

Study of stochastic aspects in the modeling of the strain-induced crystallization in unfilled polymers

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The present contribution deals with the mechanical modeling of the crystallization of unfilled polymers under consideration of stochastic aspects of the process. The framework applied is thermodynamically consistent. The model involves the diameter of crystalline regions and the distance between these regions as internal variables. The necessary evolution equations are based on the assumptions for the effective free energy and the dissipation potential of a control volume. A distribution function is introduced to express the expectation value of relevant quantities. Furthermore, the numerical implementation of probability integrals is shown. The proposed concepts are of general nature and can be taken as a basis for the modeling of similar stochastic processes involving the evolution of the internal microstructure.

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1 Introduction

Strain-induced crystallization is a phenomenon in which a part of amorphous polymer chains change their arrangement and form regular crystalline regions. These changes in the microstructure influence the macrostructural properties as documented by numerous experimental investigations [1]. The statistic aspects play here an important role, which manifests through the spatial distribution of crystalline regions and the variation of their size.

2 Statistical mechanical modeling of strain-induced crystallization

Two internal variables are introduced in order to describe the microstructural processes associated with strain-induced crystallization. Variable D specifies the characteristic diameter of a crystalline region under the assumption that the circular form well approximates the natural shape of crystalline regions, whereas, internal variable r indicates the distance between two crystalline regions measured between their centers. Here, it holds that $a_{\text{RVE}} \geq r \geq 0$, and a_{RVE} represents the size of the representative volume element (RVE). The work pursues the minimal principle of dissipation potential in order to derive the evolution laws of the internal variables obeying the second thermodynamic law. According to this theory, the Lagrange function L consists of the Helmholtz energy rate $\dot{\psi}$ and the dissipation potential Δ as follows

$$L = \dot{\psi} + \Delta + \lambda_c \left(\dot{V}_1 - \bar{V}_1 \right), \quad \psi = \psi_1 + \psi_2, \quad \Delta = \Delta_D + \Delta_r. \quad (1)$$

In this assumption, the Helmholtz energy ψ is additively split into a part due to the energy of crystalline regions ψ_1 and a part corresponding to the energy of the amorphous matrix ψ_2 . These energies represent the statistical average of energies of single phases

$$\psi_1 = \langle \tilde{\psi}_1 \rangle = \int_{\Omega} f \tilde{\psi}_1 \, dz, \quad \psi_2 = \langle \tilde{\psi}_2 \rangle = \int_{\Omega} (1 - f) \tilde{\psi}_2 \, dz, \quad f(\mathbf{z}) = k_1 D^2 \exp \left(-k_2 \left(\frac{r}{a_{\text{RVE}}} \right)^{k_3} \right), \quad (2)$$

such that $\mathbf{z} = \{D, r, \mathbf{F}\}$ is the set of statistically distributed variables and $f(\mathbf{z})$ is the probability distribution function with constants k_1, k_2 and k_3 . The model furthermore assumes the Arruda-Boyce free energy for both phases $\tilde{\psi}_i(\mathbf{F})$, $i = 1, 2$, and \mathbf{F} denotes the deformation gradient. The dissipation potential Δ is also split into two contributions each of them corresponding to a single internal variable

$$\Delta_D = \langle \tilde{\Delta}_D \rangle = \int_{\Omega} f \tilde{\Delta}_D \, dz, \quad \tilde{\Delta}_D(\dot{D}) = (A_D + B_D) |\dot{D}|, \quad (3)$$

$$\Delta_r = \langle \tilde{\Delta}_r \rangle = \int_{\Omega} f \tilde{\Delta}_r \, dz, \quad \tilde{\Delta}_r(\dot{r}) = (A_r + B_r) |\dot{r}|. \quad (4)$$

Here, A_D and A_r are material parameters determining the initiation of crystallization process, and B_D and B_r regulates the change of these limits depending on load applied. A more comprehensive explanation of this type of potentials is presented in [2, 3]. Finally, the last term in the Lagrangian in Eq. (1) is introduced to stipulate the equality of the volume fraction of crystals, also called crystallinity degree (\bar{V}_1), to the corresponding experimental values (\bar{V}_1), and λ_c is the Lagrange multiplier of the equality constraint.

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3 Thermodynamic consistency and derivation of evolution equations

The thermodynamic consistency is ensured by considering the Clausius-Duhem inequality $\mathcal{D} = \mathbf{P} : \dot{\mathbf{F}} - \dot{\psi} \geq 0$, which requires the calculation of the Helmholtz energy rate

$$\dot{\psi} = \int_{\Omega} \frac{\partial f}{\partial D} (\tilde{\psi}_1 - \tilde{\psi}_2) \dot{D} \, dz + \int_{\Omega} \frac{\partial f}{\partial r} (\tilde{\psi}_1 - \tilde{\psi}_2) \dot{r} \, dz + \int_{\Omega} \left(f \frac{\partial \tilde{\psi}_1}{\partial \mathbf{F}} + (1-f) \frac{\partial \tilde{\psi}_2}{\partial \mathbf{F}} \right) : \dot{\mathbf{F}} \, dz. \quad (5)$$

Following the Coleman-Noll procedure, the Clausius-Duhem inequality transforms in the reduced dissipation inequality $q_D \dot{D} + q_r \dot{r} \geq 0$, where q_D and q_r represent the thermodynamic driving forces

$$q_D = \int_{\Omega} 2 k_1 D \exp(-k_2 r^{k_3}) (\tilde{\psi}_2 - \tilde{\psi}_1) \, dz, \quad q_r = - \int_{\Omega} k_1 k_2 k_3 r^{k_3-1} \exp(-k_2 r^{k_3}) (\tilde{\psi}_2 - \tilde{\psi}_1) \, dz. \quad (6)$$

With these relationships at hand, the Lagrangian turns into

$$L = \mathbf{P} : \dot{\mathbf{F}} - q_D \dot{D} - q_r \dot{r} + \int_{\Omega} f (\tilde{\Delta}_D + \tilde{\Delta}_r) \, dz + \lambda_c (\dot{V}_1 - \dot{\bar{V}}). \quad (7)$$

In the next step, the minimization of the Lagrangian with respect to \dot{D} and \dot{r} , the introduction of multipliers λ_D and λ_r and the calculation of the crystallinity degree yield the evolution equations

$$\dot{D} = \frac{|\dot{D}|}{A_D + B_D} \frac{q_D}{\int_{\Omega} f \, dz} = \frac{V_{\text{RVE}}}{V_1} \lambda_D q_D, \quad \dot{r} = \frac{|\dot{r}|}{A_r + B_r} \frac{q_r}{\int_{\Omega} f \, dz} = \frac{V_{\text{RVE}}}{V_1} \lambda_r q_r, \quad \int_{\Omega} f \, dz = \frac{V_1}{V_{\text{RVE}}}, \quad (8)$$

where V_{RVE} represents the volume of the representative volume element. Note that the different signs of the driving forces in Eq. (6) lead to an increasing diameter rate \dot{D} and a decreasing \dot{r} during the loading stage. The simulation of the unloading phase is discussed in our previous works [2, 3].

4 Numerical implementation

A suitable scheme for the numerical solution of probability integrals is provided in the work by Zhou and Nowak [4]. These authors apply the Gauss-Hermite formula and the probability function of the form as in Eq. (2)c with the constants $k_1 = 1/(2\pi)$, $k_2 = 1/2$ and $k_3 = 2$ for the statistical averaging of an arbitrary function G

$$\int_{\Omega} f(z) G(z) \, dz \approx \sum_{j=1}^m w_j G(z_j), \quad f(z) = \frac{D^2}{2\pi} \exp\left(-\frac{1}{2} \left(\frac{r}{a_{\text{RVE}}}\right)^2\right). \quad (9)$$

Here, m is the number of integration points, z_j are integration points and w_i weight factors. In the case that G is a polynomial of the maximum degree of $2m - 1$, the integration formula (Eq. (9)) determines the exact solution of the integral.

5 Conclusions

The present work uses the statistical averaging concept for the investigation of the effective behavior of polymers affected by the strain-induced crystallization. It follows the minimum principle of the dissipation potential, however, the elastic power and dissipation potential are averaged by using the probability function in terms of characteristic diameter and spacing between the crystalline regions. The numerical integration over the admissible set for the statistically distributed variables is performed by using the Gauss-Hermite formula. The model is advantageous in comparison with the well established multiscale strategies since it does not require an accurate definition of the RVE and of the distribution of nuclei of crystalline regions. Moreover, it is a promising solution in regard of increasing efficiency of homogenization concepts.

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