Coupled thermomechanical model for strain-induced crystallization in polymers

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Crystallization in certain polymers, like natural rubber, is characterized by the specific geometrical arrangement of atoms in macromolecules caused by high strains. Starting from crystallization nuclei, polymer chains leave their natural entangled structure, stretch out, fold back and stack. Eventually, they build regions with a regular structure, also called lamellae. The process must be taken into consideration when planning manufacturing processes since it significantly influences mechanical and thermal properties of the final product. The present contribution deals with the thermomechanical model for crystallization of unfilled polymers, which involves displacements and temperature as global degrees of freedom, and the degree of network regularity as an internal variable. The mechanical part of the model uses the dissipation potential with two special features: Firstly, the thermodynamically consistent framework is developed to simulate the reduction of the network regularity during the unloading phase. Secondly, the microstructure evolution under the cyclic tensile load is visualized. The thermal part of the model is based on the solution of the heat equation. The resulting, coupled thermomechanical problem is solved in a monolithic way. Finally, selected numerical examples are compared with experimental data of natural rubber without fillers.

1 Introduction

The phenomenon of strain-induced crystallization (SIC) in polymers is characterized by the fact that, under the influence of high strains, polymer chains partially form a regular structure that resembles a crystalline pattern. Under the increasing strain, the evolution of the microstructure causes the strengthening of material and changes the reaction to the macroscopic mechanical and thermal influences. Experimental data for cyclic uniaxial tests (Fig. 1) show that the stress response builds a hysteresis which indicates that the process has a dissipative character. Moreover, the results show that crystallization starts at a stretch of about 430%. At the stretch of 600% the crystallinity degree reaches 15% (Fig. 1 a). The higher values of crystallinity can be achieved if the higher stretches are applied. However, additional inelastic processes occur simultaneously to the SIC in that case. It is also worth mentioning that heat produced by the formation of crystalline regions leads to an increase in temperature, whereas the regression of crystalline regions during the unloading phase yields a temperature decrease. Accordingly, the temperature diagram (Fig. 1 b) has an analogous form to the diagram of crystallinity degree (Fig. 1 a) as shown in [1].

Fig. 1: Uniaxial cyclic tension test for a vulcanized unfilled natural rubber at room temperature at the strain rate $4.2 \times 10^{-3}$ s$^{-1}$. a) Stress-stretch diagram and crystallinity degree-stretch diagram. b) Stress-stretch diagram and temperature-stretch diagram. Original diagrams are published in Candau et al. (2015) [1].

Most of the models focusing on the mechanical modeling of polymers use the Langevin expression for the free energy as a basis [2, 3]. 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 Arruda-Boyce assumption for the Helmholtz free energy and on the assumption for the dissipation potential [4]. The free energy primarily includes terms due to the deformation, regularity and temperature. The external variables are temperature and deformation, whereas the inelastic deformations and degree of the network regularity are internal variables. Their evolution equations are derived according to the minimum principle of the dissipation potential [5]. In addition to the balance of linear momentum describing the mechanical part, the heat equation is used to simulate the temperature response due to the crystallization.

2 Micromechanical modeling of SIC in polymers

The theory of finite deformations is the suitable framework for the simulation of polymers. Typical of this theory, the modeling of dissipative processes requires a multiplicative decomposition of the deformation gradient into an elastic part and an inelastic part \( F = F^e \cdot F^c \). In our case, \( F^c \) 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 \( \chi \). 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 is pursued in order to derive the evolution laws obeying the second thermodynamic law. According to this theory, the Lagrange function involves the elastic power and dissipation potential \( L = \tilde{\Psi} + \Delta \). In this work, the Helmholtz energy \( \tilde{\Psi}(F^c, \Theta) = \Psi^F(F^c) + \Psi^\delta(\Theta) \) consists of an elastic part depending on elastic deformations and a purely temperature dependent part, where \( \Theta \) is the temperature. We assume the free energy of an Arruda-Boyce material for the elastic part with a split into a volumetric and a deviatoric contribution

\[
\tilde{\Psi}(J^e, C^e) = K U(J^e) + \frac{\mu}{2} \left[ (\tilde{I}_1 - 3) + \frac{m}{10} (\tilde{I}_2^2 - 9) + \frac{11m^2}{525} (\tilde{I}_3^2 - 27) \right],
\]

\[
U(J^e) = \frac{1}{4} (J^e)^2 - 2 \ln(J^e) \quad , \quad \tilde{I}_1 = J^e - \frac{2}{3} \text{tr}(C^e) \quad , \quad \tilde{\mu} = \frac{\mu}{1 + \frac{4}{3}m + \frac{99}{175}m^2} \quad , \quad m = \frac{1}{\lambda_m^2}.
\]

In the chosen constitutive law, \( C^e = (F^e)^T \cdot F^e \) represents the elastic right Cauchy-Green deformation tensor, \( J^e = \det (F^e) \) is the elastic Jacobian, \( K \) is the bulk modulus, \( \mu \) denotes the shear modulus and \( \lambda_m \) is the limiting network stretch. We furthermore assume the dissipation potential and the evolution law for variable \( B \)

\[
\Delta = (A + B) |\dot{\chi}| \quad , \quad \dot{B} = \frac{c}{f(\chi)} \text{sgn} \left( \|M^\text{dev}\| \right) |\dot{\chi}| \quad , \quad M^\text{dev} = M - \frac{\text{tr}(M)}{3} I,
\]

where the material constant \( A \) is the crystallization limit, being a threshold for the start of the regularity evolution and \( B \) determines its evolution depending on the stress state. Symbol \( M^\text{dev} \) denotes the deviatoric part of the Mandel stress tensor \( M = F^c \cdot \nabla \tilde{\Psi} / \partial F^c \). In the present model, the regularity evolution is favored in regions with a high value of the regularity degree which is achieved by introducing function \( f(\chi) \). Finally, the evolution of the \( F^c \) is coupled with the evolution of regularity \( \chi \) through the relationship for velocity gradient \( L^e \)

\[
L^e = \dot{F}^c \cdot F^{-1} = k \dot{\chi} \text{sgn} \left( \|M^\text{dev}\| / \|M^\text{dev}\| \right) M^\text{dev} / \|M^\text{dev}\|,
\]

where \( k \) is a positive proportionality constant. The particularity of the assumption (3) is the introduction of the signum function depending on the evolution of the Mandel stress tensor. This enables the regularity to increase during the loading phase and to subsequently decrease during the unloading phase.

3 Thermodynamic consistency and thermal modeling of SIC

The study of thermal effects starts with the consideration of the dissipation inequality which is expressed by using the Clausius-Duhem formalism

\[
D = -\tilde{\Psi} - \eta \Theta + \frac{1}{\rho_0} P: \dot{F}^c + \frac{1}{\rho_0} q_0 \cdot \nabla \Theta \geq 0,
\]

This formulation of the second thermodynamic law depends on the density in reference configuration (\( \rho_0 \)), the first Piola-Kirchhoff stress tensor (\( P \)), the entropy (\( \eta \)) and the heat flux vector (\( q_0 \)). The time derivative of the free energy now reads

\[
\dot{\Psi} = \frac{\partial \Psi}{\partial F^c} \cdot \dot{F}^c + \frac{\partial \Psi}{\partial \Theta} \dot{\Theta}, \quad \dot{F}^c = \dot{F} \cdot F^{-1} - F^{c-1} - F^{-1} \cdot F^{c-1}.
\]
such that Eq. (4) is reformulated as
\[
D = \left( \frac{1}{\rho_0} P - \frac{\partial \Psi}{\partial F^c} : F^c - T \right) : \dot{F} + M : L^c - \left( \frac{\partial \Psi}{\partial \Theta} + \eta \right) \dot{\Theta} - \frac{1}{\rho_0} \Theta q_0 \cdot \nabla \chi \Theta \geq 0. \tag{6}
\]
Inequality (6) yields two consequences: Firstly, the constitutive laws for the the first Piola-Kirchhoff stress tensor \( P = \rho_0 \frac{\partial \Psi}{\partial F^c} : F^c - T \) and the entropy \( \eta = -\frac{\partial \Psi}{\partial \Theta} \) are obtained by assuming that each expression in parentheses is equal to zero. Secondly, the dissipation includes a term due to the crystallization (\( D_{\text{SIC}} \)) and a term due to heat conduction (\( D_{\text{cond}} \)). As usual, the positivity of each term is required separately:
\[
D_{\text{SIC}} + D_{\text{cond}} \geq 0, \quad D_{\text{SIC}} = M : L^c = q_\chi \chi \geq 0, \quad D_{\text{cond}} = -\frac{1}{\rho_0} \Theta q_0 \cdot \nabla \chi \Theta \geq 0. \tag{7}
\]
Dissipation \( D_{\text{SIC}} \) implies that the regularity evolution and the corresponding thermodynamic driving force \( (q_\chi) \) have the same sign, whereas the classic Fourier’s conduction law is introduced as a solution of inequality (7 c). The thermal problem is described by the local form for the balance of energy
\[
\psi + \eta \dot{\Theta} + \Theta \dot{\eta} + \frac{1}{\rho_0} \text{Div}(q_0) = \frac{1}{\rho_0} P : \dot{F} + r_\Theta, \quad \dot{\eta} = -\frac{\partial^2 \psi}{\partial \Theta^2} \dot{\Theta},
\]
where \( r_\Theta \) is the heat source. Finally, the insertion of Eq. (5) into Eq. (8) yields the heat conduction equation
\[
c_d \dot{\Theta} + \frac{1}{\rho_0} \text{Div}(q_0) = r_\Theta + q_\chi \chi, \quad c_d = -\Theta \frac{\partial^2 \psi}{\partial \Theta^2}, \tag{9}
\]
determining the temperature change caused by the SIC. At this stage, our model assumes the heat capacity \( (c_d) \) to be constant during the process.

4 Derivation of evolution equations

The minimum principle of the dissipation potential enables us to derive the evolution law for the internal variable \( \chi \) based on assumptions for the free energy (1) and the dissipation potential (2)
\[
\chi = \text{arg inf} \left\{ L(\chi) \mid \chi \right\} = \text{arg inf} \left\{ \left( \psi + \Delta \right) \mid \chi \right\} = \left\{ \begin{array}{ll}
0, & \text{for } |q_\chi| \leq A + B, \\
\lambda q_\chi, & \lambda > 0, \\
\lambda > 0, & \text{otherwise}.
\end{array} \right. \tag{10}
\]
The derivation of this evolution equation requires the application of the subdifferential since the Lagrange function is discontinuous at \( \chi = 0 \). An expression for \( \lambda \) in the closed form is obtained by using the consistency condition \( q_\chi \dot{q}_\chi = (A + B) \dot{B} \).

For the purpose of numerical implementation, the evolution equation (10) is discretized in time by using the forward Euler method: \( \chi(t_n) = (\chi_{n+1} - \chi_n) / \Delta t \). In addition, the exponential mapping is applied for the evaluation of the current \( F_n^{\text{dev}} \)
\[
F_n^{\text{dev}} = \exp \left( k \text{ sgn} \left( M_n^{\text{dev}} \right) \right) \left( \chi_{n+1} - \chi_n \right) N_n \cdot F_n^{\text{dev}}, \tag{11}
\]
where \( M_n^{\text{dev}} \approx \| M_n^{\text{dev}} \| \) indicates the numerical approximation.

5 Numerical example

The material model for SIC is implemented into the FE program FEAP [6]. In order to illustrate its application, a uniaxial tensile test for a square sample with the dimensions 100 \times 100 \text{ mm} is chosen. The lower and the upper boundaries are constrained and a gradually increasing displacement within the range [0, 250 \text{ mm}] is applied at each of these boundaries in the normal direction. Thereafter, the specimen is gradually unloaded. The total loading time amounts to 10 \text{ s} and the time increment is \( \Delta t = 1e^{-3} \text{ s} \). The regularity of the polymer network in the starting configuration has random initial values within the range [0, 1e-3], which simulates the nuclei of the crystalline regions (Fig. 2 a). During the loading phase the regularity increases and its growth is favored in regions with the higher initial values. This is achieved by introducing function \( f(\chi) \) in the evolution of \( B \) (Eq. (2 b)). Figure 2 b shows the state of the network regularity in the final loading step. The red color corresponds to the completely crystallized regions. Subsequently, the crystalline regions decrease with a lower rate during the unloading phase (results not shown here). Finally, the material becomes entirely amorphous. The temperature distributions during the loading phase at a stretch of \( \lambda = 5.2 \) and in the last loading step at a stretch of \( \lambda = 6 \) are shown in Fig. 3. The temperature development behaves similarly to the regularity evolution: The highest temperature occurs in the completely crystallized regions, whereas the temperature in the amorphous regions hardly changes during the process.
The present work shows a thermodynamically consistent model based on the assumptions for the free energy and dissipation potential. The main advantages of the approach are: i) It enables the simulation of the formation and development of crystalline regions during loading and degradation of crystalline regions during unloading. ii) The microstructure evolution is visualized, which is not possible with experimental techniques. iii) The heat production due to the SIC and the related temperature change can be observed. iv) The model is applicable for implementation within the multiscale concept [7] in order to study the influence of crystalline regions on the effective material behavior of polymers. The proposed model is suitable for further extensions and offers a good basis for simulating effects, such as damage, crack propagation and coupling with plastic deformations. In all these cases, a comparison with additional experimental results would be necessary for a reliable determination of material parameters.

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