Experimental real-time tracking and diffusion/mechanics numerical simulation of cavitation in gas-saturated elastomers

Julien Jaravel *, Sylvie Castagnet, Jean-Claude Grandidier, Mikaël Gueguen

Institut Prime, UPR 3346 CNRS – ENSMA – Université de Poitiers, ENSMA – Télport 2, 1 avenue Clément Ader, BP 40109, F86961 FUTUROSCOPE CHASSENEUIL Cedex, France

A R T I C L E   I N F O

Article history:
Received 8 August 2012
Received in revised form 23 December 2012
Available online 11 January 2013

Keywords:
Hydrogen
Decompression
Cavitation mechanisms
Pressure
Stability and bifurcation

A B S T R A C T

The effect of a gas decompression after saturation on rubbers was investigated with both an experimental and a numerical approach. Experimental results have been obtained with a commercial transparent rubber under hydrogen and a tensile machine fitted with a pressure chamber that allows a spatial and temporal tracking of damage. The influence of the decompression rate and cavity radius have been studied and compared with a numerical model based on the theory of the hollow sphere and the implementation of a Fickean law to have gas diffusion in the material. This multi-scale model was used to temporally predict the response of a spherical cavity in a hyperelastic incompressible material submitted to a coupled gas/mechanical loading. The aim of the study was to understand the gas exchanges between the cavity and the material and to temporally predict with a simple critical stretch ratio criterion when a small cavity can grow to a visible size. The influence of decompression rate, pressure level, cavity radius and position in the sample were discussed and compared with experiments.

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1. Introduction

Gas-saturated rubbers undergo very detrimental cavitation damage during fast decompression, caused by the expansion of the sorbed gas (Denecour and Gent, 1968). This decompression-induced cavitation mode is often referred to as explosive Decompression Failure (XDF). The phenomenon has been experimentally shown in several rubber-gas systems, among which carbon dioxide (Briscoe and Liatsis, 1992; Briscoe et al., 1994; Embury, 2004; Zakaria and Briscoe, 1990), argon (Gent, 1990; Gent and Tompkins, 1969; Stewart, 1970), methane (Stevenson and Morgan, 1995) but mechanisms responsible for damage are not understood yet. A few modeling predictions were proposed, but in very restricted and drastic conditions as detailed below in the Introduction. However, XDF is a major issue for several applications fields like offshore industry, carbon dioxide storage and hydrogen energy facilities. Only few authors investigated this phenomenon in hydrogen (Yamabe and Nishimura, 2009; Yamabe and Nishimura, 2012).

When rubbers are exposed to high gas pressure, no damage appears during the saturation stage (Stewart, 1970). In the previously investigated gas-polymer systems, a few cavities appear during decompression or a few minutes later. Satellite bubbles further nucleate around the primary ones, due to a local stress concentration (Gent, 1990). When decompressed from a low saturation pressure ($P_{sat}$), rubber samples do not exhibit any damage. From higher saturation pressures, the density of cavities increases with $P_{sat}$ (Stewart, 1970) except near surfaces where there exists a boundary layer without any visible damage (Stevenson and Morgan, 1995; Zakaria and Briscoe, 1990). Except for a very small number of reported works (Major et al., 2007), XDF was tracked after complete and uncontrolled decompression and removal of the sample from the pressure chamber.

Cavitation criteria developed to predict this phenomenon are mainly transferred from pure mechanical framework. Indeed, mechanical cavitation in rubber-like materials is well known since the Poker Chip Test of Gent et al. in 1959 (Gent and Lindley, 1959). The Poker Chip Test consists in inserting a thin cylinder of elastomer between two metal cylinders, which are pulled apart, creating hydrostatic stress at the center of the sample. More recently, such damage under a merely mechanical loading has been experimentally observed in real time in a transparent rubber (Cristiano, 2009). When the hydrostatic pressure was higher than 5 $\mu$2 where $\mu$ stands for the shear modulus, cavities appeared in the center of the specimen (Gent and Lindley, 1959). This critical pressure was based on the calculation of Green and Zerna in a hollow sphere under hydrostatic loading (Green and Zerna, 1954). Other studies postulated the existence of defects in the material (Butler et al., 1998; Gent and Lindley, 1959) and modeled the sudden growth of this pre-existing defect as a hyperelastic hollow sphere problem (Ball, 1982). More sophisticated models were published recently to take into account shear stresses effect and predict onset-of-cavitation surfaces upon...
three-dimensional loading (Lopez-Pamies et al., 2011). The influence of the rubber constitutive law has been addressed, considering a compressible material (Murphy and Biwa, 1997; Shang and Cheng, 2001), an incompressible material (Dollhofer et al., 2004; Hou and Abeyaratne, 1992; Jin et al., 1999) or a viscous material (Lee and Mear, 1994). Some of these works took into account the surface tension (Dollhofer et al., 2004; Gent and Tompkins, 1969; Huo et al., 1999). In most studies, the problem was solved for hydrostatic loadings only, in a uni- or bi-axial framework. Only a few works generalized the problem to tri-axial loadings (Diani, 2001). The aim of these approaches was to predict a critical mechanical loading for cavitation onset. None of them were able to predict time effects, such as the loading rate sensitivity. Previously reported models were not able to predict damage of elastomers under a real gas cycle including partial decompression or to account for the influence of the thickness of seals submitted to coupled diffusion/mechanical loading.

Since rubbers are used in many industrial applications under various loadings, it is crucial to predict the XDF sensitivity to the loading history among which saturation pressure and decompression rate. In the case of XDF, time effects are important. For instance, they may arise from variable decompression rates. In a methane-elastomer system, Stevenson and Morgan (1995) evidenced that the density of cavities does not depend on decompression rates between 40 MPa/min and 69 MPa/min, whereas it decreases by a factor of 5 between 40 MPa/min and 2 \( \times 10^{-4} \) MPa/min. It was interpreted as a gas diffusion effect. In general, there are only a few works aiming at predicting cavitation onset in a coupled diffusion/mechanics framework. Yamabe and Nishimura (2009), Yamabe and Nishimura (2012) assumed a pre-existing cavity that mimicked clusters of hydrogen molecules formed at the very early stage of decompression. They calculated the critical internal pressure to enhance fracture of the cavity wall. They considered that no desorption occurred so that they solved a time-independent problem. In the 70’s, Stewart (1970) accounted for the gas diffusion at the surface of a similar cavity, proposed an analytical solution that gives the time history of a cavity submitted to a fast decompression as a function of the cavitation time. Assuming a cavitation time and a gas concentration profile around the cavities, this solution was able to reproduce the qualitative dependence on gas diffusion parameters and saturation pressure.

In this context, the present study focuses on the very early stage of damage and has two objectives. The first one is to complete the experimental characterization of the phenomenon in extended conditions, i.e. by real-time tracking during the decompression stage, and to map the influence of key loading parameters like saturation pressure and decompression rate on the cavitation onset. A key contribution of the present work is to access the current pressure at cavitation onset and thus to discuss the relevance of hydrostatic pressure-based cavitation criteria. The second one is to improve the prediction of cavitation in the same extended conditions. In particular, a major originality is to compute the volume change of a pre-existing spherical cavity located in the core of the sample during decompression, in order to temporally predict XDF. Gas diffusion and mechanics are both solved in a hollow sphere problem with boundary conditions calculated from the macroscopic coupled diffusion/mechanics problem at the scale of the sample. This radially symmetric framework is relevant since only pure hydrostatic mechanical loadings are considered. In addition, our numerical model can take into account the distance from the cavity to the free surface of the sample, which has never been modeled before.

The present study is based on vinyltrimethoxysilane interacting with hydrogen but the approach and results more widely concern the whole field.

2. Experimental

2.1. Material and gas

Decompression experiments were conducted in a transparent and un-filled vinyltrimethoxysilane previously saturated by gaseous hydrogen. The solubility \( S_p \) and diffusion \( D \) coefficients of hydrogen into this rubber were measured using the Thermal Desorption Analysis (TDA) technique of Yamabe and Nishimura (2009) in cylindrical samples (height \( z_0 = 2 \text{ mm} \); radius \( r_0 = 6.5 \text{ mm} \)). The hydrogen desorption kinetics was analytically fitted from the series proposed by Demarez et al. (1954):

\[
Q_{H_2}^{\text{RST}} = \frac{32}{\pi^2} V_{s} \sum_{n=0}^{\infty} \exp \left[ -\frac{2(2n+1)^2}{C_2^2} \frac{D}{C_1^2} \frac{t}{C_0^2} \right] \times \frac{\sum_{n=0}^{\infty} \exp \left[ -D \left( \frac{r_0}{r_{m}} \right)^2 \left( \frac{2n+1}{C_0} \right)^2 \right]}{r_{m}^2} \tag{1}
\]

where \( Q_{H_2}^{\text{RST}} \) stands for the hydrogen quantity remaining in the volume \( V \) of the sample, \( b_n \) is the root of the \( J_0(\beta) = 0 \) equation with \( J_0 \) Bessel function. Coefficients \( D \) and \( S_p \) were fitted from a classical genetic algorithm (Renner and Ekart, 2003).

The optimized values were \( 4.22 \times 10^{-2} \text{ cm}^3 \text{ STP} \text{ cm}^{-3} \text{ bar} \) for the solubility \( S_p \) and \( 2.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) for the diffusion coefficient \( D \). STP stands for Standard conditions of Temperature (273 K) and Pressure (0.1013 MPa). These fitted values were in good agreements with data reported about hydrogen-rubber systems (Hagg, 2000).

The hyperelastic response of the rubber was calibrated from tensile Dynamic Mechanical Analysis (DMA) and monotonic tension tests. A shear modulus of 0.4 MPa was measured at room temperature with both tests. It could be argued that these mechanical tests were performed in air and further applied to the hydrogen-saturated rubber, but hydrogen was shown to have a negligible effect on the mechanical properties of rubber materials (Yamabe and Nishimura, 2011). No other transition than the glass transition—occurring at \(-68 \text{ °C}\)—could be detected from the DMA analysis, and no damping contribution was measured at room temperature. Optical microscopy did not evidence any pre-existing micro-cavity. However, sub-micron cavities or defects smaller than 1 \( \mu \text{m} \) could not be detected from such optical techniques.

2.2. Experimental results

Decompression tests were carried out in an Instron 8802 tensile machine fitted with a pressure and temperature regulated chamber which allows mechanical testing in gaseous nitrogen, hydrogen or carbon dioxide. For details about the experiment, one can refer to previous papers from the same laboratory (Castagnet et al., 2012). Regarding the state-of-art, a key contribution of the present work dealt with the ability to simultaneous spatial and temporal tracking of XDF. It was made possible by two sapphire windows inserted in the front and back doors of the chamber.

Decompression tests consisted of a pressurization stage at constant pressure rate, followed by a constant pressure stage aimed at stabilizing the temperature (at about 20°C) and saturating the sample. Finally, the decompression step was conducted under constant pressure rate. All tests were performed at room temperature, excepted that temperature variations resulting from the pressure history were not regulated. Experimental conditions, e.g. saturation pressure, pressurization and decompression rates, did not enhance any phase transformation of the hydrogen gas.

Two main series of experiments were carried out. In the first one, the saturation pressure varied from 3 up to 27 MPa and decompression always occurred at 9 MPa min\(^{-1}\), whereas in the second series, samples were decompressed at a constant rate varying from 0.1 up to 90 MPa min\(^{-1}\) from an always identical saturation pressure of 9 MPa. In this way, the influence of saturation pressure was assessed.
pressure and decompression rate on cavitation onset could be addressed separately.

This real-time tracking has demonstrated the influence of the level of gas saturation pressure and of the decompression rate on the time of appearance of damage. A fastest decompression or a lowest saturation pressure decreased the cavitation time and it was possible to avoid damage with a slow decompression or a low saturation pressure (Fig. 1a and b). These two parameters had an effect on the density of visible cavities: the faster the decompression or the higher the saturation pressure, the more cavities there were. Concerning damage morphology, another result was the absence of visible damage near surfaces in all cases.

The decompression rate \( V_d \) and the saturation pressure \( P_{sat} \) had both an influence on damage and on the time of its appearance but it was impossible to always temporally predict cavitation with a simple criterion based on a gas pressure: this value was not constant when cavitation occurred and for decompression after saturation at a low gas pressure, XDF started after the end of decompression when there was no more evolution of the gas pressure (for \( P_{sat} < 8 \) MPa and \( V_d = 9 \) MPa/min or \( V_d > 20 \) MPa/min and \( P_{sat} = 9 \) MPa) (Fig. 1c and d). These results showed the significant effect of gas diffusion and the needs for a temporal analysis taking into account both mechanics and gas diffusion.

At the macroscopic scale, the samples were exposed to pressurized hydrogen, meaning to a mechanical pressure \( P_{ext,p} \) and a gas concentration \( C_{ext,p} \), linked together by Henry’s law in the elastomer (Eq. (2))

\[
C_{ext,p} = P_{ext,p} \cdot S_p
\]

These diagrams show the influence of pressure and decompression rate on the time of appearance of cavitation and the density of cavities. The absence of visible damage near surfaces is also highlighted. The equations and figures (Fig. 1) illustrate the complex relationship between gas pressure, decompression rate, and cavitation onset.
where $s_p$ is the hydrogen solubility in the rubber. Thus, the mechanical and diffusion boundary conditions at the surface of the macroscopic sample were fully defined as soon as either the pressure or concentration history was fixed. The former was controlled in our experiments and calculations have been performed with the real external loading imposed on the real geometry of samples on Abaqus/CAE® using C3D8T elements. From a sample without gas, an external gas concentration was imposed at the outer surface of the model and gas concentration at the node in the specimen center was picked up when cavitation starts (Fig. 1e and f).

Results with decompression at 9 MPa/min showed that specimen center was still saturated when XDF begins. Same result was obtained after saturation at 9 MPa except when decompression was slow enough to have beginning of desorption when damage appears. As with the macroscopic gas pressure, gas concentration in the sample was not a parameter that allowed predicting XDF.

In order to understand why the macroscopic hydrostatic pressure or gas concentration was not sufficient to predict cavitation over all the tested configurations, it was necessary to go down to the cavity scale. Numerical simulations were performed at the local scale of a small cavity pre-existing in the sample. Boundary conditions were computed from the macroscopic sample ones, following the same gas concentration and mechanical pressure histories as in the experiments. In the same way as in experiments, a special attention was paid on the influence of saturation pressure and decompression rate.

3. Numerical modeling

The aim of this diffusion/mechanics numerical approach, based on a hollow sphere modeling, was thus to highlight gas transport phenomena at a pre-existing cavity scale and to quantify the cavity growth during decompression. For various decompression conditions, the cavity size was further post-processed with a wall fracture criterion. The resulting time-to-failure was compared to the experimental one. Details about numerical solving, implemented in Matlab®, are displayed in the following, after describing first the problem geometry and boundary conditions.

3.1. General scheme

Equations of a gas diffusion/mechanics hollow sphere problem were implemented in Matlab® to compute the time response of a single pre-existing cavity located within a rubber sheet.

This problem is actually a fluid–structure interaction problem at the microscopic scale, for which three sets of equations must be solved: mechanical equations for the solid, equations of state for the gas and mass transport between the two media. Usually, these equations cannot be written within a unified framework and are solved successively with a quantification of mass exchanges in between. This numerical scheme is reproduced here.

Despite experimental results evidenced the nucleation of many cavities upon decompression, a single cavity was studied in this numerical part. The reason was that the modeling aimed at predicting the very first stage of damage, through the instable growth of primary bubbles. A spherical cavity shape was selected because only purely hydrostatic loadings are considered here and because the material is assumed to be isotropic and homogeneous with no density variations around the cavity. This first section gives a general overview of the problem geometry. Details about each calculation step will be given in the following sections.

As depicted in Fig. 2, the hollow sphere was placed at the center of a constant thickness sheet. The internal cavity radius $R_{int}$ ranged between 50 and 500 nm. Most of the calculations were performed with a sheet thickness $e = 2$ mm and a few additional ones were carried out in 1 or 4-mm thick sheets. The main reason was that decompression conditions were more detrimental for a cavity located in the core, compared to a cavity located at the vicinity of a free surface where desorption was faster and easier. Indeed, no cavity was experimentally observed through a boundary layer of about 450 µm, even in the most severe condition. Such a pre-existing cavity approach required to prescribe its initial size. Since no new experimental information was provided here to support the initial size of a physical pre-existing defect, cavities with a diameter between 0.1 µm and 1 µm were simulated, consistently with previous works by Gent et al. (between 0.01 µm and 0.1 µm) (Gent and Tompkins, 1969), Dollhofer et al. (between 0.5 µm and 10 µm) (Dollhofer et al., 2004) and Yamabe et al. (initial size before gas exposure about 14 µm) (Yamabe and Nishimura, 2011).

The cavity was surrounded by the hollow sphere shell, obviously made of the same rubber as the sample volume. The hollow sphere had an external radius $R_{ext}$ a thousand times larger than the cavity itself. This ratio has been determined so that $R_{ext}$ had no influence on the response of the cavity. In other words, the coupled diffusion/mechanics response of the cavity did not “see” the frontier of the hollow sphere. It was checked that results obtained for a higher $R_{ext}$ were unchanged.

The cavity growth problem was treated at the hollow sphere scale. However, the mechanical and diffusion boundary conditions at the hollow sphere frontier were calculated from the macroscopic sample scale. Radial symmetry of the mechanical boundary condition at the external frontier of the hollow sphere arises from the fact that only hydrostatic loadings are considered in an isotropic and homogeneous material. Concerning the diffusion problem, the radial symmetry is an approximation. In a macroscopic cavity, the gas concentration at the hollow sphere external surface has no reason to be radial. In the present situation, the cavity is very small (the cavity radius is at least 2000 times smaller than half-thickness of the rubber sheet) and gradients arising from variable distance to the free surface at each point of the cavity wall are assumed to be negligible.

As previously explained in the Experimental section, the external pressure $P_{ext,p}$ and gas concentration at the surface of the sheet $c_{ext,p}$ were related by the Henry’s law (Eq. (2)). In our experiments, pressure was regulated. The external loading was divided into a first step of pressurization at 1 MPa/min followed by a one-hour saturation step at constant pressure $P_{sat,p}$. Then, decomposition was applied at a constant rate $V_d$ between 0.2 MPa/min and 90 MPa/min. Finally, both pressure and gas concentration were removed in the last step. In the whole study, vinyltrimetoxysilane was modeled as an incompressible Neo-Hookean rubber with a shear modulus $\mu = 0.4$ MPa.

At the hollow sphere scale, the mechanical equilibrium was solved by calculating the potential energy minimum of the system, taking into account a mechanical pressure inside the cavity and outside the sphere, and a surface tension at the cavity surface.

Regarding the diffusion problem, the cavity was assumed to be initially empty. An alternative could have been to consider an air-filled cavity: the saturation stage would have been almost the same with an air–hydrogen mixture in the cavity equilibrated at the external pressure. Diffusion of the gas was calculated first at the macroscopic scale through the sheet thickness, in a one dimensional framework in coordinates linked to the sample (i.e. Cartesian coordinates). From this concentration profile through the sample thickness, the time evolution of gas at the deepness corresponding to the outer surface of the hollow sphere could be calculated in order to apply the boundary condition at the frontier of the hollow sphere. It means that the boundary conditions applied to the hollow sphere mimicked the influence of the closest free surface of the sample, i.e. through the thickness. Then, gas diffusion.
through the hollow sphere was calculated in a one-dimensional framework as in the sheet, but in coordinates linked to the hollow sphere (i.e. spherical coordinates).

Fig. 3 summarizes the global algorithm for solving the coupled diffusion/mechanics problem at each time increment \( \Delta t \). The successive steps will be presented more in depth in the following.

The first step dealt with the sheet scale: the gas concentration \( C_{ext,p} \) and pressure \( P_{ext,p} \) at the surface of the macroscopic sheet were updated first, so that the new boundary conditions \((P_{ext}, C_{ext})\) at the outer surface of the hollow sphere \( S_{ext} \) could be calculated, as explained in Section 3.2.

The following steps dedicated to the hollow sphere problem itself. Mechanics and diffusion were incremented from the same hollow sphere geometry computed at the previous time step, except that pressure in cavity was updated from the new mechanical equilibrium to solve the diffusion problem. Practically, the
mechanical equilibrium was calculated first (see details in Section 3.3.1). Diffusion was solved as reported in Section 3.3.2, i.e. by calculating the new concentration profile in the shell and the gas flux through the cavity-rubber interface, and then updating the concentration in the cavity according to the new gas content. Still on the hollow sphere problem, the final step globalized the new mechanical and diffusion states by updating the concentration profile in the hollow sphere shell from the new equilibrium thickness.

3.2. Boundary conditions of the hollow sphere problem

Since the rubber material was assumed to exhibit a hyperelastic incompressible behavior and considering the homogeneity of the sample, the outer pressure applied at the sample surface was instantaneously transferred to the outer surface $S_{\text{ext}}$ of the hollow sphere: $P_{\text{ext}} = P_{\text{ext}}(t)$. Gas concentration at the hollow sphere outer surface $S_{\text{ext}}$ was determined from the gas concentration profile through the rubber sheet, at the abscissa corresponding to the outer surface of the hollow sphere (Fig. 2).

This concentration profile through the sheet thickness $C_p(h)$ was obtained at any time of the loading history from calculations at different points $h$ equidistant by $dh$ along the sheet thickness. An explicit second-order central difference method was implemented to solve Eq. (3) and compute the gas concentration value at each point and any time. Eq. (3) depicts the time evolution of the one-dimensional Fickian diffusion profile in a spatially discretized sheet. The Fickian law was supported by Thermal Desorption Analysis kinetics of hydrogen diffusion into this rubber.

$$C_p(h,t+dt) = C_p(h,t) + \frac{C_p(h-1,t) - 2C_p(h,t) + C_p(h+1,t)}{D dt}$$

where $D$ stands for the diffusion coefficient.

The gas concentration boundary condition for the hollow sphere was defined as $C_{\text{in}} = C_p(e/2 - R_{\text{ext}})$ where $e$ is the thickness of the sheet and $R_{\text{ext}}$ is the outer radius of the hollow sphere. $dh$ was calibrated to be able to calculate $C_p$ at the hollow sphere frontier precisely, and to get a good accuracy for the gas concentration profile through the sheet. Since time increments $dt$ were short (between $1 - 10^{-5}$ s and $5 - 10^{-4}$ s), the gas concentration increments within a given time step were small also so that $dh$ did not need to be finitely discretized to get a good accuracy.

3.3. Resolution of the hollow sphere problem

3.3.1. Mechanical equilibrium of the hollow sphere

At the hollow sphere scale, the mechanical equilibrium was solved first. Input data were the internal pressure $P_{\text{int}}$ calculated at the end of the previous time step, and the updated value of the external pressure $P_{\text{ext}}$ on the hollow sphere from Section 3.2.

Outputs were the new size of the hollow sphere ($R_{\text{ext}}$) including the size of the cavity ($R_{\text{int}}$), the temporary new internal pressure $P_{\text{int}}$, only dependent on the already contained gas quantity and on the volume change enhanced by the new equilibrium balance at the current time step. This first updating of $P_{\text{int}}$ only obeyed mechanical equilibrium without any gas transport yet.

$P_{\text{int}}$ was updated again later, after the diffusion calculation.

(1) Equations of the cavity equilibrium in an incompressible Neo-Hookean sphere, including surface tension effect, was based on the paper by Dollhofer et al. (2004) developed in a slightly different framework, i.e. an empty cavity undergoing external hydrostatic tension.

As a result of incompressibility, the basic relationship of Eq. (4) linked up the initial geometry to the current one:

$$R(t)^3 - R_{\text{int}}(t)^3 = R(t)^3 - R_{\text{int}}(0)^3$$

Eq. (4) held for any point distant by $R$ from the center of the hollow sphere. For a given time $t$, $R$ could be isolated from Eq. (4), leading to Eq. (5)

$$R(t) = (R(0)^3 - R_{\text{int}}(0)^3 + R_{\text{int}}(0)^3)^{1/3}$$

Incompressibility provided the additional relationship between the stretch ratios $\lambda_{\text{int}}, \lambda_{\text{ext}}, \lambda_{\text{eq}}$ given by Eq. (6)

$$\lambda_{\text{int}} \lambda_{\text{ext}} \lambda_{\text{eq}} = 1$$

where stretch ratios can be expressed by Eq. (7) and (8)

$$\lambda_{\text{int}} = \frac{dR(t)}{dR(0)}$$

$$\lambda_{\text{ext}} = \frac{R(t)}{R(0)}$$

$$\lambda_{\text{eq}} = \frac{R(t)}{R(0)}$$

In this context, it was then possible to determine the potential energy of the system. The potential energy of the system II was calculated following Eq. (9)–(14), taking into account the external works $W_{\text{ext}}$ and $W_{\text{int}}$ respectively due to the inner and outer pressure, the strain energy $U$ and the surface tension energy $U_{\gamma}$

$$\Pi = U + U_{\gamma} - W_{\text{ext}} - W_{\text{int}}$$

where

$$U(t) = \iiint_{\text{domain}} \left[ \frac{\mu}{2} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial u}{\partial y} \right)^2 + \left( \frac{\partial u}{\partial z} \right)^2 \right] dV$$

by using Eq. (5) and (8)

$$U(t) = \frac{2 \pi E}{3} \int_{R_{\text{int}}}^{R_{\text{ext}}} \left[ 2 \left( 1 + R_{\text{int}} \left( \frac{R_{\text{int}}}{R} \right)^3 - \left( \frac{R_{\text{int}}}{R} \right)^3 \right) \right]^{4/3} R^2 dR$$

$$U_{\gamma} = 4 \pi \gamma R_{\text{int}}^2 t^2$$

$$W_{\text{ext}} = - \frac{P_{\text{ext}} S_{\text{ext}}}{R_{\text{ext}} - R_{\text{int}}(0)}$$

$$W_{\text{int}} = \frac{P_{\text{int}} S_{\text{int}}}{R_{\text{int}} - R_{\text{int}}(0)}$$

$$W_{\text{int}} = 4 \pi \rho_{\text{int}} R_{\text{int}}^3 \left( 1 - \left( \frac{R_{\text{int}}}{R_{\text{ext}}} \right)^3 \right)^2$$

For given hollow sphere dimensions ($R_{\text{ext}}, R_{\text{int}}$), a fixed material (i.e. the shear modulus $\mu$ and the surface tension $\gamma$) and for a given couple of inner/outer pressure ($P_{\text{int}}/P_{\text{ext}}$), the equilibrium solution corresponded to the stretch ratio $\lambda_{\text{eq}}$ for which the potential energy was minimum (Eq. (15))

$$\frac{d\Pi}{d\lambda_{\text{eq}}} = 0$$

To reduce the calculation time during time-dependent simulations, solutions were previously mapped as a function of $P_{\text{int}}, P_{\text{ext}}, R_{\text{ext}}, R_{\text{int}}, E$ and $\gamma$. For each time increment, the mechanical solution was linearly interpolated between the four nearest solutions over the map. 200 values were taken for $P_{\text{ext}}$ and $P_{\text{int}}$ to create the map between $-0.5$ MPa and 10 MPa for all tests below 9 MPa. This accuracy leads to an error lower than 0.4%.

The new equilibrium size of the cavity provided a new volume $V_{\text{int}}$ which was used to update $P_{\text{int}}$ (as depicted in Eq. (16)) consid-
erating a constant gas quantity in the cavity, obeying an ideal gas law.

\[ P_{\text{int}}(t') = P_{\text{int}}(t) \frac{V_{\text{int}}(t)}{V_{\text{int}}(t')} \]  

(16)

where \( t' \) is a temporary calculation time inside the time step after updating the cavity volume \( V_{\text{int}} \).

Yamabe and Nishimura (2009) evidenced that hydrogen content in an exposed sample obeyed a Henry’s law. This result was used in the material and at the interface cavity/elastomer and elastomer/pressure chamber. Furthermore, hydrogen in the cavity was assumed to behave as an ideal gas. So, the gas concentration in the cavity \( C_{\text{int}} \) was related to the pressure \( P_{\text{int}} \) following Eq. (17), where \( R_{\text{CP}} \) is the perfect gas constant taken as 8.314 J K\(^{-1}\) mol\(^{-1}\). Temperature was fixed at 30°C.

\[ P_{\text{int}} = C_{\text{C}} R_{\text{CP}} T \]  

(17)

If the difference between \( P_{\text{int}}(t') \) and \( P_{\text{int}}(t) \) exceeded 0.1, the equilibrium calculation was iterated from \( P_{\text{int}}(t') \) not more than two more times however. Anyway, it could be shown that the problem converged towards a solution.

### 3.3.2. Gas diffusion

The objective of the gas diffusion routine was to compute the concentration profile \( C(h) \) through the hollow sphere shell and the gas concentration in the rubber at the surface of the cavity \( C_{\text{ext}} \), respectively at \( R_{\text{ext}} \) and \( R_{\text{int}} \) by the Henry’s law. Diffusion calculation was made on the fixed hollow sphere geometry at time \( t \), i.e. before mechanical balance update.

Input data were the gas concentration at the frontier of the hollow sphere \( C_{\text{ext}} \), the gas concentration profile at \( t = C(h, t) \), and the new value of \( C_{\text{int}} \) calculated from \( P_{\text{int}} \) by the Henry’s law at the end of the previous mechanical routine. Here arises a major assumption of the modelling. The internal pressure \( P_{\text{int}} \) computed from the mechanical problem in Section 3.3.1 was that inside the cavity, whereas \( P_{\text{in}} \) in the Henry’s law referred to pressure in the rubber at the surface of the cavity (i.e. at \( R_{\text{int}} \)). In the same way as Stewart before (Stewart, 1970), pressure continuity between cavity and rubber surface was assumed in the present modelling.

(i) The new gas concentration profile through the shell was calculated first. The analytical solution for hollow sphere proposed by Carslaw and Jaeger for heat transfer in a hollow sphere (Carslaw and Jaeger, 1980) has been adapted here for gas diffusion, as depicted by Eq. (18) considering a gas concentration \( C_{\text{ext}} \) and \( C_{\text{int}} \) respectively at \( R_{\text{ext}} \) and \( R_{\text{int}} \), and the gas concentration history in the material:

\[ C(R, t + dt) = \frac{R_{\text{ext}}(t)C_{\text{ext}}(t) - \left(R_{\text{ext}}(t)C_{\text{ext}}(t) - R_{\text{ext}}(t)C_{\text{int}}(t)\right)\left(R_{\text{ext}} - R_{\text{int}}\right)}{R_{\text{ext}}(t) - R_{\text{int}}(t)} + \sum_{n=1}^{N} \frac{n\pi(R - R_{\text{ext}})}{(R_{\text{ext}} - R_{\text{int}})^2} \sin\left[\frac{n\pi(R - R_{\text{ext}})}{(R_{\text{ext}} - R_{\text{int}})}\right] \]

\[ \times \exp\left[\frac{-Dn^2\pi^2dt}{(R_{\text{ext}} - R_{\text{int}})^2}\right] \]

\[ + \frac{2}{R_{\text{ext}}(t) - R_{\text{int}}(t)} \sum_{n=1}^{N} \sin\left[\frac{n\pi(R - R_{\text{ext}})}{(R_{\text{ext}} - R_{\text{int}})}\right] \exp\left[\frac{-Dn^2\pi^2dt}{(R_{\text{ext}} - R_{\text{int}})^2}\right] \]

\[ \times \int_{R_{\text{int}}(t)}^{R_{\text{ext}}(t)} RCR(t) C_{\text{int}}(R, t) \sin\left[\frac{n\pi(R - R_{\text{ext}})}{(R_{\text{ext}} - R_{\text{int}})}\right] dR \]

(18)

To estimate the integral, the radius of the hollow sphere was discretized into equidistant points and the gas concentration was linearly interpolated between successive points distant by \( dR \).

(ii) The updated gas concentration profile through the rubber shell was used to compute the gas flux at the interface of the cavity, meaning the gas quantity sorbed or released by the cavity. As already assumed by Stewart (1970), the gas flux \( F(R_{\text{int}}, t) \) at the cavity-rubber interface was taken proportional to the gas concentration gradient near the interface, as depicted by Eq. (19) where \( D \) is the diffusion coefficient:

\[ F(R_{\text{int}}, t) = D \frac{\partial C(R_{\text{int}}, t)}{\partial R} = D \frac{C(R_{\text{int}} + dR, t) - C(R_{\text{int}} - dR, t)}{dR} \]  

(19)

\( dR \) equaled 1/6 of \( (R_{\text{ext}} - R_{\text{int}}) \) in order to have converging calculation within a reasonable time. So \( dR \) and \( dt \) were related to get convergence. In the present case, \( dR \) was calibrated to have a good accuracy. One hour was needed to saturate a 2-mm-thick sample; in such case, the gas pressure around the cavity evolved slowly and \( dR \) had no influence on results.

(iii) Then, the current gas concentration in the cavity \( C_{\text{c}} \) (defined as the gas quantity inside the cavity \( N \) divided by the cavity volume \( V_{\text{int}} \) and expressed in nmol mm\(^{-2}\)) could be calculated as a function of the new gas quantity \( N \), the surface of the cavity wall \( S_{\text{int}} \) and the volume of the cavity \( V_{\text{int}} \) as given by Eq. (20):

\[ C_{\text{c}}(t + dt) = C_{\text{c}}(t) + \frac{1}{V_{\text{int}}(t)} \frac{\partial N(t)}{\partial t} - \frac{C_{\text{c}}(t) \partial V_{\text{int}}(t)}{V_{\text{int}}(t)} \]

(20)

The final value of the internal pressure in the cavity \( P_{\text{int}}(t + dt) \) could be obtained then from the perfect gas law at constant temperature.

### 4. Temporal analysis and cavitation criteria

The present model displayed the time evolution of the cavity radius in a hyperelastic material. It took into account the surface tension and gas exchange in the cavity with a direct relationship between gas concentration and pressure in the cavity. A goal of this model was to understand the driving force leading a small cavity to grow up to macroscopic damage.

In the pure mechanical case of an empty cavity (i.e. without gas diffusion) in a hollow sphere undergoing hydrostatic tension, Doolhofer et al. found out bifurcation solutions above a critical value of the hydrostatic stress applied at the outer surface of the hollow sphere (Doolhofer et al., 2004). The potential energy reached as well meta-stable, unstable and absolutely stable equilibrium. In these conditions a cavity could appear at a visible size from a small cavity.

In the present coupled diffusion/mechanics conditions the minimization solution was always unique. This issued from the compression loading at the front of the hollow sphere, as illustrated in Fig. 4 for a hollow sphere with \( R_{\text{int}} = 500 \) nm and \( R_{\text{ext}} = 500 \) μm. This graph clearly evidence a stable cavity with one minimum of potential energy only for a compression of the hollow sphere (\( P_{\text{ext}} > 0 \) and \( P_{\text{int}} > 0 \) (Fig. 4b) and more than one solution for a traction (Fig. 4a).

In this problem including an external and internal pressure, there was always a unique stable solution for \( \lambda \). No ingredient was included to the hollow sphere problem itself to enhance mechanical instability and dramatic growth of the cavity.

The model allowed temporally following the gas pressure inside the cavity \( P_{\text{int}} \) outside the hollow sphere and the sheet \( P_{\text{ext}} \) and the internal radius \( R_{\text{int}} \) of the cavity.

Typical results of the temporal follow up are presented Fig. 5, for a hollow sphere with \( R_{\text{int}} = 0.5 \) μm and \( R_{\text{ext}} = 500 \) μm located at the center of a 2-mm thick sheet. After saturation of the sheet at 9 MPa for one hour, the pressure was released at \( V_{\text{j}} = 90 \) MPa/ min.

Fig. 5 shows the time evolution of \( P_{\text{ext}}, P_{\text{int}} \) and \( R_{\text{int}} \) during saturation (Fig. 5a) and decompression (Fig. 5b). At the very early beginning of pressurization, although the external pressure \( P_{\text{ext}} \) had started to increase, the increase of pressure in the cavity \( P_{\text{int}} \)
was delayed, due to the time needed for hydrogen diffusion across the rubber and into the cavity (Fig. 5c.B). This pure mechanical pressure step led to a cavity contraction. Then, the gas started to fill the cavity and two competitive processes occurred: on one hand, \( P_{\text{int}} \) tended to open the cavity while \( P_{\text{ext}} \) kept decreasing its size (Fig. 5c.C). After \( P_{\text{ext}} \) reached the prescribed value, \( P_{\text{int}} \) kept increasing and the cavity growing up (Fig. 5c.D) until saturation was reached (Fig. 5c.E). In the saturated state, the cavity was found to be always smaller than the initial size, showing that cavitation was not possible during saturation (Stewart, 1970).

During the first step of the decompression, the decrease of external pressure made the cavity volume increase quickly. Therefore, the gas concentration in the cavity \( C_{\text{C}} \)--which is the gas quantity divided by the cavity volume-- decreased as well as the internal pressure \( P_{\text{int}} \) (Fig. 5c.F). This phenomenon occurred very fast before the beginning of global gas desorption at the center of the infinite sheet, so that the rubber was still saturated around the hollow sphere. The quick volume increase and the subsequent drop of the internal pressure enhanced pressure disequilibrium between the cavity and the rubber layer at the surface of the cavity. Since a continuous pressure was assumed at the interface, disequilibrium was compensated by a gas flux from the rubber towards the cavity. Less compensation was needed as soon as even partial desorption to the surrounding atmosphere could be possible, i.e. at slower decompression rates. Then, \( P_{\text{int}} \) and \( C_{\text{C}} \) increased again (Fig. 5c.G) before global desorption of the sample (Fig. 5c.H) and return back to the initial state (Fig. 5c.A).

To sum up, there was a cavity extension during decompression before a return to the initial state. Therefore, it was necessary to introduce a criterion accounting for irreversible growth of the cavity. As a first basic attempt, a critical biaxial elongation criterion was selected to mimic the cavity wall fracture. The time evolution of the extension ratio of the cavity wall was then post-processed and compared with the criterion to estimate the time-to-failure. In similar approaches, Gent and Wang used the critical stretch ratio \( k_{\text{crit}} \) of 10 determined in uniaxial tension on a natural rubber (Gent and Wang). Diani (Diani, 2001) picked up this value again but finally considered that a critical stretch of 2 seemed more physical. Our model sensitivity to this critical parameter \( k_{\text{crit}} \) will be discussed in the following and results will be plotted in the following sections for various influence parameters.

![Fig. 4. Solutions for the tangential stretch ratio of the cavity wall as a function of \( P_{\text{ext}} \) and \( P_{\text{int}} \) in the case of (a) negative and (b) positive hydrostatic pressure.](image)

![Fig. 5. Temporal evolution of the hollow sphere internal and external pressures \( P_{\text{int}} \) and \( P_{\text{ext}} \), and of the cavity radius during (a) saturation and (b) decompression with \( R_{\text{int}} = 0.5 \mu m \) and \( R_{\text{ext}} = 500 \mu m \), \( P_{\text{int}} = 9 \text{ MPa} \) and \( V_d = 90 \text{ MPa/min} \). (c) Schematic representation of the different phases.](image)
5. Critical stretch ratio identification and prediction of the decompression rate influence

This section now focuses on the effect of decompression rate. Simulation conditions were those of the second series of experiments, i.e. decompression at different rates from an identical saturation pressure (9 MPa). Four initial cavity sizes were simulated with internal radius of $R_{int} = 50$ nm, 100 nm, 250 nm and 500 nm. Fig. 6 plots the time evolution of the biaxial stretching ratio for cavities ($R_{int} = 500$ nm) saturated at 9 MPa and decompressed at $V_d$ between 0.2 (no damage observed during the test) and 90 MPa/min (fastest experimental decompression).

A fast decompression led to a high maximum stretch ratio. However, even under a decompression rate of 90 MPa/min, it was not possible to enhance cavitation by prescribing a cavity wall fracture criterion of $\lambda_{crit} = 10$. This value, calibrated by Gent and Wang (1991) from uniaxial tension in natural rubber, was not relevant in the present biaxial framework. The critical extension criterion was calibrated from the experiments by averaging the maximum computed extension ratios between the minimal pressure for which damage was observed (i.e. 0.3 MPa/min) and the maximal one for which no cavitation was observed (0.2 MPa/min). The calibrated value was $\lambda_{crit} = 1.25$. It was consistent with previous discussion about pure mechanical cavitation in rubbers and PMMA (Diani, 2001). For this calibrated $\lambda_{crit}$, the corresponding time could be picked up for each decompression rate and values could be plotted against the decompression rate and compared to the experimental values, as made in Fig. 7.

Numerical results were in good agreement with experiments. The modeling captured the observed increase of cavitation time with the slowing down of decompression. Moreover, the model was able to predict a decompression rate threshold below which cavitation did not occur. But for the fastest decompression, the model predicted a too early cavitation. This difference could arise from a local viscous contribution of the rubber behavior, not taken into account in the present hyperelastic modeling. More precisely, two effects could be induced: first, the transfer of the external pressure drop to the hollow sphere frontier would be delayed, and secondly, the opening of the cavity would be slowed down. Since viscosity remains weak in rubber materials, such an effect would be noticeable at high decompression rates only.

Let us comment now on the influence of the initial size of the cavity, which was not experimentally supported here and was therefore arbitrary assessed. Fig. 7 shows that simulations performed with a larger initial cavity size ($R_{int} = 250$ or 500 nm) predicted a damage limit at about $V_d = 0.27$ MPa/min whereas it was about 0.45 MPa/min with the previous $R_{int} = 100$ nm. Therefore, only the smallest cavities were expected to expand up to a visible size under slow decompression and more visible cavities were expected under faster decompression. This qualitative result was consistent with the increase of cavity density with $V_d$ observed during experiments.

This influence of the cavity size could be shown by plotting the maximum stretch ratio during decompression for various decompression rate and initial cavities sizes (Fig. 8). By extrapolating these curves from a polynomial interpolation of experimental data, it was possible to estimate the order of a minimum cavity radius that will leads to damage for a given pressure cycle. With $V_d = 1.8$ MPa/min for example, only cavities whose radius exceeds 10 nm cavitate. This result was in good agreements with considerations made by Stevenson and Morgan (1995) who consider defects in rubbers with a size between 2 nm and 200 nm or made by Yamabe and Nishimura (2009) with 20 µm in diameter defects. The good agreement between literature and the extrapolation method validates the extrapolation method. Furthermore, this extrapolation is justified by the fact that the smaller the initial cavity is, the higher the surface tension, and so the lower the maximum stretch ratio is expected to be.
This numerical analysis was done with one cavity only, making impossible the replication of the satellite bubbles initiation observed experimentally around primary cavities (Gent, 1990). Such a modeling framework was relevant here, regarding the present aim at predicting the very first stage of damage in the most severely loaded zones of the sample. It would have been a limitation however if the aim had been to predict damage growth.

6. Prediction of the saturation pressure influence

For comparison purpose with the other experiment series, decompressions were also simulated from different saturation pressures (ranging from 3 up to 30 MPa) at the same decompression rate of 9 MPa/min. Only the biggest cavity (Rint = 500 μm and Rout = 500 nm) was modeled due to the calculation time arising from small cavity sizes. Indeed, the gas quantity entering the cavity was a function of its surface which was itself a function of the square radius. So, by decreasing Rout by a factor of 10, Sat decreased by a factor 10² and the time needed for computation achievement increased by the same factor. As an example, the time needed to compute saturation in a 500 nm-radius cavity was four days, whereas it was more than four weeks to complete the same calculation in a 50 nm-radius cavity.

Fig. 9 shows a good trend between the model and experiments. Firstly, the time elapsed before the dramatic growth of the cavity increased with the saturation pressure from which decompression was applied. Secondly, the modeling could predict a saturation pressure threshold below which the cavity wall did not fracture. For instance, the computed extension ratio of the cavity wall upon decompression from 2 MPa never reached the kcrit = 1.25 criterion. An important result was also that the critical elongation criterion (kext = 1.25), calibrated from experiments at different decompression rates, led to relevant predictions for different saturation pressures.

A limitation of the current modeling was that the maximum extension of the cavity wall systematically coincided with the end of decompression (when Pint vanished). So, it would not have been possible to predict cavitation after the end of decompression based on this modeling version. Such situations corresponded to the points below Psat = 9 MPa for which the difference between modeling and experiments was the largest.

Further work, may be on the fracture criterion and on rubber viscosity, should be developed to extend predictions to situations for which damage onset occurs after the end of decompression.

7. Influence of the distance to the free surface

The goal of this last series of simulation was to evaluate sensitivity to the sheet thickness and to discuss the boundary layer phenomenon observed experimentally. Let us remind indeed that an about 450 μm-thick layer without any cavity was observed near the free surfaces of the macroscopic sample. To this aim, computations were done in a 1 mm and a 4 mm thick sheet (Fig. 10).

For a cavity located in the core of a thinner sheet, desorption started slightly earlier and Pint decreased faster. A fastest decompression rate is needed to cavitate. The decompression rate threshold between cavitation and no cavitation situations increased by more than a decade between 1 mm and 4 mm thick sheets. This was directly related to the boundary layer effect pointed out in experiments. The ability of the model to account for the free surface distance, usually impossible in previously reported approaches, is a first step towards the design of basic structures like O-rings for instance.

Another result was an appearance of damage faster when the sample was thicker because for a thick sample, diffusion at the center of specimens started later. This effect was not visible for a decompression with Vd = 90 MPa/min when damage appeared before desorption even in the 1 mm in thickness sample.

8. Conclusion

This work addressed damage decompression in a gas-saturated rubber in various conditions than reported in the literature: during decompression and with various controlled decompression rates. Experiments were carried out based on an original hydrogen facility able to track damage in real time. A significant effect of saturation pressure and decompression rate on cavitation time and cavitation threshold was evidenced, proving that cavitation criteria only based on hydrostatic pressure at the material point to predict the whole set of decompression conditions are irrelevant. Furthermore a criteria based on gas concentration at the material point was also shown to be irrelevant.

Conclusions of the experimental part argued to consider the problem at the fine scale of a single cavity in an incompressible Neo-Hookean rubber. This was numerically explored through coupled diffusion/mechanics simulations of a hollow sphere problem, whose boundary conditions were calculated from the macroscopic sample. Simulation results provided the time evolution of the radius and internal pressure of the cavity for every experimental decompression. Contrary to the case of purely mechanical loading, where cavity growth is the result of instability, cavity growth during decompression after saturation is the consequence of gas
exchange between the cavity and the rubber material. By post-
processing a cavity wall fracture criterion, it was possible to
predict the corresponding cavitation times. The major contribu-
tion of this coupled mechanical/gas diffusion approach was to tempo-
rally predict experimental results, including the lack of cavitation
for a slow decompression rate or a low saturation pressure.

The second major contribution was the ability to simulate suc-
cessfully the influence of the distance to the free surface and the
boundary layer observed near the surface in experiments.

Compared to previous studies that were only valid for complete
decompressions, the developed model provides new tools for the
design of components subjected to extended loading conditions,
such as partial decompression or cyclic loadings.

Acknowledgments

Authors gratefully acknowledge Pr. Nishimura and Dr. Fujiwara
from the HYDROGENIUS program of the National Institute of
Advanced Industrial Science and Technology at Kyushu University
(Japan) for their collaboration about measurement of the hydrogen
properties of hydrogen in the studied material. JSPS program is also
acknowledged for funding J. Jaravel’s stay in Kyushu University, as
well as CNRS and Région Poitou-Charentes for granting his PhD.

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Glossary

$\rho_{ts}$: root of the $J_0(x) = 0$ equation with $J_0$ Bessel function

$C(R)$: gas concentration profile in the hollow sphere

$C_{e,M}$: gas concentration at the outer surface of the hollow sphere

$C_{e,P}$: gas concentration at the outer surface of the sheet

$C_{e}$: gas concentration in the cavity (gas quantity inside the cavity divided by
the cavity volume)

$C_{m}$: gas concentration in the cavity (gas quantity inside the cavity divided by
the cavity volume)

$C_{e,h}$: gas concentration profile in the sheet

$D$: diffusion coefficient

$dh$: distance between two points for the calculation of the gas concentration profile
in the sheet

$dt$: temporal increment for a step of equilibrium calculation

$dx$: distance between two points for the calculation of the gas concentration profile
in the hollow sphere

$\varepsilon$: sheet thickness

$F$: gas flux at the interface between the cavity and the material

$\gamma$: surface tension coefficient

$\lambda$: tangential stretch ratio of the internal radius of the hollow sphere in spherical
coordinates

$\lambda_s$: radial stretch ratio in spherical coordinates

$\lambda_t$: tangential stretch ratio in spherical coordinates

$\lambda_{Az}$: Azimuthal stretch ratio along the radius in spherical coordinates

$\mu$: shear modulus of the material

$N$: number of gas moles in the cavity

$P_{ext}$: gas pressure at the external surface of the hollow sphere

$P_{ext,h}$: gas pressure at the external surface of the sheet

$I$: potential energy of the hollow sphere

$P_{sat}$: gas pressure in the cavity

$P_{sat}$: saturation pressure

$Q_{ext}$: gas quantity remaining in the cylinder for the determination of $D$ and $\varepsilon$

$R$: radius coordinate in the hollow sphere

$\psi$: initial radius of the cylinder used for the determination of $D$ and $\varepsilon$

$S_{ext}$: external surface of the hollow sphere

$S_{int}$: internal surface of the hollow sphere (i.e. surface of the cavity)

$\psi_c$: gas solubility in the elastomer

$U$: strain energy of the hollow sphere material

$U_{int}$: surface tension energy of the hollow sphere

$V$: volume of the cylinder used for the determination of $D$ and $\varepsilon$

$V_{DC}$: decompression rate

$V_{int}$: cavity volume

$V_{ext}$: external work of the pressure at the outer surface of the hollow sphere

$V_{int}$: external work of the pressure at the inner surface of the hollow sphere

$\delta$: thickness of the cylinder used for the determination of $D$ and $\varepsilon$. 