Covalent bond scission in the Mullins effect of a filled elastomer: real-time visualization with mechanoluminescence

Citation for published version (APA):

DOI:
10.1002/adfm.201602490

Document status and date:
Published: 01/01/2016

Document Version:
Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 22. Aug. 2019
Covalent Bond Scission in the Mullins Effect of a Filled Elastomer: Real-time Visualization with Mechanoluminescence

Jess M. Clough, Costantino Creton, Stephen L. Craig, Rint P. Sijbesma

Strain-induced light emission from mechanoluminescent cross-linkers in silica-filled poly(dimethylsiloxane) demonstrated that covalent bond scission contributes significantly to irreversible stress-softening upon the initial extension, known as the Mullins effect. The cross-linkers contained dioxetanes that emit light upon force-induced bond scission. The filled elastomer emitted light in cyclic uniaxial tension, but only on exceeding the previous maximum strain. The amount of light increased with hysteresis energy in a power law of exponent 2.0, demonstrating that covalent bond scission became increasingly important in the strain regime studied. Below ∼100-120 % strain, corresponding to an energy absorption of $(0.082 \pm 0.012)$ J cm$^{-3}$, mechanoluminescence was not detectable. Calibration of the light intensity indicated that by 190 % strain, less than 0.1% of the dioxetane moieties break. Small but significant amounts of...
light were emitted upon unloading, suggesting a complex stress transfer to the dioxetanes mediated by the fillers. Pre-strained material emitted light on straining perpendicularly, but not parallel to the original tensile direction, demonstrating that covalent bond scission is highly anisotropic. These findings show that the scission of even a small number of covalent bonds plays a discernible role in the Mullins effect in filled silicone elastomers. Such mechanisms may be active in other types of filled elastomers.

1. Introduction
Filled elastomers are ubiquitous engineering polymers demonstrating high tensile strength, deformability and toughness. These remarkable properties are mainly brought about by the addition of a large amount of nano-sized filler particles to the elastomer, but the addition of filler also gives rise to a complex mechanical behavior. Most notably, these materials have mechanical behavior that depends upon the maximum strain that they have experienced during prior mechanical testing. [1] When that maximum strain is exceeded, they undergo damage (a change in their structure) and absorb energy irreversibly. The resulting history-dependent stress-softening is often referred to as the Mullins effect or “mechanomemory”, [2] as the material appears to “remember” its previous maximum strain. This phenomenon has most often been examined in cyclic uniaxial tension, as first described in a report by Bouasse and Carrière in 1903 [3] and depicted schematically in Figure 1. On straining to $\lambda_1$, the material is not fully elastic but absorbs energy and undergoes a change in mechanical properties, as shown by the shaded area between the loading and reloading curves. Re-straining to $\lambda_1$ for a second or subsequent time, the material exhibits a lower stress than it did on the first straining and absorbs much less energy; however, on straining beyond $\lambda_1$ to $\lambda_2$, the stress response rejoins the curve that would have been obtained upon straining to failure and significant hysteresis is again observed.
Phenomenologically, a similar behavior is exhibited by a disparate array of materials, including thermoplastic elastomers,[4],[5] double networks,[6] fibrin and collagen networks,[7] biological tissues[8],[9] and shape-memory alloys.[10] All of these systems undergo a change in structure upon straining to large strains, which in turn modifies the mechanical properties on subsequent cycles.

Figure 1. Stress-softening, or mechanomemory, in uniaxial tension. On straining from $\lambda = 1$ to failure (1), filled elastomers exhibit a characteristic S-shaped stress-strain curve (dotted line). If this material is strained (2) then relaxed (3) at a certain value of strain, $\lambda_1$, hysteresis is observed (yellow line), as the network absorbs energy and undergoes permanent deformation (shaded grey area). This energy, corresponding to the area bound by the loading and reloading curves to a particular strain on a plot of nominal stress vs. nominal strain, is referred to here as the “hysteresis energy”. On restraining to $\lambda_1$ for a second or subsequent time, the material follows the reloading curve up to $\lambda_1$ (4, red line). Straining beyond $\lambda_1$ (4) and relaxing (5), the material absorbs energy again.
In spite of the technological importance of filled elastomers and the significant research interest that the Mullins effect has generated over the past few decades, its molecular origins remain unresolved. The exact mechanisms vary with the nature of the polymer and filler of the system; nevertheless, some molecular interactions are thought to be generally relevant to understanding the Mullins effect in filled elastomers, as depicted schematically in Figure 2 and well-reviewed by Diani et al.\textsuperscript{[1]} Among the most important are covalent cross-links and non-covalent interactions between the filler and the polymer, such as physical adsorptions and hydrogen bonds. Covalent bond-breaking has been demonstrated in ESR experiments indicating the formation of carbon-centered radicals in silica-filled styrene-butadiene rubber (SBR) under tension,\textsuperscript{[11]} but its involvement in the Mullins effect was not shown explicitly with this technique. Some covalent bond scission is also necessary for nanocavity formation, which has been detected with various methods, such as dilatometry,\textsuperscript{[12]} direct optical visualization\textsuperscript{[13][14]} and SAXS.\textsuperscript{[15]} However, the decreases in cross-linking density resulting from straining carbon black-reinforced SBR, as determined by solvent swelling samples post mortem, are relatively small, leading some
to claim that covalent bond scission cannot make a significant direct contribution to the stress-
softening.[16],[17]

Many authors have instead assigned decisive roles to other energy-absorbing processes. In silica-
filled PDMS, stress-softening has been ascribed to the detachment of the polymer chains from
the filler particles, in a study on the temperature dependence of the mechanical hysteresis
curves,[18] but also to polymer disentanglement by others.[19] The rupture of filler aggregates has
been scrutinized for its contribution to the mechanical hysteresis, particularly in carbon black-
filled networks, where the level of percolation of the network formed by fillers can be
characterized by conductivity measurements.[17][20] Lastly, micro- and mesoscopic changes in the
structure of the material have been proposed to account for the Mullins effect, such as the
conversion of hard blocks to soft ones under force[21] and force-induced rearrangements in a filler
super-network connected by oriented polymer chains.[22] Structural changes at these length scales
have been probed with SAXS,[23] AFM[18][24][25][26] and SEM.[27] It is clear that new experimental
techniques are required to separate the contributions to the Mullins effect from the various
interactions and assess which are the most significant.

Over the past ten years, approaches have been developed to produce optical responses to
mechanical force in polymers, enabling materials to report on the mechanical damage they have
sustained. To obtain these properties, functional groups with relatively weak covalent bonds (or
mechanophores) are incorporated in the material, which isomerize or break selectively when a
force is applied.[28][29][30][31][32][33][34] Mehanoresponsivity is thereby achieved without
significantly compromising the mechanical integrity of the material. Until now, filled PDMS has
received some attention in this area as a platform for mechanophore activation in the linear
elastic regime: the Craig group found that a spiropyran, a mechanoresponsive moiety that
changes its UV absorption and fluorescence emission under mechanical force, when used as cross-linker, was activated at ~50 % strain in the material.[35] Researchers in the Grzybowski group demonstrated mechanoradical formation in water at similar strains, [36] possibly aided by the lowered rupture force of siloxane bonds in water.[37] However, these approaches have significant drawbacks in addressing the Mullins effect. In particular, mechanoactivation of spiropyran gives an integrated signal in absorption or fluorescence, making it more difficult to record small changes over time. In a parallel line of research, piezoluminescent inorganic crystals have been employed to create mechanoluminescent materials, by creating composites,[38][39] such as in PDMS,[40] or by coating a material with a thin layer of the crystal.[41][42] In these systems, however, it is difficult to relate the mechanoluminescence output with the stresses experienced by the covalent bonds in the polymer chains of the material.

Mechanically induced chemiluminescence, or mechanoluminescence,[29][43] from 1,2-dioxetanes offers a new approach to delineate and quantify the contribution of covalent bond scission in the bulk polymer matrix to the mechanomemory of filled elastomers. In this strategy, thermally stable bis(adamantyl)-1,2-dioxetane is covalently incorporated either centrally in a linear polymer or as a cross-linker within the polymer network; under stress, the central four-membered dioxetane ring of this mechanophore cleaves preferentially to give excited ketones, which relax to the ground state with the emission of light (Figure 3). Computational studies support a partly biradical (stepwise) decomposition pathway under thermal activation;[44] such studies have yet to be performed for mechanical activation, but it is known that both triplet and singlet ketones are produced mechanically.[43] To date, this stress probe has been used to study a number of materials, including thermoplastic elastomers,[45] elastomers with multiple interpenetrating
networks\textsuperscript{[46]} and supramolecularly cross-linked materials.\textsuperscript{[47]} Whilst many of the techniques previously used to study the Mullins effect are limited to post mortem measurements of bulk properties, mechanoluminescence emission reveals when and where covalent bonds are breaking, in real-time with high spatio-temporal precision and sensitivity. Furthermore, mechanoluminescence offers an important advantage over techniques based on fluorescent mechanophores, namely that the signal is transient. The measurement of a transient instead of an additive signal boosts sensitivity, which is aided further by the absence of an excitation signal.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\linewidth]{thermoluminescence}
\caption{Thermoluminescence}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\linewidth]{mechanoluminescence}
\caption{Mechanoluminescence}
\end{figure}

Figure 3. Top: thermally induced mechanoluminescence from bis(adamantyl)-1,2-dioxetane, first discovered by Weiringa et al. Bottom: on incorporating in a polymer, chemiluminescence from bis(adamantyl)-1,2-dioxetane can be induced mechanically, as first reported by Chen et al.\textsuperscript{29}

In this study, we use commercial components (from Sylgard 184) to prepare silica-filled poly(dimethylsiloxane) (PDMS) networks containing mechanoluminescent dioxetane as an additional cross-linker to establish the role of covalent bond scission in stress-softening. We perform the study by simultaneously recording stress and light intensity when samples are subjected to cyclic tensile testing. We also investigate the role of covalent bond scission in the anisotropy of mechanomemory, which has never been addressed experimentally.
2. Results
A bis(adamantyl)-1,2-dioxetane mechanophore contained within a bis(vinyl) cross-linker (2 wt%) and 9,10-diphenylanthracene (DPA) fluorophore (0.5 wt%) were incorporated in silica-filled poly(dimethylsiloxane) (PDMS) networks by mixing them into the pre-polymer/curing agent combination of the Sylgard 184 elastomer kit. DPA serves to boost the quantum yield by accepting excitation energy from the mechanically produced excited state ketones. The excited state adamantanones, in common with most ketones, have a low fluorescence efficiency, but they can transfer their energy more efficiently via Förster resonance energy transfer (FRET) to a fluorescent acceptor, such as DPA. DPA can then emit the energy as fluorescence with a much higher quantum yield than the adamantanone (Figure 4a) and a peak wavelength of approximately 420 nm.

The curing process in this material is a platinum-catalyzed hydrosilylation reaction (Figure 4b). The bulk of the pre-polymer is comprised of vinyl-terminated siloxane oligomers and dimethylvinylated silica filler particles present in a volume fraction of at least 0.16, whilst tetravinyl tetracyclosiloxanes and methylhydrogen siloxane oligomers, incorporated in much lower proportions of approximately 0.5 wt% and 5 wt% respectively, serve to cross-link the network.[48][49] In the elastomer, the mechanophore was incorporated into the network via reaction of its vinyl end groups with the methylhydrogen siloxane oligomers, forming cross-links with a length of 27 bonds. The dioxetane cross-linker provides an excess of vinyl groups relative to the optimum stoichiometry of the Sylgard mixture. The silica filler is composed of ~100 nm aggregated spherical silica particles, the individual particles being ~10 nm in size.[19]

Reinforcement originates from a combination of covalent attachments between the siloxane oligomers and the fillers (formed via hydrosilylation with the surface vinyl groups on the silica)
and hydrogen-bonding between the silanol groups on the silica and the backbone of the siloxanes. The dioxetane-functionalized PDMS networks had good mechanical properties, including a Young’s modulus of $(0.92 \pm 0.1)$ MPa (calculated in the linear elastic region, <20 % strain) and an ultimate tensile strength of $(6.6 \pm 2)$ MPa (true stress), within the generally expected ranges for silica-filled PDMS. The dioxetane material has a Young’s modulus ~20 % lower than the unfunctionalised PDMS (see Supporting Information), as a result of the change to stoichiometry from the additional cross-linker, although the breaking strength and hysteresis energy are comparable.

Figure 4. a) Photophysical scheme. 9,10-Diphenylanthracene (DPA) accepts excitation energy from the mechanically formed excited state adamantanes via Förster resonance energy transfer

Figure 4. B) Chemical structures and reactions.
(FRET), then releases energy as fluorescence, peak $\lambda_{\text{emission}} \sim 420$ nm. b) Synthesis of silica-filled PDMS networks via a platinum-catalyzed hydrosilylation reaction.

On pulling a sample by hand to fracture, light was readily observable by eye. No light was observed from mechanically inactive control samples with bis(adamantyl)-1,2-dioxetane (without reactive vinyl functionalities) dissolved within the PDMS network, supporting the mechanical origin of the luminescence at break from mechanically active samples. Furthermore, on heating mechanically active samples, thermally induced chemiluminescent decomposition only occurred significantly at temperatures above 150 °C. These control experiments indicate that mechanical transduction of force is required to induce the chemiluminescence of bis(adamantyl)-1,2-dioxetane when it is covalently embedded in the PDMS network. Furthermore, $^1$H NMR of samples that were heated at 60 °C overnight showed that the dioxetane did not decompose significantly under the conditions of network formation.

Cycles of uniaxial tensile stress were applied to a rectangular sample at an initial strain rate of 0.1 s$^{-1}$, increasing the maximum nominal strain on each successive cycle by 50 %, 25 % or 10 % (smaller intervals were used at higher strains). The resulting stress-strain curves are displayed in Figure 5 and show the characteristic stress-strain behavior of a filled elastomer, with an approximately linear elastic regime up to 50 % strain. At higher strains, the Mullins effect is manifest: the material exhibits significantly lower stresses on re-straining below the maximum previously applied strain, indicating some damage and irreversible dissipation of energy. This energy, which we will define as the area bound by the loading and reloading curves to a particular strain, will be referred to throughout as the (permanent) hysteresis energy. It is important to note that this hysteresis is smaller than the hysteresis between loading and
unloading, a widely reported phenomenon in filled elastomers.\textsuperscript{[1]} The difference is indicative of viscoelasticity. After a time interval of one week, the samples did not exhibit significant recovery in strain, suggesting that the strain recovery due to viscoelasticity is complete in the time before the next cycle begins (during unloading and in the interval between cycles, \(~1\text{-}2\) minutes), in line with previous reports describing recovery in silica-filled PDMS.\textsuperscript{19} Furthermore, upon repeated cycling to a fixed strain, the second and consecutive cycles exhibit much less permanent residual deformation at zero stress. For a series of cycles increasing by 10 % beyond the previous strain maximum, the energy absorbed on the second and third cycles was 17 % and 3 % of the energy absorbed on the first cycle respectively. The permanent hysteresis exhibited on the first cycle represents approximately 40 % of the area bound by the loading and unloading curves on average, although its exact proportion is dependent upon the maximum strain in the cycle and the strain interval by which the maximum strain is increased. As a result of the stress softening, the small-strain modulus of the material decreases by \((26 \pm 3)\) % of its original value upon straining to 150 %.

To analyze bond scission upon failure in detail, we monitored the mechanoluminescence emission with a camera during the application of tensile strain, as shown in Figure 5. The light intensity was integrated over the sample for each 0.1 s time interval and is plotted in blue against strain. The light intensity is plotted in counts, where one count corresponds to \(~1.5\) photons received on the camera sensor, which has an area of 232.4 mm\(^2\).\textsuperscript{[50]} Several key features of the covalent bond scission processes are immediately apparent from this plot. Firstly, there is a strain threshold of approximately 100-120 % strain, below which very little light was detected. At lower strains, the material does experience some permanent damage, as indicated by the fact
that there was permanent hysteresis in the tensile cycles at these strains, yet no detectable light was produced. At strains below this threshold, it seems that softening is dominated by other mechanisms not involving covalent chain scission, such as rupture and reformation of the physical adsorptions or hydrogen bonds binding the polymer chains and the filler. Above this threshold, the mechanoluminescence intensity increased with applied strain, so that the light emitted in each 10 % increment of strain increased as the maximum strain of the cycle increased.
Most strikingly, the material only emitted significant light when it encountered a strain which it had not experienced in a prior tensile cycle. For example, on straining to 160 %, significant light was only emitted above 150 %, the maximum strain of the previous cycle. Straining a sample multiple times to a strain equal to the maximum strain previously applied produced insignificant amounts of light, in agreement with the small amounts of energy absorbed on the second and third cycles, described above. Furthermore, after leaving the samples for an extended period (~1 week) the mechanical properties were not recovered and mechanoluminescence was not emitted below the maximum all-time strain (in agreement with previous literature reports concerning recovery in silica-filled PDMS).[19] The history-dependence of the mechanoluminescence strongly implicates polymer chain scission in the Mullins effect.

On closer inspection of the emission signal, it can be seen that the light emission began immediately upon exceeding the highest maximum previous strain (Figure 6a and Figure 6b, dashed line 1), indicating the activation of covalent bond scission. The light intensity reached the maximum intensity exhibited on the previous cycle on straining (4.2 ± 0.2) % beyond the highest maximum previous strain (Figure 6a, dashed line 2; average taken over series of cycles increasing by 10 % strain). This strain interval was not related to a trivial issue, such as the permanent set (although the interval decreased to ~2.5 % on correcting for the permanent set). Interestingly, a small amount of light was emitted at the start of each unloading curve,
corresponding to ~10 % of the light emitted during the loading curve. The time over which the intensity decreases (~0.4-0.5 s) is longer than the time in which the upper crosshead of the tensile tester reverses (~0.15 s), as can be seen from Figure 6c-d, indicating that the light emission upon unloading cannot be attributed to instrumental inertia. Furthermore, intensity analysis of the movie frames shows that the intensity increases as long as the sample continues to lengthen (Supporting Information). Possibly, a delay in force transmission to the dioxetanes, mediated by the filler particles, is responsible for the small but significant amount of mechanoluminescence upon unloading. It is notable that mechanoluminescence upon unloading has not been observed in the other polymeric materials studied with this technique.

Figure 6. a) True stress vs. nominal strain (black) and light intensity vs. nominal strain (blue) graphs for tensile cycles to 180% and 190% strain. b) Close-up. (1): Once the sample is strained to above the maximum strain of the previous cycle, light starts to be emitted. (2): On straining further, the light emission intensity exceeds the maximum intensity in the previous cycle. c)
Light intensity (blue line), and nominal strain (black line) vs. time for tensile cycle to 190%. d) Close-up of peak in nominal strain and light emission. Light emission: blue line, filled circles; nominal strain: black line, open squares.

To examine the relationship between the amount of covalent bond scission occurring in the material and the degree of damage in further detail, the total light emission emitted in a series of cycles up to a certain strain (cumulative light intensity) and the total energy absorbed by the sample in those cycles up to that strain (cumulative hysteresis energy) for the tensile cycles performed on three separate samples were plotted against the maximum strain of that cycle (Figure 7a). As discussed above, we define the hysteresis energy as the area between the first and second loading curves to a particular nominal strain on a plot of nominal stress vs. nominal strain, as shown by the grey shaded area in Figure 1. The cumulative hysteresis energy is the sum of the hysteresis energies from consecutive cycles up to a particular strain. Noteworthy features of this graph include firstly a hysteresis energy threshold for mechanoluminescence of \((0.082 \pm 0.012) \text{ J cm}^{-3}\); this threshold value represents the \(\sim 100\)-120 % strain required for mechanoluminescence noted above. It is worth noting that when samples are repeatedly stretched to the same strain, the energy absorbed on the second and successive cycles falls below this energy threshold. A log-log plot of the same data gives a straight line with an exponent of 2.0 (Figure 7b), indicating that covalent bond scission becomes more important as the amount of damage increases relative to the other mechanisms participating in the Mullins effect, within the strain regime studied.
Figure 7. a) Cumulative light intensity and cumulative hysteresis energy vs. maximum nominal strain applied to sample. Each data-point represents the average cumulative light intensity (open
circles) or cumulative hysteresis energy (filled circles) for the maximum strain of the cycle for three tensile samples cut from the same PDMS sheet; error bars represent one standard deviation in the baseline. Total light intensities corrected for differences in sample volume. b) Double logarithmic plot of cumulative light intensity vs. cumulative hysteresis energy. The light intensity varies with the hysteresis energy to a power of 2.0.

The total number of bonds broken in the cyclic straining experiments was estimated by comparing the mechanically induced light output with the amount of light produced when all of the dioxetane bonds in the sample were activated thermally. To this end, unstrained tensile samples were heated to 250-280 °C until light emission had stopped (for details, see Supporting Information). The light emission was imaged with the same shutter speed, integration time and aperture as in the tensile tests. Comparison of the thermally induced light emission with the mechanoluminescence obtained on the tensile cycling experiment with a maximum strain of 190 %, depicted in Figure 5, allowed us to calculate that (0.03 ± 0.01) % of the dioxetane bonds were broken during the entire series of cycles. This estimate took account of the fact that the quantum yield of the mechanoluminescence is approximately 50 % of the thermoluminescence quantum yield.[43] However, we consider the value of 0.03 % to be a lower bound, because we observed that the quantum yield of the thermoluminescence above 200 °C is higher by a factor of five in the absence of silica filler particles (see Supporting Information). We assume that the reduction in quantum yield is a thermal effect that does not occur to the same extent at room temperature, which is partly supported by reports of degradation in silica-filled PDMS starting to occur at ~200 °C.[51] However, if the silica-induced reduction in quantum yield is also effective at room temperature, the figure for % mechanochemical dioxetane scission may be up to five times higher.

Having observed the strongly history-dependent nature of the mechanoluminescence emission, we decided to investigate an unusual and poorly understood feature of the mechanomemory
effect, namely its anisotropy. First reported by Mullins\textsuperscript{[20]} and exhibited by many filled elastomers,\textsuperscript{[19]}\textsuperscript{[52]}\textsuperscript{[53]}\textsuperscript{[54]} a sample cut perpendicularly from a pre-strained sample behaves like the virgin material in uniaxial tension, its mechanical properties seemingly unchanged. Varying the angle at which the sample is cut from the pre-strained sample gives varying degrees of hysteresis.\textsuperscript{[54]} The anisotropy is also evident under other modes of deformation.\textsuperscript{[54]} More recently, several phenomenological models have been developed to account for this effect,\textsuperscript{[52]}\textsuperscript{[55]}\textsuperscript{[56]}\textsuperscript{[53]}\textsuperscript{[57]}\textsuperscript{[58]} but these (by definition) are not directly concerned with the sources of stress-softening: generally, experimental data is fitted by means of a damage parameter which covers all possible physical mechanisms. Nevertheless, several authors have commented on the need for more physical data to validate current models and to help formulate more accurate models in the future.\textsuperscript{[59]}\textsuperscript{[60]} Some of the physical interpretations of anisotropy which have been proposed until now even exclude covalent bond scission as a significant contributor.\textsuperscript{[19]}\textsuperscript{[61]} We anticipated therefore that it would be of great interest to examine this effect with our covalent bond scission probe.

We studied this aspect of mechanomemory with mechanoluminescence in two separate sets of experiments. In the first, a large sample was pre-conditioned to a relatively high strain of 190 % via several tensile cycles, exhibiting the stress-strain behavior and mechanoluminescence shown in Figure 8a. Smaller samples were then cut from the original large sample, one set parallel and the other perpendicular to the original tensile direction. The same sequence of strain cycles was applied to the smaller samples and the resulting mechanoluminescence recorded (Figure 8b and Figure 8c). Compared to the virgin sample, the two parallel samples which were tested exhibited much less permanent hysteresis upon straining and no detectable mechanoluminescence, as
expected on the basis of the previously observed absence of mechanoluminescence on the second and subsequent cycles to a particular strain (Figure 8b). They fractured at a lower strain than the pre-conditioning strain, possibly as a result of the introduction of defects by cutting. By contrast, the perpendicular sample demonstrated significant hysteresis and mechanoluminescence emission throughout the studied strain range (Figure 8c). Remarkably, the light emission per unit energy absorbed between virgin and perpendicular samples was indistinguishable within experimental uncertainty for the perpendicular and virgin samples (Figure 8d), suggesting that the deformation experienced by the covalent bonds is predominantly uniaxial. It might be expected that the compressive stresses lead to a reduction in the anisotropy and the light intensity (per unit energy absorbed) from the sample restrained perpendicularly compared with the virgin sample, but here the light intensities from the two samples are within experimental error. In addition, on pre-conditioning to an intermediate strain, a sample cut parallel to the original tensile direction started to emit light only above the pre-conditioning strain, whilst the perpendicular sample emitted light in the same strain range as the virgin sample (see Supporting Information).
Figure 8. Anisotropy of the Mullins effect. a) A large sample was pre-strained, exhibiting mechanoluminescence as shown (blue); b) A sample cut from the large sample (a) parallel to the original tensile direction exhibited no light on straining below the pre-straining threshold (signal magnified to show absence of light); c) A sample cut from the large sample (a) perpendicular to the original tensile direction gave out light throughout the entire strain range; d) The cumulative light intensities emitted were similar for the same cumulative hysteresis energy, correcting for the dimensions of the samples. Diamonds: virgin material; empty circles: perpendicular sample; filled circles: parallel sample.

3. Discussion
The results support a scheme in which permanent hysteresis originates from (at least) two different mechanisms, one of which involves chain scission and one or more of which do not. The lack of detectable mechanoluminescence in the lower strain regime confirms that other irreversible mechanisms are operative at low permanent hysteresis energies. Furthermore, the observation that total light emission increases more rapidly with increasing strain than the total hysteresis energy in the strain regime studied, as evidenced by a power law exponent of 2.0, also
implies that covalent bond scission becomes more important relative to other damage mechanisms as the strain increases. Interestingly, triple networks containing mechanoactive dioxetane in a first sacrificial network exhibited an exponent of less than 1, 0.75;\textsuperscript{[46]} in this case, dioxetane scission became relatively less prevalent in comparison with non-specific scission of backbone bonds.

Some existing molecular-level models of the Mullins effect in filled elastomers propose such a combination of the damage mechanisms, with at least one involving covalent bond scission. Blanchard and Parkinson\textsuperscript{[62]} and Bueche\textsuperscript{[63]} ascribed Mullins stress-softening to the rupture of non-covalent interactions and covalent bond scission. In their scheme (\textbf{Figure 9}), stress-softening at lower strains is brought about by the rearrangement of chains on the fillers, facilitated by the rupture and reformation of hydrogen bonds and/or physical adsorption bonds, which break more easily than the covalent bonds. On straining further, the lengths of the polymer chains connecting the filler particles along the tensile direction increase and homogenize, the shorter chains experiencing a greater force than the longer ones on account of their lower extensibility. Covalent rupture in the polymer matrix would come into play as the polymer chains connecting the filler particles reach the limit of their extensibility in the tensile direction.

The contemporary interpretation is more complex. If the distance between particles increases in the tensile direction, in the direction perpendicular to the straining direction, the thickness of the sample is reduced, inducing very high local shear stresses and a highly non-affine deformation of the chains (i.e. chain deformation is not proportional to the macroscopic deformation) as filler particles are pushed together.\textsuperscript{[64]} It is likely that forcing undeformable particles together in the perpendicular direction also leads to covalent bond rupture. In essence, a \textit{uniaxial} macroscopic deformation applied to a nano-filled elastomer (and ours is close to the percolation limit at a
volume fraction of 0.16) leads to a very heterogeneous level of stretch of the chains and in particular very high local stresses between particles which could cause bond breakage also by cavitation. These high local stresses cannot be fully uniaxial since bonds break upon unloading i.e. a macroscopic unloading can lead to a local loading of the molecules. The sensitivity to the stretching direction that is observed, however (Figure 8), suggests that the applied local stress field, while heterogeneous, is mainly oriented in the tensile direction.

Mechanoluminescence also provided a wealth of temporal information regarding covalent bond scission within each tensile cycle. In each cycle, covalent bond scission began as soon as the previous maximum strain was exceeded, although there was a delay, corresponding to a strain difference of (4.2 ± 0.2) %, before covalent bond scission was occurring to the same extent at the maximum strain of the previous cycle. Possibly, reversible non-covalent filler-polymer interactions that can reform in a different location upon unloading in each cycle could first accommodate some of the applied strain in the new cycle. In addition, a small amount of bond-breaking was observed to occur upon unloading because of the non-uniaxial local deformation field created by the filler structure. As the structure is modified irreversibly during loading, the unloading path leads to other regions of high stress, dependent upon the filler reorganization and viscoelasticity, leading to the scission of different covalent bonds. This difference in loading path has been clearly shown in the cavitation study of Zhang et al. on filled SBR elastomers.[23]

During a typical series of cycles to 190 % strain, only a small fraction of the dioxetane bonds are broken, ~0.03 %, or $10^{16}$ dioxetane bonds cm$^{-3}$. Regardless of whether there is preferential scission of the weak dioxetane bonds (see below), this represents a tiny fraction of all cross-links, which nevertheless accompanies a decrease in modulus of 40%. This result is in line with
the inhomogeneous nature of the stress distribution in filled elastomeric networks: a wide distribution of polymer chain lengths connects the filler particles, as described above and the fillers themselves are not evenly dispersed but are more fractal structures, leading to local stress concentrations as discussed above. The energy required for thermal decomposition of bis(adamantyl)dioxetane at zero force is 150 kJ mol\(^{-1}\)[65] in comparison to the average bond dissociation energies for C—C, Si—C (in the cross-links) and Si—O (in the polymer main chain) of 350, 360 and 450 kJ mol\(^{-1}\) respectively. Therefore, we may expect that when straining a perfectly homogeneous system, the dioxetane bonds would break significantly more often than the other cross-links in the PDMS material. In the real, inhomogeneous network, the preference is less strong, but the arguments we put forward below show that to a first approximation, scission of the dioxetane cross-links contributes significantly to the observed effects.

The activation energy of the dioxetane is 150 kJ mol\(^{-1}\), but the energy that can be stored under strain is significantly smaller because the geometry of the transition state is altered by force so as to reduce the elongation from equilibrium bond length to critical bond length, and hence reduce the work that the force needs to perform to break the bond.[66] Based on the experimental activation energy for mechanically activated bond scission in PDMS (151 kJ mol\(^{-1}\))[67] relative to its thermal bond dissociation energy (450 kJ mol\(^{-1}\)), we use a value of 50 kJ mol\(^{-1}\), one third of the dioxetane thermal activation energy. When the dioxetane breaks under strain, the energy stored in that bond is irretrievably lost. A calculation (Supporting Information) shows that the energy dissipated upon breaking 0.03 % of the dioxetane cross-links by straining to 190 % is 1.2 x10\(^{-4}\) J, corresponding to 0.16 % of the permanent hysteresis energy absorbed by that strain. However, when a network is strained, not only the dioxetane ring in a strand stores potential
energy: all the bonds in the strand between cross-links are charged with potential energy, which they subsequently lose when the dioxetane breaks. In DFT studies, Saitta et al. found that a polyethylene chain could sustain on average 68 kJ mol\(^{-1}\) per C—C bond before rupturing at 18% strain;\(^6\) Hanson et al. calculated that polyisoprene could store 335 kJ mol\(^{-1}\) per monomer unit prior to scission at 40% strain, corresponding to 84 kJ mol\(^{-1}\) per C—C bond.\(^6\) In the current system, the dioxetane cross-linker connects two silicon atoms of the matrix via 26 additional bonds; assuming each of these bonds can store as much potential energy as the dioxetane, 50 kJ mol\(^{-1}\) dioxetane bond scission dissipates an additional 3.2 x 10\(^{-3}\) J. Under these assumptions, dioxetane scission and the concomitant relaxation of the cross-linkers release 4.4% of the total hysteresis energy. This calculation further assumes that dioxetane scission releases energy only from within its own cross-linker. Scission could potentially enable other parts of the network to relax, releasing additional strain energy. In any case, dioxetane scission releases more energy than from the mechanically induced decomposition of the dioxetane moiety alone.

Given that dioxetanes represent a small fraction of the bonds in filled PDMS but contribute significantly to the hysteresis energy, the assumption that the weak bond breaks preferentially appears to hold in this case. Whilst dioxetanes are weaker than normal covalent bonds, they are still considerably stronger than the non-covalent interactions present in these materials, so we do not expect the addition of dioxetane to significantly increase the prevalence of covalent bond scission at the expense of other energy-absorbing mechanisms. In addition, the dioxetane’s location in a short cross-linker may further increase its likelihood of undergoing scission. Nevertheless, only a tiny fraction of the total number of PDMS bonds would need to break to account for the Mullins hysteresis. This analysis, whilst taking a simplified view of the system,
shows that covalent bond scission in the bulk matrix does make an important contribution to the Mullins effect in silica-filled PDMS. As mentioned above, this does not necessarily imply that covalent bond scission in the polymer matrix brings about the Mullins effect; rather, the discrepancy between energy dissipated directly by bond breakage and hysteresis energy suggests that the covalent bond scission does not dissipate a lot of energy per se but rather allows a larger relative motion of fillers (in a specific direction controlled by the macroscopic deformation field) which does in turn induce a much larger viscous dissipation than if those covalent bonds had not been broken. To the best of our knowledge this is the first time that such an insight has been shown.

It is worth considering the findings of our semi-quantitative analysis in comparison with those of Grzybowski et al. They concluded that $10^{16}$ cm$^{-3}$ covalent bonds (of Si—O, Si—C or C—C) were broken in tubes of filled PDMS subjected to 5 minutes of 60 % compressive strain, corresponding to the absorption of 10 % of the mechanical strain energy input. Whilst our own calculations indicate that 190 % (tensile) strain is required to activate $10^{16}$ cm$^{-3}$ dioxetane groups, our findings do not necessarily contradict those of Grzybowski et al. Aside from the potential differences in mechanoactivation under compression and tension, bond scission processes are not homogeneous throughout the network. For example, lower rupture forces have been calculated for Si—O bonds in siloxane oligomers attached to silica surfaces,$^{70}$ $^{71}$ it is therefore possible that the scission processes on the surface of the silica are activated at lower strains than those in the bulk PDMS matrix. The synthetic protocol here permits dioxetane incorporation only in the bulk.
Figure 9. Bueche-type mechanism for mechanoluminescence response from a filled elastomer, combining rupture of non-covalent interactions and covalent bond scission. Adamantyl groups of dioxetanes not represented for clarity. (1): Applying a low strain, the weaker physical adsorption interactions between the filler and the polymer network break first. (2): On unloading, the adsorptions reform, although the length of polymer chain between the fillers is homogenized, leading to a stress-softening. (3): On applying a higher strain to the same material, the polymer chains connecting the fillers begin to reach the limit of their extensibility. This leads to either complete rupture of all the physisorptions between a filler particle and a length of polymer chain or (4) covalent bond scission, giving rise to mechanoluminescence. FRET to DPA not represented.

Lastly, we demonstrate unambiguously that the deformation mechanisms in the Mullins effect lead to a strong degree of anisotropy in the observed strain-induced covalent bond scission in these materials. This observation is significant in that it potentially helps to exclude some
previous molecular interpretations put forward to account for the anisotropy which discount covalent bond scission as a significant contributor. For example, Papkov\textsuperscript{[61]} advocated a mechanism combining rearrangement of chains on the surface of the filler particles with irreversible displacement of the filler in the polymer matrix, based on a comparison of the calorimetric output with changes in internal energy. More recently, Hanson et al. \textsuperscript{[19]} attributed the anisotropy in silica-filled PDMS to disentanglement of polymer chains, disregarding covalent bond scission as a significant contributor on the basis that it would lead to an overall degradation of mechanical properties in all directions. The experiments performed here suggest otherwise.

One can imagine a scenario shown in Figure 10, in which various dioxetane bonds are aligned to greater or lesser degrees with the applied strain. Those dioxetanes which are best aligned (A and D) or connected to a less extensible chain will experience a greater effective force and undergo mechanoluminescent scission, whilst dioxetane C remains intact. On restretching orthogonally to the original tensile direction, the scission of the chains containing dioxetane A and D would not adversely affect the mechanical properties and dioxetane C instead takes up the applied strain. Such an interpretation, whilst obviously simplified, is consistent with previous observations on the uniaxial and equibiaxial tensile activation of spiropyran mechanophores in Sylgard 184, with greater mechanoactivation observed under equibiaxial tension.\textsuperscript{[72]}

Figure 10. Simple schematic showing a proposed mechanism to account for observed anisotropy in mechanoluminescence. Dioxetanes A and D experience the most effective force as they align in the direction of the applied tensile strain. Dioxetanes B and C are less aligned with the strain and therefore experience less force.
4. Conclusion
In summary, mechanoluminescence from silica-filled PDMS subjected to cyclic uniaxial tensile testing afforded detailed insight on the covalent bond scission processes contributing to the Mullins effect in these materials. Firstly, these results provided the clearest experimental indication up till now that covalent bond scission occurs predominantly on the first cycle to a particular strain, when the material displays the greatest hysteresis. Mechanoluminescence also allowed us to visualize the timing of bond-breaking within each cycle. For the first time, mechanoluminescence was observed upon unloading, which may point to an increase in local tensile stresses while the macroscopic stress decreases. The presence of other mechanisms could also be inferred from inspection of the relationship between light emission and hysteresis energy, with covalent bond scission in the polymer matrix absorbing more energy relative to other mechanisms as the strain increases. An approximate calibration confirmed that the number of covalent bonds undergoing rupture remains small throughout (<0.1 %), in agreement with reports by others in this field, but cross-linker relaxation could nevertheless release a substantial fraction of the observed hysteresis energy. We showed unambiguously and for the first time that covalent bond scission is brought about in an anisotropic fashion and is highly sensitive to the direction of the applied strain. Taken together, these results depict covalent bond scission as having a distinct role in the Mullins effect and we envisage that this information will be essential to those designing filled elastomeric materials and developing models of these systems to predict their behavior. A molecular mechanism or model of the Mullins effect in this material should be able to account for the occurrence of covalent bond scission in the polymer matrix at high strain and may help to rationalize important effects of the elastomer crosslink density for fracture processes that have been observed.\[73\] This work could also form a starting point for other mechanistic investigations. For example, in calculations on siloxane elastomers attached to silica, the bonds
in the covalent attachment were found to be more likely to break than the bonds in the main polymer,\textsuperscript{[70]} in agreement with experimental observations in solution of cleavage of a Diels-Alder adduct covalently attached to silica;\textsuperscript{[74]} conversely, others have predicted the existence of glassy shells of polymer around the filler particles in filled elastomers,\textsuperscript{[22]} \textsuperscript{[75]} \textsuperscript{[76]} in which mobility and plastic deformation would be limited. It would therefore be of great interest to determine whether bond scission occurs closer to the fillers or in the bulk matrix. The detailed interplay between rupture of non-covalent and covalent interactions could also be probed with selective functionalisation of the silica filler particles to tailor the average density of hydrogen-bonding sites available on the surface of the fillers. Above all, we hope that this work stimulates further interest in the use of mechanoluminescence and other force-probes to build up a better molecular picture of the processes involved in the fascinating mechanical behavior of this important class of materials.

5. Experimental Section

*Preparation of PDMS samples:* Bis(adamantyl)-1,2-dioxetane was incorporated in PDMS (2 wt\%) as a vinyl-terminated cross-linker (for synthetic procedures and small molecule characterization, see Supporting Information) via a platinum-catalyzed hydrosilylation of Sylgard 184 (10:1 base: curing agent), along with 0.5 wt\% of 9,10-diphenylanthracene (DPA) to boost the light emission. A representative procedure is as follows. The bis-vinyl cross-linker (20 mg) was dissolved in a small amount of toluene (0.2 mL), together with DPA (5 mg). The solution was added to the PDMS base (1 g) and vortexed for two minutes, after which the curing agent (0.1 g) was also added and the mixture vortexed for a further two minutes. The viscous solution was then placed on a Teflon surface and put under vacuum for a few minutes to remove
air bubbles, then polymerized under nitrogen at 60 °C for 18h. \(^1\)H NMR experiments indicate that the dioxetane mechanophore does not substantially decompose under these conditions. After polymerization, the resulting material was clear, with a slightly blue color from the DPA. Rectangular samples were cut from the material with a blade (dimensions 9 x 4 x 0.4 mm, except in anisotropy experiments). In the anisotropy experiments, the large sample had dimensions 25 x 15 x 0.4 mm and the smaller samples cut from it 9 x 5 x 0.4 mm.

**Optomechanical tests:** Tensile tests were carried out on a Zwick tensile testing machine with clamps having a maximum load capacity of 100 N at an initial strain rate of 0.1 s\(^{-1}\). Dioxetane emission was recorded with a PCO 5.5 sCMOS camera at a relatively slow frame rate of 10 fps so that the emission from the entire tensile cycle could be captured in the maximum number of frames the electronic memory can store. Bright blue light was readily observable by eye on break. The camera was set up facing the sample, enclosed and covered to exclude background light, in a similar arrangement as reported previously.\(^{[29]}\)\(^{[45]}\) The region of interest of the camera sensor (the area over which the light was recorded) was specified such that it could contain the biggest area occupied by the sample during the tensile cycle.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgments**
J. M. C. thanks Gregory Gossweiler for experimental guidance. This research is supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NOW grant number 726.011.002), by the Ministry of Education, Culture and Science of the Netherlands (Gravity program 024.001.035) and by the NSF (CHE-1124694 and CHE-1508566).


Table of Contents

Applying cycles of tensile strain to silica-filled poly(dimethylsiloxane) functionalized with 1,2-dioxetanes led to the emission of mechanically induced chemiluminescence as covalent bonds broke in the material. Monitoring in real-time, we observed light emission predominantly on the first cycle to a strain. Covalent bond scission is shown conclusively to contribute to Mullins stress-softening and to exhibit strong anisotropy.

Keywords: mechanochemistry, chemiluminescence, elastomers

J. M. Clough, C. Creton, S. L. Craig, R. P. Sijbesma*

Covalent Bond Scission in the Mullins Effect of a Filled Elastomer: Real-time Visualization with Mechnoluminescence