Effect of high pressure hydrogen on the volatiles in polymers Buna-N and Viton

DeAndre Minor, Dr. Bernice Mills, Nalini Menon
Sandia National Laboratories, Livermore, California

Introduction and Objective

The hydrogen economy requires storage and delivery of high pressure hydrogen. During storage and transfer, hydrogen experiences high pressure and temperature fluctuations. Materials that can withstand these conditions are needed. In this work, samples of Buna-N and Viton A that had been exposed to high pressure (100 MPa) argon and hydrogen(HeH2) and samples with helium and hydrogen(ArH2) (argon and helium used for leak checking) were compared to unexposed samples using thermal desorption spectroscopy (TDS). In TDS, the temperature can be ramped to reach a desired constant hold temperature while recording a series of mass spectra of volatiles and total pressure. As the polymers are heated in vacuum, the outgassing composition and pressure changes are recorded. Our objective is to determine if high pressure hydrogen affects the outgassing of the polymers Buna-N and Viton. Properties such as strength and compression set are being measured by fellow researchers.*

Material Information

Material	Exposure	Before Wt.	After Wt.	% loss
Buna-N	Not Exposed	270.91 mg	248.62 mg	8.2%
Buna-N	Ar-H2	131.39 mg	120.84 mg	8.03%
Buna-N	He-H2	146.53 mg	133.98 mg	8.6%
Viton A	Not Exposed	305.62 mg	305.32 mg	0.1%
Viton A	Ar-H2	217.52 mg	217.17 mg	0.2%
Viton A	He-H2	189.72 mg	189.35 mg	0.2%

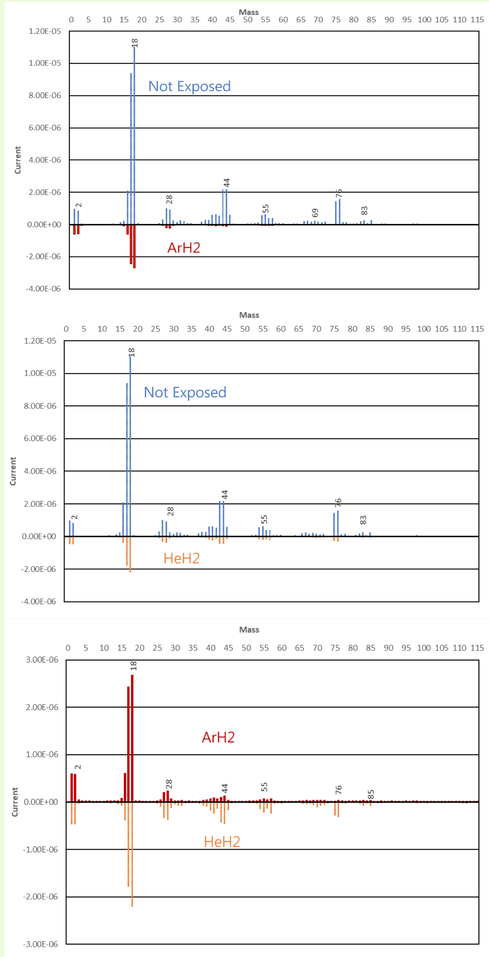
Buna-N is a polymer made up of 2-propennenitrile, 3(1,3-butadiene), and 1,2- butadiene. It is a nitrile rubber with a service temperature of about 138°C used in applications that take advantage of its oil, gasoline and solvent resistance.**
Viton A is a polymer made up of hexafluoropropylene and vinylidene fluoride. It is a fluorocarbon rubber with a service temperature of 225 °C used in various seals such as in engines, fuel systems, chemical systems and high temperature environments.***

Experimental

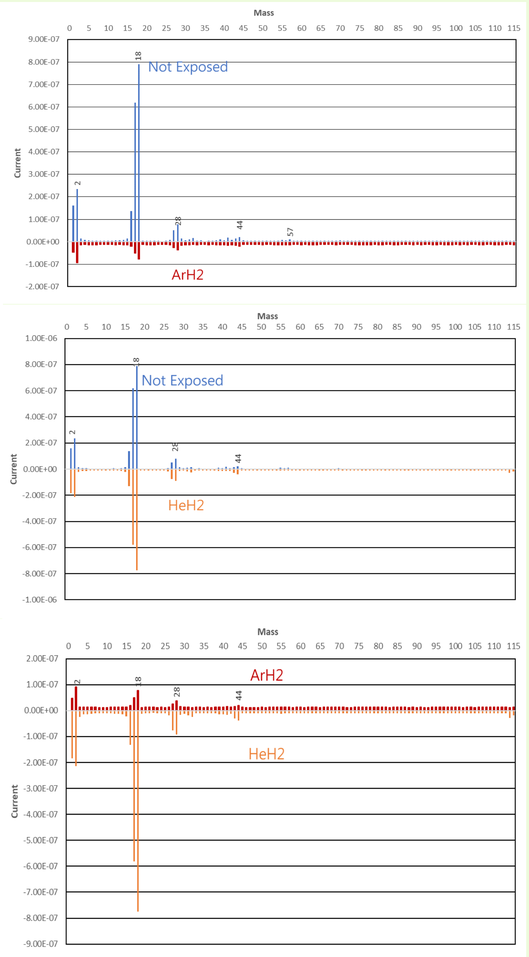
For TDS, the samples were ramped at 1°C per minute to 200°C under vacuum and held at 200°C for three hours while recording temperature, pressure, and mass spectra.

Results

Buna-N

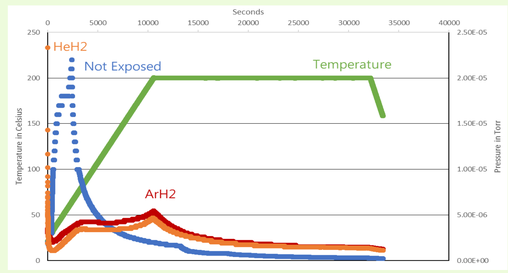


Viton A

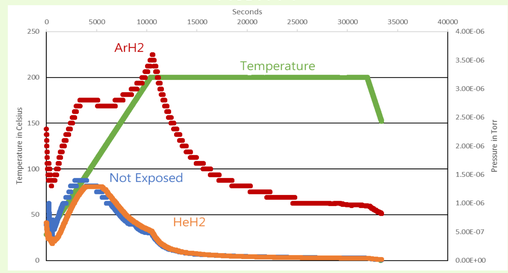


All charts have been adjusted for the difference in sample weight within each polymer.

Buna-N



Viton A



The differences in the amounts of volatiles show that there is clearly an effect on the polymers based on their exposure. ArH2 is consistently releasing the smallest amount of volatiles in both the Buna-N and Viton A. The HeH2 on the other hand do not show the same loss and in Viton show little noticeable loss as shown in the spectra.

When looking at the pressure charts, it is clear that pressure on one polymer is different from the other based on the percent loss of the polymer. For instance, the Viton A samples lost ~0.2% of its mass so the pressure is significantly lower than that of the Buna-N which lost ~8.3% of its mass.

Conclusion

Although the percent weight loss difference between the exposed and unexposed samples is small, there is a large difference in the pressure during TDS suggesting that something more is happening within the samples. There is also a significant quantitative difference in the mass spectra. For the Buna-N the exposed samples have significantly less volatiles than those not exposed. In Viton volatiles are abundant in the Argon/Hydrogen exposed samples compared with the amount in the Helium/Hydrogen exposed samples. EPDM, another polymer tested, has shown to have less volatiles in its spectra when comparing the not exposed to the exposed****. Showing that the high pressure hydrogen exposure has a demonstrable effect in removing some of the volatiles present within the samples.

Future work should include a more detailed examination of the time/temperature evolution of the individual masses seen in this data. There are plans for similar experiments using hydrogen only as well as experiments where the high pressure hydrogen is cycled.

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* Polymer Behavior in High Pressure Hydrogen, Helium, and Argon environments as applicable to the Hydrogen infrastructure, Menon, N.C., Kruizenga, A.M., Nissen, A., Mills, B. E., San Marchi, C. and Campbell, J., accepted for publication by the International Association for Hydrogen Safety.

**http://warco.com/polymer/nitrile/
***http://viton-orings.com/
****Minor,D; Mills,B; Menon,N. Effects of High Pressure Hydrogen on EPDM. SAND2017-8175.August 2, 2017. Lawrence Livermore national Laboratories