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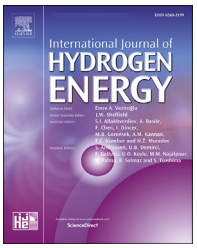

Determination of key parameters responsible for polymeric liner collapse in hyperbaric type IV hydrogen storage vessels

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ABSTRACT

Depressurization tests at a laboratory scale, coupled with numerical modelling, are used to determine the key parameters responsible for the polymeric liner collapse in hyperbaric type IV hydrogen storage vessels. X-ray tomography allows to determine the damages suffered by the sample during the depressurization step. Results show that the differential pressure induced during the depressurization step between the liner/composite interface and the free surface of the liner is the main factor responsible for the collapse of the liner. For a given temperature, this pressure gradient can be modified by changing the maximum H_2 pressure, the emptying rate or by adding a residual pressure plateau. Temperature is also of prime importance by influencing the yield point of the liner, the interface resistance and the amount of gas dissolved into the vessel. Thus, increasing temperature also increases the risk of liner collapse for the same gas exposure conditions.

Introduction

Nowadays, due to the combination of a relative low weight and a high mechanical strength, composite vessels are one of the best choice to store compressive hydrogen for automotive applications [1–4]. In the fourth generation of these vessels, the gas tightness is ensured by a thermoplastic polymer liner [5]. Most of type IV hydrogen storage vessels are composed of polyethylene [6–8] but nowadays others polymers such as aliphatic polyamides are being considered [9] due to their good mechanical and barrier properties to non-polar gases [10–13]. Because of the use of hydrogen and the need to increase the internal pressure (up to 700 bar [14]) several problems appear, among which the collapse of the liner [15]. This phenomenon, demonstrated experimentally during rapid emptying tanks, consists of a detachment and a significant deformation of the liner [16]. Indeed, during a filling/emptying cycle, the liner is submitted to stresses of various nature because of temperature and gas pressure variations [17]. This liner collapse issue

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has been already reported in literature in case of oil and gas pipes and some models predicted its appearance in terms of pressure differential [18–21]. In case of hyperbaric vessel, the collapse induces a risk of hydrogen leakage potentially linked to a liner fracture. Nonetheless, this problem of liner collapse is a hindrance to the massive deployment of composite vessels for the transport of high pressure gases. Observations of type IV storage vessel during use have revealed that the collapse of the liner depends on the operating conditions such as the initia2 filling pressure, the emptying flow rate or the time at the residual pressure plateau before emptying to atmospheric pressure. It is therefore of prime importance to better understand the key parameters responsible for the liner collapse appearance. If several studies are devoted to the mechanical strength of the composite under various conditions [22–27], few are dedicated to the issue of the liner collapse [21]. The aim of this work is to better understand the major mechanism responsible for the beginning of the liner damage. To that purpose, an identification of the main parameters governing the appearance of liner collapse during the emptying cycle will be performed. In this particular case of a heterogeneous material assembly, the appearance of the first damage may depend on differences in thermal expansion coefficient or on differences in volume change due to gas dissolution and partial pressure of dissolved gases in the liner, composite and interface. A combination of these effects can also be the driving force behind degradation.

Due to the important cost of tests performed on vessels, experimental part will be realized on representative sample as described elsewhere [28]. This representative and reproducible test on a liner/composite assembly is consistent with reservoir observations and allows the analysis of the key parameters influencing the onset of collapse in a more manageable and less expensive way than the reservoir test. This equipment allows us to characterize the influence of the hydrogen pressure cycle parameters on the initiation of the collapse phenomenon. Hence, the influence of temperature, maximum hydrogen pressure (P_{max}), depressurization rate (r_d) or even of the existence of an intermediate plateau is investigated. In parallel, a numerical modeling of the pressure/decompression cycle on both the real vessel and the assembly allows us to estimate the mechanical fields unattainable in the experimental part. The comparison between experimental and numerical results enables to discriminate the various physical phenomena potentially responsible for the onset of collapse: differential mechanical or thermal expansion, residual stresses, gas desorption.

Experimental

Materials and samples

In this work and to be consistent with a hyperbaric type IV hydrogen storage vessel, the composite is made up of an epoxy matrix reinforced by carbon fibers and two aliphatic polyamides liners were compared: a polyamide 6 (PA6) and a polyamide 12 (PA12). The samples representative of the composite pressure vessel are made of a 2 mm-thick plate of liner on which is fixed a 2 mm-thick sheet of composite material by an epoxy based adhesive as previously described [26]. These flat samples were made according to a process representative of winding. Indeed, a plane-faced mandrel was used to produce two plates on a winding machine in a 0/90° draping. In addition, a PA6 (or PA12) sheet is obtained by flattening a piece of a vessel liner. Then, this sheet was deposited onto the mandrel with a chemical treatment (confidential) which is identical to the case of vessels. Thus, the winding is carried out with the materials constitutive of a vessel (carbon + epoxy). The process ends with curing under pressure. Samples are square of 60 × 60 mm of this 4 mm-thick multi-layered material.

The comparison of these representative samples with a hyperbaric type IV hydrogen storage vessel shows that the thread tension is not homogeneous in the flat mandrel and that the flattened liner tends to return to its curved shape which can induce residual stresses on the interface. These differences are supposed to be attenuated by the curing process under pressure.

Contrary to the vessel, the test piece is flat. Nonetheless, the physical origin of the studied phenomenon is the consequence of the gas dissolution which is a local phenomenon. One may consider that the curvature will only have a minor influence on this mechanism. Differences will arise from the thread tension which will influence the debonded areas and the collapse propagation. From this point of view, the representativeness is only qualitative. Nevertheless, it will be easier to develop tools for numerical modeling on this simple configuration that can be applied, afterwards, on vessel. For this reason, it is possible to add a stress jump between the interface and the composite to evaluate its influence.

PA6 displays a rather high density of hydrogen bonds as compared to PA12 which makes it strongly sensitive to moisture [29,30]. This hydrophilic behavior gives rise to an important variation of the mechanical properties of the liner with the water content [31,32]. In order to test a liner with always the same mechanical properties, for which we have data, it was chosen to dry all the samples and keep them under vacuum at 80 °C during 15 days before depressurization tests. Indeed, the evolution of water content inside the sample was regularly measured once it was kept under vacuum. It was determined that after 7 and 10 days for PA12 and PA6 respectively, the sample weight keeps constant indicating that there is no more water to be remove from the sample. Both dried PA6 and PA12 were characterized by Differential Scanning Calorimetry (DSC) under nitrogen atmosphere at 10 °C.min^{-1} and display a glass transition temperature at 48 and 39 °C respectively, which is in agreement with literature [33]. Moreover, the transport coefficients (Pe, D, S) of these two aliphatic polyamides are different [34] and have been determined at various H_2 pressure and temperature thanks to permeation tests.

Prior to any exposure to H_2 gas, the samples were characterized by X-ray tomography (RX-Solutions) in order to determine the potential defects, especially in the liner/composite interface. The sample, a 60 × 60 × 4 mm^3 volume, was observed with a resolution of 50 μm/voxel. A complete analysis lasting for 2.5 h is made by acquiring a large number (1500 in our case) of X-ray absorption radiographs of the same sample under different viewing angles. Contrary to the liner/

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