Cavitation in rubbers exposed to high-pressure hydrogen: in-situ characterization of the phenomenon and modelling at the cavity scale

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Rubbers exposed to high-pressure diffusive gas may exhibit cavitation during decompression, when the gas contained in the polymer expands faster than desorption out of the material. This phenomenon has been reported in the literature a few decades ago in various gas-polymer systems [1-5], but quantitative data is lacking, especially to support accurate modeling framework. It has not been that much investigated since that time, especially in hydrogen. Interest for damage resistance of high-pressure hydrogen-exposed polymers was renewed about ten years ago, when hydrogen started to be considered as a new potential energy carrier. This issue is crucial to design damage-resistant parts and formulate suitable rubbers, but faces strong limitations related to hydrogen manipulation for in-situ experiments and to the relevant scales. Only a few laboratories are able today to conduct physical and mechanical experiments under high-pressure hydrogen in polymers [6-10].

The work presented here was mainly carried out in unfilled transparent EPDM, provided by Hydrogenius Laboratory, Kyushu University. Specimens (cut from 2mm-thick molded sheets) were saturated by hydrogen prior to pressure release at a constant rate. Two experimental devices were used to track damage kinetics and morphology during and after decompression:

- a mechanical testing machine in high-pressure hydrogen, fitted with a pressure vessel (hydrogen, nitrogen or carbon dioxide up to 40 MPa, temperature between the ambient and 150 °C). The major originality is the time-resolved tracking of damage morphology, during and after decompression, using visible light transmission through a 28-mm diameter window machined in the front door of the chamber. This method provides 2D projected views of the sample.
- an X-Ray tomograph fitted with the cylindrical pressure chamber that can be filled in with hydrogen, nitrogen or carbon dioxide up to 20 MPa.

Two types of information could be extracted from image analysis during the decompression test: (i) the inflation and deflation rate of single large cavities selected at different places in the sample, and (ii) a statistical analysis of cavities distribution at the full-field scale (number of cavities, size distribution and spatial distribution). Enriched evaluation of the spatial distribution of cavities was provided by a covariogram method applied to each picture of the images stack [11]. Covariogram corresponds to the probability C(h) to encounter a cavity at a distance h from another cavity along one given direction. This method allowed to discuss Representative Volume Element (RVE) features, interaction effects between close cavities and ergodicity of the cavity fields at the sample scale.

At the scale of cavity fields, the spatial distribution was shown to be influenced by the decompression conditions [12]. The number and size of cavities increased with saturation pressure and/or decompression rate with a trend to evolve from one heterogeneous population towards two populations (each of them with more homogeneous diameters) under the most severe decompression conditions. The homogeneity and isotropy of the distribution also changed with the decompression conditions.

At the cavity scale, kinetics was shown to be identical for independent cavities but different between the inflation and deflation stages. From the covariogram analysis, the relevance of modeling based on a unit cell containing one or two cavities could be discussed, and the size / isotropy of this RVE could be estimated. The morphological REV was a square in any condition, containing one or two cavities on average. However, two ranges of RVE size were obtained depending on the fact that the first cavities were nucleated under pressure of after pressure release.

These data provided the relevant distances for a Finite Element modeling of the growth of pre-existing cavities upon decompression, in diffuso-mechanical conditions. The size and shape of cavities was shown to be affected by the neighbouring cavity, as well as the gas content map around them.
Several modelling strategies have been developed to investigate the growth of a single cavity in a rubber medium exposed to hydrogen diffusion. The problem was first solved in a spherical geometry using Matlab software. As a second step, the work was extended using the Finite Element method (in Abaqus Software) with two aims: to conduct simulations under more general mechanical loadings and to address interaction between neighboring cavities. A huge difficulty for FEM convergence was to handle mechanical equilibrium and gas flux at the cavity wall. To overcome this problem, the cavity was modeled as a solid medium, with properties derived from the hydrogen state law.
As a third step, this difficulty was recently overcome by using software developed at Institut pprime (Foxtrot). Despite strong assumptions in the current version of the modelling, it is now possible to capture growth kinetics and decompression rate sensitivity in realistic decompression conditions.

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