

Computational Simulation of Mesoscopic Deformation Behavior of Semi-Crystalline Polymer

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Summary

In the present study, we clarify the micro- to macroscopic deformation behavior of semi-crystalline polymer by finite element method (FEM) analysis with a homogenization method. The crystalline plasticity theory with a penalty method for the inextensibility of the chain direction and the nonaffine molecular chain network theory were applied for the representation of the deformation behavior of the crystalline and amorphous phases, respectively, in the composite microstructure of the semi-crystalline polymer. A various directional tension is given to the 2-dimensional plane-strain unit cell model of a composite microstructure. The results reveal a highly anisotropic deformation behavior caused by the rotation of the chain direction and lamella interface, which depends on the tensile direction and manifests as substantial hardening/softening in an early stage of deformation.

Introduction

To enable the wide use of semi-crystalline polymers as structural materials, characterization of their mechanical behaviors is indispensable. Semi-crystalline polymers have a very complex hierarchical structure, and their microstructures are that of a two-phase composite material consisting of crystalline lamella and amorphous layer. In the crystalline phase, molecular chains are oriented in a specific direction along with the inextensibility is enforced. Furthermore, spherulite is formed with a radial arrangement of broad thin lamellae. Although, the deformation mechanisms of the microstructure strongly depend on the directions of the molecular chains and the lamella interface, macroscopic deformation behavior still exhibits initial isotropy [1].

In accordance with the above characteristics of semi-crystalline polymer, simplified models have been proposed to reproduce the experimental results [2], [3]. In those studies, interaction laws based on the Taylor, Sachs and self-consistent models were employed to relate microscopic and macroscopic deformations. They reproduce the initially isotropic response by modeling the aggregation of randomly oriented composite microstructures. However, these models cannot be used to evaluate interactions between adjacent composite phases.

We suggest a multi-scale model based on large-deformation FEM analysis with a homogenization method [4], which can be used to evaluate the interaction between the microstructure and the heterogeneous deformation behavior on micro- to macroscopic scales. The present investigation is mainly concerned with the characteristic deformation mechanisms in single composite microstructures consisting of crystalline and amorphous phases under various directional tensions.

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Constitutive Equation

Here, in order to express the elasto-viscoplastic deformation behavior of semi-crystalline polymer, the crystalline plasticity theory [5] with the penalty method to introduce inextensibility of the chain direction and the nonaffine molecular chain network theory [6] are employed for crystalline and amorphous phases, respectively.

The total strain rate d_{ij} is assumed to be decomposed into the elastic strain rate d_{ij}^e and plastic strain rate d_{ij}^p . With Hooke's law for the elastic strain rate, the constitutive equation that relates the rate of Kirchhoff stress \dot{S}_{ij} to strain rate becomes

$$\dot{S}_{ij} = D_{ijkl}^e d_{kl}^e - F_{ijkl} d_{kl}, \quad F_{ijkl} = \frac{1}{2} (\sigma_{ik} \delta_{jl} + \sigma_{il} \delta_{jk} + \sigma_{jl} \delta_{ik} + \sigma_{jk} \delta_{il}), \quad (1)$$

where D_{ijkl}^e is the elastic stiffness tensor and σ_{ij} is the Cauchy stress.

The plastic strain rate d_{ij}^p in the crystalline phase is modeled using the crystal plasticity theory [5], with the shear strain rate $\dot{\gamma}_{pc}$ on the α th slip system expressed by a power law [7], as

$$d_{ij}^p = \sum_{(\alpha)} P_{ij}^{(\alpha)} \dot{\gamma}_{pc}^\alpha, \quad \dot{\gamma}_{pc}^\alpha = \dot{\gamma}_{0c} \frac{\tau^{(\alpha)}}{g^{(\alpha)}} \left| \frac{\tau^{(\alpha)}}{g^{(\alpha)}} \right|^{\frac{1}{m}-1}, \quad (2)$$

where $\dot{\gamma}_{0c}$ is the reference strain rate in the crystalline phase, m is the strain rate sensitivity exponent, $g^{(\alpha)}$ is the resistance to slip, $\tau^{(\alpha)} = P_{ij}^{(\alpha)} \sigma_{ij}$ is the resolved shear stress, $P_{ij}^{(\alpha)} = (s_i^{(\alpha)} m_j^{(\alpha)} + m_i^{(\alpha)} s_j^{(\alpha)})$ is the Schmidt tensor, and $s_i^{(\alpha)}$ and $m_i^{(\alpha)}$ are unit vectors along the slip direction and the slip plane normal, respectively. Here, the penalty method is employed to approximately satisfy the inextensibility of the chain direction. The corresponding constitutive equation of the crystalline phase is expressed as [8]

$$\dot{S}_{ij} = (D_{ijkl}^e - F_{ijkl} - E_c c_i c_j c_k c_l) d_{kl} - \sum_{(\alpha)} R_{ij}^{(\alpha)} \dot{\gamma}_{pc}^{(\alpha)}, \quad (3)$$

$$R_{ij} = D_{ijkl}^e P_{kl}^{(\alpha)} + (W_{ik}^{(\alpha)} \sigma_{kj} + \sigma_{ik} W_{kj}^{(\alpha)}) \dot{\gamma}_{pc}, \quad W_{ij} = \frac{1}{2} (s_i m_j - m_i s_j),$$

where E_c is the penalty constant which has a large value, and physically, it represents the chain directional stiffness. c_i is the unit vector of chain direction.

Subsequently, the plastic strain rate d_{ij}^p in the amorphous phase is modeled using a nonaffine eight-chain model [6], with plastic shear strain rate $\dot{\gamma}_{pa}$ [9], as

$$d_{ij}^p = \frac{\dot{\gamma}_{pa}}{\sqrt{2}\tau^*} \hat{\sigma}'_{ij}, \quad \tau^* = (\hat{\sigma}'_{ij} \hat{\sigma}'_{ij})^{\frac{1}{2}}, \quad \hat{\sigma}_{ij} = \sigma_{ij} - B_{ij},$$

$$\dot{\gamma}_{pa} = \dot{\gamma}_{0a} \exp \left[\left(-\frac{A\tilde{s}}{T} \right) \left\{ 1 - \left(\frac{\tau^*}{\tilde{s}} \right)^{\frac{5}{6}} \right\} \right], \quad (4)$$

where $\dot{\gamma}_{0a}$ and A are constants, T is the absolute temperature, τ^* is the applied shear stress, $\bar{s} = s_0 + \alpha p$, $s_0 = 0.077\mu/(1-\nu)$ is the athermal shear strength [10], p is the pressure, and α is a pressure-dependent coefficient. Furthermore, B_{ij} in Eq. (4) is the back-stress tensor and the principal components are expressed, by employing the eight-chain model [11], as

$$B_i = \frac{1}{3} C^R \sqrt{N} \frac{V_i^2 - \lambda^2}{\lambda} \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{N}} \right), \quad (5)$$

where $\lambda^2 = (V_1^2 + V_2^2 + V_3^2)/3$, V_i is the principal plastic stretch, N is the average number of segments in a single chain, $C^R = nk_B T$ is a constant, n is the number of chains per unit volume, k_B is Boltzmann's constant, and $\mathcal{L}(x) = \coth(x) - 1/x$ is the Langevin function. In the nonaffine eight-chain model [6], the change in the number of entangled points, in other words, the average number of segments N , may change depending on the distortion ξ which represents the local deformation of a polymeric material [6]. The simplest expression of the number of entangled points is $N = N_0 \exp\{c(1 - \xi)\}$ with $\xi = 1$ in the reference state, and N_0 is the number of segments in a single chain in the reference state and c is a material constant.

Computational Model

Figure 1 illustrates the plane strain computational unit cell model in which crystalline and amorphous phases are assumed to be stacked periodically. In order to represent micro-to macroscopic deformation behavior, we employ the homogenization method [4]. For a 2-dimensional simulation, 2 slip systems, the chain slip and transverse slip, are modeled and the coherent boundary condition is applied to the lamella interface. The angle difference is $\theta_{c0} - \theta_{i0} = 120^\circ$, as indicated in Fig.1 [2]. The macroscopically homogeneous deformations are applied by prescribing the average strain rates \dot{E}_1 and \dot{E}_2 or stress rates $\dot{\Sigma}_1$ and $\dot{\Sigma}_2$ with respect to the coordinate directions x_1 and x_2 , respectively. In order to investigate the anisotropic deformation behavior, rotation is given to the coordinates of a unit cell, y_1 and y_2 .

For a typical unit cell, which is the microscopic element of the two-phase material, a macroscopically homogeneous strain rate $\dot{E}_0 = 10^{-5}/s$ is applied. The material parameters are specified from references [2] and [6]. For the amorphous phase, $E_{Amo}/s_0 = 23.7$, $A s_0/T = 58.3$, $\alpha = 0.01$, $\dot{\gamma}_{0a} = 1 \times 10^{16}/s$, $s_0 = 71.9\text{MPa}$, $C^R/s_0 = 0.07$, $\sqrt{N_0} = 2.83$

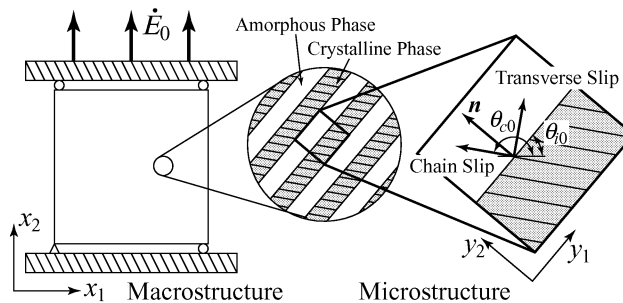


Figure 1: Computational Model for Homogenization Method

and $c = 0.33$, and for the crystalline phase, $E_{Cryst}/g^{(c)} = 125$, $\dot{\gamma}_{0c} = 1 \times 10^{-3}/s$, $g^{(c)} = 8.0\text{MPa}$, $g^{(t)} = 2.5g^{(c)}$ and $1/m = 9$ are employed with temperature $T = 296\text{K}$. Here, superscripts (c) and (t) represent chain slip and transverse slip, respectively. Furthermore, in order to reproduce sufficient inextensibility and to carry out stable calculation, the penalty constant $E_c = 10^6$ is employed.

Results and Discussion

Figure 2 indicates the relationship between (a) true stress, (b) chain direction in the crystalline phase, (c) lamella interface direction and true strain, respectively, under various directional tensions. Here, the volume fraction of the crystalline phase is fixed at 0.5. According to Fig.2 (a), deformation responses represents high anisotropy, which is attributable to preferential slip of the chain slip system in the crystalline phase which has a lower resistance of slip than other slip systems, and misalignment of lamella interface and chain directions. Chain and lamella interface directions rotate to the tensile direction as deformation increases. Due to the orientation of the chain direction in the tensile direction, the stiffness of the crystalline phase is increased by the inextensibility of the chain direction. Furthermore, the rotation of the lamella interface direction to the tensile direction causes the increase of true stress because the crystalline phase supports the deformation resistance of the overall unit cell.

In the case of $\theta_{i0} = 30^\circ$, true stress decreases at $E_2 \simeq 0.25$. When the chain direction rotates from the initial state ($\theta_c = 150^\circ$) to the tensile direction, the chain direction aligns the 135° which is the maximum shear stress direction. Then, the shear stress on chain slip rises beyond prior state while the slip resistance does not increase [2]. As a result, softening occurs in the crystalline phase.

Figure 3 indicates the relationship between mean stress in the (a) amorphous phase, (b) crystalline phase and true strain, respectively. Because each phase is assumed to be layered infinitely in a unit cell, uniform deformation occurs in each phase. For any tensile direction, mean stress in the amorphous phase exhibits a higher value than that in the crystalline phase in a later stage of deformation. In the case of $\theta_{i0} = 0^\circ$, compressive deformation along the direction normal to the tensile deformation in the amorphous phase is restricted by the hardened crystalline phase, and which causes a substantial increase of mean stress in the amorphous phase. This suggests the onset of stress concentration in a region where

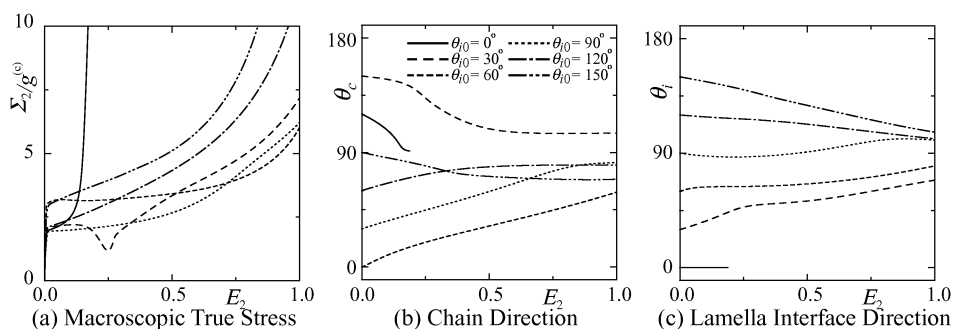


Figure 2: Deformation Behavior under Different Directional Tension

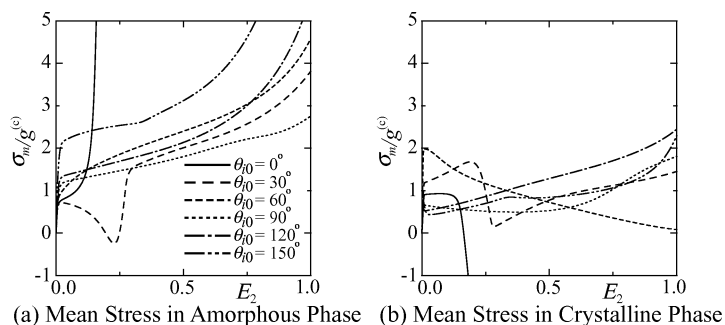


Figure 3: Mean Stress vs. True Strain

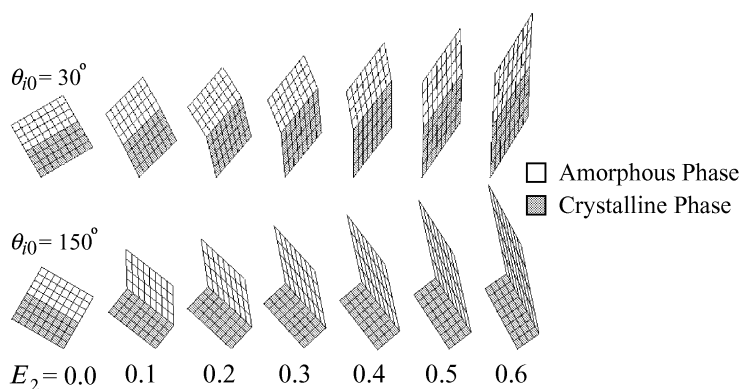


Figure 4: Deformation Behavior of Microstructure

the lamella interface normal is in the loading direction at the initial stage of deformation; this may lead to microscopic fractures. The same situation may occur in semi-crystalline polymer.

Figure 4 indicates the deformation behavior of a two-phase composite microstructure at different degrees of deformation for $\theta_{i0} = 30^\circ, 150^\circ$. These results also indicate the completely different deformation behavior. The lamella interface direction is symmetric for the tensile direction but the chain direction in the crystalline phase is nonsymmetric, which leads to a dramatic difference in plastic deformation behavior between the two cases. From these results, principal stretch direction of the microstructure of semi-crystalline polymer is differs considerably compared to the macroscopic tensile direction. This suggests that even if the macroscopic boundary condition is uniform, the deformation imposed on each composite phase is affected by the surroundings in order to satisfy the local compatibility and equilibrium.

Conclusion

A series of computational simulations clarified the characteristic deformation behavior of microstructural semi-crystalline polymer. The results are summarized as follows.

1. The microstructure of semi-crystalline polymer exhibits highly anisotropic deformation behavior due to the preferential slip deformation of the chain slip system and

the misalignment of lamella and chain directions.

2. Chain and lamella interface directions rotate to align the tensile direction as deformation increases.
3. Orientation softening occurs in the crystalline phase when the chain direction aligns the maximum shear stress direction due to the rotation caused by tension.
4. In the case that the lamella interface normal is in the loading direction, mean stress of the amorphous phase substantially increases. It causes stress concentration and leads to microscopic fractures of semi-crystalline polymer.

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