A computational study of long range surface-directed phase separation in polymer blends under a temperature gradient

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ABSTRACT

The surface-directed phase separation phenomena of a model binary polymer blend quenched into the unstable region of its binary symmetric phase diagram was studied numerically using the nonlinear Cahn–Hilliard theory coupled with the Flory–Huggins–de-Gennes theory. Long range surface potential within a square geometry, where one side of the domain is exposed to a surface with preferential attraction to one component of a binary polymer blend under a temperature gradient in the *x*-direction, was incorporated in the model. No transition from complete wetting to partial wetting for all quench depths and/or long range surface potentials was observed. The structure factor analysis for the bulk presented an exponential growth rate at the early stage of phase separation, which slowed down at the intermediate stage with a slope of 0.33, which is in agreement with the Lifshitz–Slyozov power law. As the diffusion coefficient increased, the rate of phase separation increased accordingly in the bulk. This led to faster transition time from the early to intermediate stage within the bulk. In deeper quenches, a higher rate of phase separation was observed along with lower surface enrichment. Deeper quenches also led to the faster rupture of spinodal waves in the bulk. The process of surface enrichment, however, was continuous for all quench depths studied. The effect of different temperature gradient values on the surface enrichment rate was studied for the first time within a long range surface potential setting. No noticeable change in surface enrichment was observed for different temperature gradients.

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1. Introduction

The surface-directed phase separation (SDPS) mechanism has attracted much attention and has been intensively studied [1–9]. The presence of a surface may alter the course of phase separation by spinodal decomposition in polymer blends by breaking translational and rotational symmetry. SDPS in polymer blends at a range of conditions could lead to a variety of structural morphology. Therefore, it is important to understand the phase separation behavior of polymeric materials and also the effect of different external fields (such as surface effect and temperature gradient) that could lead to the formation of structural anisotropy in polymer blends and could help produce new products with enhanced property and functionality [10–16]. The adsorption of polymers onto surfaces, whether preferred or not, has great consequences (such as undesirable morphology development leading to adverse material mechanical and/or thermal properties) in polymer product formation. Moreover, understanding and controlling such

processes is significant and is necessary in many technological features varying from paper industry and paint formulation to pharmaceutical applications [10,11], biophysics [12–14], and nanocomposite materials [15,16].

Phase separation induced through a temperature jump (for polymer blends with a lower critical solution temperature) or quench (for polymer blends with an upper critical solution temperature) into the unstable region of the phase diagram is known as thermally-induced phase separation (TIPS). Phase separation in the TIPS method occurs via spinodal decomposition (SD); this particular process of phase separation does not require an activation energy and proceeds spontaneously in the presence of minimal concentration fluctuations or thermal noise [17].

Phase separation of polymer blends can lead to different morphologies, such as the bi-continuous interconnected structure and the droplet-type morphology when altering the system characteristics such as the composition, molecular weight and structure, film thickness, solvent, or changes in the exterior environment, including the substrate, pressure, temperature, and external fields. This offers a means to create patterns in polymeric materials by controlling the phase separation conditions in thin polymer blend films.

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The first experimental observation of surface-directed phase separation (SDPS) via spinodal decomposition was reported by Jones et al. [1]. They found that in a poly(ethylenepropylene) and perdeuterated poly(ethylenepropylene) blend there is a preferential attraction of the latter component to the surface, and that phase separation by spinodal decomposition occurs with a wavevector normal to the surface which extends for some distance into the bulk. Since then, there have been numerous experimental [2–4] and numerical [2,7–9] work published on the SDPS of polymeric materials with various polymers and processing conditions.

Krausch et al. [2] studied the SDPS in a symmetric poly (ethylenepropylene) and perdeuterated poly(ethylenepropylene) blend with off-critical concentrations. They found experimentally that the growth rate of the wetting layer grows slower if the minority phase wets the surface, while the reverse is true if the majority phase wets the surface. Furthermore, their numerical studies indicate that this growth rate follows the $t^{1/3}$ diffusive scaling law when the majority phase wets the surface. Geoghegan et al. [3,4] studied the quench depth effect of the SDPS in a deuterated polystyrene and poly(α-methylstyrene) blend. They found that the growth law of the surface wetting layer follows $t^{1/3}$ for the deepest quenches, while the growth law is logarithm with time for the shallower quenches.

Brown and Chakrabarti [5] studied numerically the SDPS in a two-dimensional model incorporating the Cahn-Hillard-Cook theory for spinodal decomposition and a free energy functional composing of the Ginzburg–Landau free energy and a long range surface interaction term. They found that the thickness of the wetting layer varies with $t^{1/3}$. Moreover, although the length scales $l(t)$ in the direction parallel and perpendicular to the surface are different, they both scale as $l(t) \sim t^{1/3}$. Puri and Binder [6] used the Cahn–Hilliard equation derived from a semi-infinite model with Kawasaki spin exchange dynamics to study the SDPS. Their numerical results confirm that there exists a concentration wave growing with wavevector perpendicular to the surface. Henderson and Clarke [7] model the SDPS in a symmetric polymer blend using a model composed of the Cahn–Hilliard–Cook theory for phase separation and the Flory–Huggins–de Gennes free energy. They concluded that to model the SDPS and to be capable of replicating experimental observations, only one length scale should be used. Yan and Xie [8,9] simulated the SDPS in a polymer system by cell dynamic system. For the case of short range potential, they found that the wetting layer grows according to the logarithmic growth law if the noise term is absent, while it will grow according to the Lifshitz–Slyozov 1/3 growth law if the noise term is present. Furthermore, the length scale parallel to the surface also obeys the Lifshitz–Slyozov 1/3 growth law as well. They also found that the thickness of the wetting layer and degree and speed of phase separation all increase with surface potential.

According to the authors' knowledge of published work, the temperature has always remained constant during the SDPS in polymeric materials. The effect of a temperature gradient on the thermal-induced and polymerization-induced phase separation processes in polymer solutions has been studied numerically by Lee et al. [18–20] and Hong and Chan [21]. The presence of a temperature gradient during phase separation by spinodal decomposition significantly alters the transient morphology being formed. Temperature gradients inherently exist during the fabrication of polymeric products, such as in the extrusion, and injection molding and blow molding processes. Moreover, temperature gradients may be introduced deliberately in the phase separation process to strategically achieve a graded morphology which is required in product specifications. In this present paper, we present and solve a mathematical model composed of the Cahn–Hilliard (CH) theory for spinodal decomposition [17] and the Flory–Huggins–de Gennes (FHdG) free energy function [22,23]. The model also

incorporates the following two external forces: (1) a surface with long range surface potential, and (2) a linear temperature gradient normal to the surface. The wetting layer formation mechanisms on the surface and morphology development and evolution are examined under different conditions. The results are presented and discussed in the form of morphology formation and surface enrichment growth rate. The effects of diffusion coefficient, quench depth, temperature gradient and surface potential on the surface enrichment are as well investigated. We hope that these investigations can give a more complete view on the SDPS and promote its practical application.

2. Model development

This section explains the model development for the thermal-induced SDPS method in a binary polymer blend, involving a long range surface potential field and an externally imposed spatial linear temperature gradient. This model is developed using the nonlinear CH theory for spinodal decomposition [17] and the FHdG free energy [22,23]. The CH theory is derived using the following continuity equation:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \boldsymbol{j} \tag{1}$$

where c is the concentration of the solvent taken as volume fraction in this paper, and $\boldsymbol{j}$ is the interdiffusional flux. The flux $\boldsymbol{j}$ is related to the gradient in chemical potential through:

$$\boldsymbol{j} = -M\nabla(\mu_2 - \mu_1) = -M\frac{\delta F}{\delta c} \tag{2}$$

where M is the concentration dependent mobility, and μ_1 and μ_2 are the chemical potentials of components 1 and 2, respectively. The total free energy F is obtained from a model that incorporates the FHdG theory with a long range surface potential:

$$F = \int \left(f(c) + \kappa \|\nabla c\|^2 \right) dV + \int V(x)c\,dx \tag{3}$$

where $f(c)$ is the homogeneous Flory–Huggins (FH) free energy [23] and κ is the interfacial energy parameter. The FH free energy is expressed as:

$$f(c) = \frac{k_B T}{\upsilon} \left[\frac{c}{N_1} \ln c + \frac{1-c}{N_2} \ln(1-c) + \chi c(1-c) \right] \tag{4}$$

where k_B is Boltzmann's constant, T is the temperature, υ is the volume of a cell or segment, N_1 and N_2 are the degrees of polymerization of components 1 and 2, respectively, and χ is Flory's interaction parameter. The $V(x)$ term represents the contribution to the total free energy for the existence of a long range surface potential along the horizontal distance x from the surface on the preferred component of the mixture [24,25].

De Gennes [22] proposed that κ is the sum of an enthalpic term relating to the effective range of the interactions and an entropic term whose origin is the configurational entropy of the Gaussian coils:

$$\kappa(c) = \kappa_{\text{entropic}} + \kappa_{\text{enthalpic}} = \frac{a^2}{36c(1-c)} + a^2\chi \tag{5}$$

In polymer blends, $\kappa_{\text{entropic}} \gg \kappa_{\text{enthalpic}}$ [22] and Eq. (5) becomes:

$$\kappa(c) \cong \frac{a^2}{36c(1-c)} \tag{6}$$

Eq. (6) can be used in the CH equation to predict phase separation of polymer blends.