

# A micro-mechanically motivated approach for modelling the oxidative ageing process of elastomers

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## Micro Abstract

The mechanical response of elastomers is strongly influenced by chemical ageing, which changes the polymer network through chain scission and formation of new links. In this work, a micro-mechanical approach based on chain statistics is used to introduce ageing effects into the constitutive model. Spatial homogenisation is performed through a unit-sphere technique. As a first step, chain scission is handled by a modification of the underlying probabilistic model, and challenges of modelling a secondary network formation are discussed.

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## Introduction

Degradation of elastomers and the corresponding material performance reduction due to chemical ageing is an important engineering design consideration. The major drivers in the chemical ageing process are two competing reaction terms; chain scission and secondary network formation. This work aims to describe the ageing process in a micromechanical framework. A description of these phenomena from a micromechanical perspective is advantageous, as it provides deeper insight not obtainable from current phenomenological approaches.

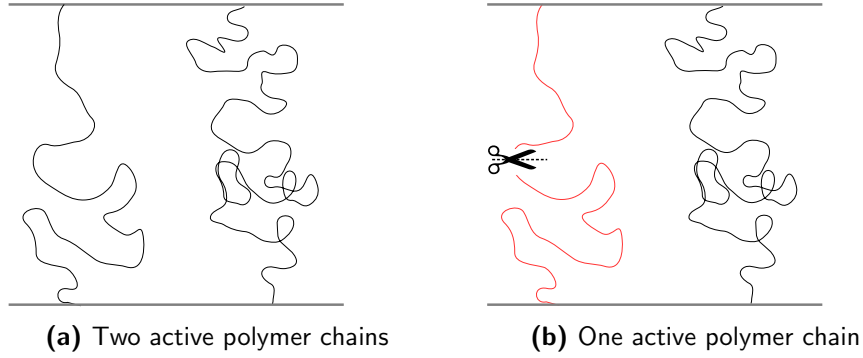
A defining characteristic of elastomers is their complex molecular structure which consists of many polymers (long chain like structures, see Figure 1a) and their interactions with filler particles and neighbouring chains. This microstructure allows elastomers to undergo large elastic deformations in comparison to metals. However, an alternative modelling approach is required. The aim is to extend the present modelling approach to include the evolution of a secondary network at a later time.

## 1 Background

Elastomers comprise of polymers which are in turn made up of repeating units of molecules to form a chain. These chains are sparsely linked to neighbouring chains and interact with filler particles. This allows sliding to occur between chains but provides a degree of structural integrity.

Chain scissions are driven by chemical reactions that sever a chain segment and introduce free radicals into the polymer network. These chemical reactions are highly dependent on the oxygen concentration in the material and constitute a coupled mechanical and reaction-diffusion process. When a polymer chain is scissioned, its load carrying ability is destroyed and the chain can be said to be *inactive*, see Figure 1b. As a first approach, we only consider chain scission that leads to a stress-softening behaviour. Consequently, this will lead to a continuously decreasing stress

response throughout time as is observed in experimental data. Opposing chain scission is the



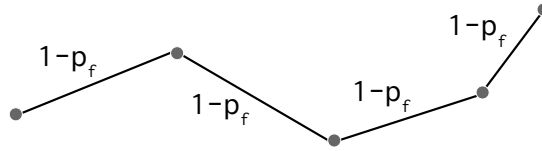
**Figure 1.** Scissioning one segment deactivates the chain

*secondary network formation* that results in the creation of additional cross-links with other polymer chains. This phenomenon is observable in the embrittlement of the elastomer.

## 2 Statistical approach for chain scission

In a polymer network, the number of unconstrained segments  $N$  between two cross-links is defined as a chain. Each chain in the polymer network has a certain number of segments and each segment has a probability  $p_f$  to undergo a scission reaction within a unit time period resulting in a *segment failure*. This probability is predominantly dependent on the reaction kinetics and in turn the availability of oxygen, temperature and other reaction rate modifiers.

Taking the complementary probability  $\overline{p_f} = 1 - p_f$  gives the probability that a given segment is still active. This can be applied to each segment of a chain as shown in Figure 2.



**Figure 2.** A chain with each segment probability to remain active

An entire chain will remain active if no scission events occur along the length of  $N$  segments, leading to the expression for the probability of a chain survival,

$$p_{cs} = (1 - p_f)^N . \quad (1)$$

Each chain has a probability to become inactive given by the complementary probability of Equation 1,

$$p_{cf} = 1 - p_{cs} = 1 - (1 - p_f)^N , \quad (2)$$

for a given polymer chain with  $N$  segments. Intuitively the longer a chain the higher the probability that it will be subject to a scission event. This observation is reflected in Equation 2, where for larger  $N$  the probability of failure increases.

A simple evolution equation is introduced to describe the change in the number of chains,

$$\frac{dn}{dt} = -np_{cf} , \quad (3)$$

where  $n$  is the number of *active* chains in the network. If  $p_{cf}$  is time-invariant and taking  $n_0$  as the initial number of chains in the network, the solution of the first order linear differential

equation in Equation 3 is given by

$$n(t) = n_0 \exp(-p_{cf}t) . \quad (4)$$

In order to implement this in a finite element framework, additional data structures are required. Firstly, we divide the total number of chains into groups which have a common number of segments  $N$  and suppose that the number of segments per chain can be described by a set with  $p$  entries,

$$N = \{N_1, N_2, \dots, N_p\} , \quad (5)$$

which can be described by an arbitrary distribution of chain lengths with the restriction that the number of segments must be greater than unity. The number of chains is then decomposed into a set with  $p$  entries

$$n(t) = \{n_1(N_1, t), n_2(N_2, t), \dots, n_p(N_p, t)\} , \quad (6)$$

where the summation of the chains with a given number of segments must yield the total number of chains in the network  $n_0$  at time  $t = 0$ ,

$$n_0 = \sum_{s=0}^p n_s(N_s, t = 0) . \quad (7)$$

A relationship between the shear modulus  $G$  and the number of chains from Equation 3 is given by  $G = nkT$ , where  $k$  is the Boltzmann constant and  $T$  is the temperature in Kelvin [2].

The affine microsphere model is used as a basis for the homogenisation [1]. A key advantage of this model is the ability to develop a one-dimensional description of the chain behaviour with a non-Gaussian description for the force on a single *unconstrained* chain,

$$F = kT\sqrt{N}\mathcal{L}^{-1}(\lambda_r) \quad (8)$$

where  $k$ ,  $T$  and  $N$  are as before,  $\mathcal{L}^{-1}$  is the inverse Langevin function,  $\lambda_r = \lambda/\sqrt{N}$  is the relative stretch,  $\lambda$  is the stretch, and homogenises this on the unit sphere to produce a three dimensional model. Modifications to this model assuming an  $m$  point quadrature scheme for the unit sphere discretisation (see Figure 3) can now be made with the aid of an assembly operator **A** which sums all of the contributions of the chain groups. Using a Padé approximation to compute the inverse Langevin function results in the deviatoric part of the Kirchhoff stress,

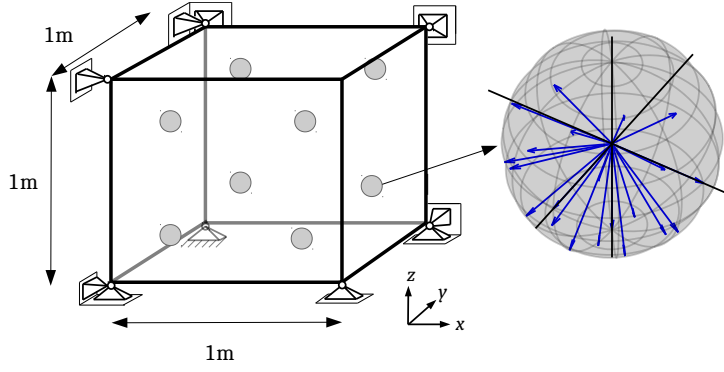
$$\bar{\tau}_f = \mathbf{A} \sum_{s=0}^p G_s \sum_{i=1}^m \frac{3N_s - \bar{\lambda}_i^2}{N_s - \bar{\lambda}_i^2} \mathbf{t}_i \otimes \mathbf{t}_i w_i , \quad (9)$$

where  $s$  is the current chain group index,  $\bar{\lambda}$  is the microstretch and  $\mathbf{t}$  is the isochoric stretch vector which is related to the integration point locations on the unit sphere. The deviatoric projection of Equation 9 is made in order to compute the Kirchhoff stress. For further information on the affine microsphere model, the reader is referred to the original paper [1].

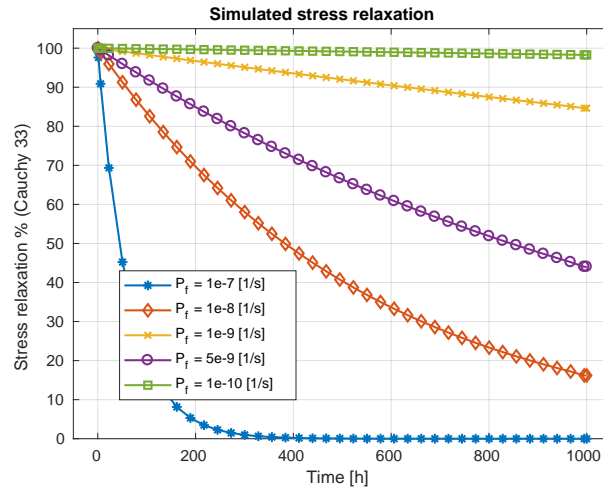
### 3 Results

A series of computational stress relaxation experiments were performed on a cube test specimen with a single hexahedron element with tri-linear shape functions. The specimen was loaded to a fixed displacement and held for 1000 hours. Symmetry boundary conditions were applied to the model as depicted in Figure 3, resulting in a homogeneous stress state. The stress component in the load direction was plotted over time, see Figure 4.

From Figure 4, it is seen that the stress relaxation exponentially decays with a rate highly dependent on the probability of scission  $p_f$ . In this idealised example, the probability of scission is uniform throughout the geometry and is not influenced by time or oxygen concentration. A physical interpretation of this scenario is an oxygen saturated specimen where oxygen is replaced as soon as it is consumed. In a more realistic example, a heterogeneous oxygen concentration affects the probability of a segment failure, therefore leading to a heterogenous stress response.



**Figure 3.** Test case cube geometry with unit sphere discretisation at each quadrature point



**Figure 4.** Numerical experiments of chain scission

## Conclusions

The model presented here draws on insights from micromechanical considerations, resulting in a simple evolution equation for the stress softening from the chain scission reactions. An elementary data structure was included to capture the effect of segment and chain distributions. The affine microsphere model was used to include the scission behaviour and the numerical experiments resulted in an exponential decay. With this micromechanical approach of the chain scission allows investigation of the influence of segment length distribution and segment probability dependencies on oxygen concentration.

## Acknowledgements

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