A micro-mechanically based continuum model for strain-induced crystallization in natural rubber

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A B S T R A C T

Recent experimental results show that strain-induced crystallization can substantially improve the crack growth resistance of natural rubber. While this might suggest superior designs of tires or other industrial applications where elastomers are used, a more thorough understanding of the underlying physics of strain-induced crystallization in natural rubber has to be developed before any design process can be started. The objective of this work is to develop a computationally-accessible micro-mechanically based continuum model, which is able to predict the macroscopic behavior of strain crystallizing natural rubber. While several researchers have developed micro-mechanical models of partially crystallized polymer chains, their results mainly give qualitative agreement with experimental data due to a lack of good micro–macro transition theories or the lack of computational power. However, recent developments in multiscale modeling in polymers give us new tools to continue this early work. To begin with, a micro-mechanical model of a constrained partially crystallized polymer chain with an extend-chain crystal is derived and connected to the macroscopic level using the non-affine micro-sphere model. Subsequently, a description of the crystallization kinetics is introduced using an evolution law based on the gradient of the macroscopic free energy function (chemical potential) and a simple threshold function. Finally a numerical implementation of the model is proposed and its predictive performance assessed using published data.

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1. Introduction

The study of strain-induced crystallization (SIC) in natural rubber (NR) dates back almost a century to Katz (1925). He discovered that NR underwent a transformation from an initially amorphous solid state to a semi-crystalline state when subjected to strain by means of X-ray diffraction, a method that is still state of the art. Ever since, SIC in NR has been a topic within the complex subject of rubber elasticity, not only because NR is widely used in industrial applications such as tires, seals, and medical devices, but also because its study might deepen the understanding of the Mullins' effect (Govindjee and Simo, 1991) and provide additional insight into the superior crack growth resistance of natural rubber (Le Cam and Toussaint, 2010). Despite this apparent significance, scant work has been done in the development of a micro-mechanically based continuum model of SIC in NR.

This type of modeling task typically includes a combination of three equally important parts:

1. A micro-mechanical model of a partially crystallized polymer chain.

2. A description of the crystallization kinetics in polymers, i.e. the time evolution of the degree of crystallinity within the material.

3. A micro-to-macro transition that connects micro-kinematic variables of the single chain with macroscopic continuum deformation measures.

The cornerstone was laid by Flory's statistical mechanical theory of extended chain crystallization (Flory, 1947). In this theory he uses a Gaussian distribution function to model the partially crystallized polymer chains and assumes that the crystallized part of the chain is oriented in the direction of stretch. There is no evolution of the degree of crystallinity involved, since equilibrium crystallization is assumed. All the relations in Flory's model are derived for uniaxial loading using an affine deformation assumption, which is known to result in inaccurate predictions for large deformations. Some years later, Gaylord (1976) and Gaylord and Lohse (1976) developed an improved theory of SIC with two modified assumptions. Unlike Flory, they took chain folding into account, which adds insight about crystal morphologies and orientation, and they used a non-Gaussian distribution function derived by Wang and Guth (1952) to model the polymer chains. At the same time another model was proposed by Smith (1976). He relaxed Flory's condition that the extended crystal has to be oriented in the direction of stretch by saying that the direction a chain takes through a

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crystal is determined by the first few links of a chain entrapped within the crystal itself. Other than giving good qualitative agreement with experimental data, all of the above mentioned models have the following three things in common: Firstly, all of them develop a detailed micro-mechanical model of a partially crystallized polymer chain. Secondly, only equilibrium crystallization is assumed and thus the time evolution of crystallinity is not considered. Thirdly, all of them lack a satisfactory micro-to-macro transition.

Crystallization kinetics itself is a widely studied phenomenon, e.g. in the study of phase changes in metals. Roughly speaking there are three different approaches. One of the most extensively used approaches to describe the process of crystallization is the model of Avrami (1939, 1940, 1941). Based on geometric considerations of nucleation and crystal growth, the equation of Avrami is given by the exponential law $\omega \propto 1 - e^{-kV_t}$, where ω is the degree of crystallinity, k is the average density of nuclei, and V_t is the volume a crystal would occupy after a time t. Here V_t depends on the growth rate and the shape of the crystal. Some years later a similar equation was obtained by Evans (1945) and applied to temperature-induced crystallization of Nylon 6,6 by Allen (1952). Gent (1954) was the first to extend the treatment of Avrami to stretched natural rubber vulcanizates and approximate the time functions governing crystal growth. Another widely used approach is taken by Becker (1938), Turnbull and Fisher (1949) and Hoffman and Weeks (1962). They use an Arrhenius equation to describe the crystallization process, $\dot{\omega} \propto \exp\left(-\Delta F/(k_B T)\right)$, where $\dot{\omega}$ is the rate of crystallization and ΔF the free energy change upon crystallization. A third approach first discussed for polymer crystallization by Roe and Krigbaum (1965) is based on a micro-mechanical model of a partially crystallized polymer chain and uses its free energy gradient (chemical potential) $\dot{\omega} \propto -\partial F/\partial\omega$ as the driving force for crystallization.

The lack of a satisfactory micro-to-macro transition has also been a challenging topic within the micro-mechanically based modeling of rubber elasticity. A good overview of constitutive models can be found in Boyce and Arruda (2000). More recently Miehe et al. (2004) have extended the micro-plane model of Bazant and Oh (1985) to the so-called non-affine micro-sphere model of rubber elasticity. This is a microscopically motivated finite deformation model for rubberlike materials. The model combines three special features: Firstly, it includes a non-affine stretch component, where micro and macro stretches are linked through a fluctuation field on a micro-sphere. The fluctuation field itself is determined by a minimization of a microstructural free energy. Secondly, polymer cross-links and entanglements are also considered using the so-called tube model of rubber elasticity, where the movement of a single chain is restricted by a tube-like constraint (Doi and Edwards, 1986). Thirdly, since closed-form solutions to the averaging integrals over a sphere are not available, a 21-point integration scheme, as derived in the original micro-plane model of Bazant and Oh (1985), is used.

The objective of this work is to leverage these ideas and develop a computationally-accessible micro-mechanically based continuum model, that is able to predict the macroscopic behavior of NR. The derivation of this model parallels the steps in Miehe and Göktepe's non-affine micro-sphere model with select changes: Firstly, on the microscopic level the free energy of a partially crystallized unconstrained single chain is considered instead of a fully amorphous chain. The model used for the chain will be a modified version of Smith (1976), which provides a way of modeling a semi-crystalline chain with extended crystals (Section 3). The microscopic model is connected to the macroscopic level using the non-affine micro-sphere model (Section 4). Secondly, on the macroscopic level an evolution law for the degree of crystallinity based on the macroscopic free energy is introduced, where the free energy gradient is used as a driving force (Roe and Krigbaum, 1965) (Section 2). Moreover, a threshold function for the evolution law inspired by phase change evolution in martensitic alloys (Govindjee and Miehe, 2001) is introduced. Thirdly, the numerical implementation using a return mapping algorithm is explained in Section 6. Finally in Section 7 the model is discussed and the predictive performance of the proposed model assessed along with a comparison to the work of Kroon (2010).

2. Macroscopic setting of model

At the macroscopic scale the model assumes a free energy function that depends on the right Cauchy–Green deformation tensor $\mathbf{C}$ and the internal variable ω, a macroscopic measure of the degree of crystallinity in the material:

$$\Psi = \Psi(\mathbf{C}; \omega). \tag{1}$$

Following the argument that the mechanical dissipation cannot be negative (see e.g. Coleman and Noll, 1963, Truesdell and Noll, 1965, Section 79, or Simo and Hughes, 1998)

$$\mathscr{D}_{mech} = \frac{1}{2}\mathbf{S} : \dot{\mathbf{C}} - \dot{\Psi} \geqslant 0, \tag{2}$$

the second Piola–Kirchhoff stress is given by

$$\mathbf{S} = 2\frac{\partial\Psi}{\partial\mathbf{C}}, \tag{3}$$

with the additional condition

$$-\frac{\partial\Psi}{\partial\omega}\dot{\omega} \geqslant 0. \tag{4}$$

The evolution of the degree of crystallinity is chosen to be governed by the macroscopic free energy function by setting the rate of the degree of crystallinity to

$$\dot{\omega} = -A\frac{\partial\Psi}{\partial\omega}, \quad A \geqslant 0, \tag{5}$$

where the free energy gradient acts as a driving force for the crystallinity. The condition $A \geqslant 0$ immediately follows from inserting Eq. (5) into Eq. (4). The degree of crystallinity however, can only evolve once a certain chemical potential threshold is reached. In order to incorporate this into the model, a chemical potential "yield function" of the form

$$g = \left|\frac{\partial\Psi}{\partial\omega}\right| - (g_c + \gamma\omega) \leqslant 0 \tag{6}$$

is introduced, where $g_c \geqslant 0$ (threshold at zero degree of crystallinity) and γ (hardening/softening parameter) are material constants. As long as $g < 0$, the degree of crystallinity does not evolve; i.e. $Ag = 0$.

Following common practice, a decoupling of the free energy function into volumetric and isochoric parts is introduced by use of the unimodular part of the deformation gradient (Flory, 1961)

$$\bar{\mathbf{F}} := J^{-1/3}\mathbf{F}, \quad J = \det\mathbf{F} \tag{7}$$

and using the form

$$\Psi = \Psi_{vol}(J) + \bar{\Psi}(\bar{\mathbf{C}}; \omega), \quad \bar{\mathbf{C}} = \bar{\mathbf{F}}^T\bar{\mathbf{F}}, \tag{8}$$

with volumetric and isochoric contributions to the free energy function. Applying (3) to the decoupled macroscopic free energy leads to the standard result in compressible hyperelasticity (see e.g. Holzapfel, 2000, Chapter 6)

$$\mathbf{S} = J\Psi'_{vol}(J)\mathbf{C}^{-1} + J^{-2/3}\left(\mathbb{I} - \frac{1}{3}\mathbf{C}^{-1} \otimes \mathbf{C}\right) : 2\frac{\partial\bar{\Psi}(\bar{\mathbf{C}}; \omega)}{\partial\bar{\mathbf{C}}}. \tag{9}$$

The volumetric response $\Psi_{vol}(J)$ can be any scalar valued function which is strictly convex, has unbounded value as $J \to 0$ and