



Micromechanical simulation of molecular architecture and orientation effect on deformation and fracture of multiblock copolymers



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ABSTRACT

Multiblock copolymers containing a large number of blocks have distinct microstructures and mechanical responses that are different from that of conventional diblock and triblock copolymers. A combined simulation method that utilized MesoDyn for morphologies and probabilistic lattice spring model (LSM) for mechanical properties was adopted in this work. Simulation results show that tensile strength increases dramatically with an increase in the number of blocks within “hard-soft” multiblock copolymers. This phenomenon can be described by the occurrence of bridging and looping chain conformations in experiment. One-dimensional lamellae were built to provide an ideal morphology for studying the influence of lamellar orientation on multiblock copolymer mechanical properties. During tensile tests different failure processes were observed with two kinds of interface strength that corresponded to a difference in chain structures (diblock, triblock or multiblock copolymers). These studies provide an efficient method for correlating the complex morphologies to the mechanical response of multiblock copolymers.

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1. Introduction

Molecular architecture affects the processing and physical properties of block copolymers in a fundamental manner [1–3]. Over the last few decades, advances in synthetic polymer chemistry have unleashed seemingly unlimited strategies for producing a broad portfolio of multiblock molecular architectures [4–8]. These multiblock copolymers have shown to have distinct microstructures and exhibit different mechanical behavior compared to conventional polymers with simple architectures, which enable a diverse and expanding range of practical applications [9–12]. For example, the toughness is enhanced by modifying the molecular structure from CEC triblock copolymer to CECEC pentablock copolymers [13], where C and E denote glassy polycyclohexylethylene and semi-crystalline polyethylene, respectively. Similarly, as for more complicated three-block-type copolymer systems, mechanical properties can be tailored by varying the number of blocks and the functionality of the connector at each block–block juncture [14–16]. Aside from the experimental findings, theoretical and

computational tools [17–19] also show an advantage for exploring mechanical behaviors of multiblock copolymers. A recent study [20] shows the influence of tie and loop molecules on the mechanical properties of lamellar block copolymers by using coarse-grained molecular dynamics simulation. More specifically, they enlarged the system in the direction perpendicular to the applied stress and the buckling instability [21,22] was observed with a wavelength that depends on the strain rate [23,24]. Most of these simulation works can show good agreement with the experiment but are computationally expensive. This shortcoming is highlighted when the system becomes more complicated.

The macroscopic mechanical properties of solid media is a topic of fundamental importance with innumerable industrial applications. From this point of view, it is time-consuming and unnecessary to perform large scale computer simulations at atomic or molecular scale, even results relative to the macroscopic properties of solids offered by these precise methods are successfully compared with experimental findings. An effective prediction method with wide applicability in polymer composites is very necessary. Based on our previous work [25,26], a computationally efficient method is developed to study the mechanical response of multiblock copolymers. Notably, the fracture process can also be obtained during the simulation. In order to compare with the

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experiment, the “hard-soft” two-block-type block copolymers are studied. As for the complex morphologies of the block copolymer system, field-based approaches are more suitable for obtaining the structural evolution information in comparison to computationally expensive atomic simulations. Dynamic density functional theory embodied in MesoDyn [27,28] was adopted to simulate the meso-structures. The output from MesoDyn served as input to the lattice spring model (LSM), a discretized method for continuum elastic media often used to simulate deformation and fracture of complicated structural systems. For more details related to LSM, see ref. [29–33]. Inspired by some simulation works [20–24], we built some artificial one-dimensional lamellar structures for orientation effect study. Microstructural orientation within the continuous phase separated structure formed by multiblock copolymers has a great impact on the mechanical behavior. To study this orientation effect of polymer layers on mechanical properties, we built a one-dimensional lamellae that can be considered as a basic unit in the phase separation structure (continuous) of block copolymers. From a micromechanical point of view, the questions to be addressed in this paper include:

1. Why is Young's modulus invariant with the increase of the number of blocks in multiblock copolymers?
2. How does molecular architecture and lamellar orientation influence the mechanical failure of hard-soft block copolymers?
3. What is the impact of the interface strength on the fracture strain in block copolymers?

2. Methods

The mechanical simulation in this work can be divided into two parts: generation of morphologies and tensile testing. The phase separation structure of block copolymer is derived from MesoDyn, while the one-dimensional lamellar structure is built by an artificial method. All structures serve as input for the LSM mechanical test.

2.1. MesoDyn simulation method

The structural evolution of block copolymers was simulated by using MesoDyn, a program incorporated in Materials Studio version 6.0, commercial software from Accelrys. The MesoDyn method is based on dynamic mean-field density functional theory, in which the dynamics of phase separation can be described by Langevin. There is a one-to-one relationship between the density distribution function of the system and the external potential field. For a detailed description of the theory of the MesoDyn, see ref [27,28]. On a coarse-grained time scale, there will be a certain distribution of bead positions, according to a function $\psi(\mathbf{R}_1, \dots, \mathbf{R}_{nN})$, where $\mathbf{R}_{\gamma s}$ is the position of bead s from chain γ . Then the collective concentration of the beads s from all chains by the average of a microscopic density operator:

$$\rho_I[\psi](\mathbf{r}) = \sum_{\gamma=1}^n \sum_{s=1}^N \delta_{I_s}^K \text{Tr} \psi \delta(\mathbf{r} - \mathbf{R}_{\gamma s}) \quad (1)$$

Interchain correlations are neglected, and the system is approximated by a set of independent Gaussian chains embedded in a mean-field. The distribution functions of the independent Gaussian chains factorize exactly, and the density functional can be simplified to a product of single-chain density functionals. In this approximation, the free energy functional can be written as:

$$F[\psi] \equiv \text{Tr}(\psi H^{id} + \beta^{-1} \psi \ln \psi) + F^{nid}[\rho^0] \quad (2)$$

where the first term is the average value of the Hamiltonian for internal Gaussian chain interactions, which include the Gaussian chain structure information. The second term in the free energy functional represents the Gibbs entropy of the distribution $-k_B \text{Tr} \psi \ln \psi$. The third term is the mean-field nonideal contribution.

The key rudiment of dynamic density functional theory is now that on a coarse-grained timescale the distribution function ψ is such that the free energy functional $F[\psi]$ is minimized. So ψ is independent of the history of the system, and is fully characterized by the constraints that it represents the density distribution and minimizes the free energy functional. This constraint on the density fields is realized by means of an external potential U_I . By taking a conditional minimum, the density functional of the free energy can be obtained as:

$$F[\rho] = -\beta^{-1} n \ln \Phi + \beta^{-1} \ln n! - \sum_I \int U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} + F^{nid}[\rho] \quad (3)$$

where I stands for different kinds of monomers, $\beta = 1/kT$, n is the total number of chains, and Φ is the partition function of a single chain. The mean-field nonideal free energy functional F^{nid} with two kinds of monomers is expressed by:

$$F^{nid}[\rho] = \frac{1}{2} \iint \varepsilon_{AA}(|\mathbf{r} - \mathbf{r}'|) \rho_A(\mathbf{r}) \rho_A(\mathbf{r}') + \varepsilon_{AB}(|\mathbf{r} - \mathbf{r}'|) \rho_A(\mathbf{r}) \rho_B(\mathbf{r}') + \varepsilon_{BB}(|\mathbf{r} - \mathbf{r}'|) \rho_B(\mathbf{r}) \rho_B(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (4)$$

where $\varepsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|)$ is an interaction energy parameter between the bead of type I at r and the one of type J at r' .

In Equation (3), the density functional is simplified to a single-chain density functional

$$\rho_I[U](\mathbf{r}) = n \sum_{s'=1}^N \delta_{I_s'}^K \text{Tr}_c \psi \delta(\mathbf{r} - \mathbf{R}_{s'}) \quad (5)$$

and ψ is the single-chain distribution,

$$\psi \equiv \frac{1}{\Phi} e^{-\beta [H^c + \sum_{s=1}^N U_s(\mathbf{R}_s)]} \quad (6)$$

where Φ is the single-chain partition function,

$$\Phi \equiv \text{Tr}_c e^{-\beta [H^c + \sum_{s=1}^N U_s(\mathbf{R}_s)]} \quad (7)$$

The intrinsic chemical potentials can be derived by functional differentiation of the free energy, $\mu_I(\mathbf{r}) = \delta F / \delta \rho_I(\mathbf{r})$. On the basis of these equations, the generalized time-dependent Ginzburg–Landau theory can be established. The time dependence is described by a diffusion equation. The Langevin equations for the diffusion dynamics of the density fields are then given by:

$$\frac{\partial \rho_A}{\partial t} = M v_B \nabla \rho_A \rho_B \nabla [\mu_A - \mu_B] + \eta \quad (8)$$

$$\frac{\partial \rho_B}{\partial t} = M v_B \nabla \rho_A \rho_B \nabla [\mu_B - \mu_A] + \eta \quad (9)$$

where M is a bead mobility parameter. The Gaussian noise η satisfies the fluctuation-dissipation theorem:

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