compared to Viton A. Thermogravimetric analysis (TGA) of the elastomers show that the percent mass loss for these unexposed elastomers in sheet form was close to each other (Figure 6). However, upon exposure to hydrogen, it seems that the polymers show lower mass loss, with Viton A exhibiting less mass loss than Buna N. This could be due to hydrogen influence on the fillers in these elastomers.

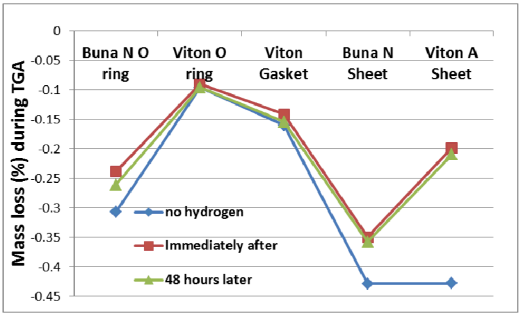

Figure 6. TGA plot for elastomers before and after hydrogen

The TGA data shown here agrees with the trend observed with the percent change in volume for the elastomers and may be related to their capacity to retain hydrogen. This can be attributed to the greater amount of free volume in the Viton A polymer microstructure compared to Buna N and may also 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 for this polymer.

Thermoplastics' Behavior in Hydrogen: As expected, a clear difference could be noted between the response of thermoplastics and elastomers to hydrogen. While the elastomers showed massive swelling, the thermoplastics did not exhibit any such change Both the thermoplastics in this study (HDPE and PTFE) are semi-crystalline and have both ordered and amorphous regions (Degree of crystallinity (DSC) HDPE = 71% and PTFE = 65%) (source: Brandrup & Immergut Polymer Handbook, 1999)). The processing during manufacture and the thermal history of these polymers, as received, strongly influence their response to high pressure hydrogen. Therefore, it is often difficult to predict permeation properties through HDPE and PTFE. DMTA plots for HDPE and PTFE (not shown here) show that the storage moduli and Tg for these polymers do not change significantly upon hydrogen exposure under the time and temperature conditions adopted in this study. 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. Density measurements on the two thermoplastics before and after hydrogen exposure revealed a similar trend as the moduli and showed no change. Thermogravimetric analysis of the thermoplastics did not reveal mass loss of any volatiles upon heating from 30°C to 200°C. Tensile testing was performed on PTFE and HDPE specimens. In previous studies, it has been reported that for semi-crystalline polymers, both tensile strength and modulus of elasticity increase approximately linearly with pressure. This increase has been attributed to an increase in T_g or increase in crystalline phase changes. Both the thermoplastics (PTFE and HDPE) behaved similarly showing an increase in Young's modulus with hydrogen exposure. This indicates that hydrogen exposure is possibly changing the polymer chain alignments sufficiently in the time frame of exposure (one week) and at room temperature, as were the conditions of the study.

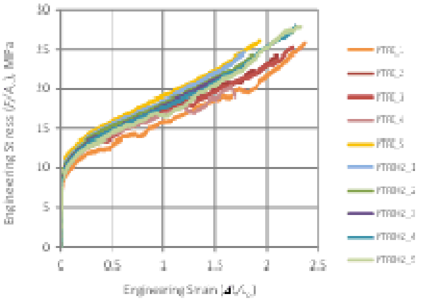

Figure 7. PTFE specimens show elastic deformation in tensile test. Table below shows the Young's modulus and tensile strength numbers for PTFE

Sample	**Young's modulus (MPa)**	**Yield Stress (MPa)**	**Strength (MPa)**
PTFE	**493±127**	**8.8±1.1**	**24.4±1.1**
PTFE in Hydrogen	**667±40**	**8.1±0.58**	**25.4±0.50**

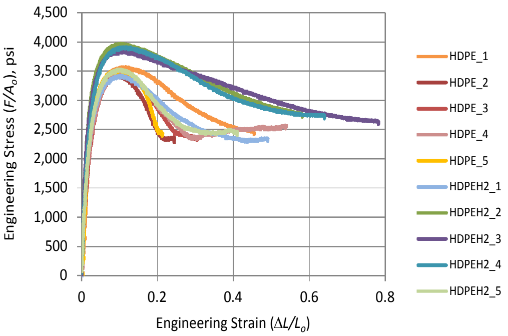

Figure 8. HDPE specimens show plastic deformation in tensile test. Table below shows the Young's modulus and tensile strength numbers for HDPE

Sample	**Young's modulus (MPa)**	**Yield Stress (MPa)**	**Strength (MPa)**
HDPE	**863±225**	**20±0.70**	**24±0.62**
HDPE Hydrogen	**990±235**	**22±1.9**	**26±1.60**

CONCLUSIONS

In this study, a select group of two elastomers (Buna N and Viton A) and two thermoplastics (HDPE and PTFE), of known grades, were exposed to static conditions of 100 MPa at ambient temperature for a week. The influence of hydrogen exposure on polymer properties such as the modulus, glass transition temperature T_g, compression set properties, density, outgassing characteristics and the tensile strength was investigated. Characterization of the polymers before and after exposure was performed. The two thermoplastics investigated did not show any significant change in major physical properties such as T_g and storage modulus. Viton A showed very significant variations in modulus, compression set, and a significant percent change in volume upon hydrogen exposure. Buna N rubber showed similar changes, but not to the same extent.

ACKNOWLEDGMENTS

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