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Review on the effects of hydrogen at extreme pressures and temperatures on the mechanical behavior of polymers

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Abstract

The effects of hydrogen on the mechanics (e.g. strength, ductility, and fatigue resistance) of polymer materials are outlined in this report. There are a small number of studies reported in the literature on this topic, and even fewer at the extreme temperatures to which hydrogen service materials will be exposed. Several studies found little evidence that hydrogen affects the static tensile properties, long term creep, or ductile fracture of high density polyethylene or polyamide. However, there has been a report that a recoverable drop in the modulus of high density polyethylene is observable under high hydrogen pressure. A research need exists on the mechanical effects of hydrogen on the wide range of polymers used or considered for use in the hydrogen economy, due to the lack of data in the literature.

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1. INTRODUCTION

The use of hydrogen as a transportation fuel has the potential to reduce the dependence the U.S. has on foreign oil imports, reduce emissions of the global warming gas, CO_2, and can be used in conventional combustion as well as advanced power-train systems, such as fuel cell vehicles. There are already approximately 500 light-duty, 250 heavy-duty, and 3000 industrial (hydrogen) fuel cell powered electric vehicles operational today[1]. In addition, there are 58 active hydrogen fueling stations in the U.S. and 143 fueling stations worldwide[2]. As the use of hydrogen as an energy carrier becomes even more widely adopted, it is critical that effects of hydrogen on the materials used in all aspects of the hydrogen economy (e.g. storage tanks, delivery pipelines and systems, etc.) are understood. Only through an understanding of the effects of hydrogen on materials can incidents, such as those recorded in the H_2 incidents database[3], be avoided. As an example, a 70 MPa, Teflon lined hose burst at a hydrogen fueling station in 2007 after two years of intermittent use.[3] This incident could have been avoided, had the material properties under hydrogen service been known, with more appropriate replacement intervals specified and/or more appropriate material selection.

The effects of hydrogen on many materials have been studied extensively and well documented over the past 100 years. Specifically, the embrittlement of metals from hydrogen is an advanced field, with a multitude of literature devoted to the topic[4,5]. The embrittlement of steels, stainless-steels, alloys, and aluminum has been observed and are active areas of research. However, there are many non-metal components used in hydrogen production, transmission, distribution, delivery, and storage systems. In addition to metal, fiberglass, carbon-fiber, and aramide are materials commonly used in hydrogen storage tanks. High-density polyethylene (HDPE) and polyphenylene sulfide (PPS) are used as piping or tank liner materials[6]. Teflon, polyetheretherketone (PEEK), acetal, PFA, Buna-N, and Viton are some common sealing materials in valves.

The focus of this review is on the effect of hydrogen on polymer components that are used or considered for use in hydrogen service. These components may be exposed to hydrogen pressures up to 15,000 psi (100 MPa). A combination of environmental conditions and expansive cooling could result in these materials experiencing temperatures as low as -70 °C. The combination of environmental conditions and compressive heating, or the required temperatures for fuel cell operation could result in these materials experiencing temperatures as high as 120 °C under high hydrogen pressure. Many of these materials will be exposed to temperature cycles under hydrogen pressure and/or pressure cycles.

Polymers are organic long-chain molecules of high molecular weight. An understanding of polymer physics did not begin until Staudinger's Macromolecular Hypothesis in the 1920's, and Sperling notes that "research into the understanding of fracture and fatigue of polymers is in its infancy"[7]. Nonetheless, there are several known degradation methods of polymers. Exposure to high temperatures causes thermal degradation, where scission of weak links in the polymers can release volatile components, reducing the molecular weight and strength[8]. High energy radiation can cause scission, crosslink formation, volatile formation, cyclization, formation and decay of unsaturated bonds[8]. Light can lead to photo-degradation, which again causes scission and cross-linking of the polymer chains[8]. Finally, chemicals can degrade polymers. For example, oxygen

exposure can lead to the formation of hydroxyl, peroxide, carbonyl, aldehyde, etc. groups along the polymer chain[8]. PPS, which is used as a piping or tank liner material, is known to be sensitive to oxidizing agents[9]. There are no reported sensitivities of polymers to hydrogen, but very few studies evaluating this relationship.

2. EFFECT OF HYDROGEN ON THE MECHANICAL PROPERTIES OF POLYMERS

Polymer mechanics includes the strength, ductility, and fatigue resistance of these materials. ASTM D4762[10] outlines the current standards for mechanical testing of polymer matrix composite materials. This standard provides a summary of test methods for composite and polymeric materials. Current static property tests methods include tensile, compressive, shear and flexural strength determination as well as fracture toughness. Dynamic tests are also outlined, including tests for the determination of fatigue, creep, and the energy of rupture. ASTM International also provides some guidance for conditioning materials in terms of temperature and relative humidity[11], but does not include other environmental factors, such as pressure or gas environment (other than humidity). An understanding of the effect of hydrogen on polymer mechanics will require such tests outlined under ASTM D4762 modified to include hydrogen pressure and extreme temperatures, as well as novel tests that include thermal and/or hydrogen pressure cycles.

Some effects of hydrogen on polymers have been studied. With the use of polymers as gas membranes for separation technology and PEM fuel cell electrolytes, the majority of the studies have focused on permeation of hydrogen[12–19], with some groups also investigating the sorption characteristics of the polymers[18,20,21]. Fiber reinforced polymers are the leading candidate for hydrogen piping systems[6], and polymers can be used as metal pipe and tank liners. The permeation properties are important to evaluate gas losses and to prevent metals embrittlement. However, an understanding of the mechanical properties of polymers under hydrogen pressure is also important for the safety and reliability of all of the components considered for use in the hydrogen economy. Only a few groups have reported studies on the effect of hydrogen on polymer mechanics.

Klopffer et al.[19] measured the permeability of hydrogen and mixtures of hydrogen at up to 20 bars through a high density polyethylene and two polyamide materials that are currently used for natural gas piping. The polyamide materials had lower permeability than the polyethylene, and each of the materials had a higher permeability at a higher temperature. The permeability of hydrogen was also found to be larger for hydrogen than CH_4 (which is likely a function of molecule size). One year of operation under hydrogen pressure did not affect the permeability. The same authors also found that under 3 MPa of hydrostatic hydrogen pressure (at room temperature), the tensile static properties, long term creep deformation, and the ductile fracture were no more than 10% different than those properties of the two materials in air.

Webster[22] performed tensile tests on three polyethylene and one PPS samples after aging the samples in an oven at 85 °C for 30 days, or leaving the samples under 70 MPa hydrogen for 30 days. Bubbles were observed under the surface of the PPS sample that was subject to the hydrogen atmosphere. This was attributed to explosive decompression, the same phenomena reported as blister fracture on rubber o-ring materials by Yamabe and Nishimura[23]. This phenomena is not unique to hydrogen, and is also observed in the chemical processing industry[9,23]. Webster[22] reported that the polyethylene materials developed curvature or became discolored after 30 days of exposure to 85 °C. With only three samples of each material under

each condition, there was significant statistical uncertainty in the tensile tests. However, the data suggested that exposure to 85 °C relaxes the residual tensile stresses (causing the shape change), increasing the tensile stress required before deformation begins. The PPS (in which the 'blister fracture' was observed) elongated significantly more than the starting material before failure. The polyethylene materials exposed to hydrogen did not have significantly different strength or elongation properties than the starting materials.

Castagnet et al.[24] have performed tensile tests in pressurized (to 10 MPa) hydrogen, nitrogen, and atmospheric pressure air for a polyethylene and polyamide thermoplastic. The authors did not measure any effect on the tensile properties of either thermoplastic due to hydrogen diffusion into the materials. In later work, the same authors [25] explore the effect of aging these two materials in up to 2 MPa H_2 for 13 months at temperatures up to 80 °C. These authors report significant uncertainty in their results, because their load cell is oversized for the small samples used in these studies. As such, no significant effect on the tensile properties or crystalline structure of the materials was observed as a result of aging over this timeframe.

Simmons[26], on the other hand, in some preliminary tests of high density polyethelyne measured a 17% drop in the modulus as the samples were exposed to hydrogen (at room temperature and 4,000psi, or 28 MPa). The modulus was recoverable after the hydrogen pressure was removed. Simmons also observed significant blister fracture in low density polyethelyne. Finally, Simmons observed that halar and high density polyethylene have better strength properties at cryogenic temperatures (down to -140 °C).

These studies suggest that hydrogen pressure can reduce the mechanical strength polymeric materials. There is little evidence to suggest that the hydrogen interacts with the polymer chains (of the polymers tested, which are polyethelene, polyamide, and PPS) causing permanent degradation[6,23], but the presence of adsorbed hydrogen can affect the mechanical properties of polymers. Therefore, in-situ mechanical testing of polymeric materials under hydrogen pressure is required to see the influence of the gas on the materials. Further testing on materials under hydrogen pressure at more extreme temperatures is also needed, as these materials may be exposed to a wide range of temperatures, and temperature cycles under hydrogen pressure. Hydrogen pressure can also cause blister fracture in polymeric materials, and the effects of blister fracture on the mechanical properties of these materials should be measured.

3. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Knowledge of the mechanical properties of all of the materials used in high pressure hydrogen service is crucial for the safety and reliability of the infrastructure related to the hydrogen economy. While much is known about the effect of hydrogen on metals, there is much less data reported on the effect of hydrogen on the polymeric materials used in hydrogen. Hydrogen is known to cause blister fracture on polymeric materials exposed to hydrogen that are decompressed too rapidly, but to our knowledge, the mechanical properties of blister fractured materials has only been measured by one group[22]. Several groups have reported the mechanical properties of polyethelene, polyamide, and PPS under hydrogen pressure[19,22,24–26], and the effect of aging under hydrogen pressure at moderate temperatures (up to 80 °C)[25]. Little influence of hydrogen on the mechanical properties of these materials is observed at moderate pressures (< 3 MPa)[19,22,24,25], but at higher pressures (28 MPa), hydrogen pressure may reduce the strength of polymeric materials[26]. The reduction in strength appears only under hydrogen pressure, and the modulus is recoverable as hydrogen pressure is removed.

Polymer mechanics data for the entirety of materials that will be used in hydrogen service is necessary for their safe use. This is a field that has not been widely explored in the scientific community. Extensions of the mechanical tests already performed by the few groups working in this field are needed for a greater understanding of the phenomena involved. Thermal cycles under hydrogen pressure, and hydrogen pressure cycles under a wide range of temperatures are needed, as these cycles may affect polymers differently than thermal cycles in air. As described earlier, these materials may experience temperatures from as low as -70 and as high as 120 °C, requiring mechanical tests to also span this wide range of temperatures. Higher hydrogen pressures, up to 100 MPa, are also necessary, to properly span the working conditions of these materials. A greater understanding of the mechanisms behind blister fracture, and the strength of blister fractured materials would allow for specifications of depressurization rates and material replacement intervals. An understanding of the relationship between hydrogen impurities and polymer mechanics would allow purity specifications to be made. Finally, the materials selection needs to be expanded to include all of the polymeric materials used in hydrogen service.

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