Visualization of Bond Scission due to Nucleation and Growth of Gas Bubbles in Elastomers.

Xavier P. Morelle*, †, ‡, §, Gabriel E. Sanoja†, §, Sylvie Castagner‡, and Costantino Creton*, †, §.

1 SIMM, ESPCI Paris, Université PSL, CNRS, Sorbonne Université, 75005, Paris, France.

2 Institut Pprime (UPR 3346 CNRS – ENSMA – Université de Poitiers), Department of Physics and Mechanics of Materials, 1 Avenue Clément Ader, BP 40109, 86961 Futuroscope cedex, France.

3 Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan.

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ABSTRACT: When an elastomer is saturated with gas and then rapidly decompressed, small cavities may nucleate, inflate, and deflate inside the material. This phenomenon, herein considered as a type of cavitation, is very important for elastomer seals because it induces damage and hampers their lifetime in use. By incorporating π-extended anthracene-maleimide adducts, a damage-activated probe, in a model unfilled poly(ethyl-acrylate) elastomer, we are able to thoroughly visualize where molecular damage occurred due to this rapid decompression. These probes yield a strong and stable fluorescent signal upon polymer chain scission enabling non-destructive detection of damage via confocal fluorescence microscopy in pristine-looking specimens. Cavities nucleated by rapid decompression of a hydrogen-saturated elastomer were examined with the present methodology. We observe that each spherical cavity in its inflated state corresponds in its unloaded configuration to a randomly oriented 2D penny-shape crack.

As a result, cavity growth in elastomers occurs through a localized fracture process with irreversible bond breakage and subsequent deformation of the initially planar damaged area into a cavity. High resolution inspection of the morphology of these penny-shape cracks suggests that cavity growth may proceed discontinuously and in a stick-slip fashion with stable and unstable crack growth. This novel visualization method has enormous potential for non-destructive inspection of complex 3D damage inside soft materials where surface tension and elastic restoring forces close cracks in the absence of loading.

Introduction

Elastomers are ubiquitous engineering materials used in applications going from classical rubber tires and seals, to more recent ones like soft robotics [1-3], and wearable electronics [4, 5]. Among classical applications, one of the most technologically relevant is that of seals where the ability of elastomers to undergo large reversible deformations is used to effectively block gas or fluid transport (the classic O-ring). Gas poses specific problems since the gas molecules can diffuse, swell, and saturate the elastomer. Upon a sudden pressure drop, the resulting imbalance in chemical potentials drives gas diffusion at a rate that is generally too slow to prevent solid-gas phase separation as well as cavity nucleation and growth. Such a process, known as rapid or explosive decompression, has been observed in elastomers saturated with gases [6], and more recently with liquids [7]. Note that such an explosive decompression process has become of particular concern for the storage and transportation of hydrogen; a highly soluble, flammable, and explosive gas increasingly used as a new energy carrier for a more sustainable economy [8].

Cavity growth was originally perceived as a deformation process (expansion of a preexisting initial flaw [9-11]), but as theoretical and experimental advances were made, it has been increasingly ascribed to fracture [12-17] involving the irreversible scission of covalent bonds in the crosslinked network [7, 17]. This consideration seems sensible when large cavities leave visible macroscopic damage [9, 13, 18] such as surface blisters, but is less obvious when small cavities completely disappear and leave the elastomer looking as-pristine [19]. The first theoretical models of cavitation [10, 11, 20] assumed the isotropic expansion of a spherical cavity under hydrostatic pressure, even if this is seldom representative of cavity growth [21]. Since then, more recent models have based their cavitation criterion not only on elastic considerations but also on the strength [22], strain hardening and fracture toughness of elastomers [12, 16]. Nonetheless, the precise shape, deformation, and growing mechanism of a cavity remains unclear [23]. Whereas some models assume that cavitation-induced fracture results from diffuse bond breakage along the cavity wall [12, 20, 24], others argue that it follows from growth of a penny-shaped crack [15, 16, 22]. Hence, direct visualization of molecular damage after cavities have inflated and deflated would provide unprecedented experimental evidence into cavitation-induced fracture while guiding the design of high-performance cavitation resistance elastomers.
Cavitation-induced damage, and more generally internal damage in elastomers, is challenging to visualize because elastic restoring forces and surface tension close cracks and flaws in the absence of a load. Techniques such as X-rays and neutron scattering are limited by the insufficient contrast between pristine and damaged regions in the unloaded state, whereas others like acoustic emission lack 3D spatial resolution and have low signal detection thresholds [25]. More recently, in situ micro-tomography has enabled 3D visualization of cavities for the case where hydrostatic tension was applied mechanically in a poker-chip geometry [26], or with a rapid gas decompression set-up [21]. However, this technique is only suitable to visualize cavities in the loaded configuration and is unable to resolve molecular damage and deformation. A method to visualize damage due to bond scission in the undeformed configuration would be more valuable to detect the extent of microscopic damage, prevent macroscopic fracture and facilitate the timely replacement of seals prior to failure. Such early detection of damage would also serve to extend lifetime, mitigate over-engineering, and ensure a safely use of seals in storage and transportation of flammable gases such as hydrogen.

Elastomers tagged with mechanophores are ideally suited to visualize molecular damage in the absence of a load. When properly positioned within a polymer chain, these mechanophores can change their photophysical properties (e.g., fluorescence, and luminescence) in response to a force-induced chemical reaction [27]. The first investigations on elastomers used mechanoluminescent 1,2-dioxetane probes that emit photons upon bond scission [28-31]. Such probes only luminesce during cavity inflation and, as such, damage visualization would only be possible by in-situ monitoring of explosive decompression with a high-sensitivity camera and would result in a much lower spatial resolution than 3D micro-tomography. Göstl, R. et al [32, 33] instead, developed a mechno-fluorescent \( \pi \)-extended anthracene-maleimide adduct (FIG1A) that upon bond scission produces a \( \pi \)-extended anthracene fluorophore of high quantum yield, and stability to photobleaching [32]. These probes have been recently randomly incorporated in polymethyl- and polyethyl-acrylate elastomers and have been shown to report quantitatively for covalent bond scission near fracture surfaces after mode I crack propagation [34].

In the present study, we used the same methodology to synthesize a poly(ethyl-acrylate) crosslinked elastomer tagged with \( \pi \)-extended anthracene-maleimide adducts (for synthetic details refer to Materials & Methods). This elastomer has a glass transition temperature \( T_g \approx -18^\circ C \), a Young’s modulus \( E \approx 1 \) MPa, and a fracture toughness \( G_f \approx 180 \) Jm\(^{-2}\); and was used as a model material to visualize damage by bond breakage after cavity nucleation and growth. Note that contrary to the PDMS undercrosslinked Sylgard PDMS elastomers used by Poulain et al. [17, 19], these elastomers do not contain any unreacted fluids inside and are in that sense more representative of poly(butadiene) or poly(isoprene) based elastomers obtained by crosslinking the polymer.

Once the materials were synthesized, we first induced cavitation with a rapid decompression set-up, similar to the one originally used by Gent and Tompkins [6] but with in-situ monitoring of cavity nucleation and growth with an optical camera (FIG1B). We then imaged the regions where cavity inflation and deflation occurred with a confocal fluorescent microscope, and reconstructed 3D maps of cavitation-induced damage in the undeformed configuration. Note that these regions were completely transparent and pristine-looking in the absence of laser exposure, meaning that damage was only detectable after fluorophore excitation.

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**Figure 1.** (A) Incorporation of mechanophores as sacrificial crosslinkers in an ethyl-acrylate (EA) elastomer. Upon force-induced activation, the \( \pi \)-extended anthracene-maleimide probes undergo cycloreversion and result in fluorescent anthracene moieties that report local bond breakage, representative of the covalent network failure. (B) Rapid decompression set-up: tests are performed in a pressure chamber where elastomer samples are exposed to high-pressure \( (P_{\text{sat}}) \) hydrogen gas during 10 \( h \) to reach full saturation. Upon fast release of that pressure, the gas trapped within the elastomer network desorbs and leads to the formation of visible cavities that progressively disappear over time. As soon as decompression starts (orange shaded regime), pictures are taken every 1 \( s \) to monitor the inflation and deflation of visible cavities.
Cavity Nucleation & Growth by Rapid Decompression

FIG2A displays optical snapshots of the rapid decompression of our model poly(ethyl-acrylate) elastomer. The specimen was saturated with H₂ for 10 h at 5 MPa, and then decompressed to 0.1 MPa at a rate of 10 MPa/min. Soon after the start of decompression (~60 s), optically visible cavities appeared randomly distributed throughout the specimen. Noteworthy, the sample thickness is 0.8 mm and thus the optical visualization of cavities is limited to 2D projections, meaning that there are some intrinsic errors in the cavity size measurement due to cavity out-of-plane tilting and overlapping.

Cavities progressively grow, reach a maximum size, and then deflate and become optically invisible over time. Most of them initially appear circular in projection and then change to a more anisotropic shape. FIG2B shows the growth of some selected cavities and highlights the transition from sphere to ellipsoid (blue dots), as well as their maximum size (red squares). Note that some small cavities appear spherical over the whole decomposition process (see the three bottom curves in FIG2B). Optical image processing enables estimation of the cavities projected area during growth and determination of their size distribution at the point of maximum inflation (FIG2C). By approximating each cavity as a circle of equivalent projected area (see details in Materials & Methods), we determined an average cavity radius of 163 µm with a standard deviation of 34 µm.

The time at which each cavity reaches its maximum size depends on their locus of nucleation. If a cavity is formed closer to the surface, the gas will diffuse out of it faster while lowering the driving force for growth, leading to smaller cavities. This is further validated by confocal fluorescent microscopy as discussed in the following section. To conclude, under the applied conditions, cavities seem to nucleate rather randomly in the 3D volume of the elastomeric network.

Damage Visualization Through Post-mortem Confocal Imaging Analysis

After rapid decompression and complete gas desorption, the specimen was removed from the pressurized chamber and cavitation-induced damage evaluated with confocal fluorescence microscopy by building 3D fluorescent maps. As illustrated in FIG3A, the specimen is pristine-looking at that point with no visible trace of cavities remaining from decompression. However, imaging regions that experienced cavitation reveals fluorescent sites of localized bond scission with size, shape, and orientation analogous to that of the observed cavities (FIG3). It is worth noting that we did not detect any localized fluorescence in regions where we did not optically observe cavities, indicating that these regions are likely to remain cavity-free (or at least without inducing any damage larger than the ~3 µm resolution of our confocal microscope). We stress that the fluorescence results from mechanophore breakage [32]. If the mechanophore is dilute and randomly incorporated in the network as it is the case here, previous studies have shown that it reports quantitatively for polymer chain scission in the crosslinked network [34, 35]. Hence, it can be concluded that each cavitation event leads to damage by covalent bond scission and local fracture (i.e., crack formation) in the elastomer network. However, while the intensity of the signal is proportional to the concentration of activated mechanophores it is also dependent on the depth from the surface of the sample (due to absorption of light). Hence an absolute value of the amount of covalent bond scission for a given cavity is more complex to obtain for an arbitrary depth and orientation and was not carried out here.

Taking a closer look at the shape of the fluorescent regions, every damaged site appears as a collection of thin penny-shape disks with random orientation (see Movie 1 in SI and FIG3B). These disks organize themselves in a flower-like pattern around a rougher region of higher fluorescence. The typical dimensions of a 3D box enclosing a damaged site are 30-50 µm thickness and 100-400 µm side, meaning that these sites, although they are not flat, have a highly planar aspect ratio. As a result, our observations demonstrate that decompression-induced cavitation in poly(ethyl-acrylate) results from the nucleation and growth of penny-shaped cracks through a close-to-2D fracture process. Interestingly, cavities as small as 30 µm still had well-resolved fluorescent damaged regions, though their optical observation was more challenging due to the limited resolution of our optical camera as illustrated in FIG S1 for another specimen under identical decompression conditions.

The maximum projected cavity size observed optically during decompression is always 120-145% larger than the size measured in the fluorescent images, as illustrated in FIG S2. This difference is because the inflated cavities are in a deformed state, whereas the damage sites result from elastic retraction of the cavity to its undeformed state. Noteworthy, the thickness of the fluorescent penny-shaped damage regions (~5-25 µm) is in close agreement with the characteristic damage zone size measured normal to the fracture plane during mode I crack propagation [34, 35], confirming that cavitation leads to localized fracture in the bulk of the material.

The morphology of the disk-like damage zone is consistent with the ellipsoidal rough fracture surface obtained by loading a poker-chip-like specimen in a mechanically confined geometry in model polyurethane elastomers [13] or with the highly planar flower-like cavities formed by (volume-controlled) needle induced cavitation in PDMS [36]. This flower-like pattern has also been observed by Scanning Electron Microscopy (SEM) on the fracture surface of a rapidly decompressed EPDM rubber [37]. As such, our strategy to combine elastomer design with cavitation-induced cavitation not only serves to non-destructively visualize damage prior to failure, but also to illustrate general features of cavity growth in a range of incumbent elastomers.

Figure 2. (A) Optical snapshots of the different cavitation stages during decompression at 10MPa/min of an ethyl-acrylate elastomer saturated at a pressure of 5 MPa of hydrogen for 10 h (corresponding movie is available as Movie S1 in the S1). (B) Evolution of approximate cavity radius ($r = \sqrt{(\text{cavity surface} / \pi)}$) for eight distinct cavities as a function of decomposition time. Red squares correspond to maximum cavity size, while blue dots indicate transition from a self-similar spherical growth to an anisotropic growth. (C) Distribution of maximum approximate cavity radius measured during decompression of the specimen depicted in (A).
From Molecular Damage to Cavity Growth Process

Because of its good spatial resolution and more importantly because of its ability to visualize damaged regions in their unloaded state, the post-mortem visualization of bond scission provides additional information on the cavitation process. Compared to state-of-the-art techniques, laser scanning confocal fluorescence microscopy enables detection down to the \( \mu m \)-size. However, we foresee significant improvements over this spatial resolution as super resolution microscopy finds space in the characterization of soft materials [38]. A cavity growth mechanism can be established by complementing the optical decompression images with a fractography analysis of the fluorescent penny-shape cracks. For that purpose, FIG4 and FIG5 respectively illustrate the optical zoom and fluorescent visualization of a representative cavity (cavity n°3 in FIG3) that is fortuitously well-aligned with the specimen xy-plane and, thus, has reduced out-of-plane tilt effects.

The lack of real time information on damage precludes a definitive analysis of the early nucleation stage of the cavity. However, as the rate of growth progressively slows down with cavity size (FIG2B) due to a decrease of the pressure differential during decompression, it becomes possible to optically monitor the evolution of the cavity shape. As previously mentioned, the transition towards anisotropic growth is typically observed around 150-200 \( s \) after the start of decompression, when the seemingly self-similar spherical growth shows distinctive concavities in the form of small “popping” events (highlighted by the dashed lines in FIG4A). This symmetry breaking is often interpreted as a signature of fracture, as reported in cavitation rheology (i.e. needle-injection induced cavitation) of other elastomers and hydrogels [39, 40]. The raspberry-like growth (i.e. in the inflated state) suggests that damage occurs through the growth of several side-cracks originating from the highly deformed wall of the original cavity. Moreover, the deflating steps (illustrated after the red square in FIG4A) seem to indicate that these bubbles disappear in a rather concave crack-closing way.

Nonetheless, without a proper visualization of the actual irreversible damage, this mechanism of cavitation remains hypothetical and in the need of proof (or disproof) of the transition from self-similar growth to a raspberry like structure (as schematized in FIG4B). The post-mortem fluorescent confocal analysis, highlighting the broken bonds in the unloaded configuration, is consistent with the postulated chronology and provides the missing information to validate that cavity growth process.

The nucleation site of each cavity can be identified from the region of high fluorescence (more or less centered) that results from numerous polymer chain scission events (FIG5) at the early (and faster) stages of cavity expansion. Indeed, as the pressure differential (and associated load) are higher at the early stages of decompression, so is the cavity growth rate and the damage by bond scission (see the time-lapse evolution of the highlighted cavity contour in FIG S3). This assertion is consistent with recent investigations of damage in mode I fracture of the same elastomer, where fast crack propagation leads to a larger and more delocalized bond breakage near the fracture plane than slow crack propagation [34]. Hence, the intense fluorescent signal over the thicker centered region (of radius \( \sim 50-100 \mu m \)) corresponds to that early cavity expansion stage, and serves as a nucleation site for multiple “planes” of very localized damage that subsequently grow outwards as large and thin petals (\( \leq 10 \mu m \) thick as illustrated by the \( z \)-slices in FIG5A). The observation of such highly planar damaged regions validates the hypothesis that anisotropic cavity growth results from the propagation of multiple penny-shaped cracks, as schematized in FIG4B-(ii), but also that it probably already applies for earlier stages where the cavity growth is seemingly spherical and isotropic in the optical recording of decompression (see FIG5). Moreover, the presence of intermediate crack-arrest lines (indicated with the green arrows in FIG5), as well as out-of-plane crack bifurcations (see cross sectional images in FIG S4), suggests a discontinuous growth process occurring at scales that could not be easily resolved optically during decompression. Such crack propagation process is often referred to as \textit{stick-slip} in mode I fracture and adhesion of soft materials [41]. It corresponds to the propagation of a crack by a series of unstable fast steps followed by temporary crack arrests. Propagation stops when the crack has advanced so much that the crack-tip reaches a region with an insufficient driving force for crack growth (i.e. subcritical energy release rate). In our case, the crack arrest could be due to the pressure drop associated with hydrogen diffusion, but the observed succession of crack arrest lines (FIG5C) confirms that stick-slip is inherent to the crack growth mechanism.
Figure 4. (A) Optical zoom snapshots of the shape of a single representative cavity (cavity n°3 in FIG 3) at different stages of inflation and deflation (white scale bar corresponds to 100 μm). Dashed lines highlight difference of concavity when transitioning from self-similar spherical growth to anisotropic growth illustrated by the blue square. The red square shows maximum expansion. (B) Two speculative 3D schematic scenarios of the cavitation process: (i) self-similar growth of a seemingly spherical cavity; (ii) explanation of the anisotropic cavity growth by propagation of multiple crack planes originating from a same nucleation site. (C) Evolution of the 2D projected area of the same cavity as function of decompression time. Inlet shows the confocal top view of the same cavity that can be easily compared to the last deflating optical picture (black scale bar corresponds to 100 μm).

Discussion

Tagging elastomers with damage-activated mechanofluorescent probes enables novel non-destructive visualization of damage in unloaded elastomers after complex 3D loading. Such visualization is used here to gain new insights on the cavitation growth process. As such, a few comments should be made to put this work in perspective.

First, due to the complex loading configuration involving gas diffusion, phase separation, and pressure drop, we are unable to evaluate the critical pressure for cavitation [42]. Nonetheless, we are in the expected regime of cavitation with a hydrostatic pressure of the order of magnitude of the elastomer Young’s modulus (P ~ 0.1 MPa) [6, 9]. Experimental studies of cavitation originally started with the application of a tensile stress to a confined elastomer layer [9, 13, 17] with the nucleation of a random number of cavities; but have more recently turned to puncture experiments where a single cavity is nucleated at the tip of a needle and subsequently expanded under controlled pressure [39] or volume [36, 40]. Cavity nucleation and growth due to rapid decompression is neither stress nor volume controlled since the cavity pressure and volume are coupled to the gas diffusion flux throughout decompression. With this caveat in mind, we compare our results with those of previous studies despite these differences in cavitation conditions.

Through the development of their cavitation rheology technique by needle-injection pressurization [39, 43], Crosby and co-workers have argued that cavity growth in soft solids (i.e. hydrogels and soft biological tissues) transitions from a reversible deformation process (driven by an elastic instability as originally proposed by Gent) to irreversible fracture where a crack is optically visible. We demonstrate here that, in our elastomers, even if the cavitation process looks optically reversible with a stable self-similar growth, irreversible internal damage still occurs. All optically visible cavities, even those that remained spherical throughout decompression (see FIG S5 in SI), locally break bonds in a highly planar but non-flat fashion with a flower-like fracture pattern. This observation is reasonable considering the difference between the size of the polymer network mesh (10nm) and that of a cavity (10-100μm).

The recent works of Kim et al. [7] and Poulin et al. [17, 19] also indirectly demonstrate that cavitation in crosslinked oligomer-containing PDMS networks, supersaturated with fluorinated oil and in their pure state respectively, must involve the creation of new fractured surfaces. Poulin et al. attributed the conical shape of expanded cavities to the growth of penny-shape cracks combining optical observations with finite element simulations, whereas Kim et al. indirectly showed through cycling that irreversible bond breakage must occur when cavitation is induced by local phase separation. To the best of our knowledge, we provide however the first direct observation of the locus of polymer chain scission during cavitation with a non-destructive visualization technique.

Kim et al. also optically observed a first stage of self-similar spherical growth and argued that it must relate to a distributed damage around the cavity surface before transitioning to a more crack-like ellipsoidal growth. In analogy with cavitation in ductile materials like metals, they argued that the transition occurs at the elasto-adhesive length L ~ G/E [44]. Despite the similarities in optical observations with our work, we show that cavitation occurs through the opening of a penny-shaped crack even at scales smaller than the elasto-adhesive length (i.e. L ~ 180 μm for our material) as smaller optical cavities still showed sign of damage and as the maximum thickness of the fluorescent penny-shape crack is ~25μm.

More generally, besides theoretical discrepancies concerning cavity nucleation, there is consensus about the occurrence of fracture at a sufficiently large cavity size and the existence of different growth regimes. By directly (and non-destructively) visualizing damage in unloaded elastomers, we can relate these different cavity growth regimes to a discontinuous crack growth process similar to that of stick-slip mode I crack propagation. This observation is consistent with a theory recently developed by Cai et al. [15] where volume-control cavitation can lead to both stable and unstable crack growth depending on the loading conditions and the crack-size. They consider a spherical cavity in a soft solid with an edge crack of a ring-shape on the cavity wall. For different ratios of the edge crack with regard to the overall cavity size, they identify unstable and stable growth regimes and how a transition from one to the other can occur with an increase of the crack length or a change of external loading conditions (i.e. volume increase). We think this description is not only appropriate for our case but is also useful in unifying other descriptions of cavitation [7, 39], as long as cavitation is always considered as a fracture process.
When an elastomer is subjected to a high-pressure gas for a sufficiently long time, gas sorbs until reaching a saturation equilibrium. Upon fast release of that pressure, the gas absorbed within the polymer diffuses out of the material. If diffusion is not fast enough, phase separation occurs leading to the formation of visible gas bubbles. Even though these bubbles eventually disappear as the gas diffuses out, such rapid decompression can lead to macroscopic failure and is of concern for the use of seals in hydrogen storage and transportation. In this work, we label a poly(ethyl-acrylate) elastomer with a mechano-fluorescent molecule that reports polymer chain scission by becoming fluorescent through a force activated cycloreversion reaction. Visual monitoring of the bubble inflation/deflation process and 3D post-mortem laser scanning confocal microscopy of the decompressed specimens demonstrate that each bubble (i.e., cavity) results from polymer chain scission. This methodology not only enables non-destructive and spatially resolved inspection of internal damage, but also brings unprecedented insights on the shape, deformation and fracture of cavities in elastomers.

The relation between fluorescence intensity and bond breakage provides a direct proof of the network damage associated with cavity growth. In our system (and likely in all elastomers), visible cavity expansion is always accompanied by an irreversible and localized fracture process presumably due to the large deformations experienced by the polymer chains during bubble expansion. Post-mortem laser scanning confocal microscopy on the pristine-looking and unloaded material demonstrate that 3D cavities correspond to randomly oriented 2D penny-shape cracks. Additionally, the anisotropic shape observed optically during cavity expansion is closely related to the nucleation and growth of several crack planes originating from a common nucleation site. A careful study of their morphology suggests that the cavitation process is discontinuous, meaning that it occurs in a stick-slip fashion with stable and unstable crack growth.

In addition to its usefulness for the fundamental understanding of fracture in elastomers, such a fluorescence-based observation technique has many practical implications. As long as optical detection is possible, the non-destructive visualization of damage by polymer chain scission in elastomers makes it possible to assess the role of multiple cycles of compression/decompression or any other complex loading configuration, on the spatial distribution of internal damage in the polymer network and its impact on seals lifetime.

Materials and Methods

Reagents: Ethyl acrylate (EA), 1,4-butanediol diacrylate (BDA) and 2-hydroxy-2-methylpropiophenone (HMP) were purchased from Sigma-Aldrich. EA and BDA were purified via column chromatography on activated alumina, and HMP used as received. The mechanofluorescent π-extended anthracene maleimide probe (DACL) was synthesized and purified according to previously established procedures [31]. All reagents were sparged with N₂ for 45 min and transferred to a N₂-filled glovebox.

Synthesis: the tagged ethyl acrylate polymer network was synthesized according to previously established procedures [29, 30, 45]. In a N₂-filled glovebox, EA (4.0 mL, 36.68 mmol), BDA (33.4 µL, 0.18 mmol), HMP (66 µL, 0.43 mmol), and DACL (5.1 mg, 0.01 mmol) were well-mixed and transferred to a polymerization mold previously sealed with rubber spacers (0.1 mm). The polymerization was conducted under UV (10 µW/cm²) for 2 h, and the resulting polymer networks dried under vacuum at 50 °C for 8 h to eliminate any residual monomer.

Material properties: the labeled elastomers that we used have a glass transition measured at -18°C through DSC. They exhibit the same mechanical properties with or without mechanophores as previously reported in [34, 35] and illustrated in the stress-stretch curves under uniaxial tension and pure-shear tests in FIG S6 of the SI. The corresponding Young’s modulus and mode I fracture toughness were measured to be ~1 MPa and ~180 J/m², respectively.

Explosive Decompression Tests: Decompression tests were performed in a pressure chamber (1.77 L; diameter 150 mm; depth 100 mm) allowing tests under a gas pressure up to 40 MPa, with con-
trolled pressurization and depressurization ramps. All experiments were conducted at room temperature, except small transient deviations due to pressure variations of the gas during pressurization and decompression steps. The applied pressure cycle was made of the following steps: (i) three initial purges of the chamber with gaseous nitrogen up to 1 MPa (in order to avoid oxygen/hydrogen mixture), (ii) pressurization at constant rate of 1 MPa/min up to a pressure for saturation P_{sa} of 5 MPa, (iii) dwell at P_{sa} for 10 h (in order to bring the sample back to thermal equilibrium and to reach hydrogen solubility in ethyl-acrylate, according to the Crank’s solution for unidirectional gas diffusion through infinite sheet [44] (iv) pressure release down to the atmospheric pressure P_{atm} at constant rate P’ dot = 10 MPa/min, and (v) maintain of the sample at P_{atm} for 2 h in order to track the delayed evolution of cavitation. In order to estimate reproducibility, the same test was applied on two rectangular specimens on two different days, and very similar results were obtained (see Movies S1-2).

Note that the diffusion coefficient D = 1.35e-11 m²/s and hydrogen solubility S = 3.05e-4 mol H₂/m³.MPa⁻¹, obtained via permeability measurements, are rather close to that of other elastomers of commercial interest such as EPDM and NBR. This confirms that full saturation is achieved prior-decompression through the applied dwell time but also validates our ethyl-acrylate elastomer as a good model system for studying cavitation under rapid decompression.

Moreover, an additional confirmation that the presence of embedded mechanophores does not impact the cavitation process in the ethyl acrylate network is given by the observation of similar cavities formation (bubble size and growth kinetics) under identical rapid decompression conditions for specimens with and without mechanophores (see Movie S3).

**Optical Recording:** Pictures of the sample were taken every second during the first twenty-five minutes of decompression and maintain at atmospheric pressure steps, using a wired light and a Sony XCD SX 90 CCD camera fitted with an Avenir TV Zoom Lens 12.5-75 mm F1.8. The device geometry clearly limited the spatial resolution as the camera had to be located far from the sample (due to the chamber size and front-door thickness – see FIG1B). In addition, the pixel size had to be compromised to allow for the monitoring of the full area of the sample surface. The retained configuration finally led to a detection limit of cavities of 10 µm.

The stack of images taken during decompression was processed using the Fuji plug-in of Image® software. First, it was cropped around each selected cavity and a dedicated macro for segmentation was applied to each of them. Particle analysis of the stack of binary images finally led to a detection limit of cavities of 10 µm.

**Fluorescent Confocal Microscopy:** All scanning confocal microscope pictures were taken with a Nikon AZ-100/C2+ confocal macroscope customized to our purpose. The objective used was an AZ Plan Fluor 5x, with a focal length of 15 mm. The objective was not inverted and can zoom from 1x to 8x. Fluorescence was recorded at an image size of 512 × 512 px with each pixel containing 12-bit digital units (intensity from 0 to 4096 a.u.). The maximal pixel size is 8.15 µm and the minimal pixel size is 1.02 µm. Confocal mapping reduces out-of-focus light and allows the measurement of intensity in local volumes x * y * z (“voxels”) of typically 2.72 × 2.72 × 12 µm inside of the material for a 3x zoom setting. A laser with 405 nm wavelength was used and the emission signal was recorded from 450 nm to 550 nm, matching absorption and emission peak of ε-extended antranichrome moieties (see FIG S7). No specific sample preparation is required except a small dusting-off and careful positioning (facilitated by a biased cut made on one of the specimen edges to keep the same orientation than during decompression).

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Elastomers are used as seals in connecting hardware for gas transport. Upon saturation with a gas followed by a sudden pressure drop, elastomers can cavitate and exhibit bubbles that progressively disappear over time, an issue that raises concern over their mechanical integrity and gas barrier properties. Here, by incorporating a mechanofluorescent damage-activated probe in a model unfilled elastomer, we demonstrate that cavity expansion is an irreversible fracture process by visualizing covalent bond scission via fluorescent microscopy. This methodology not only provides a novel and spatially resolved technique for non-destructive inspection of internal damage in 3D, but also serves to demonstrate that cavity growth in elastomers occurs through the nucleation and subsequent stick-slip propagation of randomly oriented and distributed penny-shape cracks.
Supplementary Information for

Visualization of Bond Scission due to Nucleation and Growth of Gas Bubbles in Elastomers

Xavier P. Morelle*†, Gabriel E. Sanoja†, Sylvie Castagnet2, and Costantino Creton*†,3.

1 SIMM, ESPCI Paris, Université PSL, CNRS, Sorbonne Université, 75005, Paris, France.
2 Institut Pprime (UPR 3346 CNRS – ENSMA – Université de Poitiers), Department of Physics and Mechanics of Materials, 1 Avenue Clément Ader, BP 40109, 86961 Futuroscope cedex, France
3 Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan.

* costantino.creton@espci.psl.eu, morelle.xavier@gmail.com

Fig. S1. (A) Optical snapshot of second ethyl acrylate specimen (see Movie S2) at maximum cavity expansion during decompression at 10MPa/min after 10h of saturation at a pressure of 5 MPa of hydrogen. (B) Zoom on the red square region of (A) where six cavities can be seen, among which the smaller one (yellow circle) is hardly visible by our camera. (C) is the confocal (top view) zoom of the region corresponding to the red square in (A) where a localized fluorescent damage region can be found for each of the six cavities identified in (B). The damaged region of the yellow cavity has a disc shape with a diameter size as small as 30 µm.
**Fig. S2.** Size comparison between maximum (inflated) cavity through optical visualization (top) and associated damage region, in the deflated state, visualized by fluorescent microscopy. The identified cavities correspond to the number-identification on FIG2A and are fortuitously well-aligned with the specimen xy-plane.

**Fig. S3.** (top) Cavity contour evolution at constant different (constant) time step obtained from optical visualization during decompression (NB: 2D projection limitation thus apply). (bottom) Confocal (artistic) top view of corresponding cavities in order to highlight the difference of fluorescence intensity (and overall contour) between nucleation site and the rest of the flower-like pattern. The 3 visualized cavities correspond to the number-identified on FIG2A, white and black scale bars correspond to 100 µm.
**Fig. S4.** (A) Confocal fluorescent microscopy of the biggest central cavity highlighted with a yellow square in (B) and (C), with corresponding cross-sectional images highlighting local crack bifurcation and tilt of cavity damage region. (B) & (C) are respectively the optical (in the maximum inflated state) and confocal (in the deflated state) view of overall Zone 2 identified in FIG 2.

**Fig. S5.** (A) Optical snapshot of our ethyl acrylate elastomer specimen at maximum cavity expansion during decompression, highlighting three colored regions each one with a cavity exhibiting only a self-similar spherical growth (violet circle with yellow dot). (B), (C) and (D) are respectively the confocal (top view) zoom of the corresponding fluorescent damaged regions. The three seemingly spherical cavities are numbered and highlighted with yellow circles with corresponding magnified zoom shown in (E). The fluorescent signal provides a better optical resolution and shows that the damage associated to each of these cavities also corresponds to the superposition of penny-shape cracks forming a flower like pattern (F), hence confirming the same damage growth mechanism than for larger anisotropic cavities. (note that the centered orange or purple halo in (B), (C) and (D) is an optical artifact coming from the fluorescence of the specimen surface.)
Fig. S6. Comparison of the mechanical properties of the ethyl acrylate polymer network with or without mechanophores. No significant differences in elastic and fracture properties can be noticed both under (A) uniaxial tensile tests; and (B) pure shear tests.

Fig. S7. Absorption and emission peak of π-extended anthracene moieties, data taken from [1]. Photoluminescence and excitation spectra were obtained from an Edinburgh Instrument spectrometer. The absorption spectrum was recorded between 320 nm and 450 nm for an emission at 460 nm. The emission spectrum was recorded between 420 nm and 600 nm, for an excitation at 405 nm. The reference molecule was diluted in ethyl-acetate at 6x10^{-5} mol.L^{-1}. 
**Movie S1 (separate file).** Video made of the snapshots (every 20 s until 400 s then every 100 s until 1100 s) of the different stages during and after a decompression at 10 MPa/min of an ethyl-acrylate elastomer saturated at a pressure of 5 MPa of hydrogen for 10 h. The specimen depicted is the same as the one studied through the entire article and totally or partially shown in FIG2, 3 and 4.

**Movie S2 (separate file).** Video made of the snapshots (at various intervals from 18 s to 1800 s) of the different stages during and after a decompression at 10 MPa/min of a second ethyl-acrylate elastomer specimen saturated at a pressure of 5 MPa of hydrogen for 10 h.

**Movie S3 (separate file).** Video made of the snapshots (accelerated 40 x) of the different stages during and after a decompression at 5 MPa/min of 3 samples of ethyl-acrylate elastomer (the right one with mechanophores and the two left ones without) saturated at a pressure of 5 MPa of hydrogen for 10 h, confirming no significant difference of cavitation resistance (especially no embrittlement) is observed.

**SI References**

1. Slootman, J., *Quantitative detection of damage in soft materials using mechano-fluorescence*, in *ESPCI Paris*. 2019, PSL.