Degradation of Semi-Crystalline Thermoplastic Materials in Severe Hydrogen Environments

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The increasing use of hydrogen as a clean energy carrier necessitates the development of materials capable of withstanding its challenging conditions. Semi-crystalline thermoplastic materials, because of their good gas barrier properties, are often considered for applications involving hydrogen storage and transportation. However, these materials face significant challenges when exposed to high-pressure hydrogen environments.

One of the damages that occur in the thermoplastic liner of a type IV hydrogen tank (fig.1) is blistering. This happens because gas is absorbed by the material at high pressure, and stresses are generated when the decompression rate exceeds the rate at which the absorbed gas can escape by diffusion (see the schematic representation fig.2). The defects characteristic size is on the order of micrometers, making them difficult to detect. However, some damage layer in depressurized HDPE samples have been observed in literature as in T.A. Yersak *et al* [3] (fig.3).

This study aims to investigate the degradation mechanisms of semi-crystalline thermoplastics in severe hydrogen conditions, focusing on the induced effects of damage on the mechanical and barrier properties of the materials. One of our objectives is to identify the observation and characterization techniques able to detect such micro-damage. Samples of semi-crystalline thermoplastics commonly used for liner manufacturing, including high-density polyethylene (HDPE), polyamide 6 (PA6), and polyamide 11 (PA11), are subjected to hydrogen exposure at pressures up to 700 bar until complete saturation and then rapidly depressurized (5MPa/s).

Various characterization techniques, such as tensile testing, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and permeation tests, are employed to assess the mechanical, thermal, barrier, and microstructural changes in the materials. Observation techniques, such as tomography, SAXS, and transmitted light digital imaging, are employed to detect cavities resulting from rapid depressurization.

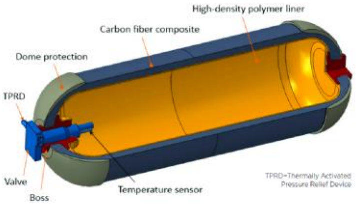

Figure 1 : Type IV hydrogen tank [1]

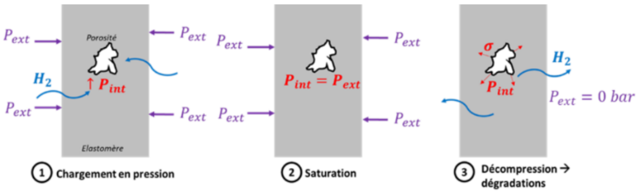

Figure 2 : llustration of the diffusion phenomenon and blistering [2]

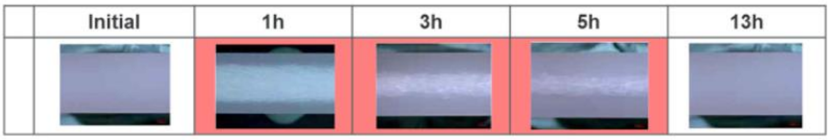

Figure 1: Cross section of HDPE monolayer liner before and after depressurization (from 87.5 MPa to 2MPa in 1, 3, 5, and 13 h depressurizations at 50 °C) observed by tomography [3]

References:

[1] E. Rivard, M. Trudeau, et K. Zaghib, « Hydrogen Storage for Mobility: A Review », Materials, vol. 12, no 1973, 2019.

[2] Q. Gardavaud, « Contribution à l'étude de l'influence des paramètres de pression sur des élastomères soumis à une décompression rapide d'hydrogène », phdthesis, Université Bourgogne Franche-Comté, 2023. Consulté le: 19 février 2024

[3] T. A. Yersak et al., « Predictive model for depressurization-induced blistering of type IV tank liners for hydrogen storage », International Journal of Hydrogen Energy, vol. 42, nº 48, p. 28910-28917, nov. 2017, doi: 10.1016/j.ijhydene.2017.10.024.

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