THERMOMECHANICAL DAMAGE MODELS FOR TYPE IV HYDROGEN VESSELS SUBJECTED TO FIRE

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Keywords: hyperbaric hydrogen tank, filament wound composite, thermomechanical loading, burst pressure, leak before burst

Abstract
In order to ensure safety of type-IV hydrogen tanks in accidental conditions, for example fire, it is necessary to develop and to validate numerical tools able to accurately simulate the time to failure of a vessel submitted to a severe thermal heat flux. To achieve this goal, two approaches may be associated. First, a computation time saving tool based on a first ply failure criterion assumes that fire leads to stiffness decrease when the temperature exceeds specific thresholds (glass transition temperature, thermal degradation onset temperature). This criterion is completed by a more advanced analysis of burst through a mechanical damage model taking into account the thermal degradation of the composite by the means of a specific variable related to the mass loss occuring at high temperature. These tools are able to forecast accurately the burst pressure of the tank and to capture the transition between a burst regime at high inner pressure and a safer falilure mode at lower inner pressure, namely leak, when the polymeric liner melts before the composite shell breaks. Thanks to its low computer time consumption, the first ply failure is a efficient tool to optimize safe vessels by promoting leak before burst.

1. Introduction

Use of hydrogen energy at a large scale necessitates mastering the reliability of storage at very high pressure. Type-IV tanks (made of a composite shell wound over a polymeric liner) are nowadays considered mature technology [1-3], but it is necessary to better characterize the conditions that need to be achieved to avoid a failure of the composite pressure vessel in any accidental conditions, in particular fire. Experimental works [4] have been carried out, in a first step, to improve understanding of the heat transfer mechanisms and the loss of strength of composite high-pressure vessels in fire conditions. From these experiments, tractable and reliable simulations of the thermo-mechanical behaviour of the high pressure vessel exposed in the same conditions are necessary. They will allow, in the future, to improve current standards and fire protection strategies in order to protect people from both cylinder burst and hydrogen flames.
The risk analysis [5] and the prediction of storage burst capability in fire are subjects of great current interest. In spite of this highly coupled framework, the numerical tools have to be simple enough to simulate large vessels, but they must also provide a high level of reliability. In this study, a basic, simple criterion approach has been first considered, in which the composite ply fails as soon as a damage criterion is satisfied. In [6], usual are compared to simulate the burst pressure of a composite hydrogen storage vessel subjected to inner pressure. It is proven that these criteria lead to very similar burst pressure predictions. Consequently, for the sake of tractability, a maximum stress failure

criterion is selected in this work: failure in a ply is assumed to occur when the stress in the fiber direction reaches the corresponding temperature-dependent strength.
However, this type of failure temperature-dependent failure criterion is not able to precisely describe the kinetics of damage mechanisms leading to burst. It also does not take into account explicitely damage due to transformation of the composite material into char when subjected to fire. That is the reason why the vessel degradation has been simulated by a more precise approach associating a Hashin-like damage model and a variable taking into account the composite mass loss due to fire exposure. This chemical reaction, which can be mechanically considered as a type of damage, substantially modifies the stress distribution within the structure: the stress undergone by the outer burnt layers is transferred to the inner layers which rapidly reach their damage threshold and the global strength is strongly reduced.
In order to check the validity of the FE simulations, a given tank geometry of 36 liters studied in the framework of the FireComp project [4] has been selected as a reference case. Coupled thermomechanical calculations are performed to reproduce the experimental conditions undergone by the vessel. The experimental bonfire tests show two different regimes: at high inner pressures, the combustion of the outer layers redistributes the mechanical stress to the inner layers and the vessel bursts when the remaining non-charred composite can no longer withstand the pressure. At lower inner pressures, the mechanical stress is not high enough to cause burst. Consequently, the liner has enough time to reach its melting temperature and the vessel leaks. The models developed in this work are found to be accurate enough to capture the transition between burst and leak regimes. They are efficient tools not only to predict tank failure but also to design safe hydrogen vessels by promoting leak before burst.

2. Damage modelling by failure criterion

A reference 36-litre tank is modelled by Finite Element Analysis (software Abaqus). A scheme of this 36-litre tank is displayed in Figure 1. It is recalled that the type IV pressure vessels are obtained by filament winding process over a polymeric liner and metallic bosses at the ends.

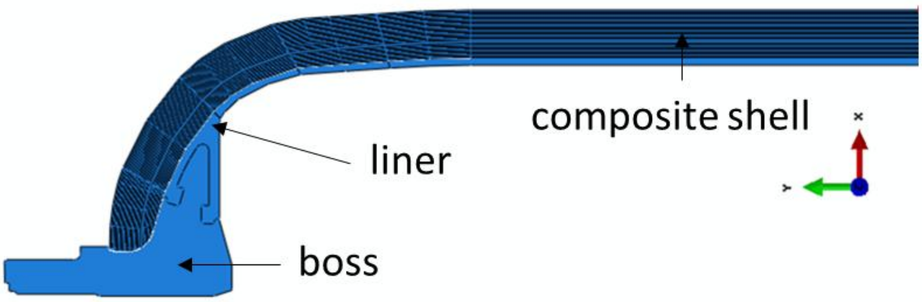

Figure 1: scheme of the reference 36-litre tank

Beside the geometry of the bosses and of the liner, the FE computations require the full stacking sequence of the wound composite shell in the cylindrical part of the vessel, that means, for each layer, the winding angle (measured with respect to the tank axis) and the thickness.

The composite material used to manufacture the pressure vessels is composed of an epoxy resin (whose glass transition temperature is about 108°C) and T700S carbon fibers [7], with a volume fiber ratio of about 55%. An extensive test campaign (tension tests at different temperatures for the mechanical properties, cone calorimeter experiments for thermochemical degradation) on composite samples cut in real pressure vessels has been carried out.

The following conclusions regarding the mechanical properties can be drawn:

- The longitudinal modulus is only slightly affected (decrease of 15%) by the temperature in the range 20°C-150°C, whereas the transverse stiffness and the in-plane shear modulus drop by a factor of around 10 once the glass transition temperature is reached.
- The longitudinal strength remains identical whatever the temperature (as long as pyrolysis does not occur), the transverse strength is strongly reduced above 108°C (the material loses more than 90% of its strength in this direction) as well as the shear strength.

Regarding the thermal properties, an inverse modelling approach based on a constant thermal conductivity and a temperature dependent heat capacity is used [8]. These tests also allow identification of the temperature at combustion onset of the composite (~350°C) and at combustion stop (~450°C). The radiative transfer at the composite surface when charring takes place has been measured [9] and set to 0.91.
The liner is High Density PolyEthylene (HDPE), whose behavior is assumed to be elastic, given its negligible contribution to the global stiffness. The bosses are made of 6061 aluminum alloy.
In order to avoid prohibitive computer times, a simplified strategy is based on the following relationships between temperature, mechanics and combustion:

- The mechanical elastic stress is assumed to have no influence on the material combustion and on the thermal properties
- As already mentioned, the mechanical stiffness is affected by the temperature. Its evolution over the interval 20°C-150°C has been addressed above. Between 150°C and the combustion start temperature (350°C), the stiffness is supposed to remain constant, since the TGA experiments do not exhibit specific chemical reactions in this temperature range.
- The temperature controls combustion, but instead of integrating coupled Arrhenius laws to model the transformation of the composite into char, combustion is implicitly taken into account by its effect on the mechanical stiffness. Starting from the experimental observation showing the char has no residual strength [10], it is assumed that the longitudinal modulus sharply drops from the combustion onset temperature (350°C). At 450°C (combustion stop), the stiffness is less than 10% of its initial value. Between 350°C and 450°C, the material density decreases from 1350 kg/m^3 to 1015 kg/m^3. Regarding the transverse and shear moduli, their values, very low at 150°C, do not need to be further affected.

The burst simulations take advantage of the symmetries of the problem: the geometry is axisymmetric (only a slice of the vessel is represented) and only one half of the tank is modeled (Figure 1). This geometry is meshed with axisymmetric quadratic elements. Thanks to this geometrical assumption, the number of elements is limited and the computation time reduced (6851 elements for the boss and the liner, 15713 for the composite; the thickness of each composite layer contains one element).
Regarding loading and boundary conditions, symmetry conditions are applied along the mirror plane (on the right-hand side of the geometry in Figure 1). The metallic boss is free to move along its axis, allowing the elongation of the cylinder. A pressure is applied on the inner surface of the liner and the boss. The incident flux is taken equal to 100 kW/m^2, according to the experimental measurement [4].

From the input described in the previous section, the objective is to simulate the burst pressure of the pressurized vessels, with an inner operating pressure of 700 bar and to compare the results to the experiments.
This needs a global burst criterion, based on the local failure of plies. As mentioned in the introduction, a simple criterion has been selected to simulate failure of the composite ply. A very simple criterion is selected in this work in order to reduce computer time. It is assumed that burst is controlled by the first fiber failure: when the following criterion

$$f_f = \left|\frac{\sigma_{11}}{X}\right| - 1 = 0 \qquad (1)$$

is satisfied at the ply scale (where σ_{11} is the in-plane longitudinal stress and X the in-plane longitudinal strength). This criterion leads to a time to burst of 228s, to be compared to the experimental time (238s). The simple approach based on a fiber failure criterion provides a satisfactory time to burst.

3. Leak before burst

The experimental tests performed on real tests in the framework of the FireComp project [4] show two different regimes: at high inner pressures, the combustion of the outer layers redistributes the mechanical stress towards the inner layers and the vessel bursts when the remaining non-charred composite can no longer withstand the pressure. At lower inner pressures, the mechanical stress is not high enough to cause burst. Consequently, the liner has enough time to reach its melting temperature and the vessel leaks.

The FE model detailed above is able to forecast this transition between burst and leak, provided a leak criterion is added: leak is assumed to occur as soon as the temperature at the composite / liner interface reaches the liner polymer melting point. Since the tightness in this type of structures is only ensured by the liner (the composite porosity is about 10%), liner melting is assumed to cause leak. In the following, this melting temperature is taken equal to 135°C, according to [11].

According to the initial pressure value, different types of behaviour can be observed for the most loaded layer, *i.e.*, the layer which undergoes the maximum stress in the fiber direction:

- At high inner pressure (f. ex. 700 bar):

The criterion (1) is rapidly satisfied. This is due to stress redistribution when the temperature of the outer layers increases and their stiffness decreases. When σ_{11}=X (*i.e.,* f_f=0), first fibres break and burst occurs (at 228s for 700 bar).

- At intermediate inner pressure (325 bar – 400 bar):

As for 700 bar, the value of σ_{11} (stress in the fiber direction) first increases in the most loaded layer but it reaches a plateau due to the constant longitudinal stiffness regime between 150°C and 350°C (see Section 2). During this period of time, the temperature of all composite layers lies between 150°C and 350°C, and the mechanical state does not evolve. When the temperature of the outer layers exceeds 350°C, their stiffness suddenly drops and the mechanical stress increases in the most loaded layer. If this stress increase occurs before the liner reaches its melting temperature, the tank bursts. Otherwise, the tank leaks.

- For low inner pressure (<300 bar):

The mechanical loading is so that the longitudinal stress σ_{11} never reaches X, the vessel cannot burst.

In conclusion, the transition from burst to leak is the result of a competition between two different kinetics: the time needed for σ_{11} to reach X and the time needed by the liner-composite interface to reach 135°C. Indeed, the vessel may leak if the melting point of the HDPE (135°C) is reached at the liner-composite interface before σ_{11} is equal to X. The melting point is reached at 470s. In the light of these considerations, it is possible to draw, by the means of FE simulations at different inner pressures, the safe pressure relief curve (Figure 2) which connects the critical (burst or leak) points and defines a safe zone (no burst / no leak). This curve is obtained in the following way:

- For a given inner pressure in the range 300 bar – 700 bar, the evolution of σ_{11} is calculated. The time to burst corresponds to the time at which f_f reaches 0.0 (black dots in Figure 2).
- If this dot is on the right side of the dashed line at 470s, the temperature rise at the liner-composite interface is rapid enough to reach 135°C before burst, and the tank leaks whatever the inner pressure. This transition occurs for an initial inner pressure of about 370 bar. Therefore the safety curve is composed of two parts: firstly a decreasing curve when the inner pressure is more than 370 bar and secondly a vertical line at the point of abscissa 470s.

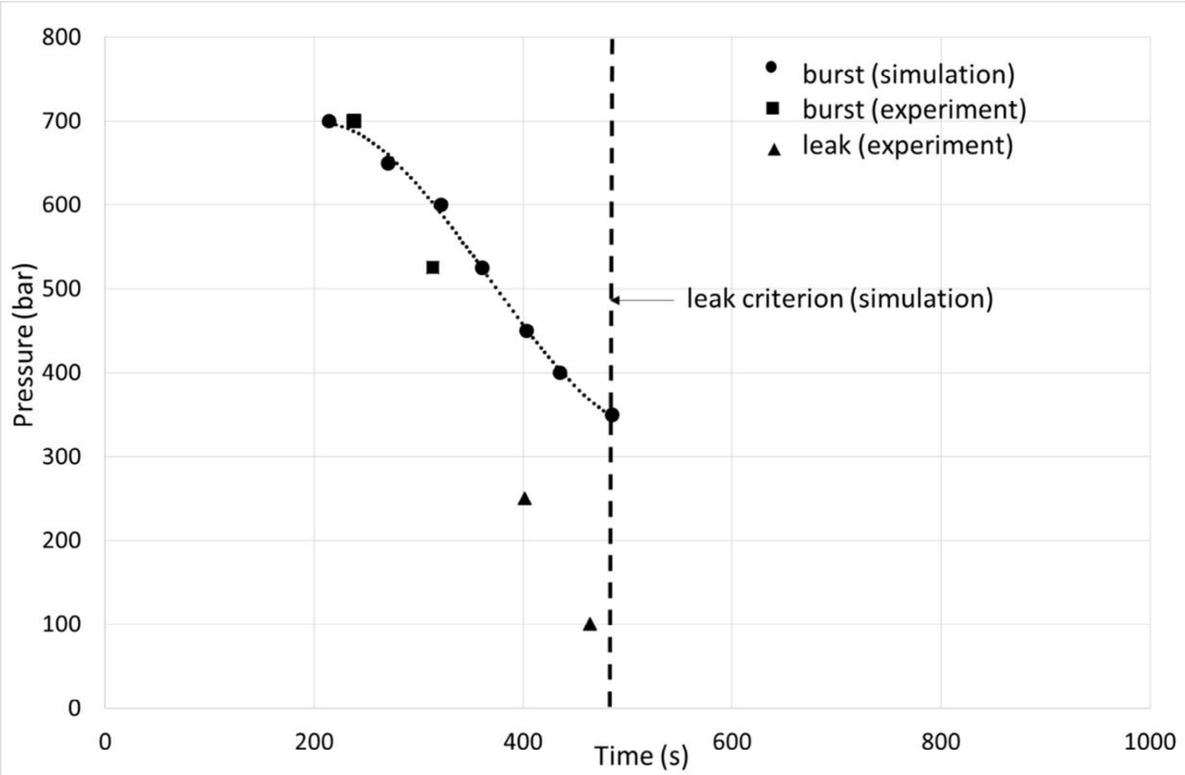

Figure 2: burst-leak curve for a flux of 100 kW/m^2

4. Damage modelling by internal variables

The approach by failure criterion presented in the previous section has been found to provide satisfactory results when simulating time to burst or time to leak of hydrogen tanks subjected to a given heat flux. However, this method is not precise enough to describe the progressive damage mechanisms and their interaction with degradation of the outer composite layers due to fire exposure. That is the reason why a more complex approach has been implemented. The effect of the mechanical damage in the composite material is simulated by the means of a Hashin-like model [12]. A set of internal variables (d_f, d_m, d_s) is selected to represent respectively fiber breakage, fiber / matrix debonding and matrix cracking. Each variable affects one or more components of the stiffness tensor and a specific evolution law is assigned to each variable, brittle for d_f and d_m, or progressive for d_s. The constitutive relation reads:

$$\sigma_{ij} = C_{ijkl}(d_f,d_m,d_s)\ \varepsilon_{kl} \tag{2}$$

The effect of combustion is considered here as an extra damage variable d_{dec}, since it leads to a stiffness reduction. In Equation (2), the stiffness $C(d_f,d_m,d_s)$ is replaced by $(1\text{-}d_{dec})C(d_f,d_m,d_s)$. The variable $d_{dec}$is related to conversion ratio of the chemical reaction transforming the composite material into char α (Figure 3), whose evolution is obtained from an Arrhenius law, identified from TGA experiments:

$$\frac{d\alpha}{dt} = \frac{\upsilon}{m_f - m_0} A * m^n * \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where ν is the stoichiometric factor, m the current mass, m_0 the initial mass, m_f the final mass, n the reaction order, T the temperature and A and E the pre-exponential factor and the activation energy. The relationship between d_{dec} and α can be classically [13] chosen as:

$$d_{dec} = 0.5 + 0.5 \tanh [\phi.(\alpha - \alpha_{mid})] \quad (4)$$

where ϕ and α_{mid} are parameters to be identified, for example, from tension tests performed on partially degraded samples [14].

This approach has been implemented in the FE software Abaqus and simulations similar to those presented in the previous section have been carried out (inner pressure and heat flux on the outer surface). It allows to monitor damage evolution in the composite shell as well as degradation due to fire exposure. For example, Figure 3 displays the fiber damage and the thermal decomposition 1-d_{dec} at two different times for an inner pressure of 300 bar.

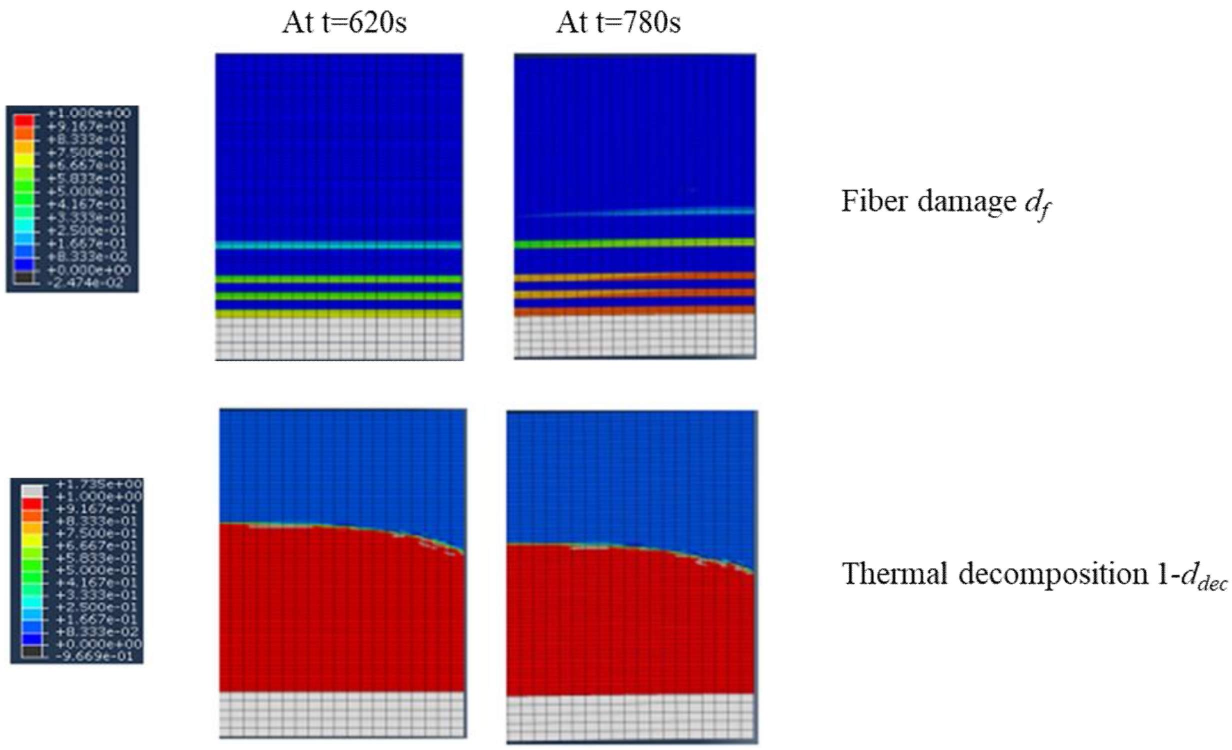

Figure 3: Fiber damage and thermal decomposition in the cylindrical part of the tank at t=620s and t=780s, for an inner pressure of 300 bar – the grey part at the bottom is the liner, the heat flux is appied at the top face

In Figure 3, it can be seen that the thermal decomposition affects almost the half of the composite wall (blue: fully degraded material, red: non degraded material) at t=620s. Between t=620s and 780s, the thickness of degraded composite hardly grows, owing to the thermal shield effect of the char whose diffusivity is much less than that of the composite. Regarding the fiber damage, Figure 3 shows very little evolution: at 780s, no new layer (wrt. 620s) is affected by damage. The damage evolution is due to the temperature rise which weakens the mechanical properties of the composite layers. This almost steady state explains that, at low inner pressure, the temperature at the composite / liner interface has enough time to reach 135°C, leading to vessel leak.
Therefore the damage model approach is able to describe more accurately the mechanical and thermal mechanisms leading to failure or to leak. However the computer time is much higher since three non linear equations (heat equation, Equation (3) and Hashin damage evolution laws) have to be simultaneously solved.

5. Conclusion

In spite of simple assumptions (axisymmetric geometry, homogeneous flux, burst at first fiber failure, leak criterion based on the temperature at liner/composite interface,…), the criterion approach is capable of predicting results in satisfactory accordance with experiments, not only for the time to burst at different inner pressures but also for the time to leak. More complex approaches combining degradation and progressive damage evolution can provide precise information about the thermal and mechanical mechanisms leading to burst or to leak.
Since the criterion approach gives a good prediction of the burst and leak of the cylinders, it is a useful tool to limit costly and complex test and to design pressure relief devices which may equip the hydrogen tanks to make sure the pressure always lies within the safe zone. A parametric study has been carried out to determine the thermomechanical properties of an ideal composite material which would promote leak before burst. It has been found that a higher conductivity reduces the time to leak, and a higher glass transition temperature increases the time to burst. More systematic optimization computations can be used as guide for the design of composite pressure vessels with reduced risk of burst in fire.

Acknowledgments

The research leading to these results has received funding from the European Union's Seventh Framework Program (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under Grant Agreement No.325329.
The authors thank all partners for the amount of work carried out in the FireComp project.
This work pertains to the French Government program ''Investissements d'Avenir'' (LABEX INTERACTIFS, reference ANR-11-LABX-0017-01).

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