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METHODOLOGY FOR THE IDENTIFICATION OF HYDROGEN GAS PERMEATION PATH IN DAMAGED LAMINATES

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Abstract: *The main bottleneck of using composites for cryogenic storage of clean hydrogen fuel is the permeation of gas molecules. In this work, the permeation of hydrogen gas through thermally cycled thermoplastic composite laminates with two different stacking sequence is investigated. The experimental study is based on a methodology of cryogenically cycling the composite specimen and measuring the permeability in a dedicated hydrogen permeation setup. An optical microscope and X-ray computed tomography scanner are employed to investigate the existence of cracks. The results reveal that thermal cycling does not have a profound influence on permeability, while the stacking sequence has a considerable effect. Laminates with dispersed 0° layers resulted in lower permeation values compared to the laminate with grouped 0° layers at the laminate's core. The imaging techniques did not reveal any observable crack which supports the hypothesis that permeation is mostly driven by bulk diffusion in the polymer.*

Keywords: Cryogenic storage; Thermoplastic composite; Hydrogen; Permeation

1. Introduction

Fiber-reinforced thermoplastics (FRTP) and hydrogen play important role in the future of sustainable aviation. FRTPs are proposed over conventional thermoset counterparts due to their superior fracture toughness and recyclability. One technological challenge in this plan is the high cost and weight of the tanks storing liquid hydrogen at cryogenic temperatures close to -253°C. The linerless composite tanks, also known as type V vessels, could lead to the weight saving of up to 30% compared to metallic tanks [1]. A linerless tank concept could potentially be manufactured by a single-step automated tape winding (ATW) process owing to the in-situ consolidation mechanism [2]. This offers the advantage of lower overall manufacturing costs. In the absence of a liner, the tank wall structure should be gas tight, which is a major challenge for composite laminates, especially after cryogenic cycling. Laminates will be subjected to thermal cycles due to the refuelling which would cause the existing cracks to propagate and more hydrogen to leak. The leaked hydrogen not only brings safety risks but also causes economical losses. Therefore, there is a prominent need for research on understanding the permeation of hydrogen gas in the FRTPs to eliminate the leakage.

Permeation of hydrogen molecules through composites is studied by various researchers for both thermosets and thermoplastic composites subjected to different mechanical and thermal loading conditions. Reported experiments make use of different permeating gases such as helium or hydrogen. Gas permeation through composite laminates can be described differently based on the damage state of the laminate. If cracks are present, as depicted in Figure 1, the intersecting microcracks allow the passage of hydrogen molecules, making permeation

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proportional to the area of the intersecting cracks which is dominated by Darcy's law. In contrast, in the absence of the microcracks, hydrogen gas molecules would first travel in the polymer, along with the fiber/resin interface, between the plies and finally reach the other side of the laminate known as near-Fickian diffusion behaviour [3].

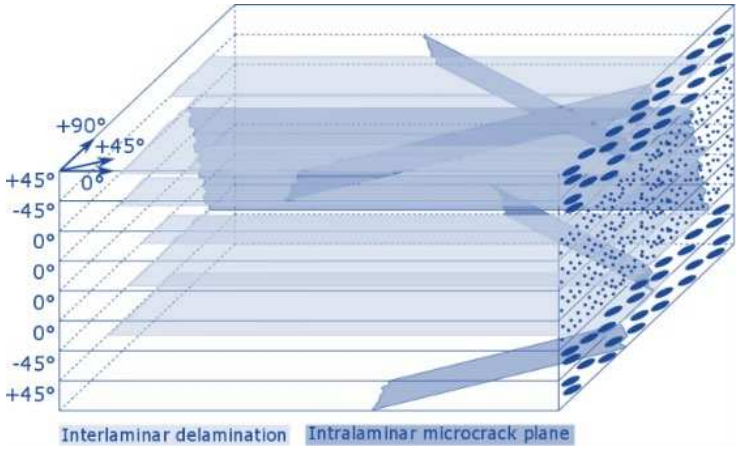

Figure 1. A schematic view of the microcrack network as the permeation path.

There are multiple research papers reporting crack formation on epoxy-based composite laminates after cryogenic cycling. Hamori et al. evaluated the gas permeability of composites made of carbon fiber (CF) and epoxy resin [4]. They performed mechanical tests at -253°C followed by leak tests at 20°C. It was observed that the microcracks were formed by the application of mechanical loads. In another study on the epoxy resin and carbon fiber, 150 thermal cycles were applied between -196°C and room temperature (RT) at the rate of 7°C /min and an X-ray computed tomography (CT) scanner was used to investigate the specimen after cycling [5]. They reported an increase in the microdefects as compared to the as-manufactured sample. In another paper, microcracks were observed in laminates made of graphite/epoxy with a layup of $[0_2/90_2/0_2]$ and thickness of 0.787mm after cryogenic cycling [6].

Thermoplastic composites could be an alternative to thermosets for cryogenic applications providing superior fracture toughness and processability enabling cost-efficient production [7,8]. It was reported that the observable crack network was limited for CF/Polyetheretherketone (CF/PEEK) laminates following thermally cycling the samples (8-layers, 50 thermal cycles between -196°C and 40°C) [9]. Similarly, for unidirectional AS4/PEEK laminate after cryogenic thermal loading between -269°C and ambient temperature, no observable crack was identified [10]. However, it was also reported that relatively thick thermoplastic laminates with 16 and 32 layers show damage, particularly with a quasi-isotropic layup, indicating laminates' thickness affects the permeation performance [9].

Another point of attention is the methodology followed for observing the cracks. The current state-of-the-art for visualization of the cracks is via CT scanning [5,8–12]. CT-scan images provide 3D visualization of the crack's location and orientations. Optical microscopy is also typically used for 2D observation of the cracks for a cross-section of the bulk material. Another parameter that plays a role in the permeation test is the permeant. Most of the reported permeability coefficient is based on helium gas which is the conventional method used by many researchers [3,6,8,9]. Permeation measurements at room temperature using hydrogen results in a higher permeability compared to helium according to Humpenöder [13].

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Based on the aforementioned observations from the literature, the focus of this work is on the thermoplastic material system made of carbon fiber and semi-crystalline low melt Polyaryletherketone resin (CF/LMPAEK). To evaluate the effect of stacking on the permeation two laminates are manufactured with grouped and dispersed layers of 0° fiber orientation. Finally, the effects of thermal cycling on the induced damage and the consequent effect on the permeability behaviour are studied. Optical microscopy and CT scan techniques are used to visualize possible cracks in the material. Permeation tests are performed using hydrogen gas as permeate.

2. Methodology

In this section, information is provided on the tested material, thermal cycling protocol, visualisation technique used for the tested specimen and the working principle of the hydrogen permeation setup.

2.1 Material

The layup used by Flanagan et al. was chosen as a guideline to be able to compare the new results to the ones available in their work [3]. Laminates made of 8 layers of unidirectional plies utilizing CF/LMPAEK with a nominal thickness of 0.14 mm per consolidated ply were manufactured by the press forming process. Disk-shaped samples for the permeation tests with a diameter of 49.9 mm were cut using a water jet. Two layups were considered to evaluate the effect of the grouping versus dispersing the plies as described in Table 1. The laminate with 4 layers of 0° direction stacked together at the core laminate is referred to as “thick”, and the laminate with a more dispersed layup is called “thin” in this study, even though the overall thickness remains the same.

Table 1. Sample definitions.

Permeation barrier layer	Layup
Thick – Grouped 0 layers	$[+45/-45/0/0]_s$
Thin – Dispersed layers	$[+45/0/-45/0]_s$

2.2 Cryogenic thermal cycles

The cryogenic cycling was performed at -196°C using liquid nitrogen (LN_2). Samples were immersed in LN_2 for 3 min and stayed at RT (20 °C) for 8 min followed by warming up by natural convection. The duration of the cooling and heating cycles was based on [3]. Two specimens per layup were subjected to 50 thermal cycles. The samples were positioned in a 3D-printed rack as shown in Figure 2 and submerged in dewar.

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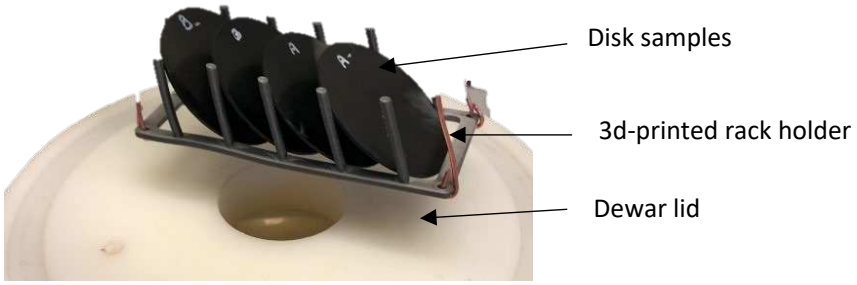

Figure 2. The setup for the cryogenic thermal cycling of the samples.

2.3 Visualization techniques

The optical microscopy and X-ray CT techniques were utilized to visualize the defects in the samples. The visualization was performed on rectangular samples (5mm x 10mm) from each layup cut from the same laminates as the disks for the permeation test and cycled cryogenically in the same manner. The optical microscopy was performed using a Keyence Laser Scanning Confocal Microscope. The CT images were taken by a Phoenix Nanotom® scanner. Images were generated at 160 kV and 28 µA with a voxel size of 3 µm. The volume rendering was completed using VGStudio MAX 2.2 software. The small size of the samples facilitated capturing images of high resolution with a 3µm voxel size which is suitable to identify cracks in the order of the fiber diameter.

2.4 Permeation setup

For the hydrogen permeation tests, the setup developed by TNO, Netherlands, shown in Figure 3 was used. This setup is capable of accommodating temperatures up to 325°C and pressures up to 2000 bars, although not necessary for this study. The working principle of the setup is based on the manometric method. The sample was mounted in the permeation cell to form the barrier between the two chambers. Both chambers were evacuated. Afterwards, one chamber was filled with hydrogen to 10 bars at room temperature. In the other chamber, the pressure increases because of the transmission through the specimen. The area available for permeation was 9.62e-4 m^2.

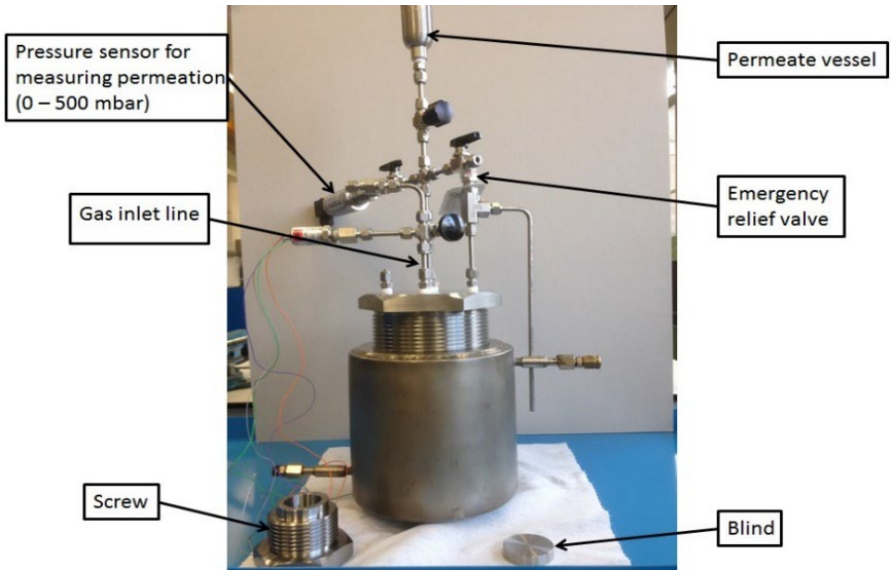

Figure 3. A view of the permeation setup.

3. Results and discussions

In Figure 4 the micrographs of the cross-section of the thick sample before and after 50 thermal cycles are shown. No evidence of cracks, voids and defects is recognized except for some resin-rich areas.

Figure 4. Micrographs of the polished cross-section of the thick laminate before -0 thermal cycles- (top) and after -50 thermal cycles- (bottom).

The CT scan images confirm the microscopic observations as shown in Figure 5 since no delamination or cracks are visible in the bulk of the material. It is of interest to mention the darker areas observed in the slices of the CT scan, indicating a variation in the fibre bundle motion, as observed also by other researchers [14].

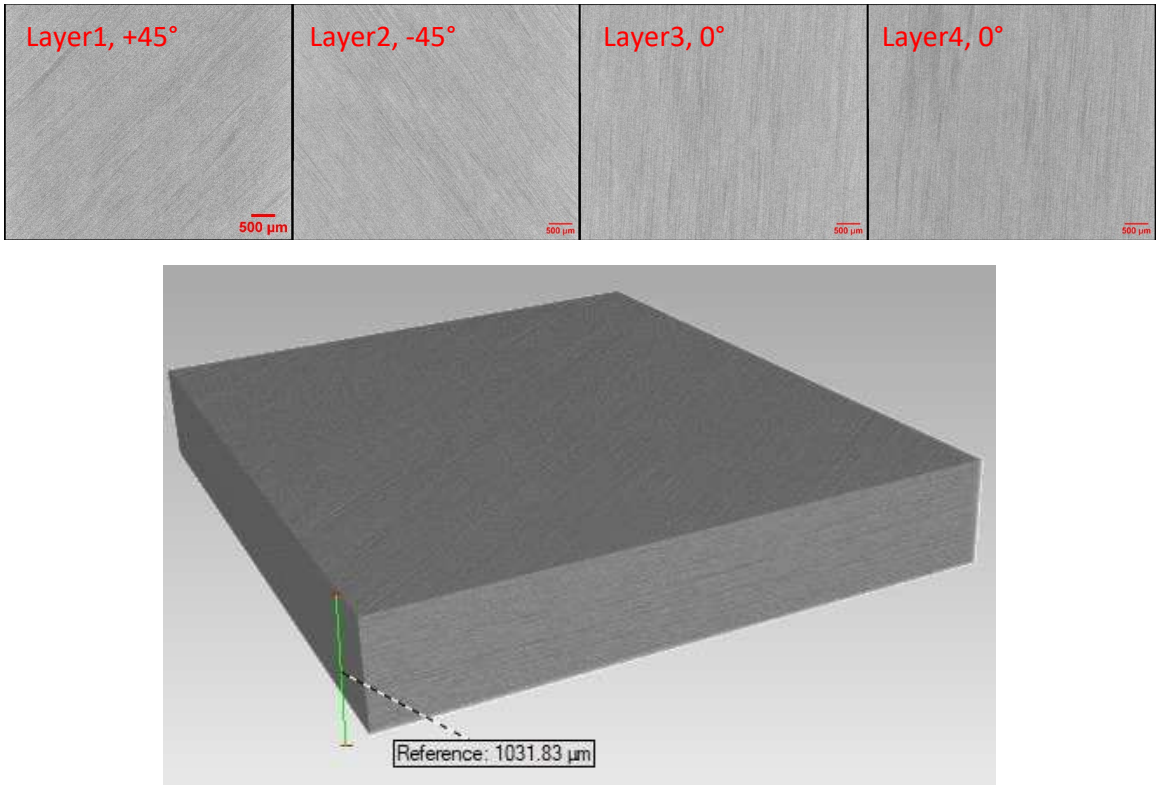

Figure 5. The CT scan images of each ply (top) and the bulk of laminate (bottom).

In Table 2, the permeability coefficients as the average of the two measurements are shown for the tested so-called thin and thick laminates. The permeability of the intact thin laminate with dispersing stacking sequence is 3.4 times higher than the thick laminate with grouped layers (i.e. 1.21e-17 vs. 4.1e-17 mol/(m.s.Pa)). A similar observation is also reported in the literature by

[6,15]. Figure 6 shows the consolidation of the layers of the thin and the thick laminates. In the thick laminate, grouped 0° layers at the centre have no clear boundaries and detecting each ply boundary is difficult, however with the thin laminates, the ply interfaces are more prominent. At the interfaces with non-similar fiber orientations, fibers are occasionally aligned very neatly with local high fiber volume fraction, which could potentially be the reason for the reduced permeability of the thin laminates (with dispersed plies) compared to the thick laminates (with grouped plies), since the aligned fibers are creating a thin physical block against the passage of the hydrogen molecules. This should be evaluated more in future work.

Table 2. Measured values of permeation tests with the unit of e-17xmol/(m.s.Pa). The percentages are the standard deviation of the two samples in the current work.

					Number of thermal cycles				
Reference	Permeant	Fiber	Matrix	Layup	0	1	10	30	50
[3]	He	AS4	PEEK	Thick	4.3 (5%)	4.5 (4%)	4.6 (4%)	5.0 (11%)	
[3]	He	IM7	PEEK	Thick	2.6 (15%)	2.3 (6%)	2.4 (7%)	3.2 (19%)	
[3]	He	AS4	PEEK	Thick	5.5 (1%)	4.9 (7%)	5.2 (6%)	4.9 (6%)	
[3]	He	N/A	PEEK	N/A	56.0				
Current Work	H_2	CF	LMPAEK	Thick	41.0 (2%)				44.6 (12%)
Current Work	H_2	CF	LMPAEK	Thin	12.1 (12%)				18.6 (19%)

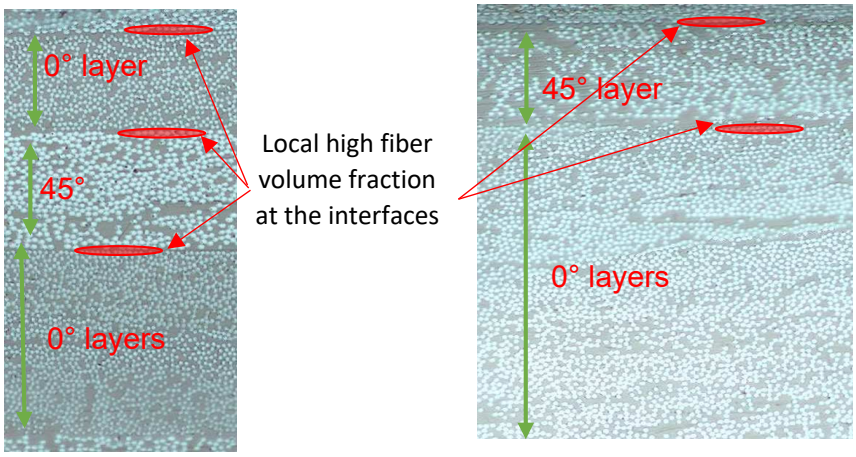

Figure 6. A zoomed view of interfaces for the thin (left) and thick (right) laminate.

Permeation data is also plotted in Figure 7. The effect of thermal cycling on the permeation measurements seems negligible for these materials, which is also observed in [3]. As compared to the literature data, the permeability values from the current work are higher, which could be because of the permeate difference (He vs H_2) or difference in the resin (PEEK vs LMPAEK). According to Humpenöder permeability measurements at room temperature using hydrogen results in a higher permeability compared to helium [13].

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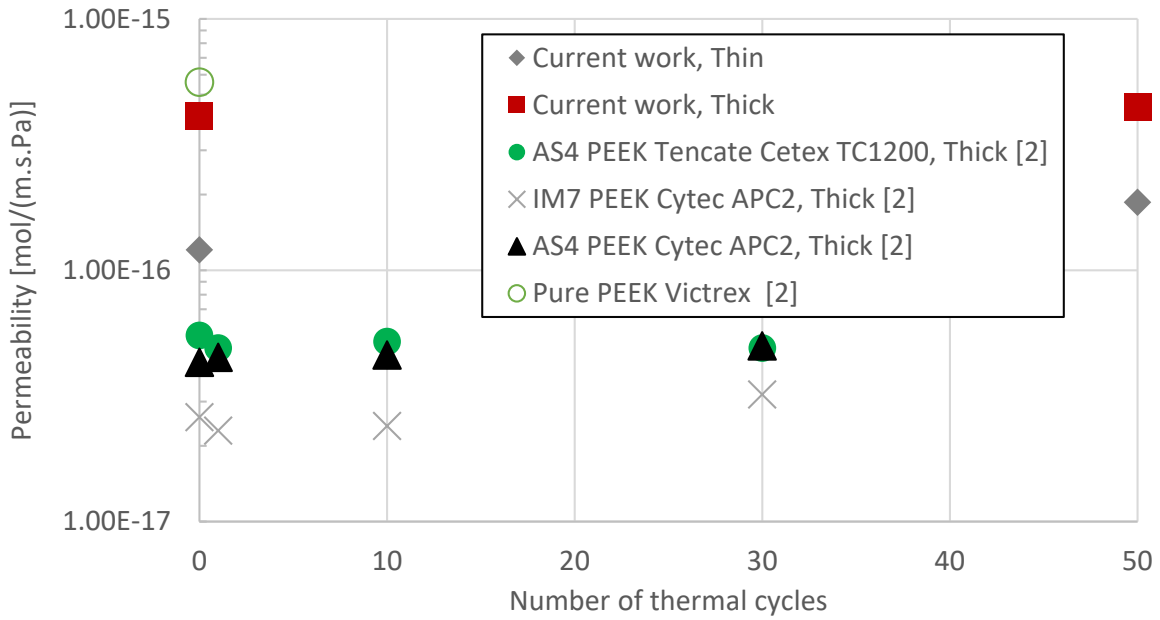

Figure 7. The measured permeation values as compared to the literature data.

4. Conclusions and future works

This work provides the hydrogen gas permeation values through laminates made of carbon fiber and high performance thermoplastic resin LMPAEK. It is encouraging to see that there is no observable crack network which would lead to permeation values that are several magnitudes higher compared to the values that are observed here. This work shed a light on the effect of the number of ply interfaces on the hydrogen permeation. Permeation measurements for "thin" specimens are lower compared to the "thick" specimen, indicating that dispersing the oriented plies through the thickness instead of grouped layers is favourable for lowering the permeation. The results show that for both "thin" and "thick" configurations, subjecting the specimen to a thermal cycle has a negligible effect on the permeation. It is confirmed by the microscopic imaging and the CT scans that there are no visible cracks in these materials. However, images with improved scanning technologies at higher resolution could help to investigate the presence of nano cracks at for instance the fiber/matrix interface. The permeation values are slightly higher compared to the CF/PEEK laminates reported in the literature. The reason could be, among other unknowns and uncertainties, the difference in permeating gas since in this current work hydrogen was used and the results from the literature are based on helium permeation. Therefore, another round of permeation tests with helium gas is suggested. Also, the type of resin is different which could lead to the observed difference. This can be also checked by testing the pure LMPEAK material using both helium and hydrogen gas. The future work may include mechanically induced cracks to represent the load cases similar to the hydrogen tanks.

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