LEAKAGE INVESTIGATION OF EPOXY-BASED COMPOSITE LAMINATES FOR REUSABLE CRYOGENIC PROPELLANT TANKS

C. Rauh, T. Reimer

German Aerospace Center (DLR e.V)
Institute for Structures and Design
Pfaffenwaldring 38-40, Stuttgart, Germany

J. Wilken

German Aerospace Center (DLR e.V)
Institute of Space Systems
Robert-Hooke-Straße 7, Bremen, Germany

ABSTRACT

Experimental studies on the gas leakage behaviour of carbon composite laminates are taking place at the German Aerospace Center to further promote the potential use of carbon fibre composites as propellant tank material for reusable launch vehicles. The leak rates of IM7/5320-1 prepreg unidirectional and cross-ply samples are measured using helium mass spectrometry. The leakage behaviour of the samples shows a significant deterioration after being cryogenically cycled with liquid nitrogen. Samples featuring thin plies with approximately 20 % of the standard ply thickness are also tested to assess their impact on leakage resistance. The latest results indicate an enhanced gas-tightness of cross-ply laminates with thin plies at helium gauge pressures of 2 bar, but no significant advantage at 4 bar compared to the UD samples. The helium leakage test bed and the test routine are presented along with the latest results and future plans of this ongoing work.

***Index Terms*—** RLV, Cryogenic Tank, CFRP, Permeation, Leakage

1. INTRODUCTION

Reusable launch vehicles (RLV) are internationally endorsed for sustainable future space transport missions. However, not only their ecological but particularly their economical benefits need to be considered for their long-term implementation in global competition [1]. An effective way to increase the performance of a launch vehicle and thus lower the specific payload cost is the reduction of the dry mass. This is even more critical for RLV than for expendable launch vehicles, due to the additional effort needed to safely return stages. In order to be cost effective, these light structures also have to be reliable and low maintenance.

For launchers with cryogenic propellants, the tank structure is a substantial mass portion of the vehicle. Hence, carbon fibre composites as structure material offer a promising weight saving potential compared to conventional aluminium designs [2]. However, the frequent temperature changes to cryogenic conditions can lead to transverse microcracks due to the complex anisotropic nature of the material, possibly reducing mechanical strength and causing the formation of gas leakage paths.

Due to the successful results of the DC-XA project in the early 1990s with the first out-of-laboratory flight test series of a reusable composite liquid hydrogen (LH2) tank [3], the composite technology was further investigated during the X-33 project of NASA and industrial partners. The X-33 was a subscale RLV demonstrator vehicle featuring a graphite composite LH2 tank [4]. Consisting of four lobes, the tank was an innovative sandwich structure with IM7/997-2 graphite/epoxy facesheets and a Korex® honeycomb core. However, it failed critically after a protoflight pressure and loads test under LH2 conditions of -258 °C in 1999. After the LH2 was drained, the outer facesheet and the core separated locally from the inner facesheet during the tank purge routine. In combination with manufacturing flaws and infiltration of external purging nitrogen, microcracking of the inner facesheet was determined as one major cause of the failure, leading to higher core pressures due to the expansion of the penetrated hydrogen, eventually causing delamination and separation of the facesheets [5].

The setback of the X-33 project was not the end of carbon composites in cryotank technology. The lessons learned were incorporated in the composite cryotank technology development (CCTD) project of The Boeing Company and NASA. Aiming for the increase of the technology and manufacturing readiness levels, two composite tank demonstrators of 2.4 m and 5.5 m diameter were built and structural, thermal and permeation tests were performed successfully [6]. The composite material was the carbon fibre/epoxy resin prepreg system IM7/5320-1, which is particularly suitable for manufacturing large structures due to its out-of-autoclave curing capability [7, 8].

Within the last decade, great progress was made in composite tank technology, but no reusable composite tank for cryogenic propellants has been matured yet for commercial use. For the use in an RLV, a suitable thermal protection system (TPS) is needed to protect the structure from high re-entry heat loads. Also the possibility of repairing or refurbishing

the composite structure to extend the tank's operating life and thus to increase the number of missions is desired. The German Aerospace Center (DLR) contributes to these fields as part of the ongoing project TRANSIENT [9]. Preliminary studies addressing the gas tightness of epoxy-based carbon composites are carried out in the project using helium mass spectrometry. The paper describes the manufacturing process of the laminate samples and both the test rig and the test routine are presented. The leak rates of uncycled samples of different laminate designs with and without thin plies are compared with samples thermally cycled using liquid nitrogen. The paper concludes with an outlook of future tests and assessments.

2. LEAKAGE AND PERMEATION IN CARBON COMPOSITES

Despite of their superiour specific strength and stiffness properties, carbon composites are still not established as lightweight cryogenic tank material. This is mainly due to their highly anisotropic thermal properties. The linear coefficient of thermal expansion (CTE) mismatch of fibres and resin matrix and the CTE differences of the individual layers depending on the fibre orientation generate residual thermal stresses after cure which can induce the formation of transverse microcracks. If it comes to RLV propellant tanks, repeated fill-and-drain cycles between cryogenic and ambient temperatures with combined pressure and vehicle body loads provoke crack propagation, in the worst case leading to distinctive transversal leakage paths.

Liquid hydrogen is a common fuel especially for heavy launchers because of its high performance in combination with liquid oxygen (LOX). But due to its small molecular size, it passes through the tiniest leakage paths, eventually posing a serious hazard if the gas mixture reaches the critical explosive limit. Moreover, gaseous hydrogen can permeate through flawless material. Permeation is driven by concentration and pressure differences and is dependent on the temperature and the material's wall thickness. Robinson [10] highlighted the importance of defining allowable hydrogen permeation rates for RLV composite laminate designs, depending on ratings like mission profile and location on the tank. He concludes that properly designed composites can meet the allowable limits if microcracking is controlled.

Many experimental studies have been conducted in order to form a better understanding of composite permeability and microcracking behaviour under cryogenic loads. Timmerman et al. [11] found that microcrack progression leveled off rapidly after the first cryogenic cycle, leading to the assumption that microcracking effects on leakage behaviour can be adequately assessed after only a few cycles. Moreover, his results showed that a higher fibre tensile modulus cause more and larger microcracks and the resin properties play a significant role in cracking behaviour.

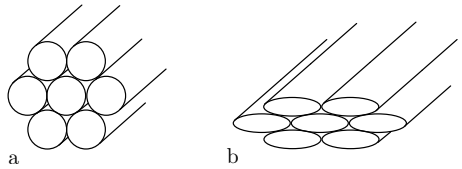

Fig. 1. Idealised scheme of a) conventional tows and b) spread tows.

Since Crossman et al. [12] stated the advantageous effect of reduced ply thicknesses of below 100 µm on the reduction of transverse cracking, the use of thin plies as permeation barrier has been investigated thoroughly [6, 13, 14]. Thin plies are realised by spreading conventional fibre tows, as schematically shown in Fig.1, resulting in a greatly reduced areal weight, improved damage tolerance and weight-specific load-carrying capability [15]. The successfully manufactured and tested LH2-cryotanks of the CCTD project are probably the most prominent examples of thin plies in cryotank technology. They were added to the conventional prepreg plies as microcrack-resistant hydrogen permeation barrier. The tank permeation test results indicated an improved performance and permeation limits for upper and boost stage composite tank applications could be met [7].

3. EXPERIMENTAL SETUP

3.1. Sample preparation

All samples for the leak rate measurements were made of IM7/CYCOM®5320-1 unidirectional 145 g/m^2 prepreg with 33 % resin content. Square panels with an edge length of 350 mm were manufactured via vacuum-bag-only cure with the vacuum bag arrangement and the cure cycle according to the product's data sheet [8]. Up to four square samples of 125 mm edge length were cut out of each panel. Most of the samples have a symmetric cross-ply lay-up with alternating 0° and 90° layers. These laminates are free of extension-bending coupling and thus do not warp with temperature fluctuations. However, the thermal residual stresses are high due to the maximum angular difference of 90° [16]. Hence, cross-ply laminates should show a sensitive reaction to thermal cycling which was considered beneficial for the study.

The thin plies were realised using TeXtreme® spread tows of the Swedish company Oxeon. The spread tows are provided as 15 mm unidirectional IM7 tapes with an areal weight of 50 g/m^2 and as plain weave fabric. No additional resin was used when applying the spread tows to the prepreg plies because the 5320-1 resin was not available separately. Nevertheless, the excess resin from the prepreg layers infiltrated the dry spread tow layers sufficiently during the vacuum process. Scanning electron microscopy proved a homogenous laminate quality with a low void content.

Table 1. Overview of manufactured and tested laminate samples.

Sample ID	Stacking sequence	Cycled?	Thickness mm
Stainless steel	–	no	2.0
UD P1	$[0^\circ_{15}]$	yes	2.1
UD P2	$[0^\circ_{15}]$	yes	2.1
5TP P1	$[0°/90°/0°/90°/0°/90°/0°/90°_{TP}/0°_{TP}/\overline{90°_{TP}}]_S$	yes	2.08
5TP P2	$[0°/90°/0°/90°/0°/90°/0°/90°_{TP}/0°_{TP}/\overline{90°_{TP}}]_S$	yes	2.08
19TP P1	$[0°/90°/0°/90°/0°/90°/0°/90°_{TP}/0°_{TP}/90°_{TP}/0°_{TP}/90°_{TP}/0°_{TP}/90°_{TP}/0°_{TP}/90°_{TP}/\overline{0°_{TP}}]_S$	yes	2.5
10TPF P1	$[0°/90°/0°/90°/0°/90°/0°/(0°/90°)_{5f}]_S$	no	2.2

The detailed laminate design for each tested sample including the sample thicknesses can be found in Table 1. A 2 mm stainless steel plate was tested for comparative reasons and to verify the gas-tightness of the test facility. All the thin ply samples (TP) and the thin ply fabric samples (TPF), contain the same number of conventional prepreg plies. This results in different sample thicknesses with the one containing 19 layers of thin plies being the thickest with 2.5 mm. Sample 10TPF P1 contains 10 layers of spread-tow cross-ply plain weave fabric instead of tapes.
Thermal cycling was carried out using liquid nitrogen (LN2). The LN2 boiling temperature is -196 °C, hence not as low as the boiling temperature of LH2 which is -253 °C, but it is a safe cryogenic substitute suitable for laboratory tests. The samples were immersed into an LN2 storage dewar for 5 minutes and then allowed to equilibrate at room temperature again before they were either cycled again or placed into the sample holder for testing.

3.2. Test facility

The leak tests were carried out with the helium leak detector ASM340 from Pfeiffer Vacuum. The ASM340 uses a mass spectrometer for quantitative measurements of helium gas leak rates down to $1{\cdot}10^{-12}$ (mbar l)/s. Helium is a safe alternative to hydrogen due to its non-toxic, non-explosive properties and is commonly used for leak testing. Due to its high sensitiveness to the test gas, the test facility is located in a vented laboratory to prevent the accumulation of helium in the surroundings of the detector in case of a leakage.
The test setup is schematically shown in Fig. 2. The sample is placed between the two chambers of the sample holder which are screwed together, enabling a varying sample thickness. Viton O-rings with an inner diameter of 100 mm seal the test area on both sides. All the measurements described in the following took place under room temperature.
During a test run, the predefined helium test pressure is applied on one side of the sample while vacuum is created on the other side by the integrated rotary vane pump of the leak detector. The helium pressure p_1 is monitored by a pressure transmitter of the PR-33X series by Keller with a range of

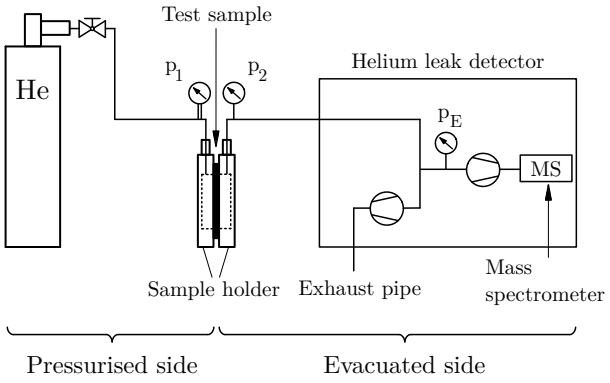

Fig. 2. Helium leakage test rig schematic.

0-10 bar relative to ambient pressure. The pressure p_2 on the vacuum side is monitored by the Keller absolute pressure transmitter PAA-33X with a range of 0-1 bar. If helium passes through the composite sample, it diffuses against the gas flow being pumped by the turbomolecular pump into the mass spectrometer, while heavier gases are held back. The leak detector outputs both the leak rate LR in (mbar l)/s and the inlet pressure p_E at the pumping port of the vacuum port. All fittings and seals have been checked for leakage with a second leak detector at 4 bar helium gauge pressure to exclude interferences caused by leakage.
The advantage of the test rig is its mobility and flexibility. The detector can also be used in sniffer mode to check large pressurised volumes for leaks. Additionally, measurements under LN2-conditions can be carried out with an adapted sample holder.

3.3. Testing procedure

After the sample is placed into the sample holder, vacuum is applied by the integrated pump of the helium detector. Following a warm-up period of at least 20 minutes, the internal leak rate calibration routine is started. After completion, the helium background, which usually results in a leak rate on the

order of 10^{-8} to 10^{-9} (mbar l)/s for the test facility, is subtracted from the signal. This is crucial to reach the desired measurement sensitivity. Otherwise, the background signal is added to the measured leak rate, consequently hiding smaller leaks. From now on, the helium gauge pressure is applied on the sample and is held constant throughout the test period. For the tests presented here, gauge pressures of 2 bar and 4 bar have been chosen to assess the influence of different test pressures on the sample leak rates.
Test time starts when the helium test pressure is applied and continues either until LR_{limit} is exceeded or until the leak rate has reached steady state. Depending on the sample properties, the test duration is less than 1 hour if leakage is present, or up to 56 hours if the leak rate increases slowly due to permeation.

4. RESULTS AND DISCUSSION

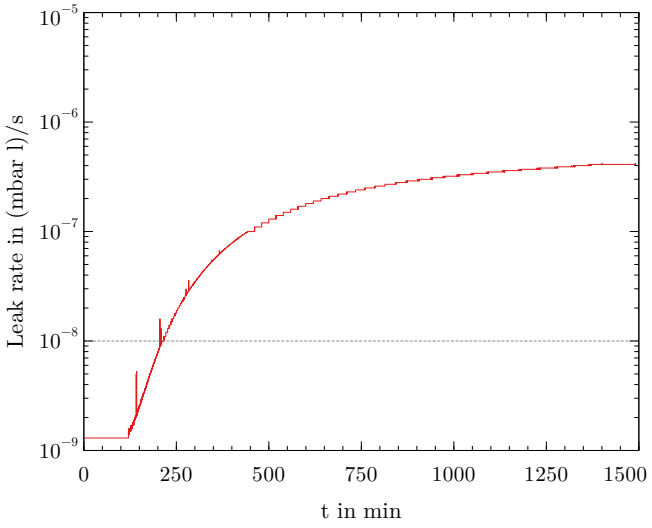

Fig. 3. Leak rate over testing time of cycled sample UD P2 at 4 bar test pressure.

The graph depicted in Fig. 3 shows a representative leak rate curve of a test run. After applying 4 bar gauge pressure, no permeating helium was detectable for 130 minutes. After that, the leak rate started increasing until it eventually approached a steady-state value of $4.1{\cdot}10^{-7}$ (mbar l)/s after over 22.5 hours. This example shows the unidirectional sample UD P2 which presumably has not developed severe distinct leak paths despite of being thermally cycled. Leak rates due to permeation are usually several orders of magnitude lower than leak rates due to transversal microcrack channel structures. The leak rate of cracked samples would show an immediate sensor response after pressurisation.
In general, $LR_{limit} = 10^{-8}$ (mbar l)/s is defined as maximum acceptable leak rate for an LH2-tank wall material, though it is difficult to find a recommendation in the literature. From the samples tested so far, all have exceeded this value, but

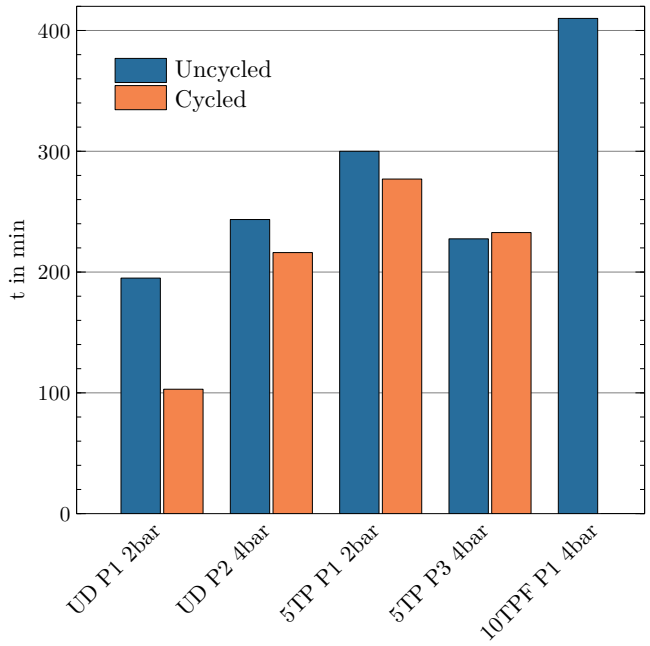

Fig. 4. Test time required to reach $LR_{limit} = 10^{-8}$ (mbar l)/s at 2 bar and 4 bar test gauge pressure for cycled and uncycled samples.

there are clear differences in the test time required to do so. Because cryogenic tanks are supposed to be drained when the launch is delayed, it is considered acceptable when LR_{limit} is exceeded after a specific time.
The bar chart in Fig. 4 illustrates the required time for uncycled and cycled samples at test pressures of 2 bar and 4 bar. Independently from the gauge pressure, the cycled samples reached LR_{limit} in a shorter test time than in their uncycled condition, except for sample 5TP P3 tested at 4 bar. However, the time difference is only 5.2 minutes compared to uncycled 5TP P3. The sample P1 from the same laminate plate tested at 2 bar deteriorated more significantly after cycling with a time difference to the uncycled condition of 23 minutes. Moreover, the doubled test pressure of 4 bar resulted in a 24 % and 16 % shorter time until LR_{limit} was reached for the uncycled plate and the cycled plate, respectively.
The results of the UD plates show an ambiguous behaviour, with the sample tested at 4 bar achieving much better values than plate P1 tested at 2 bar. The cycled UD P2 unexpectedly took 16 minutes longer to reach LR_{limit} than the uncycled thin ply-sample 5TP, however, the reason for this is most likely the higher thickness of UD P2. The comparatively short required times of 195 min and 103 min of UD P1 uncycled and cycled, respectively, is most likely due to internal flaws in the laminate. It can be expected that a flawless plate could reach similar values like 5TP P1 because both plates achieved a similar time with 4 bar gauge pressure, but further investigations are needed.

The best performance by far showed sample 10TPF whose leak rate remained below the limit for 410 minutes. Since it is also the thickest laminate, more samples need to be made to assess whether the better performance can be attributed to the usage of fabric or to the thickness. Measurements with cycled plates are still pending.
While only a few plates have been studied for their leakage characteristics yet, interesting trends are already emerging which require further investigation. Multiple samples per laminate need to be examined to capture effects actually tied to the laminate design. The future samples should also be of the same thickness to improve the comparability.
Additionally, the influence of the manufacturing method should be investigated. The residual stresses of a wound cylindrical tank vary from the ones of a flat plate. Consequently, it is assumed that the microcracking behaviour of an actual tank differ from the flat samples. The development of numerical models in combination with experimental validations could support the development of microcrack-resistant composite tank walls.
Moreover, an assessment of the applicability of the simplifications commonly made in the laboratory environment needs to be done. Hydrogen molecules are slightly smaller than helium molecules, hence their permeation capability should also be higher. Schultheiss [17] compared hydrogen and helium permeation and concluded that both gases permeate similarly. However, low leak rates can not be detected with hydrogen due to the higher hydrogen background signal within a mass spectrometer. Furthermore, hydrogen leak rates are strongly dependent on environmental parameters like sunshine duration. Because of this, Schultheiss concluded that hydrogen measurements do not reach the high quality of helium permeation measurements.
Secondly, the question arises if the results of the measurements taking place under room temperature are applicable to the cryogenic conditions of a propellant tank. However, Yokozeki et al. [18] showed that leak rates of carbon/epoxy laminates differed only slightly between room temperature and LN2 temperature. He concluded that the reduced molecular kinetics due to cryogenic conditions compensates partly for the damage-induced gas leakage increase. Further investigations are pending to prove if these results can be reproduced within the frame of the previously described experiments.

5. CONCLUSION AND OUTLOOK

As part of the ongoing DLR-project TRANSIENT, the potential use of carbon fibre reinforced plastics as cryogenic tank wall material for reusable launch vehicles is investigated. To do so, a test facility to measure the helium leak rate based on mass spectrometry is introduced. The leak rates of carbon composite unidirectional and cross-ply samples made of IM7/5320-1 were assessed at room temperature before and after being thermally cycled with liquid nitrogen. Cross-ply samples containing thin plies were also tested and showed an improved performance compared to UD samples, though more in-depth assessments are pending. More laminate variations need to be assessed as well as the influence of a higher number of cryogenic cycling on the leak rate deterioration.
Overall, the results show that the test facility is well suited for both quick leakage and detailed permeation investigations. The test bed will be upgraded with the possibility of cryogenic measurements in liquid nitrogen conditions. The currently recorded measured variables of pressure and leak rate are going to be supplemented by temperature and strain.
Furthermore, two major concerns regarding composite cryogenic tanks for RLV applications are going to be addressed in the further course of the project TRANSIENT. First, the refurbishment of the composite structure is going to be investigated. Previously leak-tested composite samples will be impacted, repaired and then tested for leakage. Second, the integration of a thermal protection system onto the carbon composite tank structure is investigated in the project. An attachment system for the TPS is designed with respect to the thermal boundary conditions of an RLV booster stage. Subsequently, an integrated test object (ITO) will be manufactured including a cryogenic insulation layer and a simplified TPS which is connected mechanically to the composite test structure. The thermal design of the ITO comprises the integration of a purge flow within the insulation system to keep temperatures in the TPS at acceptable values during steady-state cold conditions before launch. Finally, the ITO will be tested under combined re-entry thermal and mechanical loads.

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