Phase-field modeling of decompression failure mechanisms in hydrogen-exposed rubbers

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Abstract

Exposure of rubber materials to high-pressure diffusive gases can undergo cavitation and/or cracking processes upon subsequent decompression. Such decompression failure processes result from too-slow gas desorption as compared with the pressure release rate; the gas expands within the volume of the material and damages it. This phenomenon has been reported for different gas polymer systems in the past, rather qualitatively however, mostly under fast pressure release rates and in other gases than hydrogen (Gent 1969, Gent 1990, Briscoe 1994, Stewart 1970). Over the past decade, it has become a concern for the storage and transportation of compressed gaseous hydrogen. Indeed, the pressure range (up to 90 MPa) and the safety requirements specifically related to this gas challenge material formulation and component design for sealing.
The morphology and intensity of decompression failure are known to depend on the exposure conditions, as well as on the mechanical and sorption properties of the rubber material (Yamabe 2011, Jaravel 2011, Kane Diallo 2016, Schrittesser 2016, Jeon 2022). Damage initiation can be more or less delayed after decompression. Cavities usually inflate and deflate during the decompression and desorption stages. Except in the case of micro-cracks, it is very difficult and most of the time impossible to detect residual damage.

Such phenomenology results from full couplings between mechanics, temperature, and gas transport. At the macroscopic scale, the main subsequent challenge is to capture the statistics of cavity or crack fields and the damage gradients, among which edge effects (Fazal 2020). At the cavity scale, which is under consideration in the presented work, the existence of full diffuso-mechanical couplings is a key issue too. Considering a single cavity, the expansion and deflation depend on the balance between the external hydrostatic pressure and the internal pressure (which depends itself on the volume of the cavity and the gas content inside it, possibly varied by the gas flux at the cavity wall) but also on the intrinsic properties of the rubber at large strains at the cavity wall, and on the global gas content field. It depends also on the micro-cracking contribution which is very difficult to be measured in the inflated configuration (Morelle 2021). The problem even becomes more difficult when close cavities possibly interact within clusters.

A first strong limitation to experimentally characterizing the phenomenon is the inability to access all physics (e.g. the time-evolution of gas content and temperature fields). Another

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one is the complexity of performing in-situ measurements, especially in tracking the transient evolution of damage.

Only a few modelings have been proposed to simulate decompression failure (Jaravel 2013, Yersak 2017, Kulkarni 2021). Most of them were 1D solving of one cavity, taking into account (Yersak 2017) or not (Jaravel 2013) a gas flux at the cavity wall and thus a full computation of the internal pressure at the cavity scale. The effect of decompression conditions could be discussed from these works. Kulkarni et al. (Kulkarni 2021) proposed 2D FEM simulations of a cavity fields over a very small time range around the maximal value of the pressure, with a fixed internal pressure at the boundary of the cavities. They addressed interaction effects between close cavities, without diffusion effects between them however.

In such context, two key challenges for both experimental characterization and modeling of decompression failure are (i) to accurately capture the full couplings between diffusion and mechanics and (ii) to overcome the poor knowledge obtained from residual damage with time-resolved and 3D tracking of damage all along the process.

The experimental works reported here aim at a better understanding of the mechanisms of cavity growth, and some possible interaction effects at variable range, with a free surface or between close cavities, in a weakly cross-linked unfilled EPDM. The work was based on a 3D time-resolved quantification of the kinetics and morphology of the damage, from an in-situ X-ray tomography experiment initially developed on a laboratory source (spatial resolution 16μm, temporal 100s) and extended under a synchrotron environment on the Anatomix line of SOLEIL synchrotron (France). The gain in spatial (3μm) and temporal (4s) resolution made it possible to access the very first stages of growth, to track the transient growth kinetics of close cavities, and to detect residual damage.

A phase-field method, based on the Cahn-Hilliard equation, was used to simulate the growth of cavities during decompression. Such approach is particularly well-suited for modeling diffusive phenomena and phase transitions in complex systems.

In this framework, the phase field represented the local hydrogen concentration. One major advantage of this method was its ability to naturally handle the interface between the cavity and the matrix, the diffuse nature of the interface being inherently managed by the model. The coefficients governing the physical processes depended on both the mechanical and concentration fields and the coupling was facilitated through the phase field. Diffusion was modeled using Fick's law, with flux-based boundary conditions. Henry's law was applied to convert the hydrogen concentration in the cavity into pressure, which was subsequently applied as a boundary condition at the cavity wall. The mechanical behavior of the matrix was incorporated to account for stress and strain fields around the growing cavity. Cavities were initially introduced with the varying initial sizes and positions detected from the in-situ tomography views. As a first step, not all the complexity was retained in the modeling; the matrix was assumed to be linear elastic and no micro-cracking was introduced as a driving force of the cavity growth.

The simulation code was developed in Python, using the Fenics API to solve the mechanical fields around the cavities using the finite element (FE) method. Our 2D simulations provided insights into the temporal evolution of hydrogen concentration and cavity volume. The size of the simulated volume matched that of the sample for this case. In other tests with one or two cavities, the simulation domain differed. However, the integration of mechanical and diffusive aspects offers a promising tool for better understanding the contribution of various processes to the nucleation and growth mechanisms of cavities upon gas decompression.

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