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Reactive phase separation: Prediction of an occlusion morphology

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Abstract

Reaction-induced phase separation occurring by spinodal decomposition is simulated in this paper. A technique developed earlier [Alfarraj A, Nauman EB. Spinodal decomposition in ternary systems with significantly different component diffusivities. Macromolecular Theory and Simulations, 2007;16:627–31.] that allows component diffusivities to be dramatically different has been extended to reactive conditions. The example system is the formation of impact polystyrene. The final morphology is a continuous polystyrene phase and a discrete rubber phase where the rubber particles contain polystyrene occlusions. The morphology is modeled for an agitated batch reactor. Simulations of a quiescent batch polymerization also give a discrete rubber phase. This is contrary to reports in the early patent literature, the difference being attributed to crosslinking of the rubber that is not considered in the current model.

Keywords: Reaction-induced phase separation; Occlusions; Spinodal decomposition

1. Introduction

Phase separation in amorphous and even microcrystalline polymer blends occurs primarily and perhaps exclusively by spinodal decomposition [2]. The necessary displacement into the spinodal region of the phase diagram can occur by mechanisms such as thermal or compositional quenching. It can also occur by polymerization of a monomer when the polymer being formed is incompatible with one or more of the other components in the system. This mechanism is known as reaction-induced phase separation (RIPS) [3,4] and has been extensively studied [5–16].

Reaction and phase separation occur simultaneously during RIPS, and the coupling of these two non-equilibrium phenomena determines the morphology of the final product. The current study treats a ternary system consisting of a monomer, a first polymer that is formed from the monomer and second polymer that is incompatible with the first polymer. The example system, consists of styrene as the monomer, polystyrene as the first polymer and a rubber, typically polybutadiene, as the second polymer. The phase diagram for this system is shown in Fig. 1, and the dotted line represents the reaction path corresponding to a batch polymerization. A typical batch process for High Impact Polystyrene (HIPS) starts with a homogeneous solution of perhaps 6 wt% rubber in styrene. To the extent that the styrene is completely polymerized, the product, HIPS, will have the same overall composition, but HIPS is a complex blend that is sometimes called a double emulsion. There is a continuous polystyrene phase, a dispersed rubber phase, and there are occlusions of polystyrene within the rubber particles. A mechanistic model for the prediction of this morphology is presented in this paper.

A known problem in the modeling of diffusion in ternary systems with significantly different component diffusivities is that an unbalance in the fluxes can lead to un-physical concentrations [17]. A numerical method was developed [1] for simulating spinodal decomposition in ternary systems with order-of-magnitude differences in diffusion coefficients. It is possible now to more rigorously investigate phase transitions such as RIPS where the component diffusivities differ by several orders of magnitude. Reaction kinetics can be incorporated to describe the consumption of one component and the production of another.

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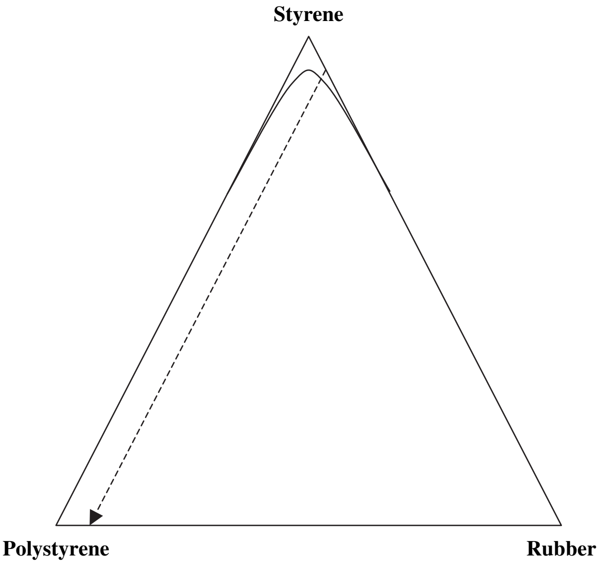

Fig. 1. Phase diagram of a ternary polymer–polymer–monomer system. The dotted line shows the reaction path.

2. Mechanism

Concentration profiles and hence the system morphology are predicted using the following equation:

$$\frac{\partial \phi_i}{\partial t} = -\nabla j_i + R_i \tag{1}$$

where ϕ_i is the volume fraction and j_i is the flux of the ith component. A reaction term R_i is added to account for the polymerization kinetics. A first order reaction, $R_i = -k\phi_i$, with rate constant k is assumed. Details to estimate the fluxes were shown in a previous publication [1]. The proportional flux method [17] is used to force a material balance. Denoting polystyrene, rubber and styrene as components 1, 2, and 3, respectively, the continuity equations for these components are:

$$\frac{\partial \phi_1}{\partial t} = \nabla \cdot D_1 \phi_1 \nabla \left\{ \begin{array}{l} (1-\phi_1)\nabla\left(\frac{\partial g}{\partial \phi_1} - \kappa_A \nabla^2 \phi_1 - \kappa_C \nabla^2 \phi_2\right) \\ -\phi_2 \nabla\left(\frac{\partial g}{\partial \phi_2} - \kappa_C \nabla^2 \phi_1 - \kappa_B \nabla^2 \phi_2\right) - \phi_3 \nabla\left(\frac{\partial g}{\partial \phi_3}\right) \end{array} \right\} + k\phi_3 \tag{2}$$

$$\frac{\partial \phi_2}{\partial t} = \nabla \cdot D_2 \phi_2 \nabla \left\{ \begin{array}{l} (1-\phi_2)\nabla\left(\frac{\partial g}{\partial \phi_2} - \kappa_C \nabla^2 \phi_1 - \kappa_B \nabla^2 \phi_2\right) \\ -\phi_1 \nabla\left(\frac{\partial g}{\partial \phi_1} - \kappa_A \nabla^2 \phi_1 - \kappa_C \nabla^2 \phi_2\right) - \phi_3 \nabla\left(\frac{\partial g}{\partial \phi_3}\right) \end{array} \right\} \tag{3}$$

The diffusion coefficients D_i can be assumed to be constant or concentration dependent. The present simulation assumes that they are constant. In these equations, g is the Flory–Huggins free energy of mixing and the κ are gradient energy parameters calculated from the following equations [18]:

$$\kappa_A = \frac{1}{3}\left(R_g^2\right)\chi_{13} \tag{5}$$

$$\kappa_B = \frac{1}{3}\left(R_g^2\right)\chi_{23} \tag{6}$$

$$\kappa_C = \frac{1}{6} R_g^2 (\chi_{13} + \chi_{23} - 2\chi_{12}) \tag{7}$$

where the two polymers are assumed to have the same radius of gyration, R_g, and χ_{13}, χ_{23}, and χ_{23} are the interaction parameters between the components.

Note that the reaction term is subtracted from the styrene equation as it reacts and is added to the polystyrene as it is formed. The rubber is assumed not to react. Grafting and cross-linking occur in the actual HIPS process, but these reactions are ignored in the current model.

3. Phase inversion and occlusion formation in agitated processes

HIPS is made commercially by a continuous process where a syrup containing about 16 wt% rubber dissolved in styrene is fed a continuous flow stirred tank reactor (CSTR) which is operated such that the continuous phase is about 30 wt% or more of polystyrene dissolved in styrene. The entering syrup is dispersed, the styrene content equilibrates between the phases, and polymerization proceeds in both phases. Adequate agitation is needed [19,20]. Polystyrene formed within the rubber particles can diffuse into the continuous phase, but this becomes increasingly difficult as the polymerization proceeds. Thus, some polystyrene formed inside the rubber particles remains inside and forms occlusions. The occlusions extend the effective volume of the rubber phase and this usually improves the impact strength of the finished HIPS. Note that the polystyrene-rich phase in the CSTR is continuous and can be modeled as well mixed. The rubber particles are not well mixed but are segregated by mass transfer limitations. Commercial processes also use multiple reactors in series. As an approximation, the rubber particle behaves as a fed batch reactor with internal concentrations that gradually evolve with time.

The situation with an agitated batch reactor is similar. The rubber phase becomes discrete and polymerization continues in both phases. The difference between the CSTR and agitated

$$\frac{\partial \phi_3}{\partial t} = \nabla \cdot D_3 \phi_3 \nabla \left\{ \begin{array}{l} (1-\phi_3)\nabla\left(\frac{\partial g}{\partial \phi_3}\right) \\ -\phi_1 \nabla\left(\frac{\partial g}{\partial \phi_1} - \kappa_A \nabla^2 \phi_1 - \kappa_C \nabla^2 \phi_2\right) - \phi_2 \nabla\left(\frac{\partial g}{\partial \phi_2} - \kappa_C \nabla^2 \phi_1 - \kappa_B \nabla^2 \phi_2\right) \end{array} \right\} - k\phi_3 \tag{4}$$

Table 1
Parameters for an agitated batch HIPS reaction

	D_i (μm^2/s)	N_i
Polystyrene (1)	10	1000
Rubber (2)	10	1000
Styrene (3)	1000	1

batch cases is the styrene concentration in the continuous phase remains constant in the CSTR case and decreases with time in the batch case.

The simulation of the HIPS particles begins immediately after their formation. Model parameters are given in Table 1. The simulation is stopped at 65% styrene, corresponding to the styrene content in the first reactor of a continuous commercial process. It also happens that the high value for $N\chi_{12}$ causes numerical difficulties at the phase boundaries due to the logarithmic term in the Flory–Huggins free energy.

The high interaction parameter between the two polymers, $\chi_{12} = 0.025$, $N\chi_{12} = 25$ reflects their substantial incompatibility. Styrene is assumed to interact equally with both polymers, $\chi_{13} = \chi_{23} = 0.5$. The initial concentrations are 26% rubber and 74% styrene in the rubber particles and 26% polystyrene and 74% styrene in the continuous phase. Polymerization proceeds in both phases (this simulation is actually for an agitated batch reactor). Fig. 2 illustrates the formation of the occluded polystyrene within rubber particles.

Fig. 3 compares experiment to theory, and the simulated morphology closely replicates the experimental results. Large rubber particles show multiple occlusions. Smaller particles show fewer occlusions until a size is reached where there are no occlusions. In such small particles, the polystyrene is

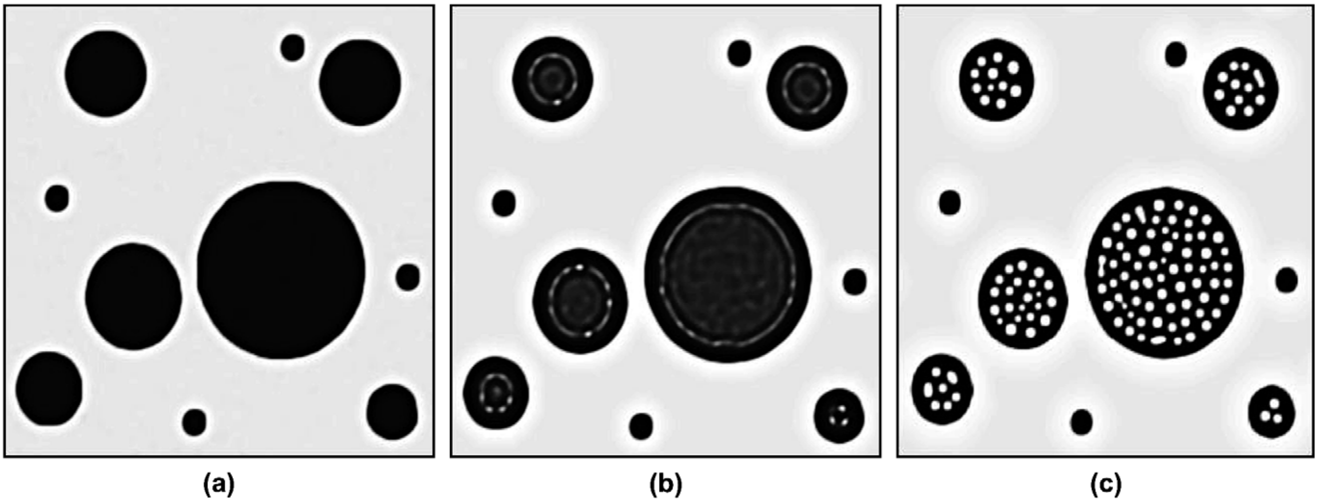

Fig. 2. Simulation of occlusion morphology (a) $\phi_{\mathrm{Styrene}} = 74\%$, (b) $\phi_{\mathrm{Styrene}} = 71\%$ and (c) $\phi_{\mathrm{Styrene}} = 65\%$.

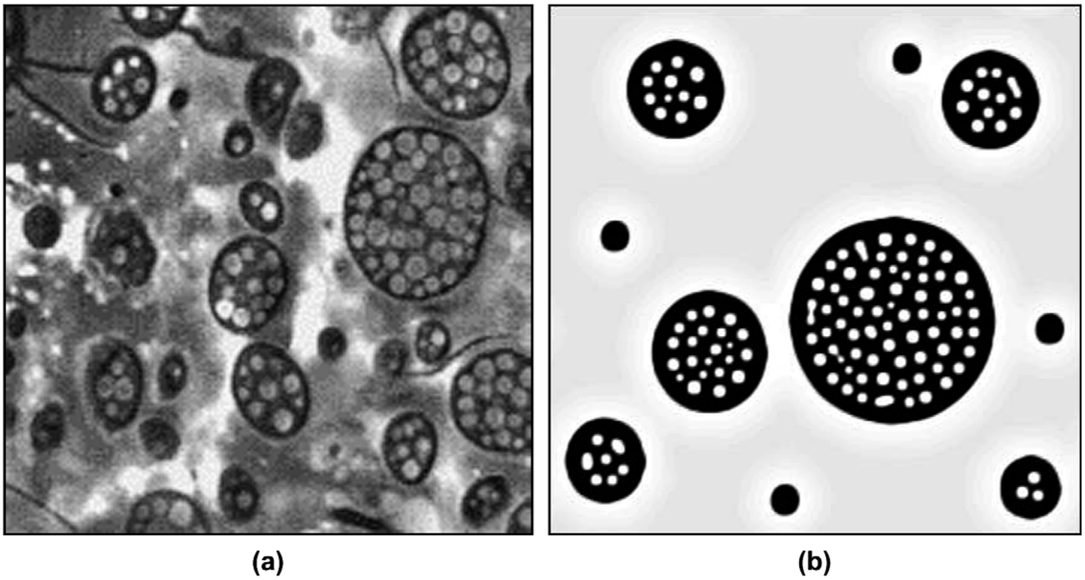

Fig. 3. (a) Experimental result adapted from Soto et al. [21]. The largest particle is about 1.5 μm in diameter. (b) Simulated occlusion morphology.

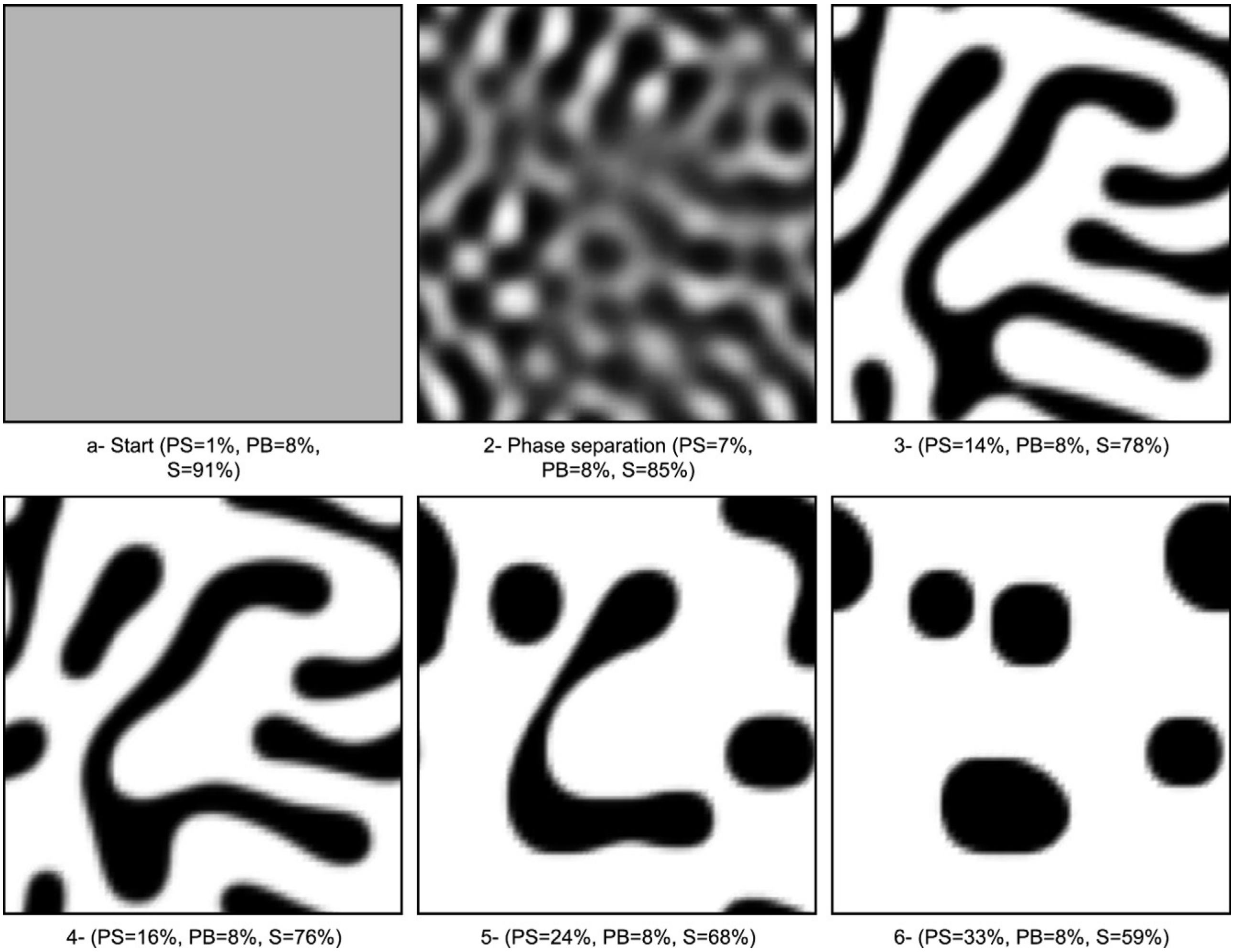

Fig. 4. Simulated morphology evolution of un-agitated batch HIPS process.

able to migrate to the preferred, continuous phase. More complicated process factors such as changes in diffusivity and cross-linking will affect the morphology but have not been considered. Thus the current model is not intended to be comprehensive but to illustrate that the formation of occlusion can now be modeled using the standard equations of nonlinear diffusion.

4. Non-agitated batch HIPS

In the early days of HIPS, polymerizations were done in agitated, batch reactors. Agitation was claimed in a patent [20]. The patent was found invalid in the United States by the standards of the time (A witch stirs her brew!), but agitation is indeed key to the formation of rubber particles. A quiescent polymerization in a test tube retains a cocontinuous rubber phase even though the rubber phase volume is low. Fig. 4 shows a quiescent batch polymerization that starts with 8% rubber, 91% styrene and 1% polystyrene. The system begins as a homogeneous mixture. The ongoing formation of polystyrene by polymerization causes phase separation, but the rubber phase is initially continuous. An initially cocontinuous structure is common in spinodal decomposition even for compositions that, upon full separation, will be particulate. The compositions simulated here evolve into a particulate morphology as polymerization proceeds. This is the expected behavior. The fact that the physical system shown in Fig. 5 remains cocontinuous without agitation is attributed to stabilization of the rubber phase by cross-linking.

5. Conclusions

Reaction-induced phase separation was simulated by a method that allows order-or-magnitude differences in the component diffusivities [1]. The example morphology was the commercially important formation of polystyrene occlusions within the particles of a dispersed rubber phase. These occlusions are not retained polystyrene-rich domains that may have existed prior to phase inversion. Instead, they form spontaneously within the rubber-rich domains because of the limited diffusion of polystyrene out of the domains. The current simulation qualitatively predicts experimentally

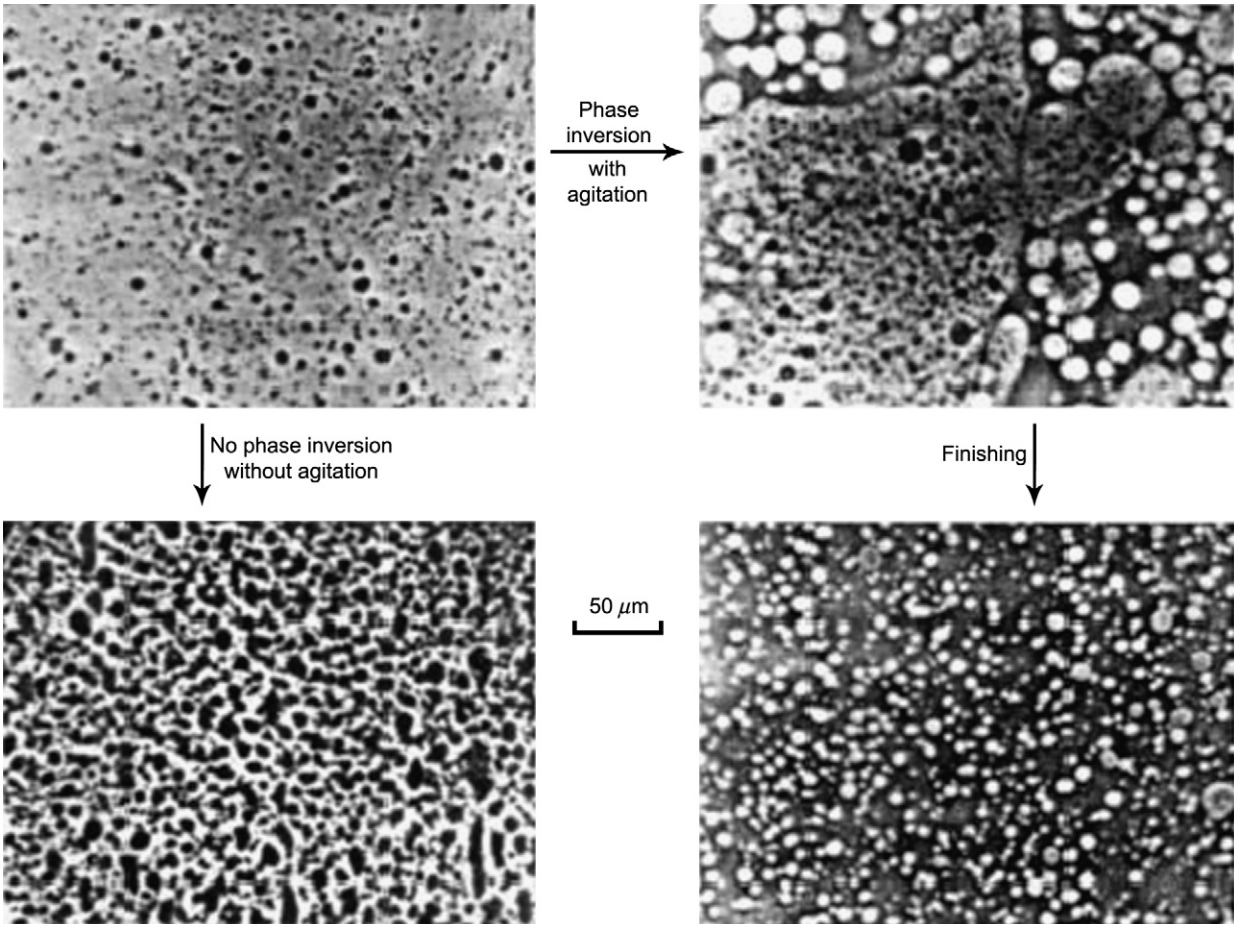

Fig. 5. Phase development in HIPS with and without agitation, adapted from Amos [19].

observed results. A more rigorous simulation could include concentration dependent diffusivities and the effects of cross-linking of the rubber phase. The failure of the simulation to predict the cocontinuous morphology of a quiescent polymerization demonstrates the need, in particular, to include the effects of cross-linking.

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