



ECF22 - Loading and Environmental effects on Structural Integrity

Mechanical modelling of self-diagnostic polymers

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Abstract

The safety level in advanced load bearing applications can be enhanced if the material would be able to detect the in-service deformation, allowing a real time evaluation of the reliability state of the components. Polymeric materials can be used to get such a functionality through the insertion of so-called mechanophore units, whose main property is to chemically respond to mechanical stimuli. In the present paper, a micromechanical approach is developed to model the response of polymers containing reporting units, whose activation is triggered by the deformation of the underneath network or by a chemical stimulus. The model, through an Arrhenius-like equilibrium reaction law, provides a quantitative evaluation of the fraction of stress-activated molecules. Moreover, if the mechanophore activation involves also a change in their geometrical conformation, it influences the network deformation and the corresponding mechanical effects must be also accounted for. The formulated micromechanical model is presented and implemented in a FE code in order to simulate structural elements made of a self-diagnostic material. In particular, we consider the fluorescence-based strain detection of pre-cracked elements made of polymers with supramolecular complexes cross-linked to the polymer's chains; the fluorescence intensity is assumed to be proportional to the volume fraction of the activated units, thus enabling to quantify the associated material's strain value.

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1. Introduction

Polymers are materials that can be usefully applied in high-performance applications, because through their microstructure they can be designed in order to get a desired behavior in response to external stimuli. Especially by using polymers in high demanding applications, the necessity to check their integrity in an easy and cheap way can be

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an important issue (Roy et al. (2010)). Damage appearing in the bulk or at the surface of the material in the form of micro cracks, cavities, growing voids, etc. are difficult to detect when their size is small; however, they can compromise the structural integrity of the material and trigger a progressive damage that can subsequently lead to a catastrophic failure. Molecules sensible to mechanical stress are ideal candidates to detect such damages and are thus suitable to prevent catastrophic collapse; if the stress or strain intensity (both related to the forthcoming damage of the material) can be quantified by simply visualizing some detectable signal out of the material, the material is identified as having self-diagnostic capabilities. Generally, in chemistry any compound whose reaction is triggered by mechanical force is termed ‘mechanophore’; their use is very appealing within the polymers field, since their insertion in the polymer’s chain network is quite straightforward from the production viewpoint, and allows to easily and economically get mechanical self-sensing materials. Mechanochemical molecules, whose reporting ability appears when activated, are characterized by two states: the first one generally occurs in absence of any mechanical stress (or when the mechanical stress is below a given threshold), while the one providing the desired signal takes place when a sufficiently high stress acts on the molecule (Black et al. (2011)). Several mechanophores have been proposed in the literature such as spiropyran units (Klajn (2014), Wang et al. (2015)), dioxetanes (Chen et al. (2014)), supramolecular systems (Früh et al. (2016)), while other detecting systems are based on physical responses to mechanical stress such as aggregation or separation-induced emission (Robb et al. (2016)), etc.

In the present paper, a micromechanical model for polymers containing reporting units is developed in order to quantitatively assess their mechanical response and to predict the emitted signal intensity under mechanical stimuli. The proposed theory, based on the statistical description of the chain network in presence of mechanically-driven units, determines the fraction of activated molecules through an equilibrium reaction law (Arrhenius equation) whose parameters are affected by the stress intensity acting in the network. Furthermore, the theory considers the possibility to trigger the reporting units through a chemical stimulus, such as in the case of a pH change; in this case the model is enriched by accounting for a solvent phase (fluid) that can permeate the polymer, influencing its volumetric deformation. Moreover, if the mechanophore activation involves a change of its size, a further effect arises on the network, whose response must consider also for this latter aspect. In order to consider the response of real elements, a continuum framework is necessary; to this aim the formulated micromechanical model is first upscaled to the mesoscale and it has been finally implemented in a FE code. In particular, we consider the fluorescence-based strain detection of pre-cracked elements made of polymers with a supramolecular complex.

Nomenclature

c_a	concentration of active chains per unit volume
\mathbf{F}	deformation gradient tensor
f_0, f	initial and generic chain length distribution function, respectively
h_r	fraction of activated molecules among those connected to chain of length r
k_A, k_D	activation and deactivation rates, respectively
k_B	Boltzmann constant
N	number of Kuhn’s segments in the single chain
\mathbf{P}, \mathbf{t}	first Piola stress tensor (nominal stress) and force in the single chain
\mathbf{r}	end-to-end vector
T	absolute temperature
$\delta G_{A0}, \delta G_{D0}$	energy barriers for activation and deactivation, respectively
λ_p, λ'_p	stretch in the single chain and corresponding amended stretch due to the molecule activation
φ_0, φ	chain distribution functions in the stress-free and in a generic state, respectively
$\Delta\Psi, \psi$	change in mechanical energy of the network and energy stored in the single chain, respectively
Ψ_{mix}, Ψ_{ext}	energy of the polymer-solvent mixing phenomenon and external energy, respectively
$Q_r, Q_{r,act}, Q_{r,inact}$	total volume fraction of mechanophores, volume fractions of activated and inactivated mechanophores in the material, respectively
$\boldsymbol{\sigma}$	Cauchy stress tensor (true stress)

2. Basic concepts on statistical-based mechanics of polymers

Differently by crystalline and crystalline-like materials, polymers are highly amorphous in their microstructure and their mechanical behavior is strongly related to the configuration of their network (entropic effects are dominant for this class of materials), rather than on the strength of the bonding existing between molecules (Treloar (1946), Flory and Volkenstein (1969)) as typically occurs in non-amorphous or crystalline materials.

2.1. Statistical-based mechanics of polymers

The distribution of chain lengths and orientations within a polymer network can be conveniently expressed by using a probability function $\varphi(\mathbf{r})$ that provides the number of chains whose end-to-end vector distance falls within a given interval (\mathbf{r} and $\mathbf{r} + d\mathbf{r}$). In the natural (or reference) state such a distribution is expressed as:

$$\varphi_0(\mathbf{r}) = c_a \cdot f_0(\mathbf{r}) \quad \text{with} \quad f_0(\mathbf{r}) = \left(\frac{3}{2\pi Nb^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3|\mathbf{r}|^2}{2Nb^2}\right) \quad (1)$$

where $f_0(\mathbf{r})$ has been assumed to be a Gaussian with a mean $\mathbf{r} = \mathbf{0}$ and standard deviation $\sqrt{N} b/3$ (N, b being the number of Kuhn segments per chain and the segment's length, respectively, Treloar (1946)) and \mathbf{r} is the chain's end-to-end vector. In (1) c_a represents the current value (chain concentration) of the active chains (i.e. chains attached to the network at their ends) per unit volume, multiplied by the standard Gaussian whose integral over the configuration space is equal to unity. Upon deformation, the function f_0 changes to f (Fig. 1) and, if no chains are lost or created, the integral over the chain space Ω is conserved, i.e. $\int_{\Omega} f_0(\mathbf{r}, t) d\Omega = \int_{\Omega} f(\mathbf{r}, t) d\Omega = 1$.

As recalled above, a deformation applied to the polymer network modifies the end-to-end vector distribution, and the corresponding mechanical energy per unit volume of the material can be written as:

$$\Psi = \int_{\Omega} \varphi(\mathbf{r}, t) \psi d\Omega = c_a \int_{\Omega} f(\mathbf{r}, t) \psi d\Omega \quad (2)$$

where ψ is the energy stored in the single chain that can be expressed, for instance, through the standard rubber elasticity for not too much stretched chains, or by using the Langevin statistics when the deformation approaches the maximum chain extension (Treloar (1946)).

Since the elastic energy stored in the single chain depends only on the actual end-to-end distances, it is zero only if $r = 0$; thus, also in the reference stress-free state of the polymer the energy stored in the chains is not zero if $r \neq 0$. The potential energy $\Delta\Psi$ per unit volume in the current state represented by $f(\mathbf{r}, t)$, can be evaluated by integrating the energy of a single chain over the chains configuration space Ω , i.e.:

$$\Delta\Psi(t) = c_a \int_{\Omega} [f(\mathbf{r}, t) - f_0(\mathbf{r}, t)] \psi d\Omega + p(t)(J - 1) = \Delta\Psi(\mathbf{F}) + p(t)(J - 1) \quad (3)$$

where p is the hydrostatic pressure that plays the role of a Lagrange multiplier to enforce the incompressibility condition herein assumed for the polymer ($J = \det \mathbf{F} = 1$, being \mathbf{F} the deformation gradient tensor). The evolution in time of the distribution function f can be expressed as follows, being $\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ the velocity deformation tensor, and δ_{ij} the Kronecker tensor (Vernerey et al. (2017)):

$$\frac{\partial f(\mathbf{r}, t)}{\partial t} = -[\nabla f(\mathbf{r}, t) \otimes \dot{\mathbf{r}} + f(\mathbf{r}, t) \otimes \nabla \cdot \dot{\mathbf{r}}] = -\left[\frac{\partial f(\mathbf{r}, t)}{\partial r_i} r_j + f(\mathbf{r}, t) \delta_{ij}\right] L_{ij} \quad (4)$$

2.2. Effect of molecule conformation change on the chain's deformation

Since we are assuming that the activation of the reporting molecules could be also eventually accompanied by a size change of the molecule (typically an expansion), the chain stretch reduces to λ'_p (Fig. 2):

$$\lambda'_p = \lambda_p - (\lambda_m - 1) \alpha \mathcal{H}(\lambda, C_s) \quad (5)$$

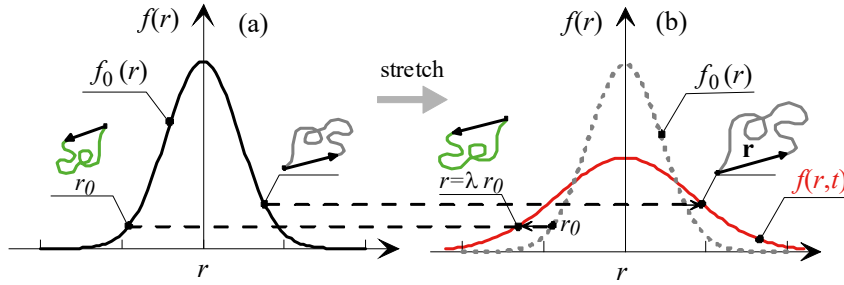


Fig. 1. Chain length distribution in the stress-free state, $f_0(r)$ (a) and in a generic stretched state, $f(r)$ (b)

where $\alpha = r_{om}/r_0$ is the initial molecule to chain length ratio, λ_p, λ_m are the stretch in the chain before the activation and the size change of the molecule, respectively, and the step function $\mathcal{H}(\lambda, r, n_s)$ is defined as:

$$\mathcal{H}(\lambda, C_s) = H(t) + H(C_s) - H(t) \cdot H(C_s), \quad H(t) = \begin{cases} 0 & \text{if } t < t'_m \\ 1 & \text{if } t \geq t'_m \end{cases}, \quad H(C_s) = \begin{cases} 0 & \text{if } C_s < \bar{C}_s \\ 1 & \text{if } C_s \geq \bar{C}_s \end{cases} \quad (6)$$

i.e. both the mechanical force in the chain, t , and the solvent concentration C_s (when the molecules are prone to be chemically-activated) have been accounted for.

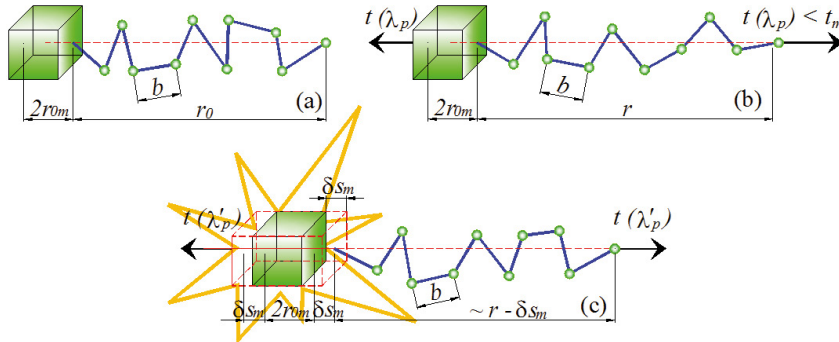


Fig. 2. Scheme of the molecule jointed with a polymeric chain. Stress-free state (a), loaded state before activation (b) and after activation (c).

Fig. 2 shows the activation process in presence of a mechanical stress: if the chain force reaches the threshold value t'_m the molecule is activated and, typically, a detectable signal takes place (such as fluorescence emission, Fig. 2c).

3. Dynamic equilibrium of molecules having multiple stable states

The activation mechanism allows the molecules to switch from the inactivated (*inact*) to the activated (*act*) state; from a chemical viewpoint, the switching follows a kinetic equilibrium law, because of the unavoidable thermal fluctuations existing in the material; the number of molecules belonging to one state or to the other must obey to:

$$\frac{d\varrho_{r,act}}{dt} = k_A \cdot \varrho_{r,inact} - k_D \cdot \varrho_{r,act} \quad \text{or} \quad \frac{dh_r}{dt} = k_A - (k_A + k_D) \cdot h_r \quad (7)$$

that provides the volume fraction of activated molecules in time ($\varrho_{r,act}$, joined to chains with length r), through the activation (k_A) and deactivation (k_D) rates, where $\varrho_{r,act}(\mathbf{F}, C_s) = h_r(\mathbf{F}, C_s) \cdot \varrho$ (the volume fraction ϱ is assumed to be uniformly distributed over all the chain lengths). In presence of an external energy, such as those coming from a mechanical force or a chemical stimulus, the activation and deactivation rates change:

$$k_A = k_{A0} \cdot \exp\left(\frac{t \cdot \delta s_m}{k_B \cdot T}\right) \cdot \exp\left(\frac{\delta G_{A0}}{k_B \cdot T} \cdot \frac{C_s}{\bar{C}_s}\right) \geq k_{A0}, \quad k_D = k_{D0} \cdot \exp\left(-\frac{t \cdot \delta s_m}{k_B \cdot T}\right) \cdot \exp\left(-\frac{\delta G_{D0}}{k_B \cdot T} \cdot \frac{C_s}{\bar{C}_s}\right) \leq k_{D0} \quad (8)$$

where $\delta G_{A0}, \delta G_{D0}, k_{A0}, k_{D0}$ are the energy barriers and the corresponding rates for the forward and backward reaction in absence of any external stimuli, respectively.

4. Continuum model and FE implementation

4.1. Continuum model

By upscaling the above micromechanical model to the continuum level, it is possible to get the governing equations that can be readily implemented in a computational framework. Upon stretching, the distribution function evolves according to Eq. (4) and can be used to evaluate the stored elastic energy in the material. By adding up the contributions of all the chains over the chain space, the stress state in a continuum material can be obtained as (Vernerey (2017)):

$$\boldsymbol{\sigma}(t) = J^{-1} \mathbf{P} \mathbf{F}^T = J^{-1} \frac{\partial \Delta \Psi}{\partial \mathbf{F}} \mathbf{F}^T = c_a \int_{\Omega} [f(\mathbf{r}, t) - f_0(\mathbf{r}, t)] \mathbf{t}(\mathbf{r}, t) \otimes \mathbf{r} d\Omega + p(t) \mathbf{1} \quad (9)$$

where $\boldsymbol{\sigma}$, \mathbf{P} are the true (Cauchy) and the nominal first Piola stress tensors, respectively, $\mathbf{1}$ is the unit 2nd order tensor and $\mathbf{t}(\mathbf{r}, t) = \partial \psi(\lambda, N) / \partial \mathbf{r}$ is the force in the single chain. The presence of a solvent phase can also be accounted for and the energy (3) must be corrected by adding the contribution coming from the dilatation induced by swelling (mixing); the variation of the total energy in this case becomes:

$$\Delta \Psi_t = \Delta \Psi(\mathbf{F}) + \Psi_{mix} + \Psi_{ext} + p(J - J_{mix}) \quad (10)$$

being Ψ_{mix} the energy of mixing and J_{mix} the volume change due to the fluid uptake (Doi (2009)).

The knowledge of the distribution function $f(\mathbf{r}, t)$ at a given time t obtained through Eq. (4), provides the chains stretch $\lambda_p = r/r_0$, eventually modified by the change in the mechanophore conformation (Eq. (5)) and by the swelling responsible for a volume dilatation induced by the fluid uptake. By using the kinetic evolution Eqs (7) equipped with the proper amended activation and deactivation parameters (Eq. (8)), the current fraction h_r of activated molecules (reasonably proportional to the intensity of the signal coming from the activated molecules) can be determined.

4.2. FE implementation

The formulated physics-based micromechanical model has been implemented in a homemade finite element code within a Lagrangian framework formulation. Standard displacement degrees of freedom are associated to the element's nodes, while the fraction of activated molecules h_r and the solvent concentration C_s are related to each element's Gauss point. The nonlinear governing equations have to be solved iteratively, for example by using a Newton-Raphson procedure, until the residual force vector norm vanishes (11₁) according to a given tolerance, and solving for the swelling equilibrium (Hong et al. (2008), 11₂), i.e.:

$$\begin{aligned} |\mathbf{R}| &= \mathbf{F}_{int} - \mathbf{F}_{ext} = \int_{B_{0e}} (\mathbf{B}^T \boldsymbol{\sigma} \mathbf{J} - \mathbf{N}^T \rho_0 \mathbf{b}) dV - \int_{\partial B_{0e}} \mathbf{N}^T \mathbf{t}_0 d\Gamma \leq \text{tol} \\ \partial \Delta \Psi_t / \partial C_s - \partial (\frac{1}{2} \zeta \dot{C}_s^2) / \partial \dot{C}_s &= 0 \end{aligned} \quad (11)$$

where \mathbf{b} , \mathbf{t}_0 are the forces per unit mass and the boundary tractions acting on the reference configuration and ζ is a friction coefficient, respectively. The stress tensor is assessed on the basis of Eq. (9) where the chain force $\mathbf{t} = \partial \psi / \partial \mathbf{r}$ is evaluated by accounting for its corrected value \mathbf{t}' in the case the molecules activate by changing their size and/or the swelling phenomenon takes place in the material.

5. Applications

5.1. Pre cracked beam under three-point bending

In the present example we consider the three-point bending test reported by Früh et al. (2017), concerning the strain sensing capability of a PDMS polymer, containing molecules cross-linked to the polymer's chains capable of a fluorescence response upon stretch. The pre-cracked beam is subjected to a downward displacement D . The material is assumed to be incompressible, with Young modulus equal to 1 GPa and $N = 10$. The contour map of \bar{h} is displayed in Fig. 34a, while in Fig. 34b the function $\bar{h}(D)$ is shown, and in Fig. 34c the contour map of \bar{h} close to the crack tip obtained through the present model, is compared with that observed experimentally. The fraction of activated molecules starts from a very low value (about 1% because of the initial kinetic equilibrium) and reaches the maximum value of about 10% close to the crack tip at the end of the loading. The experimentally measured fluorescence intensity, providing an indication of the strain, is in satisfactory agreement with the numerical FE results.

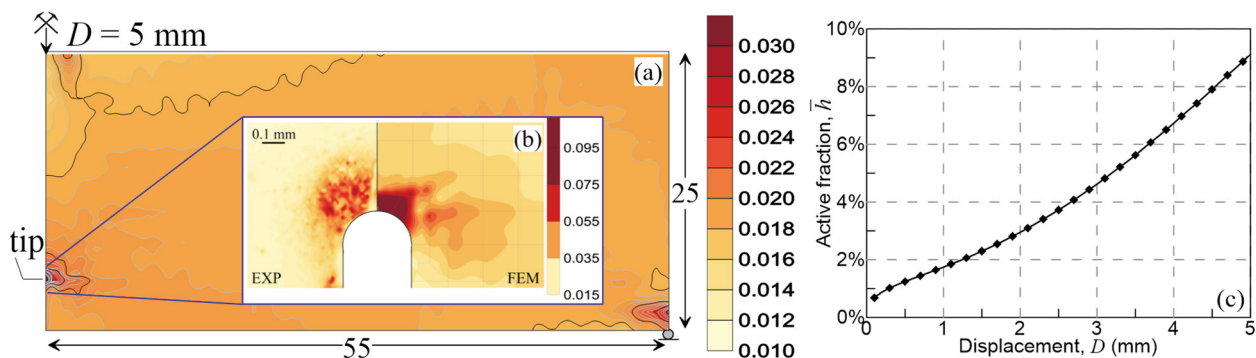


Figure 3. Self-diagnostic pre-cracked beam (mm): contour maps of activated molecules (a) and comparison of \bar{h} close to the crack tip with the experimentally observed fluorescence (b). \bar{h} vs time near to the crack tip (c).

6. Conclusions

In the present paper we considered the mechanics of polymers containing mechanophore units that are able to respond chemically to mechano-chemical stimuli. By adopting an Arrhenius-like equilibrium reaction law, the quantitative evaluation of the fraction of activated molecules has been evaluated; further, when the mechanophores activation involves a change of their geometrical conformation (size change), its influence on the network deformation has been accounted for. Moreover, the case of pH-induced mechanophore activation has also been considered and the related swelling phenomenon, taking place in presence of a fluid, was also modelled. The proposed micromechanical model has been presented and implemented in a 2-D FE code, enabling the simulation of a self-diagnostic materials. We presented the numerical simulation of a pre-cracked PDMS elastomeric beam element, taken from the literature, providing fluorescence-based strain detection; the fluorescence intensity was assumed to be proportional to the volume fraction of the activated units, thus enabling to quantify the material's strain intensity. The proposed micromechanical model, provides a comprehensive and physics-based tool for the assessment of the mechanical response of polymers with mechanophore units.

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