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Affine Full Network Model for Strain-Induced Crystallization in Rubbery Polymers

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Micro Abstract
We propose a micro-mechanically motivated material model for strain-induced crystallization in rubbers. Our point of departure is constructing a micro-mechanical model for a single crystallizing polymer chain. A thermodynamically consistent evolution law describing the kinetics of crystallization in the chain level is then proposed. The chain model is incorporated into the affine full network model. Finally, the numerical performance of the model is compared to the experimental data.

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Introduction

Natural rubber crystallizes under stretch and its amorphous structure becomes semi-crystalline. Crystallization changes the mechanical response of rubber dramatically. The tensile strength, the fatigue life and the crack growth resistance of rubber increase with crystallization. The crystallization process occurs only in those regions, which are subjected to large strains, while the rest of the structure maintains its amorphous state. Upon removal of the load, crystallites melt, which leads to a closed hysteresis loop in the loading/unloading process.

Strain-induced crystallization in rubbers was first discovered by Katz [5] using X-ray diffraction. Since then, this technique has been widely used to study strain-induced crystallization, see for example [3], [9] and [12]. Recent progress in X-ray diffraction techniques has made it possible to evaluate the real time crystalline mass fraction during loading and unloading of the rubber specimen, see [11]. Strain-induced crystallization was first theoretically treated by Flory [2]. Recently, computational modeling of strain-induced crystallization has attracted the attention of researchers. A few recent contributions can be found in [6], [8], [1], [10] and [4], among which the latter is based on the affine full network model.

Inspired by the above-mentioned works we present a multi-scale model for strain-induced crystallization in rubbers. First, we briefly discuss the macroscopic structure of the model. Next, a chain model for crystallizing rubbers is proposed. The chain model is then incorporated into the affine full network model. Finally, the performance of the model is evaluated and the results are compared to the experimental data.

Macromechanics of Crystallization

The one-to-one map $\boldsymbol{\varphi}$ defines the deformation of a body $\mathcal{B}$ undergoing finite strains. $\boldsymbol{\varphi}$ maps at time $t \in \mathbb{R}_+$ the material points $\boldsymbol{X} \in \mathcal{B}$ of the reference configuration $\mathcal{B} \subset \mathbb{R}^3$ to spatial points $\boldsymbol{x} \in \mathcal{S}$ in the current configuration $\mathcal{S} \subset \mathbb{R}^3$. In order to exclude interpenetration of matter, the deformation gradient $\boldsymbol{F} := \nabla\boldsymbol{\varphi}(\boldsymbol{X}, t)$ has to fulfill the constraint $J := \det[\boldsymbol{F}] > 0$. Furthermore, let $\boldsymbol{g}$ be the covariant spatial metric tensor. A multiplicative decomposition of the deformation gradient $\boldsymbol{F} = \boldsymbol{F}_{\mathrm{vol}}\bar{\boldsymbol{F}}$ into a volumetric part $\boldsymbol{F}_{\mathrm{vol}} := J^{1/3}\boldsymbol{1}$ and an isochoric part $\bar{\boldsymbol{F}} := J^{-1/3}\boldsymbol{F}$ is considered. We choose the macroscopic free energy Ψ per unit reference volume of crystallizing rubber to be a function of the current metric $\boldsymbol{g}$ and a vector of internal variables $\boldsymbol{\mathcal{I}}$ characterizing strain induced crystallization. In addition, the stored energy is additively split into volumetric and isochoric parts

$$\Psi(\boldsymbol{g},\boldsymbol{\mathcal{I}};\boldsymbol{F}) = \Psi_{\text{vol}}(J) + \Psi_{\text{iso}}(\boldsymbol{g},\boldsymbol{\mathcal{I}};\bar{\boldsymbol{F}}) \ . \tag{1}$$

Using the above equation and the Doyle-Ericksen formula $\boldsymbol{\tau} = 2\partial_{\boldsymbol{g}}\Psi(\boldsymbol{g},\boldsymbol{\mathcal{I}};\boldsymbol{F})$ for the Kirchhoff stress tensor, the stresses additively decompose into volumetric and isochoric contributions

$$\boldsymbol{\tau} = p\boldsymbol{g}^{-1} + \mathbb{P} : \bar{\boldsymbol{\tau}} \quad \text{with} \quad p := J\Psi'_{\text{vol}}(J) \quad \text{and} \quad \bar{\boldsymbol{\tau}} := 2\,\partial_{\boldsymbol{g}}\Psi_{\text{iso}}(\boldsymbol{g},\boldsymbol{\mathcal{I}};\bar{\boldsymbol{F}}) \ , \tag{2}$$

where $\mathbb{P}$ is the fourth order deviatoric projection tensor and prime denotes the first derivative.

Micromechanics of Crystallization

Let us consider a semi-crystalline chain molecule which consists of N segments of length l. We define the chain degree of crystallization ξ as the ratio of the number N_c of the segments in the crystalline part of the chain to the total number N of the segments, i.e., $\xi := \frac{N_c}{N}$. The total end-to-end distance r of the chain is equal to the sum of the length r_c of the crystalline portion and the length r_a of the amorphous portion. The relative stretch λ_a^r in the amorphous part of the chain is defined as the length r_a of the amorphous portion to the fully extended length $(1-\xi)Nl$ of the amorphous portion and can be written in terms of the total stretch λ in the chain and the degree of crystallization $\lambda_a^r = (\frac{\lambda}{\sqrt{N}} - \xi)/(1-\xi)$. The stored energy in the semi-crystalline chain due to stretch and crystallization is

$$\psi(\lambda,\xi) = \xi N(Ts_f - h_f) + (1-\xi)NkT\left(\lambda_a^r \mathscr{L}^{-1}(\lambda_a^r) + \ln\frac{\mathscr{L}^{-1}(\lambda_a^r)}{\sinh\mathscr{L}^{-1}(\lambda_a^r)}\right) + \psi_h(\lambda) \ , \tag{3}$$

where, similar to [4], the phenomenological term ψ_h adds the reinforcing effect of the crystallites to the model

$$\psi_h(\lambda) = \begin{cases} 0 & \text{if} \quad \lambda < \lambda^\star \\ \dfrac{h}{1+p}(\lambda-\lambda^\star)^{1+p} & \text{if} \quad \lambda \geq \lambda^\star \ . \end{cases} \tag{4}$$

Here, N, s_f, h_f, h, p and $\lambda^\star$ are material constants, T is the absolute temperature and $\mathscr{L}^{-1}$ is the inverse of the Langevin function $\mathscr{L}(\alpha) = \coth\alpha - 1/\alpha$. Applying a standard Coleman-Noll procedure, we can define the chain axial force $\mathfrak{f} := \partial_\lambda\psi(\lambda,\xi)$ and the crystallization driving force by $\mathfrak{F} := -\partial_\xi\psi(\lambda,\xi)$. The reduced microscopic dissipation $\mathcal{D}_{mic} := \mathfrak{F}\dot{\xi} \geq 0$ has to be non-negative to ensure thermodynamical consistency. To fulfill this condition we use the concept of *dissipation potential*. Assuming a convex, positive and normalized dual dissipation potential $\phi^*(\mathfrak{F})$, thermodynamical consistency is a priori satisfied if $\dot{\xi}$ is an element of the subdifferential $\partial_{\mathfrak{F}}\phi^*(\mathfrak{F})$, i.e., $\dot{\xi} \in \partial_{\mathfrak{F}}\phi^*(\mathfrak{F})$. We assume that crystallization is governed by a *rate-independent evolution law with threshold*

$$\phi^*(\mathfrak{F}) = \begin{cases} 0 & \text{if} \quad \mathfrak{F} \in [\mathfrak{F}_0, \mathfrak{F}_t] \\ +\infty & \text{if} \quad \mathfrak{F} \notin [\mathfrak{F}_0, \mathfrak{F}_t] \end{cases} \quad \rightarrow \quad \dot{\xi} \in \partial_{\mathfrak{F}}\phi^*(\mathfrak{F}) = \begin{cases} [0,+\infty] & \text{if} \quad \mathfrak{F} = \mathfrak{F}_t \\ 0 & \text{if} \quad \mathfrak{F} \in (\mathfrak{F}_0, \mathfrak{F}_t) \\ [-\infty,0] & \text{if} \quad \mathfrak{F} = \mathfrak{F}_0 \ . \end{cases} \tag{5}$$

Here, the upper threshold $\mathfrak{F}_t \geq 0$ is a constant and the lower threshold $\mathfrak{F}_0$ is the crystallization driving force in the initial state of the chain. The material parameters should be selected such that the initial crystallization driving force $\mathfrak{F}_0$ be non-positive

$$\mathfrak{F}_0 = -\partial_\xi\psi(\lambda,\xi)\Big|_{\lambda=1,\xi=0} \leq 0 \ . \tag{6}$$

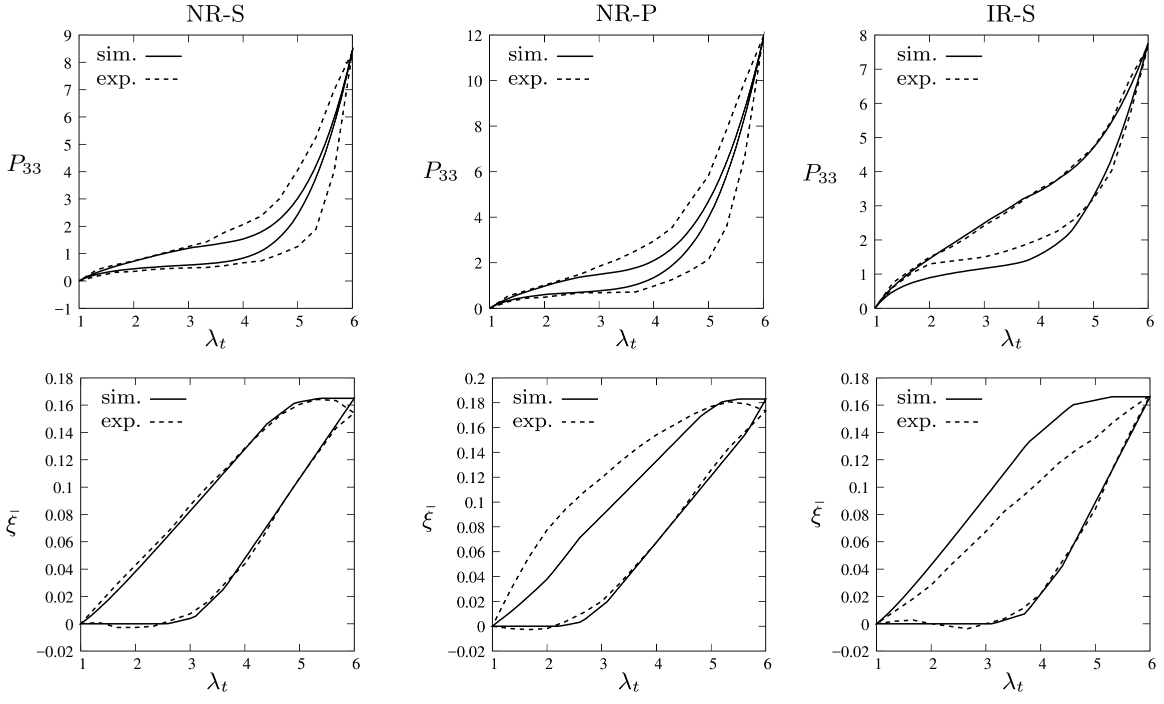

Figure 1. Stress-stretch and crystallization-stretch plots for three types of rubber are compared with the experimental results.

Affine Full Network Model for Crystallization

Consider a unit Lagrangian orientation vector $\boldsymbol{r}$ and its corresponding co-vector $\boldsymbol{r}_\flat := \boldsymbol{G}\boldsymbol{r}$ obtained by mapping $\boldsymbol{r}$ with the reference metric $\boldsymbol{G}$. The spatial isochoric orientation vector $\boldsymbol{t}$ is obtained by mapping $\boldsymbol{r}$ with the isochoric part $\bar{\boldsymbol{F}}$ of the deformation gradient, i.e., $\boldsymbol{t} = \bar{\boldsymbol{F}}\boldsymbol{r}$. The length of vector $\boldsymbol{t}$ is the stretch of a line element in the direction of $\boldsymbol{r}$ in the reference configuration

$$\bar{\lambda} = |\boldsymbol{t}|_{\boldsymbol{g}} := \sqrt{\boldsymbol{t}_\flat \cdot \boldsymbol{t}} \quad \text{with} \quad \boldsymbol{t}_\flat := \boldsymbol{g}\boldsymbol{t} \ , \tag{7}$$

where $\boldsymbol{g}$ is the current metric. We assume that deformation is affine, i.e., the stretch λ in a chain with a specific direction is equal to the stretch $\bar{\lambda}$ in the bulk rubber in that direction. The isochoric macroscopic free energy of the rubbery material is obtained by homogenizing the microscopic free energies of polymer chains over evenly-distributed orientations in space, i.e., $\Psi_{\text{iso}}(\boldsymbol{g}, \boldsymbol{\mathcal{I}}; \bar{\boldsymbol{F}}) = \langle n\psi(\bar{\lambda}, \xi)\rangle$. Here, n is the number of polymer chains per unit volume and the operator $\langle \diamond \rangle$ denotes the continuous average of the argument $\diamond$ over evenly-distributed orientations. We define the average operator on a *micro-sphere* $\mathscr{S}$ with unit radius via

$$\langle v \rangle = \frac{1}{|\mathscr{S}|} \int_{\mathscr{S}} v(\boldsymbol{r}) dA \ , \tag{8}$$

see [7]. Here, $|\mathscr{S}| = 4\pi$ is the surface area of the micro-sphere and $\boldsymbol{r}$ is the unit orientation vector. The average degree of crystallization $\bar{\xi}$ is defined as the average of the chain degrees of crystallization over the micro-sphere, i.e., $\bar{\xi} := \langle \xi \rangle$. With the isochoric macro-energy Ψ_{iso} at hand and using $(2)_3$, we are able to derive the isochoric contributions to the stresses

$$\bar{\boldsymbol{\tau}} = \langle \bar{\lambda}^{-1} n \mathfrak{f}(\bar{\lambda}, \xi)\, \boldsymbol{t} \otimes \boldsymbol{t} \rangle \ . \tag{9}$$

Evaluation of the Model

In this section we will compare the results predicted by our model with the experimental results of Toki et al. [11]. In their experimental setup, three types of rubber, namely, sulfur-vulcanized natural rubber (NR-S), peroxide vulcanized natural rubber (NR-P) and sulfur vulcanized synthetic polyisoprene rubber (IR-S) were stretched up to a total stretch of $\lambda_t = 6$ at $0°C$ and then were retracted to the initial length. They measured the mass fraction of the strain-induced crystallites at different stages of loading using synchrotron wide-angle X-ray measurements. They concluded that even at high strains, the majority of the molecules remain amorphous.

The vertical nominal stress and the average degree of crystallization obtained by the model are compared with the experimental data in Figure 1. In the crystallization plots, the average degree of crystallization $\bar{\xi}$ is considered to be the macroscopic measure of crystallization. The model is able to reproduce the experimental crystallization data very well. However, the hysteresis in the stress-stretch is underestimated. Note that in our treatment after full retraction of the material no remnant crystallization is present. This is in line with the experimental observations.

Conclusions

We proposed a micro-mechanically motivated material model for strain-induced crystallization in rubbers. Our starting point was constructing a micro-mechanical model for a single crystallizing polymer chain. A thermodynamically consistent framework for the evolution of crystallization in the chain level was proposed. This modified chain model was then incorporated into the affine full network model. Finally, the numerical performance of the model was compared to the experimental results.

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