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Breakthrough safety technology of explosion free in fire self-venting (TPRD-less) tanks: The concept and validation of the microleaks-no-burst technology for carbon-carbon and carbon-glass double-composite wall hydrogen storage systems

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HIGHLIGHTS

- Breakthrough safety technology of explosion free in fire tank is introduced.
- The tank made of 2 composites is self-venting in fire and does not require TPRD.
- The microleaks-no-burst concept of tank performance in fire is explained.
- 4 carbon-carbon and 3 carbon-glass tanks are successfully tested in 1 MW/m^2 fire.

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ABSTRACT

The paper describes the breakthrough microleaks-no-burst (μLNB) safety technology of explosion free in fire self-venting hydrogen tanks that do not require thermally-activate pressure relief devices (TPRD). The technology implies melting of the hydrogen-tight liner before hydrogen-leaky double-composite wall loses its load-bearing ability. Hydrogen then flows through the wall's microchannels and either burns in microflames on its own or together with resin. The experimental validation of the technology is presented for 7 prototypes with the nominal working pressure of 70 MPa made of carbon-carbon or carbon-glass composites. The prototypes are fire tested at the specific heat release rate HRR/A = 1 MW/m^2 characteristic for gasoline/diesel spill fires. The μLNB technology eliminates catastrophic consequences of tank rupture in fire: blast waves, fireballs, and projectiles. The technology limits hydrogen accumulation in naturally ventilated enclosures. It reduces the risk of hydrogen-powered vehicles to an acceptable level below that for fossil fuel automobiles, including underground parking and tunnels. It provides an unprecedented level of life safety and property protection.

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Introduction

Thermally activated pressure relief device (TPRD) is currently the main engineering solution for the protection of composite storage tanks against rupture in a fire. Besides safety problems with this solution, e.g. inability of TPRD to react to a localised fire or another kind of a fire of low intensity, it is notable that there had been no models to design a tank-TPRD system that excludes its rupture in engulfing fire until the HyTunnel-CS project [1] research [2]. To mitigate the pressure peaking phenomenon (PPP) [3–6] in garages, repair shops, hydrogen storage enclosures onboard of ships, trains, planes and other enclosures with limited ventilation, the diameter of TPRD release orifice should be comparatively small or enclosure venting area should be relatively large. However, TPRD orifice diameter required to avoid tank rupture in engulfing fire can be too big for compressed hydrogen storage system (CHSS) of large volumes. Thus, it is hard to impossible to avoid the destructive PPP in hydrogen storage enclosures for CHSS using TPRD. Besides, TPRD produces long flames and could jeopardise life, the integrity of structures and hydrogen system elements around it, including other hydrogen storage tanks.

The typical diameter of TPRD orifice used, for example, in current hydrogen-powered cars, is 2 mm. This diameter does not provide the required safety level for underground parking of fuel cell vehicles as demonstrated by the HyTunnel-CS project studies. Indeed, in case of unignited hydrogen release such TPRD does not exclude the formation of flammable cloud under the ceiling of parking that can deflagrate or even detonate. TPRD orifice of 2 mm diameter does not prevent the presence of hydrogen combustion products with temperature above 300 °C under the ceiling of a car park that could damage the ventilation system. The HyTunnel-CS research revealed that TPRD orifice diameter of 0.5 mm is suitable to avoid flammable cloud and hot combustion products formation under the ceiling of an underground parking. However, this is not achievable for every CHSS as the bigger TPRD diameter is needed to prevent larger volume CHSS rupture in a fire. The only acceptable solution for confined spaces like underground parking and tunnels is the release of hydrogen in the way that excludes formation of flammable hydrogen-air cloud and hotter than 300 °C combustion products under the ceiling of underground traffic facility. This is achievable with the microleaks-no-burst (μLNB) safety technology invented at HySAFER Centre of Ulster University [7].

The CHSS of conformable tanks in the SH2APED project [8] composed of several interconnected tanks, includes a few TPRDs each with an orifice diameter above 2 mm. The opening of only one TPRD creates unacceptable conditions at underground parking and could destroy a hydrogen storage enclosure unless the comparatively large vent area is available. This can be a particularly challenging engineering problem for hydrogen storage enclosures onboard of buses, trains, ships, planes, etc. The simulations performed at HySAFER using the unique in-house modelling tools have demonstrated that the breakthrough safety technology of μLNB self-venting tanks excludes conformable tanks rupture in fire as well. Validation experiments will be performed in 2023 as a part of the SH2APED project research programme.

The quantitative risk assessment of scenarios with onboard tank rupture in fire for hydrogen-powered vehicle incident in the open [9] and in the tunnels [10] is carried out. It is shown that the risk is unacceptably high for currently used standard tanks with the fire resistance ratings (FRR), i.e. time to rupture in a fire, of few minutes, e.g. 4–6 min [9,10] in typical for traffic incidents gasoline/diesel spill fires with specific heat release rate of HRR/A = 1–2 MW/m^2. To achieve the acceptable level of risk the fire resistance rating (FRR) should exceed 50 min (example of London roads) and 90 min (the Dublin tunnel), respectively. The situation aggravates by the fact that the GTR#13 fire test protocol allows reduced localised fire intensity of HRR/A = 0.3 MW/m^2, i.e. below HRR/A = 1–2 MW/m^2 characteristic for gasoline/diesel spill fires [2]. The use of thermal protection of hydrogen storage tanks by intumescent paint would require an excessive amount of protection material that implies the increase of CHSS size, weight, and cost. The sustainability of intumescent paint to cycling and wear-resistance to weather and other operating conditions has not been investigated, reported and can be unacceptable. This is impractical and can hardly be accepted by original equipment manufacturers (OEMs). The sensitivity part of quantitative risk assessment (QRA) study [10] reveals that the risk of a catastrophic failure of typical CHSS in a road tunnel fire is unacceptable. This QRA study concludes that there is a need for a safety technology that could eliminate hydrogen tanks rupture in any fire to protect life and property and underpin inherently safer deployment of hydrogen-powered vehicles.

One of CHSS designs of conformable tanks for automotive applications with several inter-connected vessels developed in SH2APED shall be placed in a metal casing. This is to protect the system from mechanical impacts, road acids, fire, etc. However, simulations of a fire scenario for conformable tanks with a metal casing located underneath a passenger car overturned in an incident demonstrated the following. For the case of metal casing being in direct contact with the composite overwrap, e.g., during traffic incident, and the fire source being a gasoline spill fire with HRR/A = 1 MW/m^2, the obtained FRR of a conformable tank is only 1 min 17 s. It is worth mentioning that the FRR of such a tank without the casing is longer, i.e., 2 min 9 s. This time is comparable and below the TPRD response to fire time, e.g. 2 min 17 s [11]. The result of such fire scenario for standard conformable tank would be its rupture in the fire. Hence, an engineering solution to prevent tank rupture is notably needed, especially when it comes to a localised fire from a fuel spill or a smouldering fire, whereby the chances of TPRD activation are close to zero.

There are several technological solutions to extend the FRR of a CHSS. In 2007 Gambone and Wong [12] suggested to use a ceramic material cover wrapped around the polymer composite layer or an insulating foam shell that has the whole storage system inside. In 2010 Webster [13] recommended a ceramic blanket wrapped by an outer steel shell. The tank withstood a localised fire for 30 min without rupture. In 2015 Villalonga et al. [14] proposed to use a silicon-filled elastomer to cover the tank. Intumescent paint has always been a popular choice for passive fire protection of structural steel buildings. The intumescent coating remains inactive at room temperature, but when heated, it may expand up to a hundred times of its original thickness forming foam/char layer to serve as a thermal insulator. In 2016 the effect of one of such paints for protection of hydrogen storage tanks was studied by Makarov et al. [15]. The experiments confirmed that a 36 L Type IV tank with nominal working pressure NWP = 70 MPa withstood a fire with HRR/A = 0.6 MW/m^2 for 2 h without rupture. Unfortunately, the use of intumescent paint increased the tank wall thickness by 72% in that case. It should be mentioned that the design of vehicle and CHSS should allow the intumescent paint to expand. The last would require additional space which is not easily available, especially onboard of vehicle. The protective measures mentioned above add weight, size, and cost to CHSS. They cannot provide protection for fires of long duration like Mont Blank tunnel fire. Intumescent paint can be eroded by high pressure impinging jet, e.g., from nearby hydrogen storage tank, etc. Thus, the use of intumescent paint cannot ultimately exclude tank rupture in any fire. The discharge of hydrogen from the CHSS protected by such means after fire extinction is another unresolved issue. Contrary to that, the μLNB safety technology provides self-venting of CHSS in a fire and reduction of pressure within the CHSS to the atmospheric pressure even after fire extinction as will be demonstrated in a separate paper we plan to publish.

There is a strong safety advantage of Type IV tanks with polymer liner compared to Type III tanks with metallic liner. The reduction of the state of charge (SoC), which is directly related to the hydrogen pressure inside the tank, to about a half of 100%, can make Type IV tank leak in a fire, rather than rupture. This phenomenon was observed experimentally in 2012 by Ruban et al. [13], confirmed later in 2019 by Blanc-Vannet et al. [9,14], and then in 2021 studied numerically and explained by Kashkarov et al. [16]. Numerical experiments [16] demonstrated that composite tank with plastic liner charged at reduced SoC can withstand a fire without losing its load-bearing ability by releasing hydrogen after liner melting. Ruban et al. [17], carried out fire tests of 36 L Type IV tanks with NWP = 70 MPa at initial pressures of 17.8, 35.6, 70.3 and 70.6 MPa. The tanks filled at the two last pressures ruptured in the fire in 5.5 and 6.5 min respectively, i.e., demonstrated typical FRR of fully filled standard tanks. One of these tests was performed with a localised fire mode. The authors concluded that FRR does not depend on whether it is localised or engulfing fire. This underpins the suggestion of the authors of current study that the fire test protocol of GTR#13 [17,16] should be amended, and include the requirement of HRR/A to be the same in localised and engulfing stages. Both tanks were filled close to NWP and ruptured in localised fire (regulated to be of 10 min duration). The authors of the experimental study [17] concluded that the tank "as a whole needs to be protected from localised fire". The tank filled at 35.6 MPa, i.e., about half of the NWP, ruptured at almost 10 min. Finally, the tank filled at 17.8 MPa did not rupture, but leaked. The hydrogen-leaky performance of similar tanks was also observed in experimental study [18], where the tanks were filled at 10, 25, 52.5 and 70 MPa and the fire source was made of 4 pipe burners releasing hydrogen-oxygen premixture producing flow with temperatures higher than hydrocarbon fires and significantly higher HRR/A estimated as 7.45 MW/m^2 [1]. The tanks pressurised at 52.5 and 70 MPa ruptured at about 5 and 4 min, respectively. The shorter FRRs compared to tests in Ref. [13] can be explained by using fire source with higher HRR/A [2]. Tanks pressurised at 10 and 25 MPa leaked in a fire without rupture.

Apart from the initial pressure in the tank directly related to SoC, there is another factor influencing the FRR of hydrogen storage tank. This is the non-uniformity of a composite wall thickness. The tank with variable wall thicknesses loses load-bearing ability in the thinnest wall thickness region, i.e., in the dome section as filament winding technology "naturally" makes dome thinner than cylindrical part. A combination of helical and hoop layers during the winding process creates a thinner wall in the dome area. The domes are the thinnest areas, as being generally wound as helical layers and located midway between the cylindrical part end and the boss neck. These thinnest areas, however, offer mechanical strength to the tank up to its required burst pressure (currently 2.25 times of the NWP). The dependence of FRR on the tank wall non-uniformity was discussed in Ref. [16]. The 36 L Type IV tank with NWP = 70 MPa had a difference in cylindrical and dome wall thicknesses of 20%, which gave a difference in FRR as big as 34%. This difference in the FRR can be resolved by providing a uniform composite overwrap wall thickness. This is a manufacturing challenge resolved in μLNB tank prototypes following Ulster's design. It was also observed that the liner thickness variations in cylindrical and dome areas can affect the minimum SoC, at which the leaky performance of Type IV tanks can be expected [16]. The technological increase of the liner thickness in the dome area, compared to the cylindrical part by 38% has led to the significant reduction of the limiting SoC for leaky performance instead of rupture from 50% to 33%. This underlines the benefits of liner manufacturing by injection moulding compared to rotomoulding due to better control of liner thickness throughout the whole internal surface of the tank.

This paper presents the original concept of the breakthrough safety technology for Type IV tanks [7] – μLNB, which resolves many if not all safety concerns of CHSS by the exclusion of storage tank rupture in any fire. It describes in detail and analyses experimental validation of the technology for carbon-carbon and carbon-glass combinations of fibres in double-composite wall.

Breakthrough microleaks-No-burst safety technology

The concept

The technology is the subject of the intellectual property (IP) of Ulster University "Composite pressure vessel for hydrogen storage" [7]. Fig. 1 shows the typical structure of the μLNB Type IV tank designed following the technology and its schematic performance in a fire.

Fig. 1a demonstrates a μLNB tank in longitudinal middle cross-section, consisting of plastic liner (yellow), metal bosses (dark blue), the first structural fibre reinforced polymer (FRP) layer (light grey), and the outside thermal protection layer (TPL) (dark grey) that is usually another load-bearing composite with lower heat conductivity or intumescent paint layer (see disadvantages of this option mentioned above).

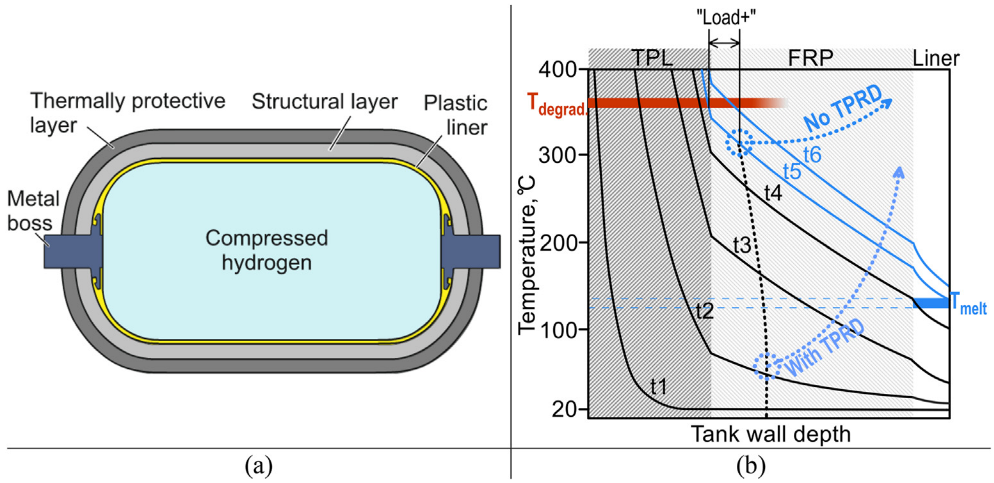

Fig. 1 – (a): Typical structure of μLNB tank. (b): Schematic performance of μLNB tank in fire [7].

Fig. 1b shows the tank wall depth (x-axis) and the temperature distribution through the wall for different moments (y-axis). The wall has three layers denoted on the upper side of the diagram: TPL, FRP and the liner. On the left-hand side of the TPL the heat flux from a fire (not shown in the diagram) is applied to the tank wall. On the right-hand side, the liner is in contact with compressed hydrogen (also not shown in the diagram). The liner limits hydrogen permeation to the regulated level (it is hydrogen-tight) and is not a load-bearing layer. For the subject of this study, both TPL and FRP are load-bearing layers of the composite overwrap. Contrary to the liner, they are not hydrogentight. To initiate hydrogen leak through the composite wall microchannels, the polymer liner must melt during the fire at least in one location through its entire thickness. The wall should not lose its load-bearing ability before the liner melts. The black and blue bold curves descending from the left to the right across the wall are the temperatures at different times labelled as t1, t2, etc. The elevation of the curve at each next moment of time demonstrates the temperature increase inside the wall as the heat is transferred from the external fire through the tank wall to hydrogen inside the tank. The temperature range corresponding to the thermal decomposition/degradation temperature of the polymer resin in the composite, is shown with the red horizontal stripe labelled "$T_{degrad.}$". The temperature range covering the melting of the polymer liner, lies significantly lower than "$T_{degrad.}$" and is denoted with the blue horizontal stripe labelled "T_{melt}". The key requirement to the design and manufacturing of a μLNB tank is ensuring the structural integrity of the composite wall thickness fraction able to bear the load of increasing in the fire hydrogen pressure until the liner melts through its entire thickness at least in one location and initiates hydrogen release through existing microchannels in the wall.

The difference between the actual non-degraded composite wall thickness and the minimum wall thickness required to bear the increasing pressure load at the moment when the liner melts is named as "Load+" [16]. In Fig. 1b, the "Load+" thickness is shown at the fire test time "t5" (blue curve "t5"), when the liner melts through its entire thickness, as the distance between the position of the degraded resin front, $T_{degrad.}$ (red stripe), and the location of minimum load-bearing wall thickness (black dotted curve). The wall thickness fraction sufficient to bear the load, and its relation with the safety factor, i.e. ratio of the actual burst pressure to NWP (regulated currently as minimum 2.25), are important parameters in the original tank failure mechanism suggested by the authors in previous studies [1,15,19].

The composite wall thickness fraction that can bear the load (black dotted curve) "bends" to the left in time, towards the exterior side of the wall. This means that this wall thickness fraction increases as the pressure inside the tank grows during the fire due to the heat transfer.

Once the microleaks are initiated after the liner melting, the pressure in the tank starts dropping until it is equal to the atmospheric pressure. It is represented with the blue dotted curve labelled "No TPRD" bending to the right. This means that the minimum wall thickness fraction needed to bear the hydrogen pressure load without tank rupture, decreases quickly following the pressure drop. This fraction can theoretically decrease to "zero" when hydrogen pressure inside the tank drops to the atmospheric pressure (no load-bearing wall thickness is needed).

The similar curve labelled "With TPRD" shows the similar decrease of the load-bearing wall thickness fraction in the case when there is a TPRD installed on the tank (the TPRD could be installed on the μLNB tank, if wanted, yet it could have significantly smaller release orifice to eliminate problems with release in underground parking mentioned above) and is initiated earlier in a fire at time "t2". This, however, is not the case for a localised fire or smouldering fire affecting the composite wall, but not the sensing element of TPRD.

Design of μLNB tank by simulations

The design of μLNB tank by simulations requires the contemporary validated CFD model and knowledge of thermophysical properties of the liner and two composites to define their thicknesses keeping in mind the regulated permeation level and minimum safety factor of 2.25. Only some of the combinations of these composites in the wall for the selected liner material and thickness may be sufficient to achieve the μLNB behaviour of the Type IV tank. The

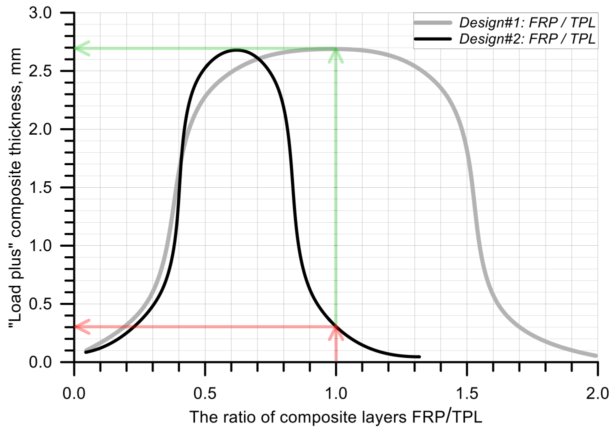

Fig. 2 – Schematic representation of the dependence of the "Load+" thickness on the ratio of thicknesses of composite layers FRP/TPL for two imaginary designs.

variations of the ratio of composite No.1 (or FRP1) thickness to composite No.2 thickness, i.e., TPL, within the same overall composite wall thickness significantly changes the "Load+", i.e., the safety margin in the wall thickness at the expected time of the microleaks initiation. For the same composite overwrap wall thickness, the ratio of the fractions of the primary load bearing FRP layer and TPL layer can vary for example, as 40%/60%, 50%/50% or 60/%/40% corresponding to FRP/TPL ratios 0.66, 1.00 and 1.50 respectively.

The numerical simulations of μLNB tank design for vessels of different volumes and length to diameter (L/D) ratios, have demonstrated that the "Load+" thickness varies as a function of the FRP/TPL thickness ratio and depends on the materials of these composites for the selected material and thickness of the liner. For demonstration purposes, the correlations between "Load+" and the thickness ratio FRP/TPL are schematically depicted in Fig. 2 for two different imaginary μLNB tank designs.

The μLNB tank of Design#1 has a notably wider peak of "Load+", with its highest value of 2.7 mm (y-axis), as shown by the grey curve and light green arrows in Fig. 2. This value is achieved at the thicknesses ratio FRP/TPL = 1 within the double-composite wall (x-axis). This means that the fractions of wall thickness occupied by FRP and TPL are 50% and 50%. This ratio provides the safest possible design for the chosen composite materials with the largest "Load+". If the ratio FRP/TPL equal or more than 2 for selected composites, the tank will rupture in a fire even it is built of two composites.

The μLNB tank of Design#2 (black curve in Figure) has the same maximum value of "Load+", but the peak is narrower and shifted towards lower ratio of FRP/TPL. The ratio FRP/TPL = 1 being suitable for Design#1 can result in significantly reduced "Load+" (in this case by 9 times!) for Design#2 (red arrows in Figure), i.e. only 0.3 mm. In fact, the peak value of "Load+" for Design#2 is achieved at FRP/TPL of about 0.6. The reduced "Load+" can compromise the safe performance of the μLNB tank in a fire due to routine deviations of fibre/resin ratios during composite winding, the liner thickness tolerance, etc. The wrong design or manufacturing of the double-composites wall with FRP/TPL more that 1.3 will results in its rupture in a fire.

It is highly important not to only control the thicknesses of both composites of the μLNB tank during manufacturing, either during the use of tow-pregs or wet-winding, but also to control the liner thickness uniformity, e.g., by using injection moulding technique instead of rotational moulding.

Experimental validation of the technology and discussion

The μLNB tank prototypes discussed in this paper, were designed at Ulster University and based on the original 7.5 L Type IV tanks with NWP = 70 MPa manufactured by our collaborator in the USA. Over 40 tank manufacturers and OEMs worldwide were reached out before the selection of the first μLNB tank manufacturer was concluded.

Several series of μLNB tank prototypes were designed, manufactured and assessed up to now and will be described in follow-up papers. Each series had the own distinct feature, e.g., different liners, FRP and TPL parameters, FRP/TPL ratios, different fire conditions, etc.

Each series of the manufactured prototypes underwent hydro-static and hydro-burst tests in accordance with [17,20,21] prior to fire testing. The hydro-static testing was set for pressures up to 150% of NWP and the actual pressures were in the range 104–105 MPa. The hydro-burst test was performed to demonstrate that the burst pressure is above 225% NWP, i.e., 157.5 MPa. The tank manufacturer conducted both types of tests using a Haskell hydrostatic equipment with a calibrated Omega pressure transducer.

Then the prototypes were tested in the fire following the GTR#13 protocol [17,16]. The tests were performed without TPRDs and at realistic HRR/A = 1 MW/m^2. Different fire scenarios to assess the μLNB tank performance were assessed in our studies, including the extreme conditions of impinging hydrogen jet fire from a nearby tank in the same CHSS, fire extinction by the firefighters, and hydrogen car removal from a fire. However, due to large volume of information they are out of scope of this paper and will be published in due course.

Carbon-carbon combination of fibres in double-composite wall

The first series of μLNB tank prototypes was designed using "carbon-carbon" (CC) combination of composites, i.e., the overwrap consisted of the first layer of carbon fibre reinforced polymers (CFRP), next to the liner, and the outside TPL, also being CFRP but manufactured using different resin. Two carbon fibres of different thermophysical and mechanical properties were used in the prototypes. They had different predetermined fibre/resin ratios. Four prototypes of composite overwrapped pressure vessel (COPV) with the same high-density polyethylene (HDPE) liner, were manufactured for the fire testing in this series, see Table 1. Tank prototype COPV#CC-4 had wall thickness equal to the original tank (increase of outside diameter of the tank is 0%) as requested by one of OEMs.

The typical pressure and temperature transients inside the μLNB tanks during the fire tests are shown for COPV#CC-1 (Fig. 3a) and for COPV#CC-4 (Fig. 3b). The initial pressure and

Table 1 – Parameters of a series of μLNB tanks with carbon-carbon fibre combination.

Tank No.	Liner	Layer No.1	Layer No.2	Outside D increase
COPV#CC-1	HDPE	CFRP#1	CFRP#2	1.3%
COPV#CC-2	HDPE	CFRP#1	CFRP#2	0.3%
COPV#CC-3	HDPE	CFRP#1	CFRP#2	0.2%
COPV#CC-4	HDPE	CFRP#1	CFRP#2	0.0%

temperature in the tank at the beginning of the fire test, pressure in the tank when microleaks start, as well as the time of leak initiations and time of leak durations are summarized in Table 2. The initial pressure in all four tests was almost equal to tank's NWP = 70 MPa and initial temperature of hydrogen in the tank was in the range 10.9–23.1 °C. The tanks started to leak at time from 4 min 26 s (COPV#CC-2) to 6 min 2 s (COPV#CC-4) when the pressure increased minimum to 74.11 MPa (COPV#CC-2) and maximum to 76.57 MPa (COPV#CC-4). Shortest blowdown of hydrogen from a tank duration was 12 min 35 s (COPV#CC-1) and the longest 14 min 31 s (COPV#CC-3).

The pressure transients in Fig. 3 and Table 2 show the increase of hydrogen pressure by 4–6 MPa in the tank before the leak due to the heat transfer from the fire. The corresponding increase of hydrogen temperature in the location of thermocouple is by 18–25 °C–29 °C in test COPV#CC-1 and 46 °C in test COPV#CC-4. The Ulster's model developed and validated in Refs. [1,15] shows that at the moment of COPV#CC-4 leak at 6 min 2 s (see Table 2), the total amount of energy transferred to the liner from the composite minus energy transferred from the liner to hydrogen, increases the liner's temperature to 128 °C, which falls within the range of HDPE melting temperature of 110–130 °C. This, indeed, is supported by the experimentally observed pressure and temperature decrease inside the tank at 6 min 2 s (Fig. 3b).

The start of pressure drop identifies the beginning of microleaks. In test COPV#CC-4 (Fig. 3b) the sharp decrease of pressure is associated with sudden decrease of hydrogen temperature due to gas expansion. The sharp drop of pressure in test COPV#CC-1 (Fig. 3a) is preceded by its slower decrease, and this is why temperature decrease in this test is shifted to the time of the sharp pressure drop stage. At the time of the first pressure drop in this test, hydrogen temperature at the location of its measurement was 20.2 °C. By the moment of the second, the sharper pressure drop, the temperature was raised to 28.4 °C at the same location. Then, the temperature dropped to 0 °C and after that the heating of gas through the wall, undergoing resin combustion, compensated and started to prevail over the cooling of hydrogen due to expansion. The temperature of hydrogen increases and at the end of the release, when the pressure inside the tank drops to the atmospheric pressure, reaches about 180 °C. The pressure transient is not monotonic in the test with COPV#CC-1, and in the test with COPV#CC-4 the pressure recording has a plateau. This plateau is due to the contraction of tank with the pressure decrease and thus the decrease of diameter or even "closure" of some of microchannels. Then, the temperature of hydrogen continues to grow and at about 100 °C (could be corresponding to more than melting temperature 110–130 °C in the HDPE liner) the microleaks intensify and promote pressure drop again. The further degradation of the resin in fire contributes to

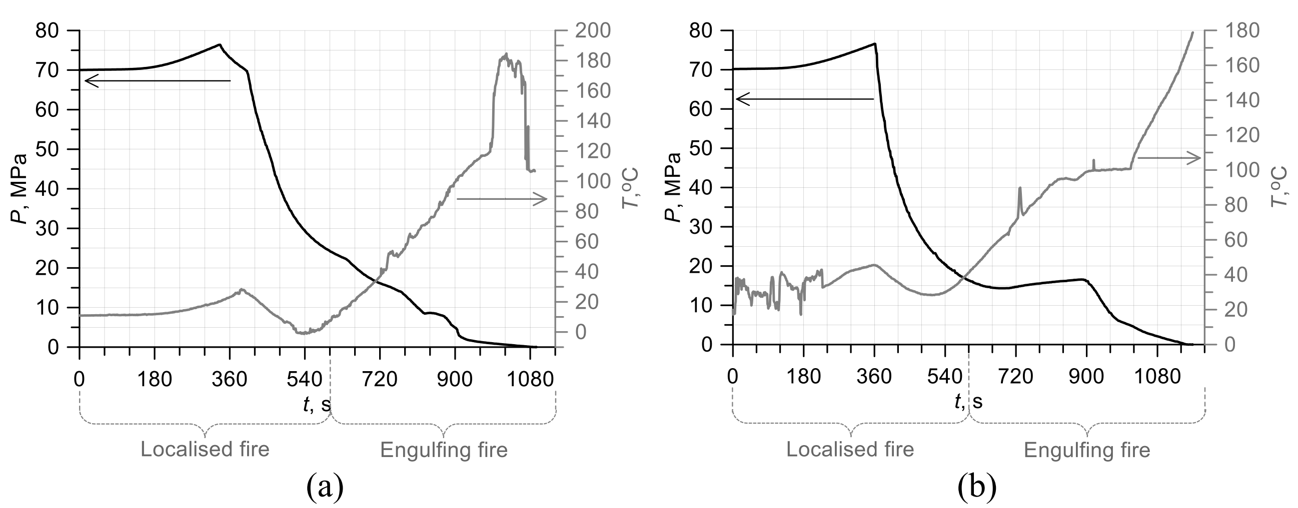

Fig. 3 – Pressure and temperature transients inside the μLNB tank prototypes during the fire tests with HRR/A = 1 MW/m² (a): COPV#CC-1; (b): COPV#CC-4.

Table 2 – Results of fire testing of the series of μLNB tanks with carbon-carbon combination.

Tank No.	P initial	T initial	P at leak	Leak start time	Leak duration
COPV#CC-1	70.02 MPa	10.9 °C	76.39 MPa	5 min 36 s	12 min 35 s
COPV#CC-2	70.09 MPa	20.7 °C	74.11 MPa	4 min 26 s	12 min 40 s
COPV#CC-3	70.22 MPa	23.1 °C	76.34 MPa	5 min 44 s	14 min 31 s
COPV#CC-4	70.17 MPa	19.8 °C	76.57 MPa	6 min 2 s	13 min 24 s

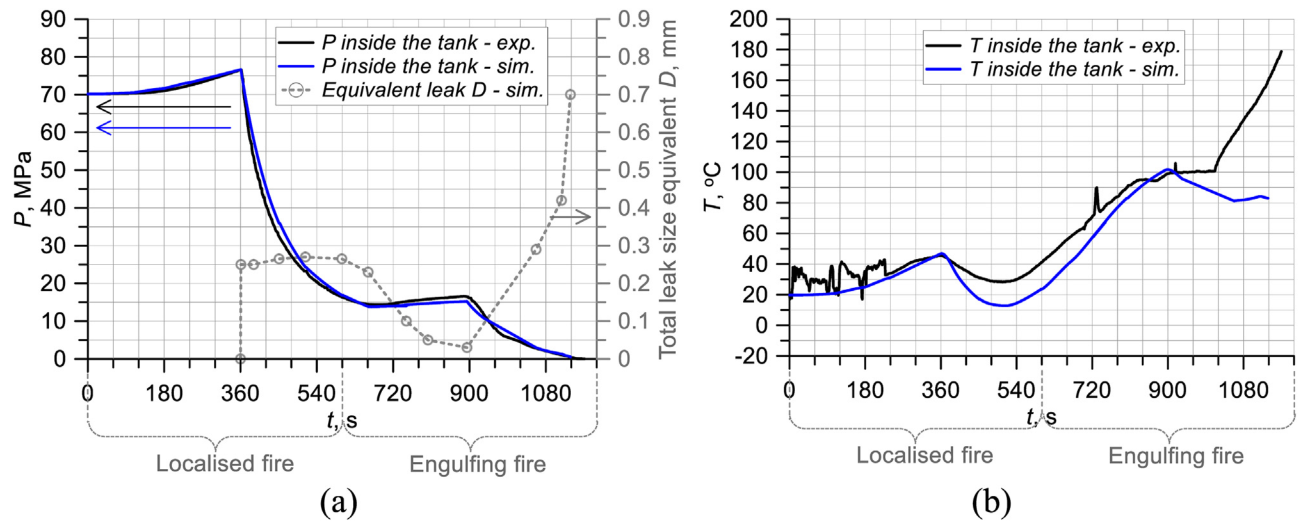

Fig. 4 – Experimental and simulated pressure dynamics (a, left y-axis) and temperature transients (b) inside the μLNB tank COPV#CC-4, and equivalent microleaks diameter (a, right y-axis).

this pressure drop as well, e.g., by increasing the number of microchannels and/or their cross-section area and decrease of pressure losses in microchannels of reduced length.

The non-adiabatic blowdown model [2] was applied to simulate pressure and temperature transients in fire test with HRR/A = 1 MW/m^2 with COPV#CC-4. Fig. 4a shows experimental and simulated pressure dynamics inside the tank (left y-axis), and the numerically derived diameter of the equivalent orifice which would have a cross-section area equal to the total effective cross section area of the microleaks in the tank wall. Fig. 4b demonstrates experimental and simulated temperature transients in the tank.

Fig. 4a and b demonstrate that the pressure and temperature dynamics in the tank are reproduced with the reasonable engineering accuracy by the model [1]. The grey dashed curve with circular symbols in Fig. 4a represents the dynamically changing equivalent diameter of the “orifice” equal to the total effective cross-section area of microleaks in the tank wall. The value of the varying cumulative microleaks area can be estimated using the right y-axis. The “orifice” diameter is equal to 0.25 mm at the start of microleaks (6 min 2 s). This “orifice” diameter remains almost constant until about 10 min, when the fire test switches from localised to engulfing mode following the GTR#13 fire test protocol [17,16]. The pressure drops from initial 76.57 MPa at 6 min 2 s to below 15 MPa at 10 min, i.e., more than 5 times in 4 min. Three factors, i.e., the contraction of the wall due to pressure drop that reduces microchannels cumulative area or even close some of them, cooling of liner and resin by cooled during expansion hydrogen, and the increase of heat transfer to hydrogen in the engulfing fire, are responsible for the plateau in the pressure transient. The wall contraction is thought to be the main factor that is evidenced by the decrease of cumulative area of microleaks from initial 0.25 mm at the start of the hydrogen escape through the wall to only 0.03–0.04 mm at the end of plateau at about 15 min of the process. The pressure starts to drop again after 15 min down to atmospheric. This is due to further decomposition of resin in the composite and associated formation of new microchannels and/or increase of cross-section area of existing microchannels. The cumulative area of microleaks grows after 15 min and reaches 0.7 mm at the end of hydrogen release when pressure in the tank equals to atmospheric pressure. Because of the pressure decrease by more than 5 times at 10–15 min to that when microleaks start, the wall thickness needed to bear the load is significantly thinner compared to the original, i.e., by about the same 5 times and multiplied by the safety factor (currently minimum is 2.25 to pass the burst test). The decrease of cumulative microleaks area after about 9 min due to tank wall contraction, and other mentioned above factors, changes a balance between hydrogen cooling and heating in favour of heating (see Fig. 4b). The increase of temperature afterwards is further supported by switching to the engulfing fire mode when the whole tank surface is subject to the fire. One of key conclusions from this test is that the equivalent leak “orifice” never closes during the blowdown, even with the composite wall shrinkage during the pressure drop.

Fig. 5 shows snapshots of tank COPV#CC-4 behaviour in a fire test with HRR/A = 1 MW/m^2.

The regulated by GTR#13 [17] and R134 [16] fire test protocol requires to start with the localised fire stage, which lasts for the first 10 min, and then switch to the engulfing fire mode. During the localised stage, the fire source extends for 250 mm of the tank's longitudinal expanse (snapshot “0 s”), from the end further from TPRD (any end in our case as μLNB tank does not have TPRD). Snapshot “3 min” shows the appearance of a first isolated flame on tank surface. This is resin combustion alone as hydrogen microleaks will start later at 6 min 2 s as evidenced by the pressure drop. Snapshot “3 min 30 s” shows several flames on the tank surface, which is also resin combustion. These flames are observed where the localised fire affects the tank. Snapshot “4 min 30 s” reveals a separated flame at some distance from the localised fire area. This is resin combustion on its own too. Snapshot “5 min” demonstrates a small jet fire which could be combustion of ejected from below the plies evaporated products of resin decomposition.

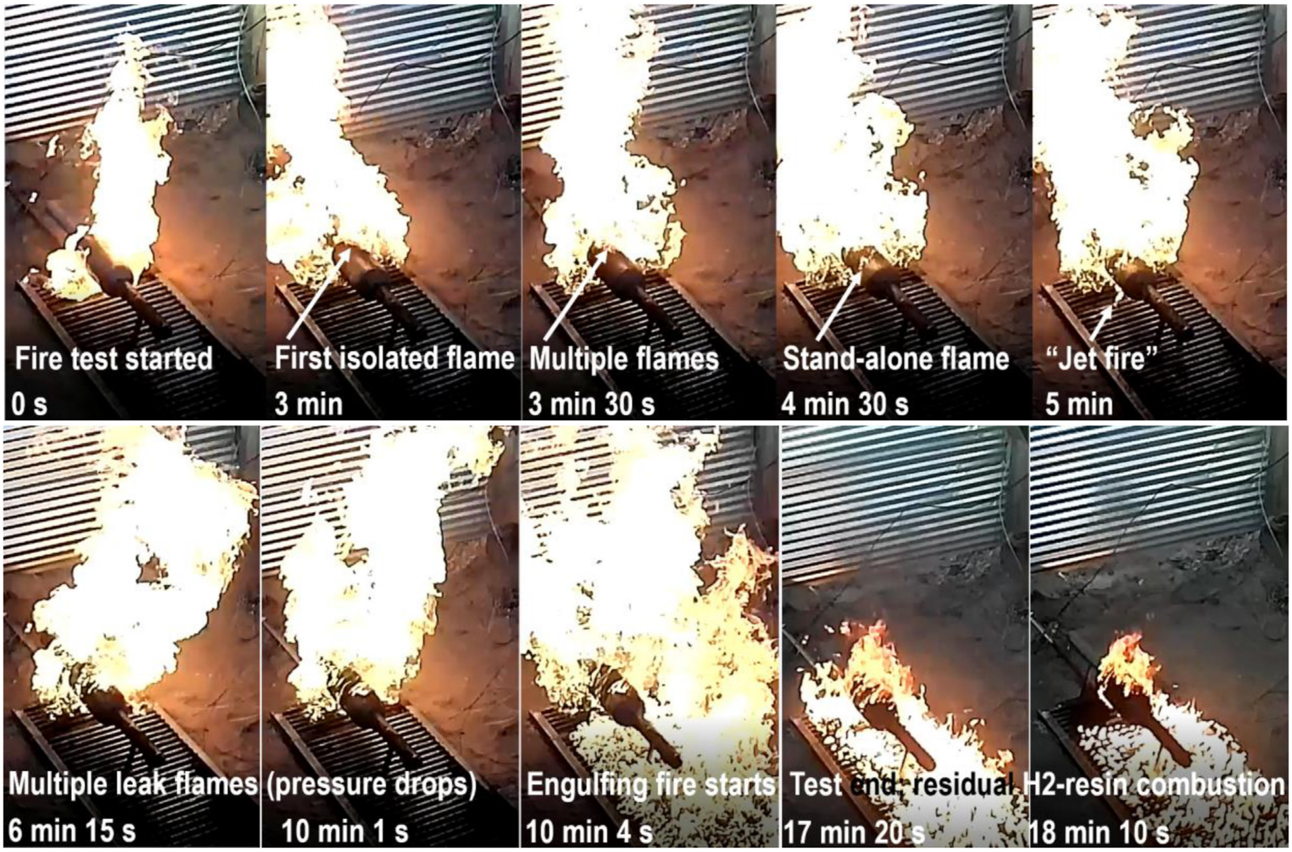

Fig. 5 – Snapshots of μLNB tank COPV#CC-4 behaviour in a fire test with HRR/A = 1 MW/m^2.

The notable decrease of hydrogen pressure inside the tank (start of microleaks) is observed in this fire test at 6 min 2 s. The snapshot "6 min 15 s" in Fig. 5 is the first after the pressure in the tank begins to drop, i.e., when the liner melted, and hydrogen started to flow through microchannels in the wall. It doesn't show any significant visible change in the burner flame (assuming small contribution of leaking hydrogen to the heat release rate of the burner fire). Only a few more little flames around the tank surface make the difference with previous snapshot "5 min" (before the blowdown of hydrogen starts). During the blowdown, at 10 min, i.e., when the fire is switched from localised to engulfing mode (snapshot "10 min 4 s") and after that time there is no visible change in combustion around the tank. The duration of the fire test is defined by the reduction of hydrogen pressure in the tank to atmospheric at 19 min 30 s. Thus, the blowdown time through microleaks was 13 min 28 s. The equivalent TPRD "orifice" diameter of the microleaks at the start of the blowdown was 0.25 mm, and the flow rate was about 2 g/s and reduced afterwards for this tank design.

Let us assume that separate hydrogen microflames on the tank surface have similar length to the observed resin combustion flames. Then, the dimensionless flame length correlation [22] gives the microchannel diameters in the range of 10–40 μm. This is of the order of carbon fibre size of 7 μm and thus of microchannels around them. Not all microleaks can sustain microflames. The lowest leak possible to sustain a flame from a miniature burner configuration is reported as 3.9–5.0 μg/s, which is the quenching limit for hydrogen flames [22–24]. The quenching mass flow rate limit for fittings is somewhat higher 28 μg/s [23]. Along with the quenching limit there is the blow-off limit. Thus, for a given leak size, there is a range of mass flow rates within which hydrogen microleak can support a stable microflame. Butler et al. [23] studied quenching and blow-off limits for pinhole type of burner, which can be considered as the closest configuration for microchannels in the wall, for pinhole diameters ranged from 0.008 mm to 3.18 mm. For the pinhole diameter 0.15 mm the flame cannot be sustained for flow rates above 1.5 mg/s, for the diameter 0.5 mm the blow-off limit increases to 20 mg/s. We can now conclude that hydrogen flame can exist if, for a particular microchannel, the flow rate is above the quenching limit and below the blow-off limit. There is a distribution of sizes of microleaks on a tank surface during blowdown. Some of the microchannels will not sustain flame as the hydrogen flow rate is below the quenching level and some will not sustain flame as flow rate is above the blow-off limit. This hydrogen will either burn in surrounding fire or, if the fire is extinguished, will decay below the lower flammability limit close to the tank surface in accordance with the similarity law stating that the flammable envelope size is proportional to the leak diameter size [25].

What is known about the visibility of microflames? Lecoustre et al. [24] reported that the burner with an internal diameter of 0.15 mm and an outside diameter of 0.30 mm can produce an invisible flame, even in a dark room (can be detected only with a thermocouple). This explains "no change" in the visible picture of small flames around the tank

Table 3 – Parameters of a series of μLNB tanks with carbon-glass fibre combination.

Tank No.	Liner	Layer No.1	Layer No.2	Outside D increase
COPV#CG-1	HDPE	CFRP#3	GFRP	11%
COPV#CG-2	HDPE	CFRP#3	GFRP	14%
COPV#CG-3	HDPE	CFRP#3	GFRP	15%

Note: CG – CFRP/GFRP combination in one over another composite overwraps.

surface when the hydrogen blowdown process starts (see Fig. 5). Hence, there is either no hydrogen flames on the surface, or they are invisible (unless the fire creates a big hole in the tank wall), or hydrogen trivially contributes to the resin combustion. Thermal cameras can be used in future studies to assess the radiation from the tank.

Carbon-glass combination of fibre in double-composite wall

Another series of μLNB tank prototypes was designed using the combination of CFRP layer (next to the liner) of modification CFRP#3, and the glass fibre reinforced polymer (GFRP) serving as TPL. The materials and the increase of the outer diameter compared to the original tank made fully of CFRP for each prototype are given in Table 3. The increase of outside diameter is due to substitution of carbon fibre by cheaper and less stronger glass fibre to meet the regulation requirement of minimum safety factor of 2.25.

The μLNB carbon-glass tanks of this series of prototypes were assessed differently from the series of carbon-carbon tank prototypes. They were subjected to the engulfing fire test exclusively as per specific sections of GTR#13 [19] and R134 [20], and fire intensity of HRR/A = 1 MW/m^2 throughout all the experiments. This allowed investigation of differences in hydrogen blowdown dynamics, as compared to the first series of prototypes (entailing both localised and engulfing stages of the fire test). Fig. 6 shows three carbon-glass tanks prior to the testing (a), a fully developed engulfing fire with a tank immersed into it (b), and one of the prototypes before (c) and after (d) the fire test.

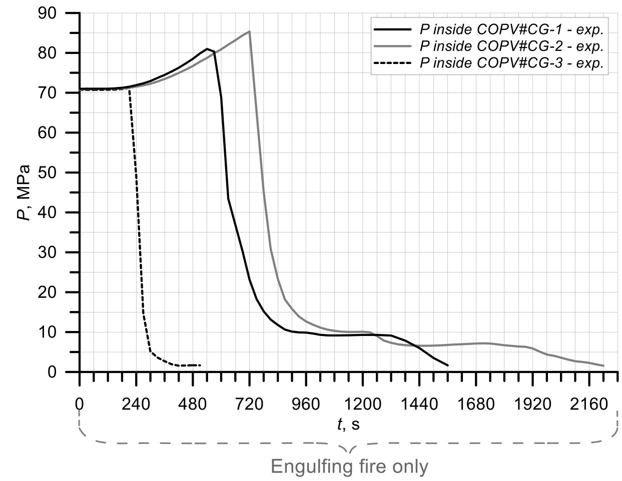

Fig. 7 – Pressure transients inside three μLNB carbon-glass fibre combination tanks during the fire tests with HRR/A = 1 MW/m^2.

Fig. 6 (d) demonstrates that the tank after the fire test has, as expected, no signs of rupture, visible holes or plies detachment. The fibres are in place while the resign is burnt out, at least in the outer layer(s). This observation is in line with the statement by Ruban et al. [17], that after the fire test experiment with Type IV tank the "epoxy resin seems to have disappeared but the carbon fibres did not burn". Indeed,

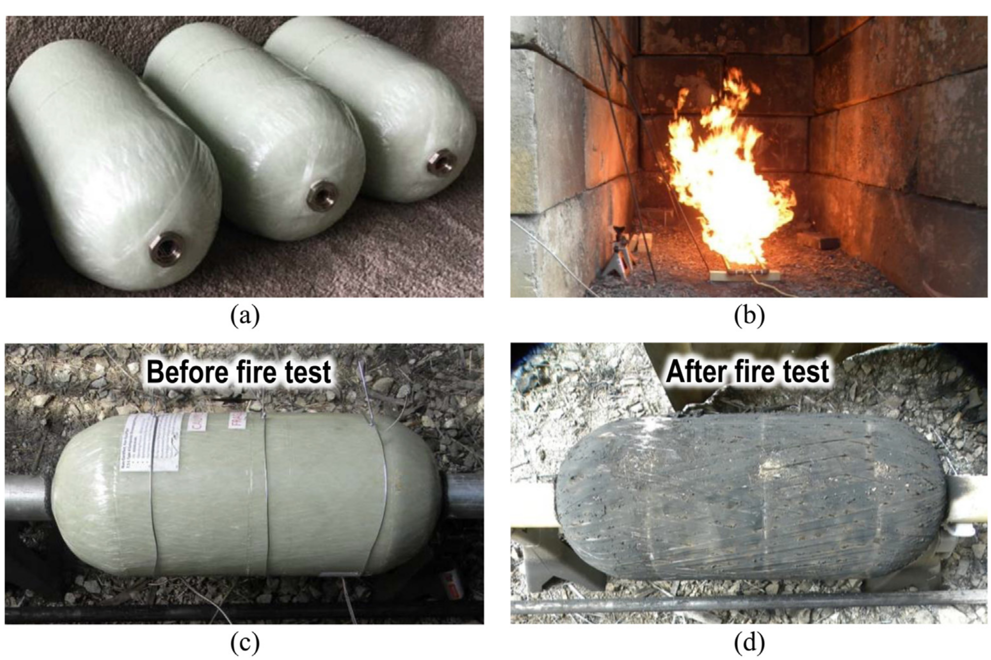

Fig. 6 – Carbon-glass μLNB tanks (a), arrangement of fire test with HRR/A = 1 MW/m^2 (b), and one of the prototypes exteriors before (c) and after (d) the fire test.

Table 4 – Testing outcomes for COPVs with carbon-glass composite layers combination.

Prototype No.	P initial	T initial	P at leak	Leak start time	Leak duration*
COPV#CG-1	70.99 MPa	N/A	80.98 MPa	9 min	17 min
COPV#CG-2	70.76 MPa	N/A	85.35 MPa	12 min	25 min
COPV#CG-3	70.69 MPa	N/A	71.22 MPa	3 min 30 s	5 min

Note: * The experimental pressures readings were interrupted when pressure dropped to 2 MPa (the duration of the final blowdown period can be estimated as 30 s to few minutes from the pressure transients during testing of carbon-carbon fibre tanks).

thermal decomposition of typical epoxy resin requires about 350 °C [26–29] and about 700–750 °C for carbon fibres [28,29].

Fig. 7 presents pressure transients for three experiments with carbon-glass μLNB tanks. Due to technical reasons at the testing laboratory, temperature readings inside the tanks during these fire tests are not available.

Fig. 7 shows pressure dynamics like that observed in the tests with carbon-carbon fibre combination in the double-composite wall. There is a notable pressure drop after the leak initiation and there are pressure plateaus too. The three carbon-glass fibre prototypes withstood the realistic engulfing fire of HRR/A = 1 MW/m^2 without rupture, as predicted by their numerical design.

The initial pressure, the pressure at the start of microleaks, the microleaks start time, and the microleaks duration are given in Table 4. The scatter of microleaks start time and its duration is defined by the difference in thicknesses of carbon and glass layers. Using Ulster's model [2] it was estimated, that similarly to the carbon-carbon prototypes, the initial overall leak flow rate in carbon-glass prototypes was also 2 g/s. The flow rate then decreased with the blow-down, as the pressure inside the tank dropped.

Comparison of Table 4 with Table 2 shows that for carbon-carbon composite walls the leak starts after about 4.5–6.0 min when hydrogen pressure in the tank reaches 74.11–76.57 MPa, while for carbon-glass walls the time to start microleaks is wider, i.e., from 3.5 min to 12 min with pressure at leak start of 71.22–85.35 MPa respectively. It can be concluded that the pressure in the tank at the leak start is a function of leak start time. The longer the leak delay the higher is the pressure. The leak start depends on the tank design, including geometrical and thermophysical parameters of liner and composites.

Conclusions

The *originality* of this paper is in the explanation of breakthrough safety technology of explosion free in fire self-venting (TPRD-less) Type IV tanks, and a detailed description of the microleaks-no-burst (μLNB) behaviour of the tank in a fire.

The *significance* of this work is in the development and demonstration of the hydrogen storage tank designs that exclude rupture in a fire. This engineering solution reduces the hazards and associated risks of hydrogen-powered vehicles and storage systems use, including in confined spaces like underground parking and tunnels, to the level below that for fossil fuels vehicles. Safety concerns regarding hydrogen storage rupture in a fire onboard of road, rail, maritime, aviation vehicles and at hydrogen refuelling stations can be reduced to a negligible level with the use of μLNB self-venting tanks: no blast waves, no huge fireballs, no projectiles (the largest projectile is a vehicle itself), no long flames from TPRD, no pressure peaking phenomenon in garages and hydrogen storage enclosures, no formation of flammable cloud and hot products under the ceiling of underground parking and in tunnels, no loss of life and property from tank rupture in a fire. It is shown that the design and manufacturing of the explosion free in a fire self-venting tank with no additional size compared to the original tank is possible for carbo-carbon systems. The reduction of amount of carbon fibre in μLNB tank is possible by using glass fibres in the design.

The *rigour* of this study is in the experimental validation of the technology for 4 carbon-carbon and 3 carbon-glass fibre combinations and different resins in the composite tanks of NWP = 70 MPa. The μLNB tanks are tested in localised and engulfing fire regimes, and at realistic specific heat release rate of HRR/A = 1 MW/m^2, in which many of standard tanks will rupture already at the localised fire stage when their TPRD is not yet affected by the fire. The Ulster's model of non-adiabatic blowdown, together with the original mechanism of tank failure in a fire, were used to analyse the dynamic change of cumulative area of microleaks. The model reproduced experimental pressure and temperature transients inside the tank and gave insights into the underlying physical phenomena. It is revealed that leakage through the microchannels never fully closes during the blowdown in conditions of the composite wall shrinkage with the pressure drop. The pressure inside the μLNB tank drops to atmospheric at the end of fire. This facilitates safer intervention of responders and dealing with hydrogen storage tanks after the incident. The real incident conditions, such as fire extinction by first responders or removal of a hydrogen-powered vehicle from a fire, as well as an extreme scenario of high-pressure hydrogen jet fire impingement onto a μLNB tank remain as subject of a future work.

The authors have explained in detail the concept and examples of the technology validations for carbon-carbon and carbon-glass systems, however some of proprietary information is not disclosed to protect intellectual property (IP) rights of Ulster University as the IP holder.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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