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Modelling of the High-Impact Polystyrene Morphogenesis

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Summary: High-impact polystyrene (HIPS) is a hetero-phase polymer with the so-called salami morphology. Salami morphology is formed by a continuous PS phase containing micron-sized PB domains. PB domains contain submicron-sized irregular PS occlusions. In our modeling work we addressed several weak points of Cahn-Hilliard model of HIPS salami morphology evolution. The weakest point of Cahn-Hilliard model is the inherently present Ostwald ripening destabilizing or competing with graft-stabilized domains. Two mechanism of formation of HIPS morphology are supported by the model: (i) encapsulation of graft-stabilized PS-rich domains in PB particles, and (ii) polymerization of styrene dissolved in PB-rich phase and subsequent phase separation leading to PS occlusions in PB domains.

Keywords: cahn-hilliard model; grafting; high-impact polystyrene; morphology evolution

Introduction

High-impact polystyrene (HIPS) is a hetero-phase polymeric material whose morphology can be described on two spatial levels: (i) the glassy continuous polystyrene (PS) phase with distributed particulate domains of polybutadiene (PB) of size 0.5 to 10 μm, and (ii) PB particles containing submicron domains (occlusions) of PS. This type of two-level structure is generally called ‘salami morphology’. Polystyrene inside the PB domains increases the volume fraction of rubber particles. Example of HIPS morphology is shown in Figure 1, which displays AFM (atomic force microscope) image of the material with the salami morphology. The relations between morphology and application properties of HIPS, such as impact resistance and gloss, were empirically described by Echte.[1]

The process of salami morphology evolution in a batch reactor with free-radical polymerization was experimentally investigated by Fischer and Hellman [2] and in a more detail by Leal and Asua.[3] These experimental studies provide a similar description of HIPS morphology evolution from the initially homogeneous mixture of polybutadiene dissolved in styrene: (i) phase separation at low styrene conversion resulting in precipitation of small PS domains, (ii) grafting reaction stabilizing PS domains by PB-g-PS chains, (iii) phase inversion at medium conversion of styrene resulting in continuous PS + styrene phase and particulate PB + styrene phase containing graft-stabilized PS occlusions, thus resulting in salami morphology. Fundamental studies of grafting reactions applicable to HIPS were conducted by Huang and Sundberg [4] and Estenoz et al.[5] Number of secondary processes are affecting HIPS morphology, e.g., mixing and Ostwald ripening. The most dramatic change of morphology takes place during the phase inversion at intermediate styrene conversion. The schematic drawing of morphology evolution is presented in Figure 2.

One possible approach to mathematical modeling of HIPS morphology evolution is based on Cahn-Hilliard model adopted by Nauman and coworkers [6–8] and applied to spatially 2D formation of hetero-phase polymer morphologies. Basic assumptions

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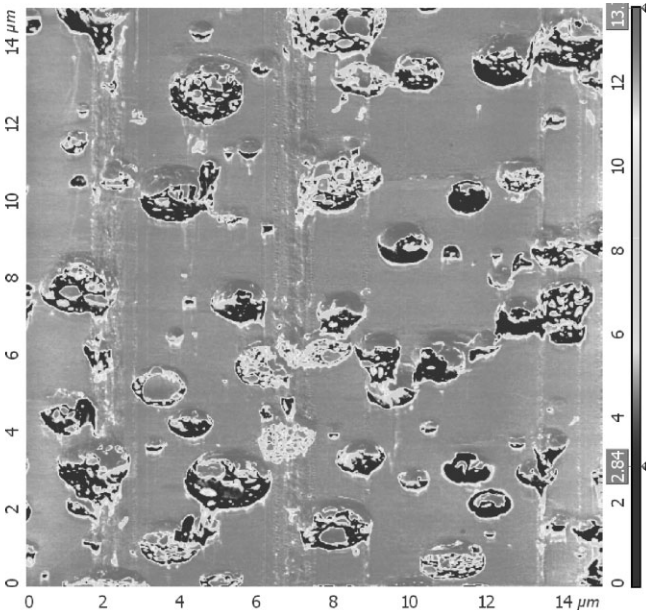

Figure 1.
The salami morphology of HIPS visualized by AFM (orange = PS, blue = PB).

of the Cahn-Hilliard model are described below in the text. As reported by Nauman and coworkers, this type of model successfully represents number of morphogenesis features, for example: (i) phase separation by the mechanism of spinodal decomposition, (ii) Ostwald ripening, and (iii) phase inversion. The computational feasibility limits the realistic selection of model parameters, e.g., chain lengths. Thus the results of Cahn-Hilliard models have to be considered as qualitative predictions of morphology evolution.

Here we attempt to develop a phenomenological model of HIPS morphology evolution by extending the Cahn-Hilliard model employed by Nauman and coworkers. Three-component model considering PS, PB and styrene (S) species is employed in our modeling. Particularly, we concentrate on: (i) nucleation of PS domains at low styrene conversion, (ii) modeling the graft-stabilized PS domains, (iii) modeling the effect of mixing on morphology, and (iv) modeling of phase inversion resulting in salami morphology. The limitations of the employed model are critically discussed and future efforts aimed on development of better models is outlined.

Mathematical Model

Cahn-Hilliard model is capable to describe formation and behavior of various multiphase systems. The fundamental assumptions of this model are: (i) concentration profiles of state variables are smooth, i.e., there are no sharp boundaries between phases, (ii) Cahn-Hilliard model consists of material balances of species, (iii) the transport of species is governed by diffusion driven by the gradient of chemical potential rather than by concentration gradient, (iv) interphase tension is locally approximated by Landau-Ginzburg functional employed as a penalty function. Cahn-Hilliard model can be combined with other equations, e.g., with Navier-Stokes equations and with the constitutive equation for the local density.

Let us now briefly describe the model in detail. In the case of classical Fick's

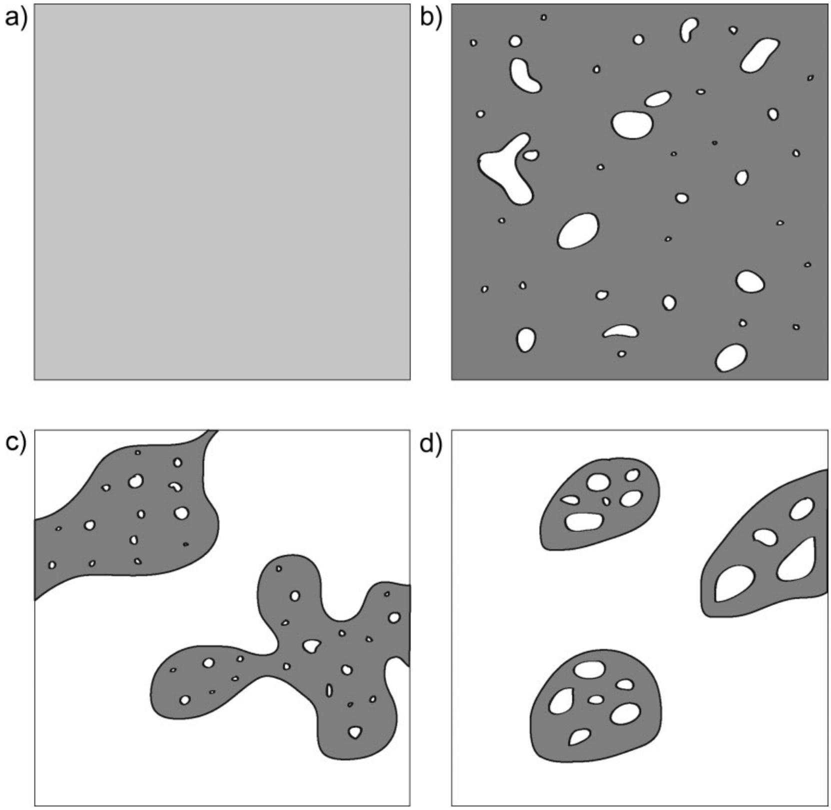

Figure 2.

Evolution of HIPS morphology. (a) homogeneous blend of styrene and PB at the beginning; (b) phase separation at approx. 3% styrene conversion – droplets of PS are dispersed through the styrene/PB phase; (c) phase inversion at styrene conversion around 20% – PS phase becomes continuous instead of styrene/PB phase; (d) resulting salami morphology of HIPS – PB domains with PS occlusions surrounded by PS continuous phase.

diffusion the gradient of concentration is the driving force of the diffusion. The Fick's law can be expressed as

$$j_i = -D_i \nabla c_i, \tag{1}$$

where j_i, D_i and c_i are the molar flux intensity, the diffusivity and the concentration of i-th species, respectively. More generally, the intensity of the diffusion flux can be defined with the gradient of chemical potential as the driving force

$$j_i = -D_i x_i \frac{\nabla \mu_i}{RT}, \tag{2}$$

where x_i is the molar fraction of i-th species, μ_i is the chemical potential of i-th component, R is the universal gas constant and T is the temperature. Let us note that eq. (2) predicts no diffusion flux between phases which are in thermodynamic equilibrium because the chemical potential of species μ_i is the same in all phases. Non-Fickian diffusion governed by eq. (2) allows to describe phase separation, i.e., species can not only smooth concentration disturbance introduced into the system as in the case of Fickian diffusion, but also amplify the concentration disturbance in the direction of phase separation.

The thermodynamics of a three-component system of PS, PB and styrene is described by the Flory-Huggins equation

$$g_{FH} = \frac{a\ln(a)}{N_A} + \frac{b\ln(b)}{N_B} + \frac{c\ln(c)}{N_C} + ab\,\chi_{AB} + ac\,\chi_{AC} + bc\,\chi_{BC}, \tag{3}$$

where g_{FH} is the scaled Gibbs free energy of mixing, a, b, and c are volume fractions of the three components PS, PB and styrene, respectively, N_A, N_B and N_C are numbers that express the sizes of the molecules, χ_{AB}, χ_{AC} and χ_{BC} are the interaction parameters between pairs of components.

The actual shape of $g_{FH}(a,b,c)$ function determines regions of total and partial miscibility of components (i.e., one and two-phase regions) and spinodal regions of spontaneous separation into two phases as described elsewhere in literature.[9] Phase separation from the initially homogeneous mixture of PB and styrene theoretically happens when the boundary of spinodal region is crossed. However, such a theoretical event is unlikely to happen and therefore nucleation events are artificially introduced in our model once the system composition crosses the boundary of binodal region.

The surface energy between the phases plays a significant role during the morphology evolution. Cahn-Hilliard model approximates the surface energy locally by introducing the penalty function known as the Landau-Ginzburg functional into the expression for the Gibbs free energy. The steep concentration gradients in the concentration field indicate the surface between phases. The gradients are multiplied by surface tension parameters and thus increase the Gibbs free energy. In a three component system the Landau-Ginzburg functional can be formally expressed either as a linear combination of squared spatial gradients $(\nabla a)^2$, $(\nabla b)^2$ and $(\nabla c)^2$ or alternatively by a formula

$$g = g_{FH} + \frac{\kappa_1}{2}(\nabla a)^2 + \frac{\kappa_{12}}{2}(\nabla a)(\nabla b) + \frac{\kappa_2}{2}(\nabla b)^2, \qquad (4)$$

where g is the generalized scaled Gibbs energy of mixing including the approximation of the surface tension. The parameters κ_1, κ_{12} and κ_2 formally represent the surface tension between phases. Values of surface tension parameters κ strongly influence the morphology evolution. Large values of parameters κ introduce high penalty to presence of interfacial surface, hence the system tries to minimize the interfacial surface during the morphology evolution.

The Cahn-Hilliard model does not distinguish between mole and volume fraction of species.[7] This rough approximation is utilized with respect to computational feasibility and does not affect the qualitative morphology predictions. Without this assumption the problem would become far more complex.

The generalized chemical potentials of species PS, PB and styrene are formally defined as:

$$\frac{\mu_A}{RT} = g + (1-a)\frac{\partial g}{\partial a} - b\frac{\partial g}{\partial b} - c\frac{\partial g}{\partial c}, \qquad (5)$$

$$\frac{\mu_B}{RT} = g + (1-b)\frac{\partial g}{\partial b} - a\frac{\partial g}{\partial a} - c\frac{\partial g}{\partial c}, \qquad (6)$$

$$\frac{\mu_C}{RT} = g + (1-c)\frac{\partial g}{\partial c} - a\frac{\partial g}{\partial a} - b\frac{\partial g}{\partial b}. \qquad (7)$$

By introducing the generalized driving force defined by eq. (2) into local material balances we obtain equations

$$\frac{\partial a}{\partial t} = \nabla \cdot \left(a\frac{D_A}{RT}\nabla\mu_A \right) + kc, \qquad (8)$$

$$\frac{\partial b}{\partial t} = \nabla \cdot \left(b\frac{D_B}{RT}\nabla\mu_B \right), \qquad (9)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(c\frac{D_C}{RT}\nabla\mu_C \right) - kc, \qquad (10)$$

for the evolution of species concentration. Symbol t here denotes time. The reaction term (kc) formally describes the consumption of monomer and polymerization. Rate constant can generally depend on time and local concentration of species, $k = k(t,a,b,c)$. Local mass balances are solved on a spatially periodic 2D domain to eliminate the effect of boundary conditions. The initial conditions are described below for each considered case study.

The system of equations (8), (9) and (10) has been processed by a finite volume method on a regular rectangular grid and integrated numerically. The size of the grid varied from 60×60 to 120×120 finite volumes.

Phase Diagram of Ternary System PS, PB and Styrene

Before we start dynamical simulations with Cahn-Hilliard model, we have to define thermodynamic phase behavior of ternary system PS, PB and styrene defined by Flory-Huggins eq. (3) introduced above. The selection of model parameters N_A, N_B, N_C, χ_{AB}, χ_{AC} and χ_{BC} in eq. (3) is seriously constrained by computational feasibility of Cahn-Hilliard system. Therefore selected values of parameters required in eq. (3) result in smooth and not very steep concentration profiles predicted by Cahn-Hilliard model on a regular non-adaptive grid of finite volumes. The second constraint imposed on selection of parameters was the requirement of initially homogeneous mixture and precipitation of (PS + styrene) phase at low conversions of styrene. The resulting phase diagram for selected values of parameters is shown in Figure 3.

The condition for binodal curves is the equality of chemical potential of components in phases I and II located on binodal curves

$$\mu_A^I = \mu_A^{II}, \tag{11}$$

$$\mu_B^I = \mu_B^{II}, \tag{12}$$

$$\mu_C^I = \mu_C^{II} \tag{13}$$

where chemical potentials of components are calculated from eqs. (5) - (7) without the Ginzburg-Landau term. Moreover, the condition $a + b + c = 1$ has to be satisfied in both phases I and II. Binodal curves border the two-phase (binodal) region, where nucleation of a placed seed disturbance can result in its growth.

In practical computation, binodal curves and tie-lines were reconstructed by varying of the volume fraction of styrene in PB-rich phase. The points on the spinodal curves were localized as inflection points of the dependence of Gibbs free energy of mixing on composition $g_{FH}(a,b,c)$ along a tie-line. A program capable of automatic construction of triangle phase diagram shown in Figure 3 has been coded and this triangle diagram serves as a guide for interpretation of results obtained with Cahn-Hilliard model.

The average composition of reaction mixture formally evolves in Figure 3 along the straight line starting from the initial homogeneous mixture containing 80% of styrene and 20% of PB and ending in a final state consisting of 80% of PS and 20% of PB. At a low conversion of styrene the system crosses a binodal curve and thus enters the binodal region, where various disturbances can cause local phase separation similarly to the growth of seeds

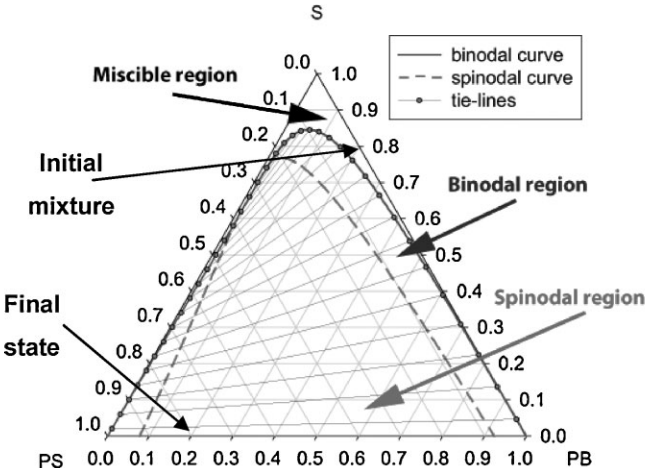

Figure 3.

The phase diagram of ternary system. The parameters of the Flory-Huggins equation are $N_A = N_B = 14$, $N_C = 4.2$, $\chi_{AB} = 0.5$, $\chi_{AC} = 0.3$ and $\chi_{BC} = 0.5$.

in crystallization. In a theoretical case (with no disturbances) the system can cross the spinodal curve and undergo a spinodal decomposition at a somewhat larger conversion of styrene. The detection of phase inversion in a spatially 2D domain of limited size is problematic because a presence of two co-continuous phases is required for phase inversion.

Grafting and Stabilization of Small PS-Rich Domains

At low styrene conversion, PS-rich domains are formed due to the growth of disturbances (i.e., nucleation) and due to the stabilization of PS-rich domains by grafted copolymers. The mechanism of creation the copolymer during the free-radical polymerization was extensively studied by Huang and Sundberg [4] and by Cavanaugh et al.[10] The grafted copolymer PB-g-PS organizes itself on the interface of PS and PB phase and acts similarly as surfactant. Moreover, grafting improves the mechanical properties of HIPS because the PS and PB phases are linked by covalent bonds.

In the Cahn-Hilliard model employed in this study we don't explicitly account for the presence of grafted copolymer as the fourth component of reaction mixture, although we don't exclude this possibility in our future efforts. The formation of grafted copolymer causes the reduction of interfacial energy parameters κ in the Ginzburg-Landau functional (4) similar to the reduction of surface tension by surfactants. There are several possible strategies how to reduce parameters κ during the simulation of HIPS morphology evolution. First, parameters κ can be reduced spatially uniformly, either empirically or in the relation to the radius of gyration. Second, parameters κ can be reduced spatially non-homogeneously according to the 'age' of phase boundary between PS-rich and PB-rich phases at a considered location. Coding of such an age-based strategy hasn't been finished yet. Third, we can reduce values of parameters κ in dependence on the size of PS-rich domains. This third strategy is driven by the goal of preserving the small PS-rich domains that become PS occlusions in PB particles during phase inversion. Small PS-rich domains otherwise disappear quickly due to the Ostwald ripening mechanism inherently present in Cahn-Hilliard model. Ostwald ripening causes the slow growth of large PS-rich domains and gradual shrinking and disappearance of small domains. Especially small PS-rich domains thus need 'a protection' against Ostwald ripening.

The example of protection of small PS-rich domains by grafting is shown in Figure 4. Here the program in the system separated into PS-rich domains and continuous PB-rich phase automatically determines the sizes of domains as shown in Figure 4b. Surface tension parameters κ are selectively lowered only for small domains. Larger particles thus coagulate and grow by Ostwald ripening and can gradually form a continuous PS-rich phase during phase inversion while smaller particles are preserved and remain in the system as shown in Figure 4a. This protection mechanism, however, only prolongs the life of small PS-rich particles, but is not capable to save them for a long time period from Ostwald ripening.

Effect of Mixing on Morphology Evolution

The agitation rate may influence the resulting morphology significantly due to the high stress inside the polymer blend of HIPS. The agitator may cause breaking of PB domains before PB chains are cross-linked. Thus the increased agitation rate in initial stages of polymerization can increase the number of PB domains.

In our phenomenological model, the shear stress was approximated by swapping and shifting of concentration field along the randomly placed line of shear during the dynamic simulation, cf. illustrative Figure 5.

The stability of small domains was enhanced by utilizing the grafting effect, i.e., by lowering the surface tension para-

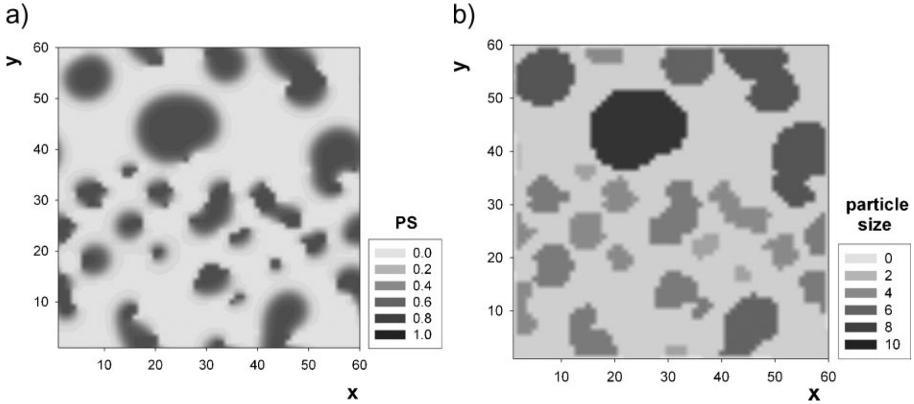

Figure 4.
Non-homogeneous stabilization of particles. (a) Small particles of PS are preserved and have enhanced surface area by lowering the surface tension parameters. (b) Corresponding binary field for determining the PS particle size.

meters κ for the whole system just before shifting or swapping the concentration field. The resulting morphology when many randomly applied shear lines were applied during the dynamic simulation is shown in Figure 6. Let us note that PB-rich domains (with no PS-rich occlusions) become smaller and more numerous due to the mixing.

Evolution of HIPS Salami Morphology During Phase Inversion

Detection of phase inversion in spatially 2D simulations is complicated due to the requirement of two co-continuous phases in a 2D domain of limited size. However, spatially 3D simulations of the phase inversion process would be very demanding for computational resources.

Phase inversion is a key stage of formation of salami morphology in a considered batch-reactor. It is not difficult to simulate the formation of PB-rich particulate system from the PS-rich particulate system as demonstrated in Figure 7.

Here Figure 7a represents the profile with graft-stabilized small domains after the phase separation at low styrene conversion. In Figure 7b corresponding to styrene conversion of roughly 50% we can observe

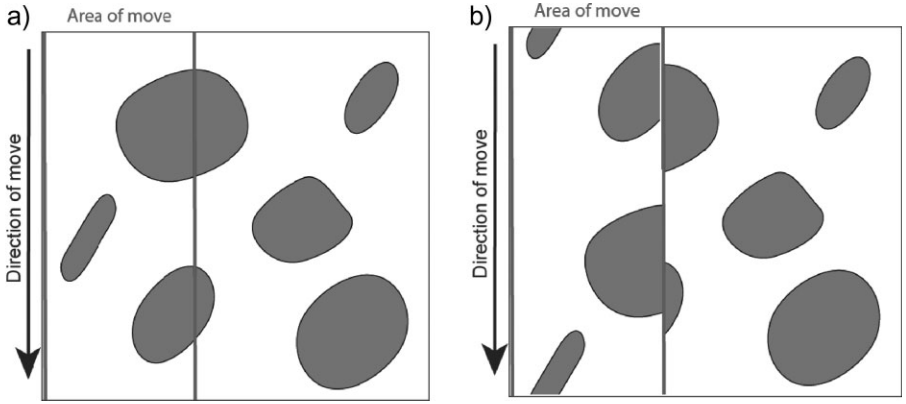

Figure 5.
Schema of shift of the concentration field: (a) before shifting, (b) after shifting.

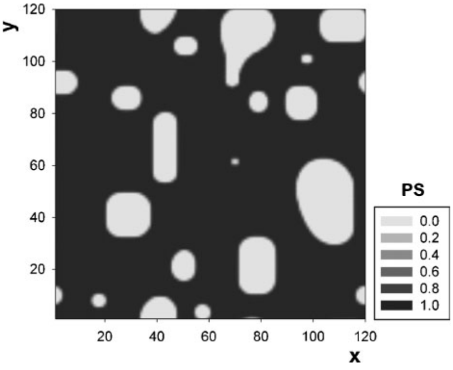

Figure 6.
PS profile after applying multiple shifts and swaps. Note that PB domains, marked by light color are smaller and more numerous.

situation close to two co-continuous phases. As the conversion of styrene increases, PB-rich particulate phase is gradually formed (Figure 7c). Let us notice, that grafting protection of PS-rich domains is weak when compared to Ostwald ripening, so that no PS-rich occlusions survived the phase inversion in Figure 7.

Experimentally observed conversions of styrene corresponding to phase inversion are around 20 to 25% for the initial mixture composition of 90% styrene +10% PB. Such a conversion at phase inversion could be obtained by adjusting the model parameters employed in the reconstruction of triangle phase diagram (Figure 3). The lever rule applied at conversions of 20 to 30% to a system containing initially 10% of PB predicts equal amounts of PS-rich and PB-rich phases and is thus in agreement with experimental observations. However, for a system starting from initial mixture containing 20% PB the phase inversion is shifted to higher conversions. Spatially 3D simulations shall result in an interval of

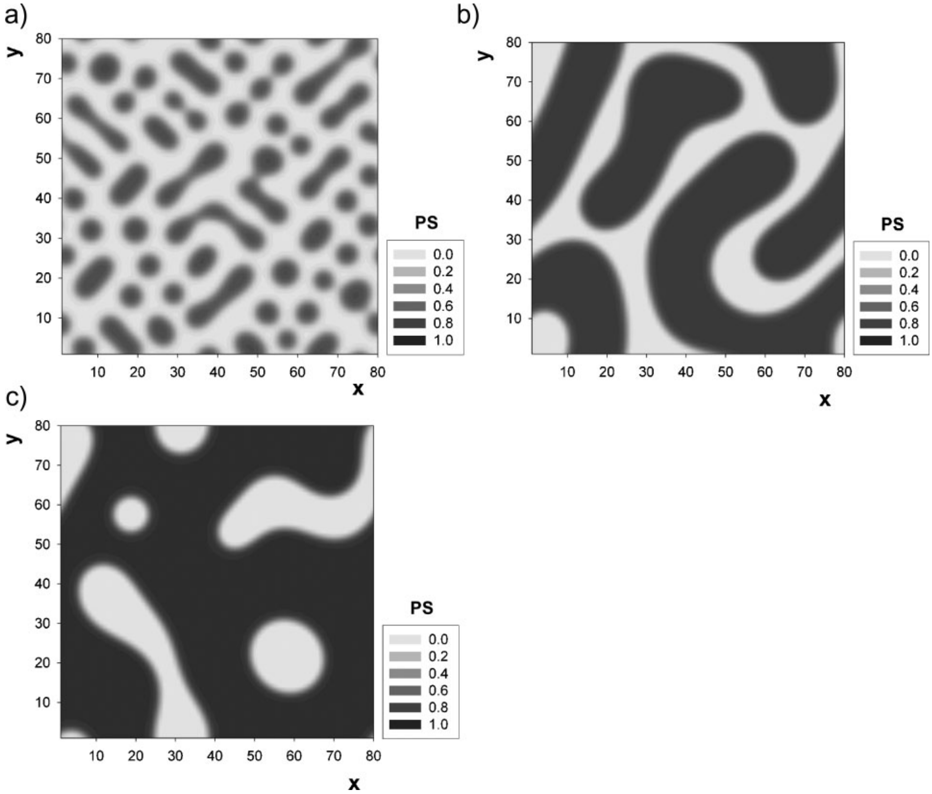

Figure 7.
Phase inversion: (a) system after the phase separation. (b) phase inversion with two co-continuous phases. (c) particulate PB-rich domains inside the PS-rich continuous phase.

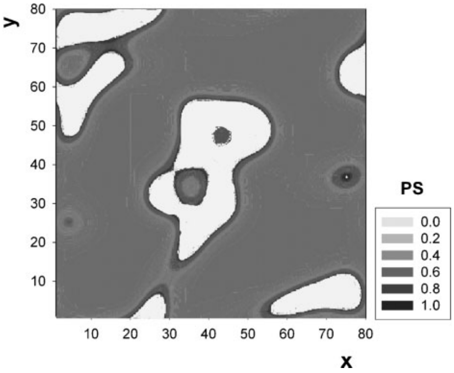

Figure 8.
Creation of PS occlusions inside the PB domains by application of the shear stress and preserving PS particles by grafting effects.

styrene conversion corresponding to two co-continuous phases.

The salami morphology of HIPS can be formed by two different mechanisms or by their combination. First, graft-stabilized PS-rich domains can 'survive' the phase inversion and will form the occlusions in PB domains of HIPS. This process is identified as a key mechanism of salami morphology evolution in experimental studies of Fischer and Hellman [2] and Leal and Asua.[3] Unfortunately, realization of this mechanism by Cahn-Hilliard model is possible only for very limited set of model parameters, cf. successful example shown in Figure 8. The realization of this mechanism depends also on the application of shear lines approximating the mixing process.

The second possible mechanism is the formation of PS occlusions from unreacted styrene dissolved in PB-rich phase just after the phase inversion. According to triangle phase diagram in Figure 3, the composition of PB-rich phase after phase inversion is approx. 70% of styrene. This styrene can either slowly diffuse out of PB phase, or can react and form PS occlusions due to phase separation going inside PB-rich domains. The presence of this second mechanism acting simultaneously is supported by our unpublished experimental data investigating HIPS morphology. Experimental evidence shows, that PS occlusions inside PB domains slowly coagulate either due to their mechanical movement or due to Ostwald ripening. Formation of salami morphology by the second mechanism is shown in Figure 9.

Conclusion

Nauman and coworkers [6,7] conducted a lot of pioneering work in modeling of evolution of hetero-phase morphologies in polymeric system. We continued in their effort by addressing several weak points of Cahn-Hilliard model of morphogenesis of

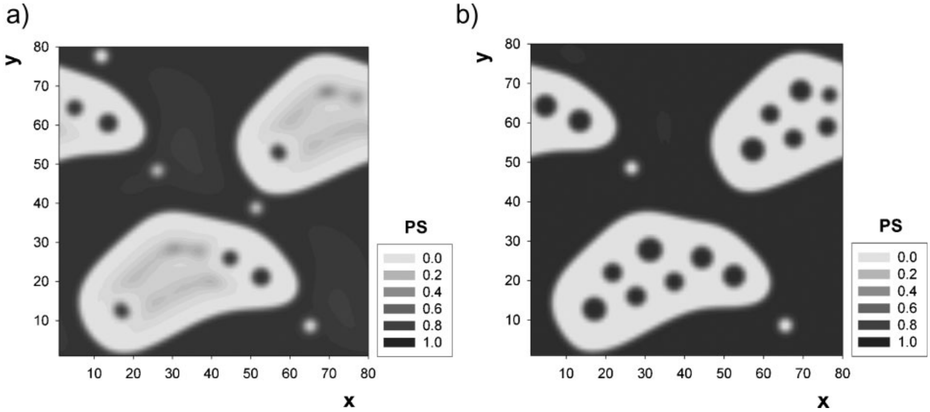

Figure 9.
Polymerization of styrene dissolved in PB-rich domains: (a) PS profile with first occlusions inside the PB domain, (b) formation of additional PS occlusions resembling the salami morphology.

high-impact polystyrene (HIPS) with salami morphology. Cahn-Hilliard model is currently phenomenological, i.e., it includes all relevant phenomena and its goal is to simulate morphology evolution in a qualitative agreement with experiments.

Ternary diagram of PS + PB + Styrene mixture with binodal and spinodal curves and tie-lines is a rich source of information enabling to estimate styrene conversion at phase separation and phase inversion and mechanism of evolution of salami morphology. It is advantageous to construct this triangle diagram before each new set of parametric studies. Our experience shows, that phase separation at low conversion of styrene proceeds more likely by nucleation rather than by spinodal decomposition.

PS-rich small domains are stabilized by grafting resulting in PB-g-PS copolymer. However, in numerical simulations based on Cahn-Hilliard model these small domains are destabilized by the inherently present Ostwald ripening. Therefore a stabilization mechanism of grafted domains has been implemented and their stability has been prolonged many times. However, still better stabilization of graft-stabilized domains (up to infinite-time stability) is required and the work on this computationally demanding fix of Cahn-Hilliard model is in progress. Two mechanism of salami morphology evolution during phase inversion are supported by our model: (i) encapsulation of graft-stabilized PS-rich domains in PB particles, and (ii) polymerization of styrene dissolved in PB-rich phase and subsequent phase separation leading to PS occlusions in PB domains.

Our future efforts shall concentrate not only on weak points of Cahn-Hilliard model, but also on the gradual development of semi-quantitative model of HIPS morphology evolution including realistic description of density, viscosity and diffusion processes, PB cross-linking and polymerization kinetics.

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[1] A. Echte, Rubber-toughened styrene polymers, *Advanced Chemistry* **1989**, *222*, 15–64.

[2] M. Fischer, G. P. Hellman, Block-graft copolymers on the basis of a styrene butadiene diblock copolymer, *Polymer* **1996**, *37*, 4547–4554.

[3] P. G. Leal, J. M. Asua, Evolution of the morphology of HIPS particles, *Polymer* **2009**, *50*, 68–76.

[4] N. Huang, D. C. Sundberg, Fundamental studies of grafting in free radical copolymerization. I.A. detailed kinetic model for solution polymerization, *Journal of Polymer Science* **1995**, *33*, 2533–2549.

[5] D. Estenoz, J. Vega, H. Oliva, G. Meira, Grafting efficiency in high-impact polystyrene by SEC combined with theoretical prediction-sec model, *Journal of Liquid Chromatography & related technologies volume 25 issue* **2002**, *18*, 2781–2793.

[6] E. B. Nauman, D. Q. He, Morphology predictions for ternary blends undergoing spinodal decomposition, *Polymer* **1994**, *35*, 2243–2255.

[7] E. B. Nauman, D. Q. He, Nonlinear diffusion and phase separation, *Chemical Engineering Science* **2001**, *56*, 1999–2018.

[8] A. Alfarraj, E.B. Nauman, Spiniodal decomposition in Ternary systems with significantly Different Component Diffusivities, *Macromolecular Theory and Simulations* **2007**, *16*, 627–631

[9] R. J. Young, P. A. Lovell, *Introduction: to polymers*, Chapman & Hall (**1991**).

[10] T. J. Cavanaugh, K. Buttle, J. N. Turner, E. B. Nauman, The study of various styrene-butadiene copolymers as compatibilisers in bulk blends of polystyrene/polybutadiene. *Polymer* **1998**, *39*, 3611–3621,