

Continuum Mechanical Modeling of Strain-Induced Crystallization in Polymers

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Micro Abstract

The strain-induced crystallization in polymers is a phenomenon manifesting itself as the natural reinforcement caused by the high deformation. The current contribution, treats a polymer affected by the SIC as a heterogeneous medium consisting of regions with a different degree of network regularity. Such a concept allows us to simulate the nucleation and the growth of crystalline regions. The model proposed is based on the assumptions for the free energy and dissipation potential.

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Introduction

The phenomenon of the strain-induced crystallization (SIC) in polymers is characterized by the fact that the polymer chains under the influence of high strains partially leave their natural entangled structure, stretch out, fold back and stack. The new structure is regular and resembles the crystalline pattern typical of metals. Under the increasing strain, the evolution of the microstructure causes the strengthening of material and changes the reaction to the macroscopic mechanical influences. Experimental data for cyclic uniaxial test (Fig. 1) show that the stress response builds a hysteresis which indicates that the process has a dissipative character. Moreover, the results show that the crystallization starts at a strain of 200-400%, whereas maximal possible strains, which do not cause any rupture, amount to 700%.

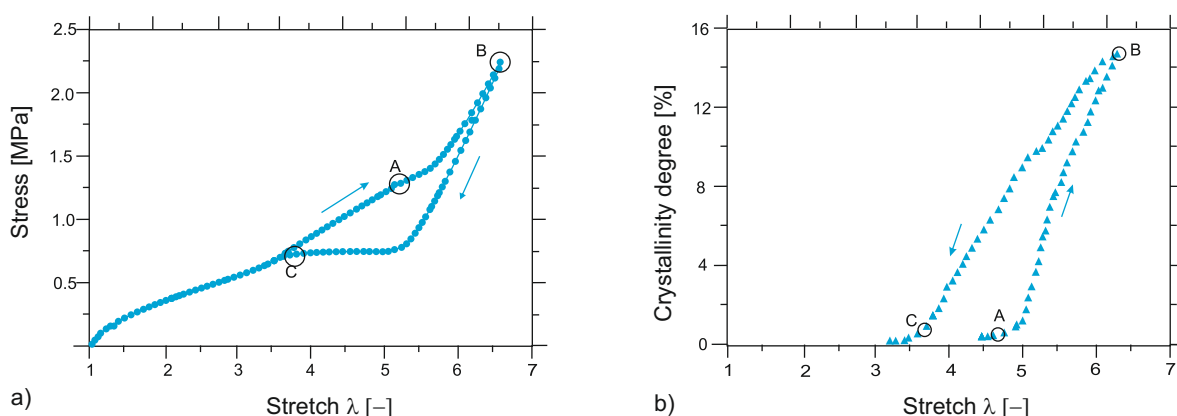


Figure 1. Uniaxial cyclic test for natural rubber under constant temperature $T = 295$ K and constant speed 2 mm/min. (a) Stretch-stress diagram. (b) Stretch-crystallinity degree diagram. Original diagrams are published in [5].

Most of the models focusing on the modeling of polymers use the Langevin expression for the free energy as a basis [1, 4]. However the model presented here, treats a polymer affected by the strain induced crystallization as a heterogeneous medium consisting of regions with a different

degree of network regularity. The model proposed is thermodynamically consistent. It is based on the assumptions for the free Helmholtz energy and dissipation potential. Both of them primarily include bulk terms due to the deformation and crystallization. The external variable is the deformation, whereas the inelastic deformations and degree of the network regularity are internal variables. Their evolution equations are derived according to the principle of minimum of dissipation potential [2].

1 Micro-mechanical modeling of SIC in polymers

The theory of finite deformations is the suitable framework for the simulation of polymers. Typically of this theory, the modeling of dissipative processes requires a multiplicative decomposition of the deformation gradient into an elastic part and an inelastic part $\mathbf{F} = \mathbf{F}^e \cdot \mathbf{F}^c$. In our case, \mathbf{F}^c represents the deformations caused by the crystallization. However, the multiplicative decomposition alone is not enough to describe the phenomena such as the formation and growth of crystalline regions. For this purpose, we introduce an internal variable denoting the regularity of the polymer chain network χ . This variable takes values from range $[0,1]$, where 0 corresponds to a totally amorphous polymer and 1 to the completely crystalline regions. The minimum principle of the dissipation potential [2] is pursued to derive the evolution laws obeying the second thermodynamic law. According to this theory, the Lagrange function consists of the elastic power and dissipation potential $L = \dot{\Psi} + \Delta$. In this work, we assume the Helmholtz free energy of a Neo-Hookean material for the elastic part

$$\Psi = \Psi^e(\mathbf{F}^e) = \left(K - \frac{2}{3}G \right) U(J^e) + \frac{G}{2} (\text{tr}(\mathbf{C}^e) - 3 - 2 \ln(J^e)) , \quad (1)$$

$$U(J^e) = \frac{1}{4} (J^{e2} - 1 - 2 \ln(J^e)) . \quad (2)$$

Here, $\mathbf{C}^e = (\mathbf{F}^e)^T \cdot \mathbf{F}^e$ is the elastic right Cauchy-Green deformation tensor, $J^e = \det \mathbf{F}^e$ is the elastic Jacobian, K is the bulk modulus and G is the shear modulus. We furthermore assume the dissipation potential in the form

$$\Delta = k_1 \lambda_0 |\dot{\chi}| + \frac{1}{2k_2 \chi^2} \dot{\chi}^2 , \quad (3)$$

where k_1 and k_2 are material constants. The term $k_1 \lambda_0$ stipulates that the deformations due to the crystallization starts after stretch limit λ_0 has been exceeded. The quadratic term enables us to simulate the variation of hysteresis depending on the velocity $\dot{\chi}$. Moreover, the change of the regularity is favored in the regions with the high value of regularity degree by introducing the factor χ^2 in the second term of the dissipation. We furthermore couple the evolution of the \mathbf{F}^c with the evolution of the regularity χ by introducing the following relationship $\mathbf{L}^c = \dot{\mathbf{F}}^c \cdot \mathbf{F}^{c-1} = k \dot{\chi} \mathbf{I}$. Here, \mathbf{L}^c represents the velocity gradient due to crystallization. In the next step, we consider the Clausius-Duhem inequality for isothermal deformations

$$D = \mathbf{P} : \dot{\mathbf{F}} - \dot{\Psi} = \left(\mathbf{P} - \frac{\partial \Psi}{\partial \mathbf{F}^e} \cdot \mathbf{F}^{c-T} \right) : \dot{\mathbf{F}} + \mathbf{M} : \mathbf{L}^c \geq 0 , \quad (4)$$

where $\mathbf{M} = \mathbf{F}^{eT} \cdot \partial \Psi / \partial \mathbf{F}^e$ denotes the Mandel stress tensor. The inequality (4) yields two consequences: First, the constitutive law for the the first Piola-Kirchhoff stress tensor is obtained by assuming that the expression in parantheses is equal to zero $\mathbf{P} = \partial \Psi / \partial \mathbf{F}^e \cdot \mathbf{F}^{c-T}$. Second, the remaining term $\mathbf{M} : \mathbf{L}^c = \mathbf{M} : (k \dot{\chi} \mathbf{I}) = k \text{tr}(\mathbf{M}) \dot{\chi} \geq 0$ implies the relation: $\text{sign}(\dot{\chi}) = \text{sign}(k \text{tr}(\mathbf{M}))$. Since the free energy (1) and the dissipation potential (3) are defined, the principle of maximum of dissipation potential enables us to derive the evolution law for the internal variable χ :

$$\dot{\chi} = \text{arginf} \{ L(\dot{\chi}) | \dot{\chi} \} = \begin{cases} 0 , & \text{for } |k \text{tr}(\mathbf{M})| \leq k_1 \lambda_0 \\ k_2 \chi^2 (|k \text{tr}(\mathbf{M})| - k_1 \lambda_0) \text{sign}(k \text{tr}(\mathbf{M})) , & \text{otherwise} \end{cases} \quad (5)$$

Here, the subdifferential is applied to define the minimum value of the Lagrange function since it is not differentiable at $\dot{\chi} = 0$. For the purpose of numerical implementation, the evolution equation (5) is discretized in time by using the forward Euler method: $\dot{\chi}(t_n) = (\chi_{n+1} - \chi_n) / \Delta t$. In addition, the exponential mapping is used for the evaluation of the current \mathbf{F}^c

$$\mathbf{F}_{n+1}^c = \exp \left(\int_{t_n}^{t_{n+1}} k \dot{\chi} dt \right) \mathbf{F}_n^c = \exp (k (\chi_{n+1} - \chi_n)) \mathbf{F}_n^c . \quad (6)$$

According to the standard notation, n and $n + 1$ denote two successive time steps.

2 Numerical example

The material model for SIC is implemented into the FE program FEAP [6]. In order to illustrate its application, a tensile test for a square sample with the dimensions 100×100 mm is chosen (Fig. 2 a). The lower and the upper boundary are constrained and a gradually increasing displacement in the range $[0, 300$ mm] is applied at each of these boundaries. The total loading time amounts to 10 s and the time increment is $\Delta t = 0.1$ s. The regularity of the polymer network in the starting configuration has small random initial values which simulates the nuclei of the crystalline regions. Fig. 2 b shows the state of the network regularity in the final loading step. Note that the red color corresponds to the completely crystallized regions.

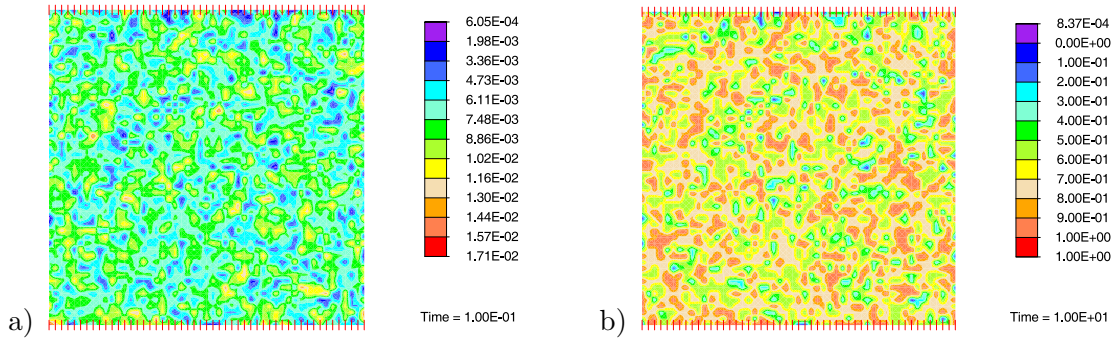


Figure 2. a) The initial random distribution of the regularity for a square sample consisting of natural rubber. b) The distribution of the regularity in the final loading step. The distribution of the regularity in the final loading step. The applied material parameters are $K = 2 \text{ e}6$ Pa, $G = 4 \text{ e}4$ Pa, $k_1 \lambda_0 = 4 \text{ e}3$ Pa, $k_2 = 6 \text{ e}-3$ Pa $^{-1}$ and $k = 1 \text{ e}-2$.

Additional numerical examples, not presented here, have shown that the model proposed needs a further improvement to simulate the material behavior during the unloading phase. The evolution equation (5) intrinsically contains a condition that the regularity can only grow. As a consequence, the regression of the regularity occurring during the unloading phase cannot be simulated. The consideration of this behavior type requires an alternative proposal for the dissipation potential. This dissipation potential has to enable us to derive a thermodynamic driving force corresponding to the evolution of the regularity, which changes its sign depending on the change of the stress state.

Conclusions

In the present work, we show a thermodynamically consistent model based on the assumption for the free energy and dissipation potential. The main advantage of our approach is that it enables the simulation of the formation and of the development of crystalline regions. In our continuing work, we will focus on the modeling of degradation of crystalline regions during the unloading. An implementation of the model within the multiscale concept [3] and the study of the influence of crystalline regions on the effective material behavior of polymers are envisaged as well. Furthermore, the model will be extended by introducing temperature effects and material

parameters will be identified by using the inverse analysis in a combination with experimental results.

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