Influence of Filler Particles and Clusters on Phase Separation in Binary Polymer Blends

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ABSTRACT

Motivated by recent experiments on filled polymer thin films, we study the effect of the presence of filler particles on phase separating mixtures. Using a generalized Cahn-Hilliard-Cook model, we show that the preferential wetting of one phase on the filler surface generates transient composition waves in the phase separating blends. The interference of the composition waves from different particles can stabilize the transient patterns, leading to desirable control of the morphology.

INTRODUCTION

Polymer materials are rarely used in their pure form in applications. They are often filled with additives that improve their processability and mechanical or electrical properties [2]. An understanding of the polymer-filler interaction and the ramifications for the properties of filled polymer blends is a matter of significant practical interest. Phase separation plays an important role in determining the morphology and properties of filled polymer composites, which usually are a blend of various macromolecular fluids, and additive particles. Despite the wide application of these blends, the development and the stability of the phase separating morphology are not fully understood. In particular, the interference of the filler induced composition waves remains unstudied.

The presence of a surface induces a composition wave, which consists of stripes parallel to the surface and only exists close to the surface. The morphologies in the bulk takes form of the characteristic spinodal decomposition patterns, i.e. the convoluted stripes. This surface directed phase separation has been studied both theoretically [3] and experimentally [4]. Recent numerical results show that an immobile spherical filler particle introduces *transient* target patterns in two-dimensional polymer thin films [5], and experimental results have confirmed the observations [2].

We report simulation results of the effect of filler geometry on phase separation morphology, focusing on the interference of the composition waves on the stability of two-dimensional polymer blends (polymer thin films). Theoretical analysis will be presented elsewhere [6].

THEORETICAL MODEL

We adapt the modified Cahn-Hilliard-Cook model for studying the phase separation of a binary mixture with immobile filler materials [5]. The framework is based upon mass balance of the polymeric materials. Consider a binary blend, we use the local volume fraction of one of the components ϕ as the order parameter,

$$\frac{\partial \phi}{\partial t} + D\nabla \cdot \vec{j} = 0, \tag{1}$$

where D is the diffusion constant, which is assumed to be a constant independent of location and concentration. The flux $\vec{j}$ is defined as the gradient of chemical potential μ:

$$\vec{j} = -\int d\vec{r}\nabla\mu = -\int d\vec{r}\nabla(\frac{\partial F}{\partial \phi}), \tag{2}$$

where the free energy F takes the usual Ginzburg-Landau functional

$$F(\phi) = k_B T \int d\vec{r}[\frac{1}{2}\kappa(\nabla\phi)^2 + \frac{1}{2}\alpha\phi^2 + \frac{1}{4}\beta\phi^4] \tag{3}$$

with $\alpha \propto T - T_c$ negative when the temperature is quenched below the critical temperature T_c. Combining the above equations, and rescaling the variables, we have the evolution equation for the order parameter ϕ

$$\frac{\partial \phi}{\partial t} = \nabla^2[\nabla^2\phi - \phi + \phi^3] + \sqrt{\epsilon}\eta(r,t), \tag{4}$$

where the dimensionless noise strength parameter

$$\epsilon = 2\beta/(\kappa|\alpha|), \tag{5}$$

which is inversely proportional to the quench depth. The Gaussian noise, η, satisfies

$$< \eta(r,t)\eta(r',t') >= -\nabla^2\delta(r-r')\delta(t-t'). \tag{6}$$

The existence of a surface, usually treated such that one of the components preferentially wets the surface, adds a surface energy

$$F_s = k_B T \int dA[h\phi + \frac{1}{2}g\phi^2], \tag{7}$$

where h corresponds to a first order bias between the two polymeric materials on the surface, and g relates to the number of broken bonds due to the surface. This surface energy effectively adds a boundary condition to the evolution equation

$$\hat{n} \cdot \nabla\phi + h + g\phi = 0, \tag{8}$$

as the local equilibrium condition must be satisfied. A no-flux boundary condition for the chemical potential, $\hat{n} \cdot \mu = 0$, must also be satisfied.

The equation of motion is solved numerically using a central finite difference scheme for the spatial derivative and a first-order Euler integration for the time step. In all the simulations, the two-dimensional lattice is of size 256^2, with periodic boundary conditions in both directions. We show here only results for the critical composition, i.e. $\langle\phi\rangle = 0$. The time step is chosen sufficiently small to avoid numerical instabilities. The surface equilibrium and no-flux boundary conditions are both satisfied at the filler surface. A homogeneous initial phase configuration was used for all the simulations showed here.

RESULTS AND DISCUSSIONS

In Figure (1), we show the influence of a surface on the development of the composition wave of the phase separating blend. The thermal noise is small in this simulation ($\epsilon = 10^{-5}$), corresponding to high molecular weight or a deep quench. The earlier stage of the phase separation shows a series of parallel stripes originating from the surface. As the characteristic scale of the bulk phase separation pattern coarsens, the extent of the surface induced composition wave gradually decays into the bulk phase separation pattern. The lower right corner of Figure 1 is obtained with the same conditions as in the upper right corner figure 1, except that the noise is larger ($\epsilon = 10^{-2}$), with fewer layers of stripes. The extent of the composition wave depends on the noise level or quench depth, the higher the noise, the weaker the extent of the composition wave, consistent with the findings in [5].

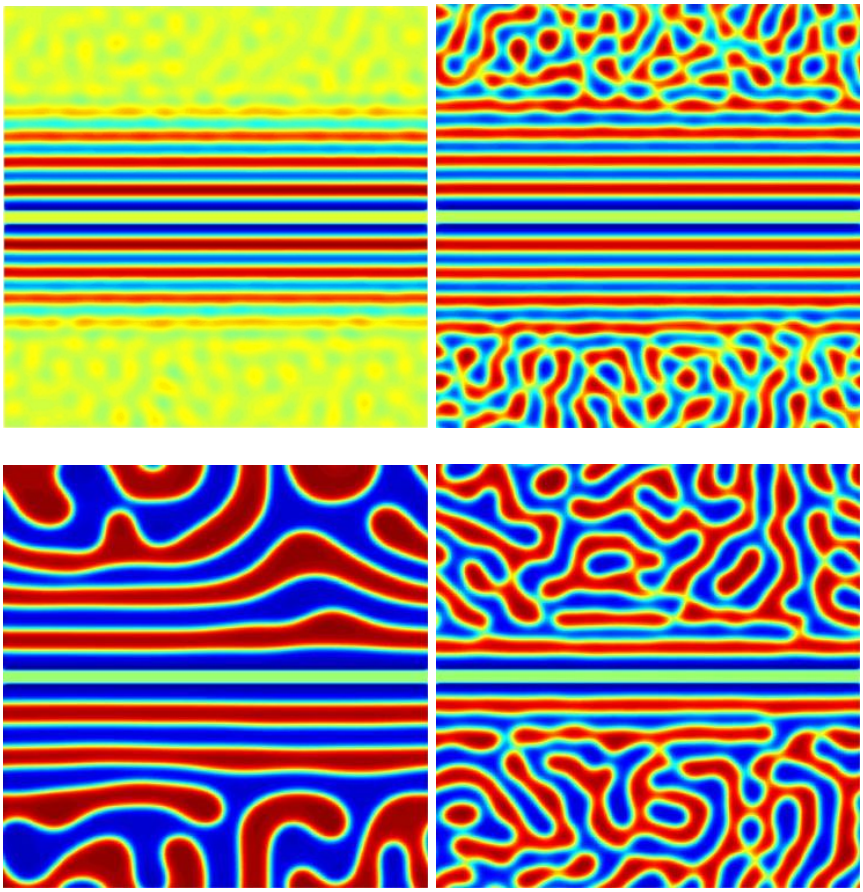

Figure 1: *Effect of a surface on phase separation in a critical composition blend, i.e. the blue phase and red phase each occupy 50% volume. Blue phase preferentially wets the surface in the center of the picture. Calculations are performed with* $\epsilon = 10^{-5}, g = 1, h = 1$, *in the reduced units. The parallel stripes fragment as the phase separation pattern coarsens. Upper left: t=24; upper right: t=56; lower left: t=400; lower right: T=56 with* $\epsilon = 10^{-2}$, *in comparison with upper right.*

There is a common tendency for particles in suspension to aggregate and form diffusion

limited aggregate (DLA) like fractal structures. Recent experiments on phase separating blends filled with nanoscale buckyballs show that the phase separation process is profoundly affected by the aggregating particles. Instead of spinodal decomposition pattern formation, the aggregate structure appears to drive the phase segregation process. Having seen the surface directed stripe patterns (Figure 1) and the single particle induced target patterns [5], it is not very surprising to see the patterns generated with a fractal cluster of particles. Figure 2 shows two early stage morphologies of the fractal cluster induced phase separation. One of the components tends to enrich the filler aggregate and that the interface tends to become increasingly rounded as the segregating coexisting phase "grows" on the aggregate. Small scale aggregate features become rounded first, followed by larger scale features.

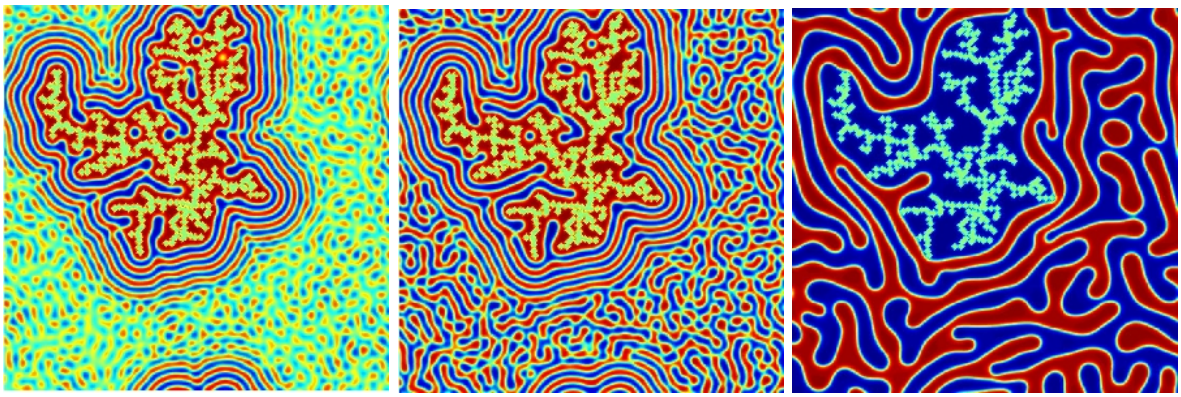

Figure 2: *Effect of a fractal cluster on a critical composition blend. Calculations are performed with* $\epsilon = 10^{-5}, g = 1, h = 1$ *in the reduced units. Blue phase wets the surface. The small scale features of the surface become rounded followed by larger scale features. Left: t=20; Center: t=28; Right: t=50.*

Figure 3 shows the structure factors as a function of time. The peak shifts to the lower wave number in time, corresponding to coarsening of the characteristic length. The large wave number (short wave length) tail corresponds to the fractal cluster pattern, thus remain unchanged in time. Rescale the wave number k by $t^{1/3}$ (Figure 3 inset), we see that the long wavelength peaks overlay on top of each other. This indicates that the structure factor, $s(k)$, reaches a universal scaling state, namely, the late stage coarsening evolves into the normal scaling state with the characteristic lengthscale $L \propto t^{1/3}$ for the conserved dynamics (or model B). A recent report on a numerical study of the late stage coarsening of the phase separation patterns with a fractal cluster also showed the same result [7].

Instead of allowing the filler particles form aggregates, it is possible and often times desirable to control the filler configurations in order to control the resulting phase separating morphology. Filler particles with non-vanishing concentration could result in striking patterns due to the interference of the composition waves from every single filler particles. Figure 4 shows a long time pattern due to an array of filler particles. The target waves induced by single filler particles interfere with each other when the waves overlap. On the upper left corner and lower right corner, the two filler particles induce target waves. The

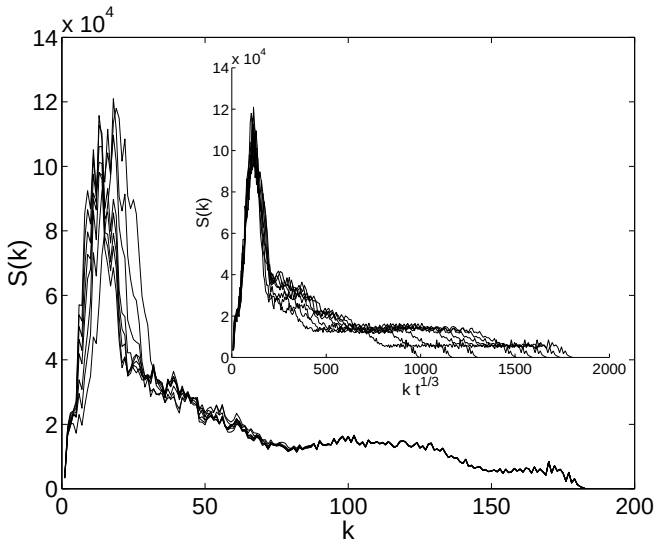

Figure 3: *Structure factors of the evolving phase separation pattern induced by a fractal cluster of filler particles. Different curves correspond to time from* $t = 10$ *to* $t = 220$ *with an interval of 30 in dimensionless units. Inset plots the same structure factors but with* k *scaled by* $t^{1/3}$.

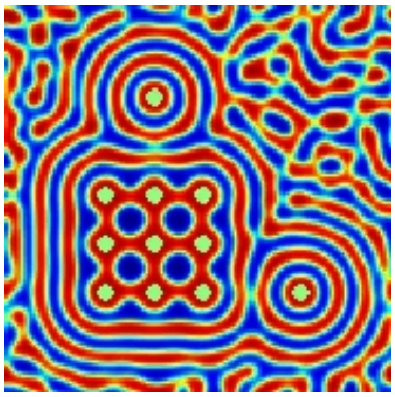

Figure 4: *Effect of a designed cluster configuration on the phase separation pattern. With* $\epsilon = 10^{-5}$, $h = -1$, $g = 1$.

array of 3×3 particles form a connected network pattern, which is stable even when in time the target patterns of the single particles are overtaken by the bulk pattern.

The interference provides a potentially very powerful means of controlling the phase separating morphology of polymer blends. By designing the location and surface properties of the filler particles, the resulting morphology and stability of the phase separating blends can be designed and controlled.

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