Mechanics of Active Mechano-Chemical Responsive Polymers

R Brighenti1,*, F Artoni1 and M P Cosma1
1Department of Engineering & Architecture, University of Parma
Parco Area delle Scienze 181/A, 43124 Parma, Italy

*Corresponding author: brigh@unipr.it

Abstract. The need for smart materials in advanced applications, has promoted significantly the research in the field of responsive (or active) materials. They are capable of some physical response to external stimuli, such as temperature, pH, light, mechanical stress, etc. so they can adapt themselves to the surrounding environment. In the present paper, we propose a mechanical model to describe the response of polymers containing mechanically responsive molecules (mechanophores), having the ability to assume two distinct geometrically stable configurations under mechanical actions or due to a change of the environment’s pH. When linked to the polymer’s chains, under a proper mechanical stress, they switch from one state to the other, triggering a macroscopic deformation of the material. Such an internal deformation, driven by the mechanophores’ activation, can be exploited to get a desired functionality of the polymer. Our model starts from the mechanical behavior at the microscopic level, and through the mechanics of a single chain and chain statistics, it is scaled-up to the (mesoscopic) continuum level. An energy-based approach is adopted: the free energy $W$ is obtained by adding up the contribution of the network deformation ($W_{\text{net}}$), of the mixing term related to the solvent uptake ($W_{\text{mix}}$) and of the switching of the hosted responsive molecules ($W_{\text{sw}}$).

Numerical simulations demonstrate that the material response under chemical or mechanical stimuli, shows a permanent deformation due to the activation of the switchable molecules, enabling the design of smart self-adaptive polymers.

1. Introduction
Polymeric materials have been subjected to a wide diffusion in engineering applications, thanks to their affordability and to their wide range of relevant mechanical properties, such as lightweight, tunable stiffness, fracture toughness, etc.; for these reasons a growing demand of proper mechanical predicting models is steadily increasing [1].

By harnessing their special microstructure, made of a network of long entangled linear chains connected together in several junction points, various macromolecular-based theories have been proposed [2, 3]. Models based on some simplifying assumptions of the spatial chains arrangements have also been successfully proposed [4, 5] as well as models based on phenomenological aspects of their observed mechanical behavior [6].

Thanks to the network-like molecular structure, in recent years molecules having particular responsiveness have been inserted into the polymer backbone, leading to materials with unusual properties, usually referred to as ‘smart’. Smart materials are capable to respond to various external stimuli such as temperature change, pH [7], mechanical stress [8], light, electric and magnetic fields [9], etc.
Responsive polymer-based materials are able to modify their chemical and/or physical properties upon external stimuli, and they open the way to the solution of complex problems where the stimuli come from living systems, such as controlled drug delivery, tissue repair, artificial muscles, biosensing, etc. [10, 11].

Among the above listed responsive materials, the sensibility to mechanical stress play a relevant role. The well-known term "mechanophore" has been introduced for molecules that undergo chemical modification – usually because of the presence of weak bonds – when triggered by mechanical forces transmitted by the polymer chain to which the mechanophores are connected.

Furthermore, pH sensible molecules [7] have also attracted attention because of the possibility to develop materials suitable to face complex problems, such as controlled drug delivery, development of smart membranes, viscosity control, etc.

We present, here, a micromechanical-based model for polymers whose cross-links have been replaced by mechanophores, which are constituted by molecules able to change their shape and size through the switching mechanism between two stable conformation states. The conformation change is triggered by mechanical stress or chemical stimuli and is captured based on the deformation features taking place at the molecular level. Through the statistics of the chain network, the micromechanical model is scaled-up to the mesoscopic level, and it can be readily adopted to model smart responsive polymers at the continuum scale. The last part of the paper is devoted to the simulation, through the developed theoretical framework, of the response of polymers with embedded chemo-mechanical molecules under various stress history, with or without the presence of a solvent responsible for pH change.

2. Mechanics of a polymer chain linked to a switchable molecule

We consider here the kinematics and the mechanics of a single polymeric chain linked to a switchable molecule.

2.1. Deformation of a polymer chain linked to a switchable molecule

Let us consider a single chain with an initial end-to-end distance $r_0 = l_{0p} = b \cdot \sqrt{N}$ ($N, b$ are the number of Kuhn’s segments in the chain and their length, respectively), linked to a switchable molecule (Fig. 1a) with an initial size $l_{0m}$. Under a force whose intensity is below the molecule’s switching threshold value $f_m'$, the chain only deforms and stretches to $\lambda_p$ (Fig. 1b). If the threshold force is overcome, $f_p > f_m'$, the switchable molecule opens an amount $2\delta s_m$ and the stretch in the chain decreases to:

$$\lambda'_p = \lambda_p - (\lambda_m - 1) \cdot \alpha$$

being $\lambda_m = \delta s_m / l_{0m}$ and $\alpha = l_{0m} / l_{0p}$.

In a real polydisperse polymer, the chains of the network have an end-to-end distance that can be described through a statistical distribution of the number of their Kuhn’s segments, $p(N)$.

Let us assume that the average chain has $\bar{N}$ segments and that the stretch referred to such a

![Figure 1](attachment:Figure_1.png)

**Figure 1.** Scheme of a single polymer chain linked to a switchable molecule (a). Deformation before (b) and after (c) the molecule switches.

chain is $\lambda_0 = l_p / (b \sqrt{N})$; by adopting the affine deformation hypothesis, the average stretch of the network $\bar{\lambda}$, is:
\[ \tilde{\lambda} = 1 + (\lambda_0 - 1) \sqrt{\frac{N}{N_{\text{min}}}} \int_{N_{\text{min}}}^{+\infty} \frac{p(N)}{\sqrt{N}} dN \]  

Finally, the stretch in a chain with \( N \) segments can be referred to the above mesoscopic deformation:

\[ \lambda_p(N) = 1 + (\tilde{\lambda} - 1) \sqrt{\frac{N}{N}} \]  

The effective stretch is

\[ \lambda'_{p}(N) = \frac{l_p - \delta s_m}{\sqrt{N} \cdot b} = 1 + \frac{(\tilde{\lambda} - 1) \sqrt{\frac{N}{N}} \cdot b - \delta s_m \cdot \mathcal{H}(\tilde{\lambda}, N)}{\sqrt{N} \cdot b} \]

being \( \mathcal{H}(\tilde{\lambda}, N) \) the step function that defines the close (\( \mathcal{H}(\tilde{\lambda}, N) = 0 \)) or open (\( \mathcal{H}(\tilde{\lambda}, N) = 1 \)) state of the molecule. Its value depends on the average stretch \( \tilde{\lambda} \) and on the number \( N \) of the chain, being the force induced in the chain by the average stretch \( \tilde{\lambda} \) dependent on the number \( N \), i.e. \( f_p = f_p(\tilde{\lambda}, N) \).

In the following step, a standard Gaussian probability function will be adopted for \( N \), i.e.

\[ p(N) = \frac{1}{\delta N \sqrt{2\pi}} \exp \left[ - \frac{(N-N)^2}{2 \delta N^2} \right], \]

where \( \delta N^2 \) is the variance and \( \bar{N} \) the mean value of the distribution.

2.2. Mechanics of the chain-switchable molecule system

The mechanics of rubberlike polymers is dominated by entropic effects, and their response is mainly governed by the entropy of the polymeric chains, that depends on the chain’s length and on the statistical distribution of the chains’ end-to-end distance within the network. The force \( f_p(N) \) in a chain with \( N \) segments can be determined through the strain energy function \( \psi \) as follows:

\[ f_p = \frac{\partial \psi}{\partial r} = k_B T b \beta, \quad \psi = N k_B T \cdot \left( \beta \frac{r}{b N} + \ln \frac{\beta}{\sinh \beta} \right), \quad \beta = \mathcal{L}^{-1} \left( \frac{r}{b N} \right) = \mathcal{L}^{-1} \left( \frac{\lambda_p}{\sqrt{N}} \right) \]

where the length-dependent Langevin-chain model, suitable for polydisperse polymers stretched close to their maximum extension (\( \lambda_{\text{pmax}}(N) = \sqrt{N} \)), has been used (\( \mathcal{L}^{-1}(x) \) is the inverse of the Langevin function defined as: \( \mathcal{L}(x) = \coth(x) - x^{-1} \)); \( k_B \) and \( T \) are the Boltzmann constant and the absolute temperature, respectively, and \( r = \lambda_p \cdot r_0, \quad r_0 = b \sqrt{N} \) are the end-to-end chain distance in the deformed and in the stress-free state, respectively. If a switchable molecule is linked to the polymer chain, the force \( f_p \) transmitted to the molecule (Fig. 1b), can trigger the switch to the open state, leading to a reduction (chain relaxation) of the force itself to the value \( f_p = \frac{k_B T}{b} \beta' \), with \( \beta' = \mathcal{L}^{-1}(\lambda'_{p}/\sqrt{N}) \). For the sake of simplicity, all chains with \( N \) segments are assumed to have the same initial end-to-end distance \( r_0 \), so that \( p(r, N) = \delta(r, r_0) \), where \( \delta \) is the Dirac delta function.

3. Molecule switching in the presence of a pH change

The volume fraction, at a given time, of the open molecules embedded in the polymer, must be determined according to the kinetic equilibrium concept, since the thermal fluctuations of the network can induce opening/closing mechanisms until a proper balance is reached [12]. For a given chain length \( N \), the following kinetic equation provides the fraction \( h_{N,\text{op}} \) of the open molecules among the total volume fraction \( \phi_N \) of those linked to chains with \( N \) segments:

\[ \frac{\partial}{\partial t} h_{N,\text{op}}(F, C_s) = k_A - (k_A + k_D) \cdot h_{N,\text{op}}(F, C_s) \]

where \( \phi_{N,\text{op}} = h_{N,\text{op}} \phi_N, \quad \phi_{N,\text{cl}} = (1 - h_{N,\text{op}}) \phi_N \) (\( \phi_N = \phi_{N,\text{op}} + \phi_{N,\text{cl}} \)); an equivalent value of \( h_{\text{op}} \) can be defined for all the chain lengths as: \( h_{\text{op}} = \int_{N_{\text{min}}}^{+\infty} h_{N,\text{op}} \cdot p(N) dN \). In (6), reaction rates constants \( k_A, k_D \) (where the subscripts ‘A’ and ‘D’ stand for activation, i.e. opening, and deactivation, i.e. closing) depend on the chemical nature of the switching phenomenon, and are influenced by both the mechanical stress and by the pH (the standard Arrhenius equation can be used for quantifying such influences). The dependence on the deformation and the solvent concentration has been indicated by
writing \( \mathbf{F}, C_s \) (deformation gradient tensor and solvent concentration, respectively) as arguments of \( h_{n,op} \). Since the switchable molecules are randomly distributed in the 3D space filled by the polymer, their effect on the network is to induce an isotropic expansion. By considering all the chain lengths, the total volume fraction of open molecules is \( \phi_{op}(F, C_s) = \hat{h}_{op}(F, C_s) \cdot \phi \), where \( \hat{h}_{op} = \phi_{op}(F, C_s) / \phi = \int_{N_{min}}^{\infty} h_{n,op}(N) \cdot p(N) dN \) is the fraction of open molecules over the total number of switchable molecules, irrespectively of the chain length. The variation in volume induced by the molecule opening is provided by:

\[
J_{op} = 1 + ((J_m) - 1) \cdot \hat{h}_{op}(F, C_s) \cdot \phi
\]

where \( (J_m) = \det(\mathbf{F}_m) = \det(\int_{\Omega} A^T \mathbf{F}_{op} A d\Omega) = [(\lambda_{m1} + \lambda_{m2} + \lambda_{m3})/3]^3 \) is the variation of volume of an ideal material made only by open switchable molecules characterized by the principal stretches \( \lambda_{m1}, \lambda_{m2}, \lambda_{m3} \). The mean isotropic stretch due to the opening mechanisms of the involved molecules is \( \lambda_{op} = J_{op}^{1/3} \). The presence of the solvent induces also swelling of the polymer with a further volume increase (polymer-solvent mixing). By solving the equilibrium equation \( \partial W_{mix}/\partial J_{sw} = 0 \) (see below) the steady-state volume increase, \( J_{sw} \), due to swelling can be obtained. Being the polymer network uncompressible, the total volume change \( J_{tot} \) is induced only by swelling and by the opening mechanism:

\[
J_{tot} = J_{sw}(1 - \phi) + \phi \cdot J_{op}
\]

Finally, the concentration of the solvent \( C_s \) results to be proportional to \( (J_{sw} - 1) \), i.e. to the volume increment of the polymer due to swelling and the related average chain stretch is \( \lambda_{sw} = J_{sw}^{1/3} \).

4. Continuum model of a polymer containing switchable molecules

For a polymer whose chains are linked together only through switchable molecules, the mechanical energy per unit volume is given by:

\[
W = W_{net} + W_{mix} + W_{op}
\]

where

\[
W_{net} = (1 - \phi) \cdot n \cdot \bar{N} \cdot k_BT \left( \frac{\beta'}{b'N} r + \ln \frac{\beta'}{\sinh \beta'} \right) - \pi \cdot (J_e - 1) - \sum_{i=1}^{3} P_{ei} \cdot \lambda_{ei}
\]

\[
W_{mix} = \frac{k_BT}{v_s} \left[ (J_{sw} - 1) \ln \left(1 - \frac{1}{J_{sw}}\right) - \frac{\chi}{J_{sw}} \right] , \quad J_{sw} = (J_{tot} - \phi \cdot J_{op}) (1 - \phi)^{-1}
\]

and \( W_{op} \) is the energy associated to the switchable molecules open per unit volume. In the above relations, \( \bar{N} \) is the number of segments of the representative chains depending on the distribution function \( p(N) \), \( \pi \) is the hydrostatic pressure constraint, \( P_{ei} \) are the components of the applied external stresses, \( v_s \) is the volume of a single solvent molecule and \( \chi \) is Flory’s parameter that governs swelling. In (10a) \( J_e = [1 + J_{tot} - J_{sw}(1 - \phi) - \phi(1 + J_{op})](1 - \phi)^{-1} \approx 1 \) is the volume change of the polymer network due to external mechanical actions and \( n \) is the number of units per unit volume; the chain stretch \( \lambda_p \) can be evaluated according to the 8-chain model [4] as

\[
\lambda'_p = J_{tot}^{1/3}
\]

by using the total volume change \( J_{tot} \) of the polymer. Finally, \( \lambda'_p \) is used to calculate \( \beta' \), see Eq. (5).

The above stated problem, involving non-trivial mathematical functions, can be solved numerically by linearizing the stationary condition \( \partial W_{net}/\partial \mathbf{F} - P_e = 0 \).

5. Numerical examples

The above presented model is used to simulate the mechanical response of a polymer with switchable molecules under the action of a pH change and under a mechanical stress history. The chains distribution \( p(N) \) has been assumed to follow a Gaussian law, with an average value \( \bar{N} = 100 \).
and deviation $\delta N = 5$; the problem’s parameters adopted for all the simulations are as follows: shear modulus $\mu = \pi k_B T = 2 \text{ MPa}$, $\chi = 0.6$, reaction rates without chemical or mechanical stress $k_{A0} = 10^{-6}\text{Hz}$, $k_{D0} = 10^{-4}\text{Hz}$.

### 5.1. Polymer with switchable molecules exposed to an acid environment

In the first example, the polymer with switchable molecules ($\langle J_m \rangle = 2.5$) is exposed to an acidic solvent. We assume that the stoichiometric ratio is equal to 1 (i.e. 1 mol of solvent is required to open 1 mol of switchable molecules), and that the acid concentration in the solvent is 0.1%; the volume fraction of the molecules has been assumed equal to be 2% (Fig. 2a) and 10% (Fig. 2b). The volume expansions of the polymer, $J_{sw}, J_{op}, J_{tot}$ vs time are illustrated; it appears that the molecule expansion enhances the volume increase of the polymer. The fraction of open molecules $\tilde{h}_{op}$ increases in time more rapidly for $\phi = 2\%$ than for $\phi = 10\%$ because a higher quantity of acid is required at a given time to open the switchable molecules.

**Figure 2.** Evolution in time of the fraction of open switchable molecules for a polymer under the action of pH changing for $\phi = 2\%$ (a) and $\phi = 10\%$ (b).

### 5.2. Polymer with switchable molecules under a cyclic mechanical stress

In the second example, the polymer with switchable molecules (two cases are considered: $\langle J_m \rangle = 2.5$, and $\langle J_m \rangle = 8.0$) is subjected to a mechanical stress history; the volume fraction of the molecules has been assumed equal to 2% and the resulting expansion and stretches are shown in Fig. 3 and in Fig. 4. Molecule expansion, triggered by the mechanical force, promotes a greater deformation of the material with respect to the case without switchable molecules.

**Figure 3.** Evolution in time of the fraction of open switchable molecules ($\langle J_m \rangle = 2.5$) and of the volumetric deformation under the action of a cyclic mechanical stress (a). Longitudinal ($\lambda_1$) and transversal stretches ($\lambda_2, \lambda_3$) vs time (b).
6. Conclusions

In the present paper we have considered the mechanics of a polymer network containing switchable molecules (mechanophores) that can assume only two different conformation states, close and open. The switching mechanism can be induced by a pH change or by mechanical stress. The theoretical framework, developed at the microscale level, accounts for the deformation induced in the polymer by both the switching of the molecules and by solvent uptake (swelling). The model has been readily upscaled to the continuum, and has been used to simulate the mechanical response of a polymeric material under the influence of a solvent which induces a pH change, and also under a mechanical stress history. The model is physically-based and is suitable to be straightforwardly implemented in a FE code for real simulations of elements made of smart responsive materials.

7. References

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