HYDROGEN PERMEABILITY OF CARBON FIBER REINFORCED CASTED POLYAMIDE 12

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Keywords: Hydrogen, Permeation, Barrier-design, CFRP, PA12C

Abstract

Green hydrogen (H_2) has a high potential to substitute fossil fuels to reduce climate harmful CO_2 emissions in several sectors. From a mechanical point of view carbon fiber reinforced plastic (CFRP) is a very good material choice for lightweight high pressure and cryogenic H_2 storage tanks due to the high strength of carbon fiber and the possibility of an anisotropic laminate design. However, the leak-free storage of the highly diffusive hydrogen gas in CFRP tanks is a huge challenge, due to the combination of high storage pressures and micro-crack propagation in the matrix induced by thermal stresses. Thermally induced cracks in composite materials arise through different thermal expansion coefficients of fiber and matrix which again results in high internal stresses. These stresses accumulate during repeated thermal cycling which increasingly weakens the fiber-matrix interface and leads to crack initiation and propagation, that causes eventually leakage. [1,2]
The aim of this research is to analyze failure mechanisms and permeation through thermoplastic CFRP in cryogenic tanks based on casted Polyamide 12 (PA12C) as a promising matrix material. Based on the gained insights crack resistant single layer designs and robust laminate stackings are developed. Research has shown, that the polymer PA12C has good permeation properties, a high strain to failure (%ε) and is also economically valuable due to the fast polymerization. [3]
The test set up allows measuring the permeation in- and out-of-plane of circular plates with a diameter of 77mm and a thickness from 1mm up to 10mm. The tests are performed under defined climate conditions with inlet pressures up to 10 MPa. The inlet gas used in the following permeation tests is helium, which has comparable permeability values to gaseous hydrogen in polymers and CFRP. [2] An extensive test program was conducted, varying not only the climate conditions, and the inlet pressure (from 2-10bar) but also the material, ranging from neat PA12C to short glass fiber reinforced PA12 to PA12 coated composite materials. The specimens were extracted from CFRP sheets via milling, which were produced using the T-RTM process. For this purpose, the monomer Laurolactam was melted and mixed with activator/ catalyst and infiltrated with overpressure into an evacuated mold in which dry carbon fibers were already present. The low-viscosity monomer melt polymerizes within a short time while soaking in the 160°C hot mold.
Some of the test specimens were subjected to cryogenic loads and tested for permeation before and after the thermal loads were induced to identify the effect of thermal induced stresses.

[1] Choi, Sukjoo, Snkar, Bhavani V.: “Gas permeability of various graphite/epoxy composite systems, 2007
[2] Schultheiß D.: Permeation Barrier for Lightweight Liquid Hydrogen Tanks, 2007
[3] Petzinger G.; Rothenbacher T.; Laufer N., Nowakowski P.; BW-Projekt FKZ BWZPH222114 „Entwicklung eines Wasserstoffspeichers im T-RTM-Verfahren auf Basis von Gusspolyamid 12 (WaGuPa)“ 1.1.20222 – 31.12.2023

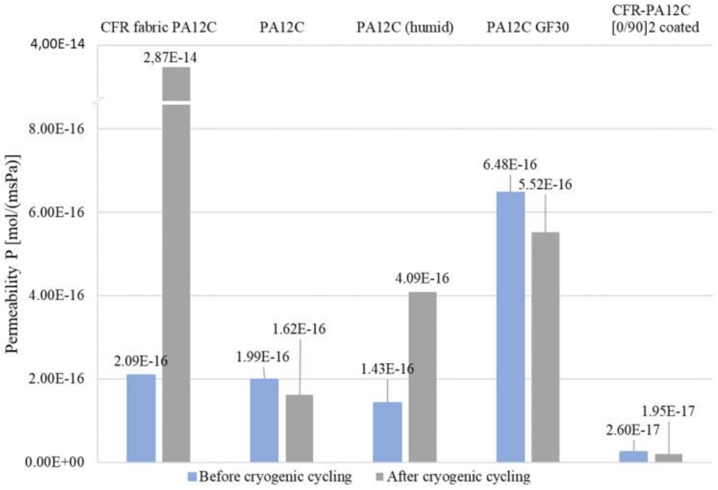

Figure 1 Permeability of unreinforced PA12C and CFRP-PA12C before and after cryogenic cycling

All samples underwent pressure tightness tests, µCT images and micrographs in order to correlate the permeation results with porosities and defects such as microcracks. The tests have shown that thermoplastic composites with a PA12C matrix can achieve a comparatively low permeation rate as long as a damage-free microstructure is ensured. The helium permeabilities of the tested samples are shown in Figure 1. Pure Polyamide 12C has nearly unchanged permeability rate before and after cryogenic cycling. The same result applies to short glass fiber reinforced PA12C (PA12C GF30). The short fiber reinforced composite is a promising material as an integrated load-bearing gas barrier in the laminate.

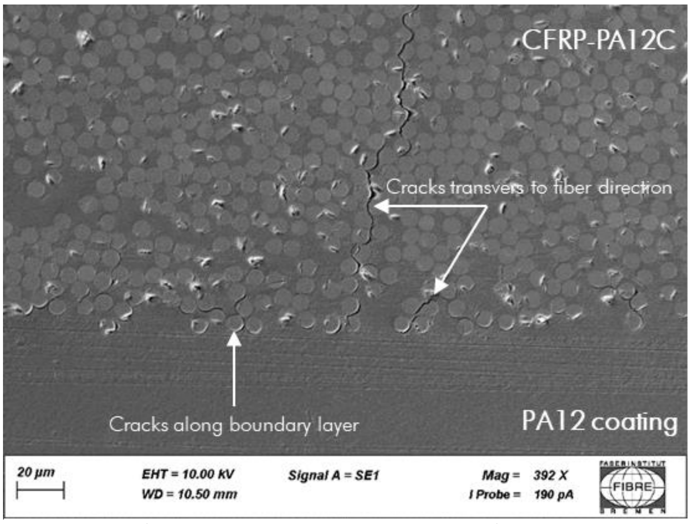

Figure 2 SEM of PA12 coated CFRP-PA12C specimen after 5x cryogenic

It was also shown that CFRP-PA12C specimen with a thin PA12 coating have remarkable barrier properties that maintain the permeation of the composite very low even after thermal induced stresses by cryogenic cycling. In Figure 2 µCT and an electron microscope scan of a cryogenic cycled PA12C coated CFRP sample is shown. Thermally induced damage leads to cracks in CFRP with a high fiber volume content and in the boundary section. In the fiber-free boundary layer, the material remains undamaged, which has no effect on the tightness against helium. Carbon fiber reinforced PA12C in combinations with an additional PA12 barrier is a promising laminate design for H_2 storage. The induction of thermal stresses by multiple cryogenic cycles creates a growing crack network within the composite layup causing a gas flow. However micro cracks are not visible in a µCT. In addition, the research has shown, that the inlet pressure, causing a smaller pressure gradient, has no notable influence on the permeation for undamaged materials. This effect and the impact on crack formation by fiber volume content, orientation and gradients will be analyzed in a follow up project aiming a suitable design of laminate stacking. All in all, results show that CFRP-PA12C tanks have a high potential to make composite H_2 storage tanks safer and more economical, which is highly interesting for future mobility.

[1] Choi, Sukjoo, Snkar, Bhavani V.: "Gas permeability of various graphite/epoxy composite systems, 2007
[2] Schultheiß D.: Permeation Barrier for Lightweight Liquid Hydrogen Tanks, 2007
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