

POLYAMIDE 12 COMPOSITES AS PERMEABILITY BARRIER FOR CRYOGENIC HYDROGEN STORAGE

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Abstract

Introduction/ Motivation

From a mechanical point of view, carbon fiber reinforced plastic (CFRP) is a very good material choice for lightweight high pressure or cryogenic H₂ storage tanks. However, the leak-free storage of the highly diffusive hydrogen gas in CFRP tanks remains a huge challenge, due to the micro-crack propagation in the matrix induced by cryogenic thermal stresses. Thermally induced cracks in composite materials arise through different coefficients of thermal expansion 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 eventually leads to crack initiation and propagation, causing leakage. [1,2] Adding fillers like short fibers to the matrix can reduce the micro crack propagation due to more homogeneous stress distribution during thermal loading. [3] Thermoplastic resins such as Polyamide 12 (PA12) promise several advantages, e.g. a high strain to failure (%ε), and high fracture toughness, which could improve thermal fatigue resistance. Previous studies have already demonstrated that PA12-based composites, incorporating carbon fiber, exhibit significantly lower gas permeability than the neat polymer [4,5,6].

The aim of this research is to investigate the influence of short fibers and ceramic particles as fillers on the hydrogen gas permeability and mechanical properties of PA12 at room and cryogenic temperature. The permeation tests are performed with a newly developed test bench.

Materials & Methods

The thermoplastic matrix was modified with short glass fibers, short carbon fibers (Tenax™-A HT P722, 3 mm), and alumina ceramic particles (CT1200 and CT3000 from ALMATIS). This approach aims to mitigate the coefficient of thermal expansion (CTE) mismatch between fiber and the filled matrix, thereby reducing internal stresses in a future continuous fiber reinforced CFRP by cryogenic exposure, while simultaneously enhancing gas tightness. The modified PA12 granulate was produced via a compounding process. Using injection molding, 2 mm thick plates were manufactured, from which permeability test specimens with a diameter of 55 mm were extracted.

The helium gas permeability test setup is shown in Figure 1. The test cell is divided into a pressurized feed side and a vacuum side, divided by two metal flanges. The specimen is clamped between the metal flanges sealed by elastomer O-rings. Both sides of the test cell hold a gas permeable sintered material to inhibit any specimen deformation. On the feed side a pressure of 5 bar is applied to the specimen, while on the vacuum side the test cell is connected to a leak detector from Pfeiffer Vacuum (ASM 340) maintaining vacuum of 10⁻³ mbar by the integrated turbo pump and measuring the leakage rate by the internally calibrated mass spectrometer. All tests were performed in a temperature-controlled lab environment of 20 ± 1 °C.

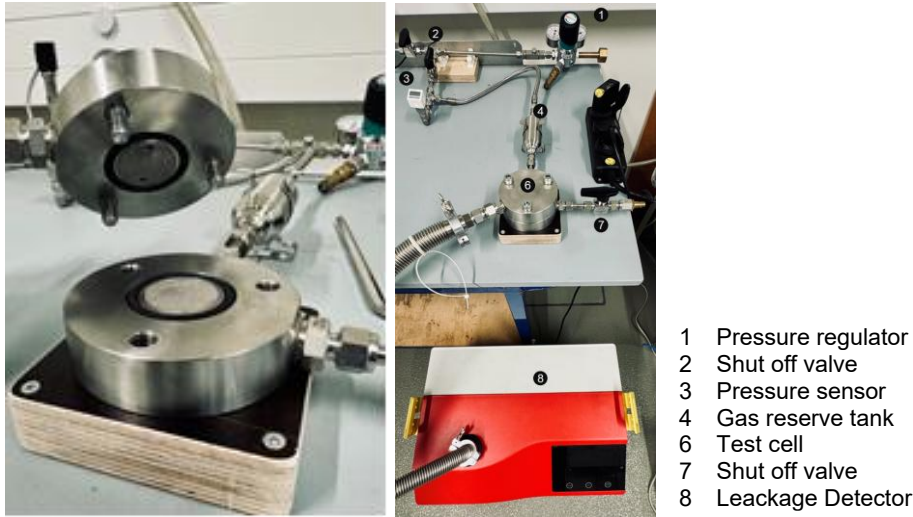


Figure 1 Helium gas permeability test setup

The measured leak rate (L_R), given in units of $\text{mbar}\cdot\text{l/s}$, represents a pressure–volume flow rate ($P \times V / t$). This value is converted into a molar flow rate (\dot{n}) using the ideal gas law ($PV = nRT$). Permeance (P_m) describes the gas transport through a specific sample of given thickness. It is defined as the molar flow rate per unit area (A) and per unit pressure difference (Δp). Permeability (P) is the intrinsic, thickness-independent property of the material. It is obtained by multiplying the permeance by the material thickness (l) and is expressed in units of $\text{mol/ m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$.

Results

The results of the permeability tests (see Figure 2) show that the addition of short fibers—particularly carbon fibers—significantly improves permeability performance. Even at a filler content of 10 vol.-%, a threefold reduction in permeability is observed. Doubling the fiber content to 20 vol.-% still yields a slight improvement; however, this effect is negligible compared to the reduction already achieved at 10 vol.-%.

PA12 reinforced with 30 vol.-% short glass fibers exhibit a similar effect to that of carbon fiber reinforcement. In contrast, the addition of ceramic particles shows almost no improvement in helium gas tightness compared to unreinforced PA12.

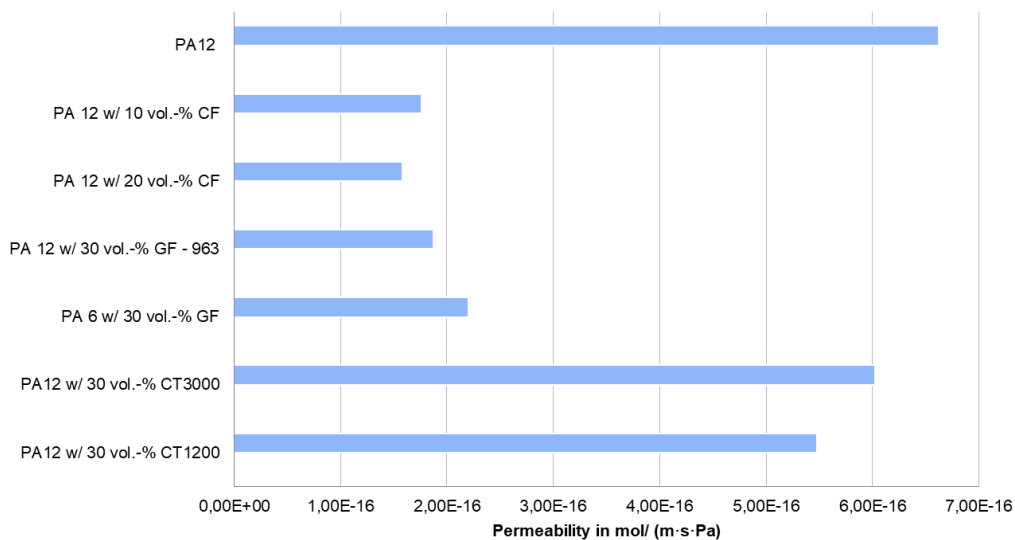


Figure 2 Permeability of a) neat PA 12 b) PA 12 w/ short CF c) PA 12 w/ short GF d) PA 12 w/ Ceramic Particles

Comparing the mechanical properties at 77 K Figure 3 shows a significant decrease of the elongation at break of each material compared to room temperature. The PA12 with Ceramic particle fillers show a much higher brittleness compared to the short fiber reinforced materials. Therefore, it is expected that the ceramic filled polymer will develop microcracks when used in a composite during cooling to cryogenic temperatures.

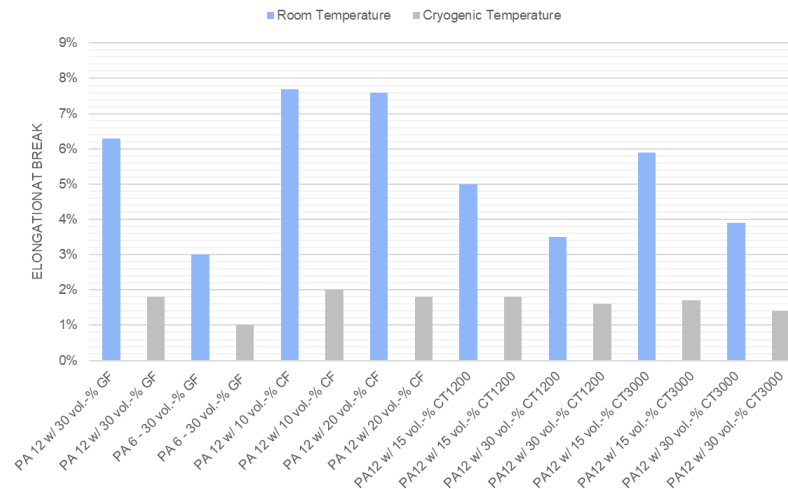


Figure 3 Elongation at break at Room Temperature and 77 K

Conclusions

As expected, the PA 12 samples filled with short fibers show a significantly reduced permeability. Unexpectedly, however, the ceramic particles exhibit almost no effect, while showing increased brittleness at both room temperature and 77 K, making this material combination unsuitable for cryogenic applications. Carbon fibers have a positive effect on gas tightness and still maintain an acceptable elongation at break; therefore, the focus is placed on carbon fibers and carbon nanostructures as fillers. The CTE from T_g down to 20 K will be measured for each material combination, aiming at a constant CTE for the whole temperature range. Furthermore, the permeability specimens will be subjected to several cryogenic thermal cycles down to 20 K, after which the permeabilities are determined to detect potential formation of leakage paths.

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