Localization of spherical nanoparticles within lamellar AB diblock copolymer melts through self-consistent field theory

Seung Ha Kim, Eric W. Cochran*

Department of Chemical and Biological Engineering, Iowa State University, Ames, IA 50011, United States

ARTICLE INFO

ABSTRACT

Here we report the results of a three dimensional hybrid self-consistent field theoretic (HSCFT) model describing the equilibrium particle distribution of spherical nanoparticles within symmetric AB diblock copolymer melts. Holding the polymer composition and morphology fixed, we consider a comprehensive parameter space comprised of the Flory interaction parameter describing interactions between B segments and the particle surface compared to the segment–segment interaction parameter (χ_{BP}/χ_{AB}), the particle volume fraction (ϕ_P), and the ratio of the particle diameter to block copolymer domain spacing (d_P/d_{AB}). Analysis of the free energy over this parameter space yields phase diagrams showing the conditions under which particles segregate to the intermaterial diving surface (IMDS) or the center of the domain. Interestingly, w e predict a particle concentration-dependent "reentrant" phase transition in which particles move from the domain interior, to the IMDS, and back as ϕ_P increases. These results are interpreted as a subtle consequence of the competition between enthalpic polymer–particle interactions and the chain packing frustration imposed by the particulate inclusion. These results are consistent with recent experiments on block copolymer nanocomposites.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer nanocomposites (NCPs), mixtures of nanoscale filler particles and polymers, have been a topic of increasing importance over the past decade. As a consequence of the enormous surface area of the particle/matrix interface, synergistic interactions arise with potential applications exploiting the unique electrical [1], optical [2], or mechanical properties [3,4] characteristic of these materials. Fundamental to the development of NCP technology is the ability to control the particle distribution [4]; for this reason researchers have turned to block copolymer (BCP) matrices due to the ability of microphase separation to selectively direct the localization of the nanoparticles, allowing the properties of the composites to be tailored by molecular design [5]. Block copolymers tend to organize themselves into exquisitely ordered periodic mesophases [6], and the positioning of particles within meso-domains can be dictated, in principle, by controlling the preference of the particle for one domain over the others.

In the simplest case, the matrix is an AB diblock copolymer, which in the absence of particulate inclusions typically assumes one of essentially four periodic equilibrium phases, dictated by the fraction of A segments (f_A) and the Flory segment–segment inter-action parameter (χ_{AB}) [7–11]. The introduction of nanoparticles is accompanied by considerable complexity. The least complicated possibility has to date received the most attention, i.e. mono-disperse spherical nanoparticles, introducing at the minimum 5 additional parameters:(**1**) the particle volume fraction (ϕ_P), (**2**)the ratio of particle size (d_P) to a characteristic dimension of the matrix, e.g. the BCP domain spacing (d_{AB}), (**3**)particle–particle interactions, (**4**) particle-A interactions, and (**5**) particle B-interactions. In prac-tice a reduced set of only 3 parameters should dictate phase behavior: native particle–particle interactions are so strong as to preclude dispersion in favor of aggregation, and in experiments particles are generally passivated through the attachment of ligands chemically similar to A (or B) segments [5,12]; this effec-tively eliminates particle–particle interactions and renders the particle surface neutral to A segments, yielding a single domain selectivity parameter χ_{BP} which characterizes enthalpic interac-tions between the particle surface and B segments. Even when $\chi_{AP} \neq 0$, so long as macrophase separation is not an issue one can define $\chi_{AP}^* = \chi_{AP} - \chi_{AP}$ as a reference state such that $\chi_{AP}^* = 0$ and $\chi_{BP}^* = \chi_{BP} - \chi_{AP} > 0$.

As a consequence the particle distribution becomes a function of the canonical parameter set f_A, χ_{AB}, χ_{BP}, ϕ_P and d_P/d_{AB}. Formulated

* Corresponding author.
  E-mail address: ecochran@iastate.edu (E.W. Cochran).

in this manner, nanospheres will tend to distribute to the A domain interior (DOM) or the intermaterial dividing surface (IMDS) subject to these parameters; a number of experimental and theoretical approaches have been conducted over the years to elucidate the conditions favoring these two extreme states.

Of the numerous experimental studies, Lauter-Pasyuk et al. performed the neutron specular reflection to study the morphology of iron oxide nanoparticles in the lamellar phase of a symmetric polystyrene-polybutylmethacrylate (PS-PBMA) diblock copolymer. They found that the preference of the particle position in the diblock copolymer matrix is dependent on the size of nanoparticle, such that small particles exhibited IMDS placement while larger particles are concentrated in the center of the PS domain [13,14]. Bockstaller et al. reproduced this behavior using thin films of poly (styrene-b-ethylene propylene) embedded with mixtures of aliphatic-coated gold (small particles, IMDS) and silica nano-particles (large particles, DOM) [15]. This behavior was rationalized based on entropic effects according to the particle size (d_P/d_{AB}), but the enthalpic interactions (i.e., by changing the nature of the ligands, χ_{BP}) were not investigated. To explain the enthalpic inter-action between nanoparticles and block copolymers, Chiu et al. synthesized particles coated with controlled mixtures of A and B oligomers at fixed particle size and concentration, demonstrating directly how IMDS vs. DOM placement can be tuned through χ_{BP} [12]. Kim et al. showed similar behavior by controlling the PS ligand graft density on gold nanospheres in a lamellar poly(styrene-b-vinyl pyridine) (PS-PVP) block copolymer; here the Au particle surface prefers the PVP domains, and thus the PS graft density directly influences χ_{BP} [16–19]. In summary, experimental studies show that entropy-dominated NCPs, i.e. with small particle size, favor IDMS positioning whereas enthalpically dominated systems favor DOM positioning.

In parallel, various theoretical approaches have been conducted to understand the morphology of nanocomposites according to changing the physical and chemical properties of nanoparticles, e.g., Monte Carlo [20], molecular dynamics [21,22], and dissipative particle dynamics [23]. Huh et al. study a phase diagram of nano-composites with particles using Monte Carlo simulation [24]. These methods are able to illustrate the kinetics of the evolution of the nanoparticle distribution within the block copolymer, however it is difficult to discern the equilibrium structure of the system. On the other hand, statistical field theories provide no kinetic data but can provide an effective way of studying the ordered phases of nano-composites at equilibrium [25]. There are many methods for statistical field theory, like an analytical method, self-consistent field theory (SCFT), and a nonlocal density functional theory (DFT). For an analytical approach, Pryamitsyn and Ganesan have per-formed the density distribution of particle calculation using the strong-stretching theory (SST) with several approximations [26].And using DFT, Cao and Wu predict the preferred position of particles with nanocomposites like experiments [27]. In particular, self-consistent field theory (SCFT) has been remarkably successful in the prediction of equilibrium mesophases in various heteroge-neous polymer systems [8,10,25,28,29]. Moreover, field theoretic approaches readily allow the decomposition of the free energy into entropic and enthalpic terms; thus applied to BCP nanocomposites, SCFT can be used to quantify how entropic and enthalpic terms control the phase behavior of the nanoparticles in the matrix [4]. However, the strong excluded volume interaction associated with solid particles in a polymer matrix complicates the application of SCFT to these systems. Two approaches to this problem have pre-dominated the literature. In 2000 Thompson et al. described the system through implementing a density functional theory (DFT) to describe the nanoparticles in conjunction with the use of SCFT for the BCP matrix [30]. Although ordered phases of the

nanocomposites are well explained by the theory, the interaction between the polymers and the particles is described by the mean field approach, in which the polymers are effectively excluded from the average particle positions [31].

To improve the excluded volume interaction of nanoparticles and polymers, Matsen introduced the use of "cavity" functions to explicitly exclude the polymer segments from areas prescribed to be occupied by nanoparticles; this approach was first used to model block copolymer thin films confined between two planar "walls", i.e., the polymer/substrate and polymer/air interfaces [32]. In this study, the confined surface density profile at the interfaces was described by a continuous function $\rho_P(\mathbf{r})$, which assumed a value of 1 in the "wall" regions and 0 in the polymer film. Polymer-interface enthalpic interactions are encapsulated at non-limiting values of $\rho_P(\mathbf{r})$ through the introduction of a Flory-like binary interaction term of the form $\chi_{BP}\rho_B\rho_P$. Application of the incompressibility constraint enforces $\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) + \rho_P(\mathbf{r}) = \rho_0$ throughout the simulation volume. Since the specification of ρ_P is arbitrary, this method allows both polymer thin film calculations as well as polymer systems with particulate inclusions of arbitrary shape and size. Numerous case studies involving both BCP thin films and BCP nanocomposites have appeared over the past decade based upon this approach [33–36].

A limitation of the "cavity" method is that once prescribed, ρ_P is a static function and thus particle coordinates are fixed — i.e., there is no direct method to simultaneously equilibrate both polymer and particle degrees of freedom. As a first attempt at circumventing this restriction, Sides et al. introduced a hybrid SCFT (HSCFT) method which retains the nanoparticle positions as explicit degrees of freedom to calculate a coupling between the nanoparticles and the polymers [37]. Here a two-dimensional simulation was employed in which an ensemble of cylindrical nanoparticles were positioned randomly within the simulation area, and SCFT was used to calculate the nearest saddle-point for this configuration. Equilib-rium particle positions were estimated using a steepest-descent scheme (i.e., Brownian dynamics with no stochastic term), with additional SCFT saddle-point calculations between particle moves until the polymer morphology stabilizes. Using this method these researchers were able to reproduce experimentally observed phase transformations in pseudo-analogous experimental systems with spherical nanoparticles in lamellar and cylindrical BCP phases. Due to the computational complexity of these simulations, however, calculations were constrained to 2D and more sophisticated algo-rithms such as force-biased Monte Carlo particle moves were impractical. Nonetheless this study was instrumental in validating the application of the "cavity" method to experimental systems, highlighting that not only does the BCP matrix direct the assembly of the nanoparticles, but also that the nanoparticle excluded volume can also have a strong effect on the BCP morphology.

Recently, Matsen and Thompson calculated the particle distri-bution including the explicit interaction between spherical nano-particles and block copolymer in a lamellar phase, to investigate the dependence of the surface affinity and diblock composition using the hybrid SCFT method, which is based on the cavity function like Sides et al. to describe the particle−polymer interface, in the dilute limit for the nanoparticles, so that particle/particle interactions are negligible [31]. They fixed the particle position at a specific point in the nanocomposite and also simplified the system to use an axial symmetry in the z axis with reflecting boundary conditions for reducing the computational time, allowing the expansion of the system from 2D to 3D as compared to the Sides study. In this study a continuous particle distribution was inferred from the free energy as a function of the particle position with respect to the IMDS. Neutral and partially selective particles were considered for two different particle sizes and 3 nearly symmetric polymer