How accurately do mechanophores report on bond scission in soft polymer materials?

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Abstract
Mechanophores are molecules that are incorporated into a host material and react to the local mechanical condition—the state of stress or strain—of that host material. Among their many purposes is that of a reporter: Mechanophores whose optical activity changes in response to mechanical cues can reveal bulk material processes that are ordinarily hidden, such as fatigue and fracture. Moreover, they may do so well before a material is fully fractured. To extract quantitative information from the optical signals from embedded mechanophores it is important that the mechanophores, which are generally a minority component of the material, report proportionally and unambiguously on the mechanical condition of the bulk. This is particularly important for early reporting of damage and wear, for which the optical signal from the mechanophore should accurately reflect bulk bond scission. In this article, we develop and analyze a general theory for the quality of optical mechanoreporting by mechanophores in soft materials, based on the Bell-Evans theory of bond breaking. We find, that at the typical low fractions in which mechanophores are incorporated the overall change in strength is limited, but that the proportionality of the reporting can be off by significant amounts, particularly at short times after loading but, for non-scissile bonds, at long times as well.

KEYWORDS
mechanophores, modeling, polymer networks, polymer physics, theory

1 | INTRODUCTION
The catastrophic mechanical failure of a material is generally marked by some abrupt macroscopic event that irreversibly destroys its structural integrity. Breaks, tears, cracks, or splits appear suddenly and propagate quickly; once they are visibly present little can be done to avert further damage. Despite its apparent unpredictability at larger length scales, however, complete failure is preceded by a phase of microscopic build-up which is often more gradual and spread out over time.1,2 Early detection of the microscopic and molecular scale events leading up to failure is therefore crucial for damage prevention and mitigation in materials. Likewise, the ability to identify molecular damage or wear at their earliest manifestation may expose the processes that trigger failure at the smallest scales and can inspire both a fundamental understanding of the operational principles of...
novel materials with exceptional resistance to failure such as tough hydrogels,\(^3,^8\) as well as their further rationally designed performance enhancements.

Detecting molecular-scale precursory processes to failure clearly must involve some form of mechanoreporting: The presence of components incorporated inside the material that relay—preferably, in an accurate and calibratable manner—information on the local mechanical state of the material. Depending on the precise implementation, these permit to map out the highly heterogeneous distributions of local forces (stresses), the local deformations (strains) or the local topology (connectivity), or combinations of these quantities. Such molecular components, capable of undergoing mechanically induced chemical reactions or conformational changes, which are accompanied by a measurable reporting signal are more commonly termed mechanophores, and an increasing number of such molecules has been identified\(^9,^{12}\) in recent years. In this work, we will be focusing on mechanophores which can be incorporated as minority fractions into a polymer matrix (gel or elastomer) and which either change color (mechanochromism), or become fluorescent/ emissive (mechanoluminescence) in response to local forces—see Figure 1.

**FIGURE 1** Schematic of the systems we discuss in this article.
A crosslinked polymer network (blue strands, black dots) is exposed to an external stress and has, embedded inside it, mechanophoric molecules (red) connecting network strands. These mechanophores may either act as crosslinkers themselves, or they may be incorporated directly into the polymer chains. Mechanophores come in two basic types: Scissile mechanophores like \(\pi\)-extended anthracenes and 1,2-dioxetanes respond with some optical signal when they break under an external force; non-scissile mechanophores like spiropyrans fluoresce when they change conformation in response to the local force, but retain their network connectivity. At sufficiently high stresses, network chains will start breaking and the mechanophores will become increasingly activated. We ask to what extent the signal intensity from the mechanophores accurately reports on the breaking of network chains [Color figure can be viewed at wileyonlinelibrary.com]

These molecules fall within one of two classes: Scissile mechanophores break into two pieces in response to a force, and colorize, emit light or fluoresce when they do. Commonly used examples of scissile mechanophores are \(\pi\)-extended anthracenes,\(^12\) hexaarylbiimidazole\(^13\) and dioxetanes.\(^14\) In contrast, non-scissile mechanophores retain their mechanical integrity but undergo a conformational change that is accommodated by luminescence, color change, or fluorescence. By far the most commonly used non-scissile mechanophane is spiropyran\(^9,^{15–17}\) which for sufficiently high forces “unfolds” to form merocyanin which fluoresces red. Merocyanin, moreover, may undergo further reversible isomerizations resulting in further color changes.\(^9\) Although in most practical applications both scissile and non-scissile activation are effectively irreversible processes, there is no a priori reason to rule out some degree of reversibility via spontaneously reversion back to the activatable state. In non-scissile bonds this would require the force to drop below the activation threshold, but in scissile bonds this may happen at all forces via a process of spontaneous reconnection. Both scissile bonds\(^18,19\) and non-scissile bonds\(^9,^{15–17}\) have been used to spectacular effect to visualize stresses and the onset of damage in a range of soft materials and as such have become indispensable tools in mechanochemistry and (soft) materials science.

The elevation of molecular mechanoreporting toward a truly quantitative, calibrated method to measure local stresses, however, is still some way away. Among the important open questions that remain to be addressed are (1) to what extent is the reporting faithful—that is, is the mechanochromic or mecanofluorescent signal intensity proportional to the invisible extent of broken bonds in the matrix? and (2) To what extent is the reporter noninvasive—that is, does its incorporation into the polymer matrix alter the strength of the material?

Clearly, an ideal mechanoreporter should report completely faithfully. This has been called “the strong hypothesis” by Creton:\(^20\) The instantaneous signal intensity from the embedded mechanophores, normalized to its maximal value, should be proportional to the fraction of broken bonds in the embedding matrix at all times and at all stresses, and the constant of proportionality should be, indeed, constant:

\[
\text{Proportionality} : \frac{\text{Mechanophore signal}}{\text{Total [mechanophore]}} = \frac{\text{Broken matrix chains}}{\text{Total [matrix chains]}}. \tag{1}
\]

At the same time, the reporter should be completely noninvasive; its presence should not alter the mechanical
quality of the host matrix in any way to ensure that the information gained from the mechanophore-matrix composite can be reliably extrapolated to the pure matrix:

Noninvasiveness: Strength of matrix
+ Mechanophores \( \approx \) Strength of matrix. \( (2) \)

The reader will likely realize that such ideal reporting is only attainable if the properties of the mechanoreporter are identical to those of the matrix polymers. Because matrix and mechanophore are, generally, distinct molecules this condition, in practice, will not be met. This, then, is the scope of our article: we investigate the extent to which ideal reporting is violated by mechanophores that are mechanically distinct from the matrix.

2 | THEORETICAL MODEL AND RESULTS

Let us consider a polymer material consisting of polymer strands connected by crosslinkers. Mechanophores are incorporated into such a network either in the main chain of the polymer strands, or they may act as crosslinkers between strands. For the discussion that follows, the distinction between these two cases is inconsequential, and we will refer to both matrix connections (chain or crosslinker) and mechanophores (chain or crosslinker) as bonds. Regardless of whether the mechanophore is scissile or non-scissile the reaction or conformational change that prompts the optical signal can be described as a barrier crossing process which, in the absence of a force, occurs at a rate \( k_0 \) [s\(^{-1}\)], and may be described as an Arrhenius process: \( 21,22 \)

\[
k_0 = \left( \frac{1}{\tau_{\text{att}}} \right) \exp \left( \frac{-\Delta E_0}{k_B T} \right). \tag{3}
\]

In this expression, \( \tau_{\text{att}} [s] \) is the attempt time, \( \Delta E_0 [J] \) is the barrier height, \( k_B [JK^{-1}] \) is the Boltzmann constant and \( T [K] \) is the absolute temperature. This equation expresses the fact that the frequency at which a barrier crossing (activated) process happens spontaneously decreases exponentially with the height of the energetic barrier. The same barrier crossing process may be considered in the presence of an external force \( f [N] \), where we will use the sign convention that \( f > 0 \) corresponds to forces that promote barrier crossing, that is, positive forces increase the activation rate. Bell theory \( 23 \) prescribes that in this case, we may write the force-dependent activation rate \( k_a(f) [s^{-1}] \) as

\[
k_a(f) = k_0 \exp \left( \frac{fx^\ddagger}{k_B T} \right), \tag{4}
\]

where \( k_0 \) is the zero-force rate from Equation (3), and \( x^\ddagger [m] \) is the reactive compliance or dissociation length. This overall activation rate \( k_a(f) \) increases exponentially when a load \( f \) is applied, and the activation process of an individual mechanophore may be thought of as arising in a trade-off between the height of the intrinsic energy barrier \( \Delta E_0 \) and the external force \( f \).

It is, of course, possible to assign actual figures to the parameters that specify the response of different mechanophores as, for instance, is done in ref. 16 where the value of \( k_0 \) for two different spyropirans is measured to be on the order of \( 10^{-6} \) s\(^{-1}\), and \( x^\ddagger \) to be around 1.8 Å. In this article, we are first and foremost interested in extracting the generic behaviors that are common to all mechanophore types, and for this reason it will be convenient to nondimensionalize our equations; we will do this by firstly measuring all times in units of \( \tau_{\text{att}} \), which means all rates are to be normalized as \( \bar{k} \equiv \tau_{\text{att}}k \). Furthermore, we will use the nondimensional force \( \phi \equiv fx^\ddagger/k_B T \), and rewrite the barrier height in terms of another nondimensional force as \( \Delta E_0 \equiv \phi_0 k_B T \). After this, we are left with

\[
\bar{k}_a(\phi) = \exp(\phi - \phi_0), \tag{5}
\]

which summarizes in compact form the competition mentioned above: activation is promoted by the force \( -\phi \), and counteracted by the barrier height \( -\phi_0 \). In what follows we will drop the bars over scaled rates, and the scaling with \( \tau_{\text{att}} \) will be assumed. What exactly does this rate mean? Now, suppose we have a number \( N_{\text{tot}} \) of such bonds, all identical and all subjected to the same force \( \phi \). Let us use \( N_i(t) \) to denote the (ensemble-averaged) number of inactive bonds at scaled time \( t \), the evolution of the average number of inactive bonds is then prescribed by the following equation

\[
\frac{d}{dt} N_i(t) = -k_a(\phi)N_i(t), \tag{6}
\]

expressing that the system is losing inactive bonds (because they become activated) at a rate \( k_a(\phi) \). Note, that here and in what follows, quantities like \( N_i(t) \) measure cumulative activation. After initial activation, many mechanophores remain active for some period of time, which implies the instantaneous mechanophore signal at time \( t \) is proportional to the cumulative activation up to time \( t \). This cumulative activation is experimentally accessible even for mechanophores that only emit at the
moment of activation, but in that case clearly additional, time-resolved information is available. At time \( t = 0 \) all bonds start out inactive; \( N(0) = N_{\text{tot}} \); and substitute Equation (5) for \( k_a(\phi) \), we find the full evolution problem for \( N_{\text{tot}} \) independently forced mechanophores:

\[
\begin{align*}
\frac{d}{dt} N(t) &= -N(t) \exp(\phi - \phi_0), \\
N(0) &= N_{\text{tot}}
\end{align*}
\]

This problem is easily solved to yield the expected exponential decay of the number of inactive bonds. Because the number of activated bonds \( N_a(t) = N_{\text{tot}} - N(t) \), we find that the number of activated bonds as a function of time is given by

\[
N_a(t) = N_{\text{tot}}[1 - \exp(-k_a(\phi)t)].
\]

So far, we have been making the greatly simplifying assumption that all bonds experience the same force \( f \). Obviously, in a network material the overall load on the system is collectively borne, by multiple bonds, and the rupture of one bond increases the load on the others. In the following, we explore the effects of such load sharing.

### 2.1 Reference case: Pure matrix

Let us begin by studying the reference case, in which there is only matrix material, held together a total number \( N_{\text{mat,tot}} \) of matrix bonds. These bonds can break, and the rate at which they do so is given by Equation (5); to be able to distinguish matrix form mechanophores in what follows we will denote the scaled barrier height of a single matrix bond by \( \phi_{\text{mat}} \). Consider, now, the case where a total force \( \Sigma \) is acting on the network. How this force is distributed across all the load-bearing bonds inside the polymer matrix is obviously dependent on a great number of factors, but we will make the crudest of approximations here; that the total force \( \Sigma \) is distributed uniformly across all intact bonds, the number of which we will refer to as \( N_{\text{mat,c}}(t) \) (the subscript \( c \) stands for “closed”). This applies, for instance, when the total force is spread out over an effectively two-dimensional failure plane; in those case where the total force is distributed over a volume the precise implementation of load sharing may need to be refined; for now we will primarily be interested in the generic effects of distributing the load. In the case of load sharing among \( N_{\text{mat,c}} \) bonds in an effectively parallel arrangement, the scaled force that each intact bond experiences is \( \phi = \Sigma / N_{\text{mat,c}}(t) \). Substituting all this into the matrix equivalent of Equation (7) produces the following initial value problem (in essence, a modified version of the Bell model\(^2\) for multiple adhesion) for the evolution of the number of intact matrix bonds

\[
\begin{align*}
\frac{d}{dt} N_{\text{mat,c}}(t) &= -N_{\text{mat,c}}(t) \exp \left( \frac{\Sigma}{N_{\text{mat,c}}(t)} - \phi_{\text{mat}} \right), \\
N_{\text{mat,c}}(0) &= N_{\text{mat,tot}}
\end{align*}
\]

The basic behavior of solutions to this initial value problem is presented in Figure 2. After an initial phase of near-exponential decay (evidenced by the straight lines in the single-logarithmic plots) the system abruptly fails, in an avalanche-like fashion, and the number of intact bonds reaches zero at some time \( t_b \), the breaking time. Since we do not keep track of the deformation of the pure matrix materials (nor of that of the matrix/mechanophore composites in what follows) our theory, which focuses on connectivity and bond breaking does not allow access to the area-under-the-curve measure of toughness that can be computed if the stress-strain...
relation is known. As a proxy for overall strength, we will use instead the time until complete dissociation of all bonds at a given total force $\Sigma$.

As Figure 2(A) shows $\phi_{\text{mat}}$, the scaled activation energy for matrix bonds, controls the strength of the matrix as evidenced by a longer breaking times $t_b$ for increasing values of $\phi_{\text{mat}}$. This is clear, as $\phi_{\text{mat}}$ is directly proportional to the activation energy and larger values correspond to a higher barrier that must be overcome to break the bond, which will take exponentially longer at constant temperature $T$. Figure 2(B) confirms another intuitive behavior; that the breaking time $t_b$ should decrease with increasing total force $\Sigma$.

We have confirmed that these numerical findings agree with an analytical expression for the breaking time $t_b$, which (see Appendix A) is given by

$$t_b = -e^{\phi_{\text{mat}}} \text{Ei} \left(\frac{-\Sigma}{N_{\text{mat,tot}}}\right),$$

where $\text{Ei}(x)$ is the Exponential Integral.\textsuperscript{24}

Note that this finite-time breaking behavior is a consequence of the load sharing, and markedly different from the exponential approach to zero intact bonds we would have seen in the case of constant forces on all bonds. In $t_b$, the time until complete failure, we now have a reference metric for the strength of material (note, that this is not a toughness or a yield strength, it is a measure of how long the material is able to withstand a given load). When we add mechanophores in what follows, we will compare $t_b$’s to establish the extent to which the material is weakened by the addition of mechanophores. Also, we will assess to what extent the bond breaking in the system is faithfully reported on by the mechanophores.

### 2.2 Scissile mechanophores

Now, we add a number $N_{\text{mp,tot}}$ of scissile mechanophores to those $N_{\text{mat,tot}}$ matrix bonds. The optical signal from the mechanophores is proportional to the number of broken mechanophores. We will ask two questions: (i) Is the signal from the mechanophores proportional to the total fraction of broken matrix bonds and (ii) how is the breaking time $t_b$ affected by the addition of the mechanophores? Matrix bond parameters are defined as in the previous section, and we will write $\phi_{\text{mp}}$ for the scaled energy barrier of the mechanophores; this barrier can and likely will be distinct from its matrix counterpart $\phi_{\text{mat}}$. We will call the instantaneous number of inactive mechanophores $N_{\text{mp},i}$. In the case of scissile bonds, inactive means intact; the mechanophore signal comes only from broken bonds. All intact bonds, matrix and mechanophore, share the total load $\Sigma$ and thus the force experienced by each bond is $\Sigma/(N_{\text{mat},i}(t) + N_{\text{mp},i}(t))$. At $t = 0$, all matrix bonds are connected and all mechanophores are inactive. This gives the following initial value problem for the evolution of $N_{\text{mat},c}$ and $N_{\text{mp},c}$:

\[
\left\{ \begin{array}{l}
\frac{d}{dt}N_{\text{mat},c}(t) = -N_{\text{mat},c}(t)\exp \left( \frac{\Sigma}{N_{\text{mat},c}(t) + N_{\text{mp},c}(t)} - \phi_{\text{mat}} \right) \\
\frac{d}{dt}N_{\text{mp},c}(t) = -N_{\text{mp},c}(t)\exp \left( \frac{\Sigma}{N_{\text{mat},c}(t) + N_{\text{mp},c}(t)} - \phi_{\text{mp}} \right) \\
N_{\text{mat},c}(0) = N_{\text{mat,tot}}, N_{\text{mp},c}(0) = N_{\text{mp,tot}}
\end{array} \right. 
\]

(11)

Now, because we should compare “apples to apples” (i.e., eliminate spurious effects in proportionality and non-invasiveness due to changes in overall number of bonds) it will be helpful to keep the overall number of bonds (matrix plus mechanophores) constant. For this reason, it will be convenient to work with bond fractions rather than absolute numbers. Using the total number of bonds $N_{\text{tot}} = N_{\text{mat,tot}} + N_{\text{mp,tot}}$ we may convert to fractions as follows:

$$n_{\text{mat},c} = \frac{N_{\text{mat},c}}{N_{\text{tot}}}, n_{\text{mp},c} = \frac{N_{\text{mp},c}}{N_{\text{tot}}},$$

(12)

The total force, likewise, is scaled with $N_{\text{tot}}$ to reveal the initial force-per-bond $\sigma = \Sigma/N_{\text{tot}}$, a measure of the total load that is proportional to the stress. In these new variables, we may work directly with the fraction of mechanophore bonds $\rho_{\text{mp}}$ defined as

$$\rho_{\text{mp}} = \frac{N_{\text{mp,tot}}}{N_{\text{tot}}}$$

(13)

Since in analogy to Equation (3), $\phi_{\text{mat}}$ sets the reference timescale it is also convenient to rescale time some more, setting $\tau = e^{-\phi_{\text{mat}}} t$ which leaves only the difference in energy barriers $\Delta \phi = \phi_{\text{mp}} - \phi_{\text{mat}}$ as a final parameter. Overall, this reduces the system of evolution equations to

\[
\left\{ \begin{array}{l}
\frac{d}{d\tau}n_{\text{mat},c}(\tau) = -n_{\text{mat},c}(\tau)\exp \left( \frac{\sigma}{n_{\text{mat},c}(\tau) + n_{\text{mp},c}(\tau)} \right) \\
\frac{d}{d\tau}n_{\text{mp},c}(\tau) = -n_{\text{mp},c}(\tau)\exp \left( \frac{\sigma}{n_{\text{mat},c}(\tau) + n_{\text{mp},c}(\tau)} - \Delta \phi \right) \\
n_{\text{mat},c}(0) = 1 - \rho_{\text{mp}}, n_{\text{mp},c}(0) = \rho_{\text{mp}}
\end{array} \right. 
\]

(14)

For every external load $\sigma$, this system has two adjustable parameters: First, $\rho_{\text{mp}}$, a number between 0 and 1,
sets the number fraction of incorporated mechanophores ($\rho_{mp} = 0$ corresponds to pure matrix, $\rho_{mp} = 1$ to only mechanophores; in practice we will consider a minority fraction of mechanophores and will set $\rho_{mp} = 1$). Second, we have $\Delta \phi$ which sets the difference in energy barriers between matrix bonds and mechanophores. If $\Delta \phi > 0$ mechanophores are stronger and break, on average, at higher forces than the matrix bonds, and if $\Delta \phi < 0$ mechanophores are weaker and break, on average, at lower forces than the matrix bonds. Figure 3 shows the typical evolution of the bond numbers (to be compared to Figure 2(A)) in the presence of mechanophores. While the overall behavior of the matrix bonds is the same, the addition of 10% of slightly weaker ($\Delta \phi = -0.1$) mechanophores has subtly changes the response in the sense that the breaking time is about 1% shorter. So, for this particular setting, the strength does not appear to suffer much from the presence of the mechanophores. Figure 3 also shows the evolution of the fraction of inactive mechanophores, which is decreasing at approximately the same rate as the fraction of connected matrix bonds. This shows that indeed the mechanophores are reporting on matrix chain scission, but the question is to what extent is this reporting quantitatively reliable.

To address this question, we turn to the proportionality of reporting which is defined as the extent to which the intensity of the optical signal (produced, in this case, when a mechanophore bond breaks) accurately reflects the invisible broken bonds in the matrix. This proportionality will be quantified by a time-dependent $P$-function, defined as

$$P(\tau) = \frac{(N_{mp,tot} - N_{mp,i}(\tau))/N_{mp,tot}}{(N_{mat,tot} - N_{mat,c}(\tau))/N_{mat,tot}}. \quad (15)$$

This $P$-function is an exact representation of Creton’s “strong hypothesis”; the numerator in the right-hand side of Equation (15) is the quantity on the left-hand side of the equal sign in Equation (1), and the denominator in the right-hand side of Equation (15) is the quantity on the right-hand side of the equal sign in Equation (1). In short

Normalized optical signal = $P(\tau) \times$ Fraction of broken matrix bonds.  

From which it is clear that we would like $P(\tau)$ to be equal to one, and independent of time. In terms of the various fractions, $P(\tau)$ may be computed as

$$P(\tau) = \left(1 - \frac{\rho_{mp}}{\rho_{mp}}\right) \frac{\rho_{mp} - n_{mp,i}(\tau)}{1 - \rho_{mp} - n_{mat,c}(\tau)}. \quad (17)$$

Note, that the $P$-function is not only a function of time, but also of the chosen parameters $\rho_{mp}$, $\Delta \phi$, and the force $\sigma$. The proportionality of reporting is perfect if $n_{mat,c}(\tau)$ and $n_{mp,i}(\tau)$ evolve in exactly the same way. In that case, at all times, the ratio of intact bonds is constant and set only by its initial value:

$$\frac{n_{mp,i}(\tau)}{n_{mat,c}(\tau)} = \frac{n_{mp,i}(0)}{n_{mat,c}(0)} = \frac{\rho_{mp}}{1 - \rho_{mp}}. \quad (18)$$

which means for perfect reporting, $P(\tau) = 1$. If $P(\tau) > 1$ the mechanophores are over reporting matrix bond breaking; if $P(\tau) < 1$ they are underreporting. In Figure 4 we plot the temporal evolution of $P(\tau)$ for the same set of parameter values used in Figure 3. Here we see that despite the suggested co-evolution of the activation of mechanophanes and matrix bond breaking the mechanophanes actually do not report completely faithfully; for relatively small breaking strength differences $\Delta \phi$ the over- or underreporting can quickly reach 10% or more. Expanding and solving the equations for the short time regime, we have found that the limit of $P(\tau)$ is determined only by the difference in bond strength between mechanophanes and matrix, and not by the fraction $\rho_{mp}$ or the scaled stress $\sigma$: $P(0) = \exp(-\Delta \phi)$. The value of $P(\tau)$ does change over time; during the build-up to fracture the actual amount of bond breaking in the invisible part of the material stands in different

**FIGURE 3** Typical evolution of the fractions of connected matrix bonds $n_{mat,c}(\tau)$ (solid line) and inactive mechanoreporters $n_{mp,i}(\tau)$ (dashed line) as a function of scaled time $\tau$. Curves were obtained for a material composed of 90% matrix bonds and 10% mechanophanes ($i.e., \rho_{mp} = 0.1$), scaled stress $\sigma = 0.001$. The difference in activation energy barriers was $\Delta \phi = -0.1$. That is, mechanoreporters in this case are weaker than matrix bonds. At these forces, the overall material strength is hardly affected; the breaking time of this composite is $\tau_{b,comp}^{\text{pure}} = 6.28$, while for a pure matrix at the same density it would be $\tau_{b,comp}^{\text{pure}} = 6.33$ (i.e., $\Delta S = 0.99$)
proportion to the optical signal observed. At longer times, the proportionality measure does self-adjust to its desired value of 1, but by then the material is nearly fully fractured and, moreover, mechanophore reporting is of particular interest in the early stages of damage before full failure.

In addition to the quality of reporting, the addition of a certain fraction $\rho_{mp}$ bonds with a different strength (quantified by the strength difference $\Delta \phi = \phi_{mp,b} - \phi_{mat}$; negative $\Delta \phi$ means the mechanophores are weaker than the matrix bonds) will alter the overall strength of the material. We will quantify this invasiveness by comparing the scaled breaking time $\tau_b$ for the mechanophore/matrix composite to its pure-matrix value:

$$\Delta S = \frac{\tau_b(\sigma, \Delta \phi, \rho_{mp})}{\tau_b(\sigma, 0, 0)} - 1.$$  \hspace{1cm} (19)

If $\Delta S > 0$ the addition of mechanophores has strengthened the overall material, and if $\Delta S < 0$ the mechanophores have weakened the overall material. Figure 5 shows the behavior of the strength difference $\Delta S$ for a similar set of parameters compared to Figure 4: We keep the overall scaled stress constant and as how much longer, or shorter, the matrix/mechanophore composite can withstand the force. Obviously, for mechanophore bonds that are weaker than matrix bonds ($\Delta \phi < 0$), $\Delta S < 0$ for all values of $\rho_{mp}$ and for stronger bonds $\Delta S > 0$. This figure however overemphasizes these strengthening and weakening effects; it is clear that for typical minority fractions of mechanophores $\rho_{mp} < 0.1$ the effect is quite small, suggesting that in optimizing mechanoreporting mechanical invasiveness, relatively, is a lower risk than disproportional reporting.

A final note on $\Delta S$: While strengthening by mechanophores may appear to be beneficial, an ideal reporter, arguably, has $\Delta S = 0$. The objective of mechanophores as early damage reporters is to report on what is happening in the matrix at a particular level of loading. If the presence of the mechanophore greatly increases the load-bearing capacity of the material overall then at similar external load the mechanophore-less matrix will experience different local forces and likely break sooner. While the material may have been strengthened, the optical signal from the reporter can no longer be used to infer a bulk matrix behavior in the reference system—the mechanophores are mechanically invasive.

**FIGURE 4** Do the mechanophores report proportionally? Red lines: Evolution of the proportionality function $P(\tau)$ as a function of scaled time $\tau$. Dashed black line: $P(\tau) = 1$, corresponding to the perfect-proportionality condition; if $P(\tau) > 1$ the mechanophores are overreporting (breaking at a higher rate than matrix bonds), for $P(\tau) < 1$ they are underreporting (breaking at a slower rate than matrix bonds). Curves were obtained for a material composed of 90% matrix bonds and 10% mechanophores (i.e., $\rho_{mp} = 0.1$), scaled stress $\sigma = 0.001$. From bottom to top, we tune the relative strength of the mechanophores and the matrix bonds by changing the difference in activation energy barrier; from bottom to top $\Delta \phi = +0.3, +0.2, +0.1, -0.1, -0.2,$ and $-0.3$ respectively. As $\Delta \phi$ is decreased, the mechanophores become weaker relative to the matrix bonds [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 5** Do the mechanophores change the strength of the material? Red lines: Strength difference $\Delta S$ (as defined in Equation (19)) between the matrix-mechanophore composite and the pure matrix plotted as a function of the fraction $\rho_{mp}$ of mechanophores added for different values of the difference in activation energy barrier (breaking strength) $\Delta \phi$ between mechanophore and matrix. Black line: Ideal mechanophore limit $\Delta S = 0$ (only possible if $\Delta \phi = 0$; no mechanical difference between mechanophore and matrix). All curves computed for a scaled stress $\sigma = 0.001$. From top to bottom: $\Delta \phi = +0.3, +0.2, +0.1, -0.1, -0.2,$ and $-0.3$ respectively [Color figure can be viewed at wileyonlinelibrary.com]
2.3 Non-scissile mechanophores

The approach for non-scissile mechanophores is very similar to what we have done for scissile bonds, with the total fraction of activated mechanophores (broken and unbroken) relative to the total number of mechanophores, broken and unbroken. All this is summarized in the following set of evolution equations:

\[
\begin{aligned}
\frac{d}{dt} N_{\text{mat},c}(t) &= -N_{\text{mat},c} \exp \left( \frac{\Sigma}{N_{\text{mat},c}(t) + N_{\text{mp},u}(t)} - \phi_{\text{mat}} \right) \\
\frac{d}{dt} N_{\text{mp},u}(t) &= -N_{\text{mp},u}(t) \exp \left( \frac{\Sigma}{N_{\text{mat},c}(t) + N_{\text{mp},u}(t)} - \phi_{\text{mp},b} \right) \\
\frac{d}{dt} N_{\text{mp},a}(t) &= + N_{\text{mp},u}(t) \left( 1 - \frac{N_{\text{mp},u}(t)}{N_{\text{mp},u,tot}} \right) \exp \left( \frac{\Sigma}{N_{\text{mat},c}(t) + N_{\text{mp},u}(t)} - \phi_{\text{mp},a} \right) \\
N_{\text{mat},c}(0) &= N_{\text{mat},tot}, N_{\text{mp},u}(0) = N_{\text{mp},tot}, N_{\text{mp},a}(0) = 0
\end{aligned}
\]

The quantity between the first brackets in the third line is the fraction of the unbroken mechanophores that has not yet been activated. As before, $\Sigma$ is the total force and $\phi_{\text{mat}}$ is the energy barrier for network chain scission; the new quantity $\phi_{\text{mp},b}$ is the energy barrier for mechanophore strand breaking and $\phi_{\text{mp},a}$ is the energy barrier for mechanophore activation. We may rescale these equations again, as we did with Equations (11), and introducing the two relative energy barrier heights for breaking and activation

\[
\Delta \phi_b = \phi_{\text{mp},b} - \phi_{\text{mat}}, \Delta \phi_a = \phi_{\text{mp},a} - \phi_{\text{mat}},
\]

to obtain the full set of scaled equations for non-scissile bonds:

\[
\begin{aligned}
\frac{d}{d\tau} n_{\text{mat},c}(\tau) &= -n_{\text{mat},c}(\tau) \exp \left( \frac{\sigma}{n_{\text{mat},c}(\tau) + n_{\text{mp},u}(\tau)} \right) \\
\frac{d}{d\tau} n_{\text{mp},u}(\tau) &= -n_{\text{mp},u}(\tau) \exp \left( \frac{\sigma}{n_{\text{mat},c}(\tau) + n_{\text{mp},u}(\tau)} - \Delta \phi_b \right) \\
\frac{d}{d\tau} n_{\text{mp},a}(\tau) &= + n_{\text{mp},u}(\tau) \left( 1 - \frac{n_{\text{mp},u}(\tau)}{\rho_{\text{mp}}} \right) \exp \left( \frac{\sigma}{n_{\text{mat},c}(\tau) + n_{\text{mp},u}(\tau)} - \Delta \phi_a \right) \\
n_{\text{mat},c}(0) &= 1 - \rho_{\text{mp}}, n_{\text{mp},u}(0) = \rho_{\text{mp}}, n_{\text{mp},a}(0) = 0
\end{aligned}
\]

mechanophore bonds that are unbroken and not yet activated can become activated. We assume irreversible activation (for completeness, the case of reversible binding is briefly treated in Appendix B), and that the amount of activated, unbroken mechanophores relative to the total number of unbroken mechanophores is the same as the behavior of solutions to these equations is graphed in Figure 6(A),(B). In Figure 6(A), we show what happens when the mechanophores are practically unbreakable by setting $\phi_{\text{mp},b} = 100$. The flat long-dashed line at $n_{\text{mp},u} = 0.1$ indicates that indeed, all mechanophores remain unbroken. In this limit of
mechanophores that are very strong relative to the matrix bonds, all mechanophores remain available for non-scissile activation and indeed, at long times, all will become activated. The situation is identical to what happened in the scissile case, save for the fact that breaking is replaced by activation. In this admittedly artificial limit, since there is a fraction of the material that never breaks the abrupt and collective fracture is also absent, and the fraction of connected matrix bonds \( n_{mp,i} \) goes to zero exponentially instead of abruptly, as evidenced by the straight line in the log-lin plot Figure 6(A). What happens when we allow for mechanophore breaking as well as activation is shown in Figure 6(B), where we set the relative breaking strength of the mechanophores to \( \phi_{mp,b} = -0.1 \), as in Figure 3. The fractions \( n_{mp,i} \) and \( n_{mp,u} \) track the behavior of the scissile mechanophores in Figure 3. This is to be expected; the activation state of the non-scissile mechanophores does not affect the load distribution, which is also why we do not study \( \Delta S \) separately for the non-scissile bonds; the results depend in the same way on \( \rho_{mp} \) and \( \phi_{mp,b} \) as in the scissile mechanophore case. Again we see the fraction of activated mechanophores \( n_{mp,a} \) rise. Its value at breaking, however, is just over 0.07 in this case; that is—only about 70% of all activatable mechanophores actually become activated. This number is not equal to the total number of mechanophores since in some cases activation of mechanophores in this case is preempted by their breaking.

This is an important distinction between the scissile and the non-scissile case, with consequences for the proportionality of reporting in this situation. Simply put, because a number of activatable mechanophores are “taken out of the game” as the bonds they are incorporated in break before the mechanophore is activated, there is a sizeable fraction of “dark” reporters whose lack of reporting does not correspond to a lack of matrix bond breaking. For every mechanophore that does break, relatively more matrix bonds break and this drives the system into a generic underreporting state. This is also borne out by the graphs in Figure 7. In red we plot, again, the hypothetical case of unbreakable mechanophore bonds, which in this case, too, mirrors the phenomenology of the scissile case: depending on whether the mechanophores activate at lower forces \( (\phi_{mp,a} < 0) \) or at higher forces \( (\phi_{mp,a} > 0) \), the activation initially respectively over- or underreports on matrix bond breaking; for larger times the proportionality tends to 1 as before. More interesting is the situation for the blue curves, where we have set the

![FIGURE 6](wileyonlinelibrary.com)

**FIGURE 6** Evolution of the fraction connected matrix bonds \( n_{mp,i} \) (solid black line), the fraction of unbroken mechanophores \( n_{mp,u} \) (long-dashed black line) and the fraction of activated mechanophores \( n_{mp,a} \) (short-dashed blue line) as a function of scaled time \( \tau \). (A): In the extreme case of unbreakable mechanophores \( (\phi_{mp,b} = 100) \), the fraction of activated mechanophores (with \( \phi_{mp,a} = -0.3 \)) gradually approaches the initial fraction of mechanophores as these all become activated. (B): Evolution for the same breaking parameters as Figure 3 \( (\phi_{mp,b} = -0.1) \), but with mechanophore activation happening, on average, before breaking \( \phi_{mp,a} = -0.3 \). The ultimate fraction of activated mechanophores is just over 0.07. Other parameters for both figures: \( \sigma = 0.001, \rho_{mp} = 0.1 \) [Color figure can be viewed at wileyonlinelibrary.com]

![FIGURE 7](wileyonlinelibrary.com)

**FIGURE 7** Evolution of the proportionality function \( P(\tau) \) as a function of scaled time \( \tau \). Dashed black line: \( P(\tau) = 1 \), corresponding to the perfect-proportionality condition. Red curves: In the case of practically unbreakable \( (\phi_{mp,b} = 100) \) but activatable mechanophores, \( P(\tau) \) behaves as it did for scissile bonds; see Figure 4. Blue curves: For mechanophore bonds that break at the same force as the matrix bonds \( (\phi_{mp,b} = 0) \) both the short-time and the long-time proportionality \( P \) are significantly different from 1. Other parameters for both red and blue curves: \( \sigma = 0.001, \rho_{mp} = 0.1 \), bottom to top \( \phi_{mp,a} = +0.3, +0.2, +0.1, 0.0, -0.1, -0.2, \) and \(-0.3 \) [Color figure can be viewed at wileyonlinelibrary.com]
energy barrier for breaking the same for mechanophore-carrying bonds as for ordinary matrix bonds. This is the appropriate setting when the mechanophores are incorporated into the same polymer backbone as the one that makes up the matrix. In this case, we see that while the initial values remain the same (for short times, there is little crosstalk yet between mechanophores and matrix bonds and they behave, effectively, decoupled) there is a universal tendency toward underreporting for longer times. This, once again, is the effect we described earlier in the discussion of Figure 6(B); activations pre-empted by breaking of the bond in which the mechanophore is incorporated may remove a significant amount of reporters from the system and leads to generic and structural underreporting for longer times.

3 | DISCUSSION AND CONCLUSION

In this article, we have presented and analyzed a simple Bell-type model and have drawn from it some very general conclusions about the accuracy with which scissile and non-scissile mechanophores can report on bulk chain breaking. The model assumes equal sharing of the external load across all intact bonds, mechanophore and matrix. We have shown that very generally, the addition of small (< 10% of all bonds) amounts of mechanophore does not change the overall ability to withstand a force; this is evidenced by the fact that the time until complete fracture does not change much as long, again, as small amounts of mechanophore are added. Of course, the measure that we use for strength here does not translate directly to a bulk modulus, or toughness. Also, the load sharing condition as we have implemented it will need to be reconsidered for general, and in particular three-dimensional, distributions of the load. It will be interesting to implement realistic, 3D stress fields into the load-sharing condition. We do not, however, expect this to qualitatively change the outcome of our model as long as the essential feature that breaking of a single bond increases the average load on all other load-bearing bonds, and that this increases the likelihood of their breaking, holds. The first criterion is readily met, but the second may be violated for instance in materials containing catch bonds; bonds whose unbinding rate decreases with increasing force. We have previously studied how collective rupture proceeds in catch bond materials. As we stated above, load sharing as we have implemented it applies to loads distributed equally across a planar interface of parallel bonds. At higher forces, or for very soft and visco-elastic materials, the stress field will penetrate deeper into the material, and stresses may irreversibly dissipate decreasing the overall force available for distribution. That is, quantities like $\Sigma$ will likely have their own relaxational dynamics, dictated by the mechanical properties of the matrix. It will certainly be interesting to investigate in more, three-dimensional detail if and when the assumption of local load sharing holds.

Our model suggests generic and relevant differences in the proportionality of reporting for scissile and non-scissile mechanophores. Scissile reports may be over- or underreporting—depending on their relative strength—on short timescales after the load has been applied but for longer times revert to a generically ideal proportionality. How this affects an experiment, of course, depends on the applied forces. For higher forces, scission happens at an exponentially accelerated rate and the initial regime of disproportionate reporting may be very short indeed. Our model suggests different issues with non-scissile mechanophores, which suffer from the same potential short-time departures from ideal proportionality, but in addition—due to activations pre-empted by breaking—show a structural tendency to underreport at longer times. For mechanophores embedded in the backbone of the polymers that also make up the matrix, this is all but unavoidable.

A valid question to ask is whether these are, ultimately, serious issues. The answer, we feel, is yes and no. No, because regardless of whether the reporting by mechanophores is completely faithful and calibratable, they certainly do report on bulk bond breaking in the sense that more signal from the mechanophores corresponds to more bond bond breaking in all cases considered here. Absent other methods to reveal the earliest, molecular scale onset of damage in soft materials mechanophores remain a remarkable tool for qualitative diagnostics. The answer is also yes, however. To elevate this technique from mostly qualitative to an accurate quantitative tool, we must learn how to properly interpret mechanophore signals, which will involve the experimental establishment of quantities like $P(\tau)$. Once this is known, the optical signals from mechanophores may be transformed, in a time- and force-dependent manner, which in essence is division by $P(\tau)$, to back out the actual, instantaneous condition of their invisible host matrix. Our article outlines what such transformations might look like, and which signature to be on the lookout for in experiments.

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**APPENDIX A.**: Analytical result for the breaking time in the pure matrix

The breaking time problem for the pure matrix amounts to solving the following initial value problem for $N_{mat,c}(t)$, and determining $t_b$ defined by $N_{mat,c}(t_b) = 0$.

\[
\begin{cases}
\frac{d}{dt} N_{mat,c}(t) = -N_{mat,c}(t) \exp \left( \frac{\Sigma}{N_{mat,c}(t)} - \phi_{mat} \right), \\
N_{mat,c}(0) = N_{mat,tot}
\end{cases}
\]  

(A1)

Rescaling $\tau = e^{-\phi_{mat}} t$, $n(\tau) = N_{mat,c}(\tau)/N_{mat,tot}$, and $\sigma = \Sigma/N_{mat,tot}$ this reduces to

\[
\begin{cases}
\frac{d}{d\tau} n(t) = -n(t) \exp \left( \frac{\sigma}{n(t)} \right), \\
n(0) = 1
\end{cases}
\]  

(A2)

If we now define $u(\tau) \equiv -\sigma/n(\tau)$, the force $\sigma$ moves to the initial condition:

\[
\begin{cases}
\dot{u}(\tau) = u(\tau) e^{-u(\tau)} \\
u(0) = -\sigma
\end{cases}
\]  

(A3)

with the overdot a shorthand notation for derivatives w.r.t. scaled time $\tau$. Since, apart from at the actual singular time $t_b$, $u(\tau) > 0$ we may divide the left-hand side by the right-hand side and integrate both side over $\tau'$ from 0 to $\tau$ to obtain

\[
\int_0^\tau \frac{\dot{u}(\tau')}u(\tau) e^{-u(\tau')} d\tau' = \int_0^\tau d\tau'.
\]  

(A4)

The right-hand side is simply $\tau$, and by changing integration variables from $\tau'$ to $u(\tau')$ we may rewrite (dropping the explicit $\tau'$s) this to

\[
\int_{u(0)}^{u(\tau)} \frac{du}{u} = \tau.
\]  

(A5)
The Exponential Integral $\text{Ei}(x)$ is a special function defined\(^{24}\) as

$$\text{Ei}(x) = \int_{-\infty}^{x} \frac{e^t}{t} dt,$$  \hspace{1cm} (A6)

and by splitting the integration interval in Equation (A4) we can therefore express the solution $u(\tau)$ as

$$\text{Ei}(u(\tau)) - \text{Ei}(u(0)) = \tau + \text{Ei}(u(0)).$$  \hspace{1cm} (A7)

With the aid of the formal inverse of the Exponential Integral, and substituting the initial value $u(0) = -\sigma$, we find the complete solution

$$u(\tau) = \text{Ei}^{-1}(\tau + \text{Ei}(-\sigma)).$$  \hspace{1cm} (A8)

The breaking time $\tau_b$ corresponds to the time when the argument reaches zero, and is given by $\tau_b = -\text{Ei}(-\sigma)$. Transforming back to the original time variable, this gives the final answer

$$t_b = -e^{\phi_{\text{mat}}}(\tau + \text{Ei}(\phi_{\text{mat}})), \hspace{1cm} (A9)$$

which we have verified numerically to be correct.

We thank prof. Mark Peletier and Prof. Adrian Muntean for pointing us to this way of solving the problem.

**APPENDIX B. Equations for the general problem including rebinding**

For completeness, we include here also the most general set of equations for non-scissile mechanophores that can also break, but where we also include the possibility of rebinding of both matrix bonds and mechanophores. This rebinding is implemented using the rebinding rates $\gamma_{\text{mat}}$ and $\gamma_{\text{mp}}$ for matrix and mechanophores, respectively, which multiply the instantaneous numbers of broken bonds of each type to reconnect a certain fraction of previously broken chains in the material. After reconnecting, an embedded mechanophore also becomes activatable again. Then, the equations (which are rebinding-extended versions of Equations (20)) become

$$
\begin{align*}
\frac{d}{dt} N_{\text{mat,}\text{c}}(t) &= -N_{\text{mat,}\text{c}}(t) \exp \left( \frac{\sum}{N_{\text{mat,}\text{c}}(t) + N_{\text{mp,u}}(t)} - \phi_{\text{mat}} \right) + \gamma_{\text{mat}}(N_{\text{mat,tot}} - N_{\text{mat,}\text{c}}(t)) \\
\frac{d}{dt} N_{\text{mp,u}}(t) &= -N_{\text{mp,u}} \exp \left( \frac{\sum}{N_{\text{mat,}\text{c}}(t) + N_{\text{mp,u}}(t)} - \phi_{\text{mp,u}} \right) + \gamma_{\text{mp}}(N_{\text{mp,tot}} - N_{\text{mp,u}}(t)) \\
\frac{d}{dt} N_{\text{mp,a}}(t) &= +N_{\text{mp,a}} \left( 1 - \frac{N_{\text{mp,a}}(t)}{N_{\text{mp,tot}}(t)} \right) \exp \left( \frac{\sum}{N_{\text{mat,}\text{c}}(t) + N_{\text{mp,u}}(t)} - \phi_{\text{mp,a}} \right) \\
N_{\text{mat,}\text{c}}(0) &= N_{\text{mat,tot}}, N_{\text{mp,u}}(0) = N_{\text{mp,tot}}, N_{\text{mp,a}}(0) = 0
\end{align*}
$$  \hspace{1cm} (B1)

Applying our usual scalings and transformations ($\tau = e^{-\phi_{\text{mat}}} t$, $N_{\text{tot}} = N_{\text{mat,tot}} + N_{\text{mp,tot}}$, $n_{\text{mat,c}} = n_{\text{mat,c}}/N_{\text{tot}}$, $n_{\text{mp,u}} = N_{\text{mp,u}}/N_{\text{tot}}$, $n_{\text{mp,a}} = N_{\text{mp,a}}/N_{\text{tot}}$, $\Delta \phi_b = \phi_{\text{mp,b}} - \phi_{\text{mat}}$, $\Delta \phi_a = \phi_{\text{mp,a}} - \phi_{\text{mat}}$, $\sigma = \Sigma/N_{\text{tot}}$, $\rho_{\text{mp}} = N_{\text{mp,tot}}/N_{\text{tot}}$) and transforming the two rebinding rates as $\gamma_{\text{mat}} = e^{\phi_{\text{mat}}} \gamma_{\text{mat}}$ and $\gamma_{\text{mp}} = e^{\phi_{\text{mat}}} \gamma_{\text{mp}}$, we may bring this problem to its scaled, nondimensional form as

$$
\begin{align*}
\frac{d}{d\tau} n_{\text{mat,}\text{c}}(\tau) &= -n_{\text{mat,}\text{c}}(\tau) \exp \left( \frac{\sigma}{n_{\text{mat,}\text{c}}(\tau) + n_{\text{mp,u}}(\tau)} \right) + \gamma_{\text{mat}}^* \left( 1 - \rho_{\text{mp}} - n_{\text{mat,}\text{c}}(\tau) \right) \\
\frac{d}{d\tau} n_{\text{mp,u}}(\tau) &= -n_{\text{mp,u}}(\tau) \exp \left( \frac{\sigma}{n_{\text{mat,}\text{c}}(\tau) + n_{\text{mp,u}}(\tau)} - \Delta \phi_b \right) + \gamma_{\text{mp}}^* \left( \rho_{\text{mp}} - n_{\text{mp,u}}(\tau) \right) \\
\frac{d}{d\tau} n_{\text{mp,a}}(\tau) &= +n_{\text{mp,a}}(\tau) \left( 1 - \frac{n_{\text{mp,a}}(\tau)}{\rho_{\text{mp}}} \right) \exp \left( \frac{\sigma}{n_{\text{mat,}\text{c}}(\tau) + n_{\text{mp,u}}(\tau)} - \Delta \phi_a \right) \\
n_{\text{mat,}\text{c}}(0) &= 1 - \rho_{\text{mp}}, n_{\text{mp,u}}(0) = \rho_{\text{mp}}, n_{\text{mp,a}}(0) = 0
\end{align*}
$$  \hspace{1cm} (B2)