Computational Design of Polymer Nanocomposite Coatings: A Multiscale Hierarchical Approach for Barrier Property Prediction

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In the development of polymer nanocomposites (PNCs), computational prediction of material properties is of great advantages in achieving rational and cost-effective design. This paper introduces a new multiscale hierarchical approach specifically tailored for PNCs property prediction. Due to its distinct features of generality and comprehensiveness, the introduced methodology outperforms most existing computational methods in this area. By this methodology, a wide range of PNCs containing any-shaped nanoparticles dispersed in a thermoplastic or thermoset polymer matrix can be thoroughly investigated for multiple property prediction. Furthermore, a reliable prediction is promoted by a systematic consideration of the intrinsic multiscale hierarchical structure of PNCs. Most importantly, an effective integration of different methods and theories at individual scales offers unique opportunities for gaining in-depth scientific understandings on the molecular structural origin of macroscopic property enhancement.

Introduction

Polymer nanocomposites (PNCs) are promising coating materials as they may significantly enhance the properties or even introduce new functionalities in the final coating products. Although scientific and technological advances have been made in this field over the past decades, it is widely recognized that cost-effective design of PNCs for the best possible coating performance remains as a very challenging task.1–3 A major reason is the lack of fundamental understandings on this type of nanostructured composite materials. Due to the structural complexity of PNCs, it is extremely difficult to derive and validate quantitative correlations between their composition, processing, structure, property, and performance. Moreover, because of the design complexity and the restrictions on product development cost and time, a thorough investigation of the huge design space for the best design solution identification becomes a formidable task.

Computer modeling and simulation is widely accepted as a tool for effective design of nanomaterials,4 since it can help generate new scientific understandings on material properties and allow virtually any number of “free” in silico experiments.5,6 Note that a critical task for effective computational design is how to ensure the reliable predictions of material properties. Among various important coating properties, this work will focus on the barrier property that directly determines the corrosion prevention performance when the coating is applied on a metal surface.

Extensive computational efforts have been devoted to the prediction of the permeability of gases through PNC coatings, which is a quantitative indicator of the barrier property. Generally speaking, the known methods for the prediction can be divided into two groups: the analytical and the numerical methods. Choudalakis and Gotsis thoroughly reviewed the analytical permeability models,7 which include two well-known equations proposed by Nielsen and Cussler et al.,8,9 as well as their extended versions. A common feature in those models is the calculation of permeability as a function of the volume fraction, aspect ratio and orientation of nanoparticles. Although those simple models can provide a quick estimation of the gas permeability of PNC coatings, they are only applicable to some ideal cases, where the platelet particles have a regular and uniform shape (i.e., rectangular or circular) and form a regular array in space.

To investigate the nanocomposites containing realistic variable-size complex-shape nanoparticles, a few finite-element-based numerical methods (FEM) were proposed.10–14 By using FEM, various morphological imperfections typical for actual nanocomposites (including incomplete exfoliation, platelet disorientation, and agglomeration) can be fully taken care of.

According to Choudalakis and Gotsis,7 the analytical models and FEM listed above cannot provide an accurate enough prediction. This is because they assume that (i) the physical characteristics of the polymer remain unchanged after adding inorganic nanoparticles and (ii) the permeability is independent of the nature of the penetrant molecules. In reality, the presence of nanoparticles can lead to a considerable molecular level transformation in the polymer matrix, especially in the vicinity of the nanoparticles.11 Recently, Thornton et al. demonstrated that the same coating material could give significantly different permeability for different penetrant molecules.15

Since molecular level structure and interactions are critical in determining the overall coating performance, molecular-scale modeling and simulation methods for permeability prediction have attracted considerable attention as well, which include molecular dynamics (MD)16–20 and Monte Carlo (MC) methods.21–25 These methods are computationally very expensive, which restricts their application to the characterization of the fundamental transport processes in a nanoscale structure only.

In recent years, multiscale modeling and simulation methods are highly valued for PNCs property prediction. The methods are capable of simultaneously taking the structural properties at different scales into account, thus giving more holistic and comprehensive understandings of the material and more reliable predictions of the properties than any monoscale effort does. Sheng et al. developed a multiscale micromechanical model for the prediction of the mechanical properties of polymer–clay nanocomposites.26 Quantitative geometric features of nanoparticles (extracted from experimental measurements), together with the estimates of silica lamina stiffness obtained from MD

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Multiscale Hierarchical Modeling and Simulation

The morphological complexity of PNCs arises from their multiscale hierarchical structure, which is especially true for polymer-clay nanocomposites. This structural hierarchy is shown in Figure 1. At a length scale of millimeter and beyond, the high aspect ratio particles are randomly dispersed in a polymer matrix. At a micrometer length scale, the clay particle structures are a mix of the exfoliated clay sheets of nanometer-level thickness and the intercalated clay sheets with interlayer galleries of nanometer-level height. At a nanometer scale, the polymer chain configurations near a clay sheet surface and in a gallery space are significantly different from those in the bulk matrix. To gain a holistic understanding on the material behavior of PNCs and to predict accurately their properties, the development of a multiscale hierarchical approach is essential.

In this work, a general multiscale modeling and simulation framework will be introduced for the reliable prediction of properties of PNCs. In this framework, multiple properties including barrier and mechanical can be evaluated with a full consideration of the intrinsic multiscale hierarchical structure of PNCs. The framework also allows the investigation of various types of PNCs with either symmetric or asymmetric nanoparticles dispersed in a thermoplastic or thermoset polymer. The remaining part of this paper is organized as follows. The need for a multiscale computational method is discussed at the outset, which is followed by a general multiscale modeling and simulation framework tailored for PNCs property prediction. After that, detailed methods at individual length scales as well as those for integrating information across different scales will be presented. Finally, the attractiveness of the developed methodology will be demonstrated through detailed case studies.

Figure 1. Hierarchical morphology of polymer–clay nanocomposites.

Figure 2. Multiscale hierarchical modeling framework.

The hierarchical framework involves two levels of models at macro- and microscales, which are interacted through a coupling block. The complete domain $\Omega$ of a macroscopic coating sample consists of $N$ subdomains:

$$\Omega = \bigcup_{j=1}^{N} \Omega_j$$

where subdomain $\Omega_j$ represents the $j$th phase of the nanocomposite material.

Microscopic models are responsible for generating microscale structures in each distinct phase, which can be generalized as

$$\tilde{Y}_j(\tilde{t}_{i+1}) = \Gamma_j(\tilde{Y}_j(\tilde{t}_i),\delta \tilde{t}, \tilde{X}(\tilde{t}_i)) \quad j = 1, 2, ..., N$$

where $\tilde{Y}_j(\tilde{t})$ is the microscale system state (structure) in phase $j$ at the time instant $\tilde{t}_i$, $\delta \tilde{t} = \tilde{t}_{i+1} - \tilde{t}_i$ is the time interval used in microscale system description; and $\tilde{X}(\tilde{t}_i)$ is a set of system input variables that include various material parameters, such as the type and size of nanoparticles, the polymer molecular weight distribution, the functional group distribution, etc. Function $\Gamma$ is a black-box time-stepper, which uses $\tilde{Y}_j(\tilde{t}_i)$ and $\tilde{X}(\tilde{t}_i)$ as the inputs, evolves over the time interval $\delta \tilde{t}$ and produces $\tilde{Y}_j(\tilde{t}_{i+1})$. The microstructural structure evolution described by function $\Gamma$ can be realized through molecular simulations, such as MC and MD. Note that the microscopic domain $\Omega_j$ belongs to the domain of the $j$th phase:

$$\Omega_j \subset \Omega$$

The information of the microstructures is then fed into the coupling block, which is developed for correlating the microstructures to the macroscopic properties, i.e.,

$$\tilde{Y}_{\text{micro}}(t,\Omega_j) = f_{\text{micro}}(\tilde{Y}(\tilde{t}),t,\mathbf{z})$$

where $\mathbf{z}$ is the vector of spatial coordinates and $\tilde{Y}_{\text{micro}}(t,\Omega_j)$ gives a specific property value for the phase $j$ material. It can be
modulus or diffusivity if, respectively, a mechanical or barrier property is investigated. Establishment of (micro)structure—property correlation expressed by the function \( f_{\text{mod-nu}} \) is the most challenging task. It may involve molecular simulations for property evaluation, where the differences between properties obtained in a microscopic domain and those for macroscopic samples have to be properly taken into account.

In silico testing of the composite coating sample, such as a tensile test or a gas diffusion test, is described by a macroscopic model, which can be generalized as

\[
F(\partial Y/\partial t; \nabla Y; Y(t,z),X(t),F_{\text{mod-nu}}(t,\Omega),t,z) = 0
\]

where \( F \) is a nonlinear vector function. System input vector \( X \) contains the parameters related to the materials and testing conditions. System output vector \( Y \) gives the test results, which can be the stress—strain relations in a tensile test or the gas concentration profiles in a diffusion test. The gradient of \( Y \) is represented as \( \nabla Y \). Note that phase properties \( Y_{\text{mod-nu}}(t,\Omega) \) given by the coupling block are the essential inputs for the macroscopic model (see Figure 2). The model set will be associated with its initial and boundary conditions in the boundary domain \( \partial\Omega, j = 1, 2, ..., N \).

Test results should be further analyzed to obtain the overall property \( Q \) of the composite material, i.e.,

\[
Q = H(Y(t,z),X(t))
\]

The general modeling and simulation framework (see Figure 2) is applicable to the prediction of multiple properties for a range of PNCs. As stated earlier, this paper focuses on the barrier property of polymer—clay nanocomposites only. The detailed methods for each block in Figure 2 are developed in the following sections.

**Molecular Modeling of PNCs.** A critical need for studying PNCs design is to create computational models that are capable of describing how polymer and nanoparticles are represented in a 3D space and how they interact physically and chemically with each other. A PNCs model should be able to (i) quantify the interactions among polymers and nanoparticles and between them in a nanocoating system, (ii) characterize the specific features of the polymers (especially for thermostet materials), such as molecular weight distribution, functional group distribution, functional group ratio, and polymer matrix as a 3D cross-linked network, and (iii) allow investigations on the impact of the nanoparticles with different shapes, sizes, and surface modification mechanisms. As such, the following model sets are needed, i.e., a polymer (network) model set, a nanoparticle model set, and a polymer—nanoparticle interaction model set.

**Polymer (Network) Modeling.** The known coarse-grained bead—spring (CGBS) modeling technique has been successfully used to model linear polymer chains, which is ideal for modeling both thermoplastic and thermostet resins. For the thermostet resin, new bonds will be continuously created between the monomers and the cross-linkers to form a highly cross-linked 3D polymer network during nanocoating formation. In the polymer network, each effective unit (either an effective monomer or a cross-linker molecule) will be represented by a polymer bead. All the polymer beads of the same size will be created through a careful selection of the degree of coarse-graining (i.e., the number of real atoms contained in each coarse-grained entity). Each bond connects two adjacent effective monomers in a precursor polymer chain or one effective monomer with one cross-linker molecule. Each bond will be represented by an anharmonic spring. The same representation technique can be used for the thermoplastic polymer, where the situation is much less complicated, since no cross-linking reaction is involved and the simulation system contains precursor polymer chains only.

It must be pointed out that the description of the interaction between any pair of polymer beads is essential for determining a realistic microstructure. Both the bonded and the nonbonded interactions are considered. Any pair of nonbonded polymer beads interacts via a standard Lennard-Jones (LJ) potential:

\[
\Gamma^{\text{LJ}}_i = 4\varepsilon_{\text{pp}}\left(\frac{\alpha_{\text{ij}}}{r_{\text{ij}}^\text{max}}\right)^{12} - \left(\frac{\alpha_{\text{ij}}}{r_{\text{ij}}^\text{min}}\right)^{6}
\]

where \( r_{\text{ij}} \) is the distance between beads \( i \) and \( j \); \( \varepsilon_{\text{pp}} \) is an energy parameter; \( \sigma \) is a distance parameter; \( r_{\text{ij}}^\text{min} \) and \( r_{\text{ij}}^\text{max} \) are, respectively, the minimum distance and the cutoff distance between any two polymer beads. Note that the potential energy is set to zero when \( r_{\text{ij}} > r_{\text{ij}}^\text{max} \).

To count the bonded interactions, the finite extention nonlinear elastic (FENE) potential will be added to quantify the effect of the anharmonic spring between two bonded beads:

\[
\Gamma^{\text{FENE}}_{ij} = 4\varepsilon_{\text{pp}}\left(\frac{\alpha_{\text{ij}}}{r_{\text{ij}}^\text{max}}\right)^{12} - \left(\frac{\alpha_{\text{ij}}}{r_{\text{ij}}^\text{max}}\right)^{6}
\]

where \( r_{\text{ij}} \) is the distance between blanks \( i \) and \( j \); \( \varepsilon_{\text{pp}} \) is an energy parameter; \( \sigma \) is a distance parameter; \( r_{\text{ij}}^\text{min} \) and \( r_{\text{ij}}^\text{max} \) are, respectively, the minimum distance and the cutoff distance between any two polymer beads. Note that the potential energy is set to zero when \( r_{\text{ij}} > r_{\text{ij}}^\text{max} \).

**Nanoparticle Modeling.** A nanoparticle (NP) model must be general enough so that it can be used to simulate NPs of different sizes, shapes, and surface modification mechanisms. NPs can be modeled by NP beads held together by NP bonds (see examples in Figure 3). Each NP bead has the same size as a polymer bead. The interaction between any pair of nonbonded NP beads will be characterized by the LJ potential, while the interaction between any pair of bonded NP beads will be described by the sum of the LJ potential and the FENE potential. It is worth noting that by this modeling method, the NP deformation during nanocoating formation can be satisfactorily investigated. The NP deformation phenomenon was observed in many experiments, but it is neglected in most known computational work.

**Polymer—Nanoparticle Interaction Modeling.** The interaction between a polymer bead and an NP bead will be modeled using the LJ potential approach. Through adjusting the energy parameter, different strengths of interactions can be derived. The model will also allow bond creation between a polymer bead and an NP bead. Between them, an anharmonic spring characterized by the FENE potential will be utilized. The modeling in this way represents certain surface modifications on NPs.
Microscopic Modeling and Simulation. The task for microscopic modeling and simulation is to generate 3D material structures in each distinct phase (see Figure 2). In this work, an off-lattice MC simulation method is developed for this purpose. A representative volume of the system shown in Figure 4 is selected for investigating polymer–clay nanocomposites, where two layers of nanoparticle sheets are involved and the periodic boundary condition (PBC) is applied on all six faces of the simulation box. This volume contains all essential phases in a polymer–clay nanocomposite system, i.e., the bulk polymers (domain \( \Omega_1 \)), the polymers in the interfacial region (domain \( \Omega_2 \)), nanoparticles (domain \( \Omega_3 \)), and the polymers in the gallery space (domain \( \Omega_4 \)).

Simulation Methodology Overview. The evolution of the microstructures within each domain \( \Omega_j \) is one of the most critical tasks in simulation. It will be realized through generating a Markov chain of configurations using the basic Metropolis algorithm and its variations. The algorithm contains two essential elements: a type of perturbation (or move) in the current configuration and a criterion for accepting/rejecting a new trial configuration. This algorithm is applied to simulate two types of ensembles: the constant entity-number/volume/temperature (NVT) ensemble and the isobaric–isothermal (NPT) ensemble. Each configuration in a Markov chain for an NVT ensemble will be the result of a trial move involving a random nanoparticle/polymer bead displacement. An additional type of move (i.e., the volume change of the simulation box) will be allowed in the NPT ensemble to remain a constant pressure. The trial configuration will be accepted as a new configuration with a certain probability given by the Metropolis criterion.

Simulation Method. Xiao et al. have developed a seven-step procedure to construct microstructures of a thermoset nanocomposite sample accounting for the effect of processing conditions. This procedure, originally designed for the PNCs containing spherical nanoparticles, is extended to the investigation of polymer–clay nanocomposites. The seven steps are those for (i) simulation system setup, (ii) initial configuration generation, (iii) first-stage system relaxation in an NVT ensemble, (iv) cross-linking reaction realization, (v) second-stage system relaxation in an NVT ensemble, (vi) cooling, and (vii) third-stage system relaxation in an NPT ensemble. Note that if thermoplastic nanocomposites are investigated, no cross-linking reaction will be involved and thus steps (iv)–(vii) need to be omitted. The approaches used in this procedure are described below.

Simulation System Setup. For a given thermoset nanocomposite (TSNC) material with known polymer number average molecular weight and functional group ratio, a large number of linear precursor polymer chains and cross-linker molecules can be created by assuming the most probable molecular weight distribution. Succeedingly, with specified polymer number density and the number of NP beads involved in the simulation, the size of the rectangular simulation box is determined. Three types of functional groups can be considered in the study. Type A functional groups are randomly distributed to the precursor polymer chains. They react with type B functional groups in the cross-linker molecules to form a polymer network. In some cases, type C functional groups are attached to the nanoparticle surfaces, which can be specified to react with either type A or type B functional groups to form polymer–nanoparticle networks. Note that cross-linker molecules associated with their functional groups will not be included for a simulation system of thermoplastic nanocomposites (TPNCs).

Initial Configuration Generation. An algorithm is developed to ensure the effective placement of simulation entities. First, the NP beads are placed in the simulation box so that the two layers of NP sheets are both parallel to the top face of the simulation box and separated by a specified distance (see Figure 4). Then the polymers are placed through (i) generating a queue of polymer chains, according to their lengths (with the longest one first and the molecules of individual effective monomers and cross-linkers not involved in any chain in the end of the queue), and (ii) placing the entities in the queue one by one into the simulation box. Each placement should satisfy the minimum distance restriction. To construct an initial structure that is close to an equilibrium state, the initial bond length is set as the equilibrium length between two bonded polymer beads and any polymer chain backfolding during the placement is avoided.

Multistage System Relaxation. The purpose of a relaxation process is to obtain an equilibrated system. Three relaxations need to be performed for TSNCs. The first occurs before introducing cross-linking reactions, and the other two are before and after the cooling process. Only the first relaxation step is required for investigating TPNCs. This multistage system relaxation is necessary because for any MC simulation, an acquisition of property data is typically not performed until most of the important thermodynamic quantities (i.e., energy, pressure, etc.) appear to reach a statistical steady-state condition.

A system relaxation in the NVT ensemble is realized as follows. In each MC step, a random displacement of a randomly selected entity (either a polymer bead or an NP bead) will be attempted. The attempted move is judged for either acceptance or rejection using an NVT ensemble criterion. This process continues until a preset maximum number of MC steps is reached. Note that each displacement must satisfy the minimum distance and the maximum bond length restrictions. A system relaxation in an NPT ensemble is a relatively simple modification on the relaxation in an NVT ensemble. In addition to the attempted entity displacements, which are accepted or rejected according to an NVT ensemble criterion, the simulation box volume fluctuation will be required to remain a constant pressure. The change of volume is accepted or rejected according to an NPT ensemble criterion.

Cross-Linking Reaction Implementation. A novel method is developed to simulate nanocoating microstructure evolution under realistic nonisothermal curing conditions. Two types of cross-linking reactions are considered. One type is between the monomers and the cross-linkers to generate a polymer network,
and the other is between nanoparticles and polymers to form a polymer–nanoparticle network. The reactions proceed along MC steps until a desired cross-linking conversion percentage is reached. A two-stage implementation approach for each MC step is developed. The first one is an attempted entity displacement, which is exactly the same as a step in the system relaxation process. The second one is for conducting reactions for the selected entity. New bonds will be generated with a probability (a function of the current curing temperature given in Xiao et al.), if the following three requirements are satisfied: (i) the selected entity is reactive (i.e., it has unreacted functional groups), (ii) within a predefined reaction distance, other reactive entities exist, and (iii) two types of functional groups are allowed to react with each other. This two-stage approach should be reasonable for characterizing the continuous reaction and random movement of polymeric materials and nanoparticles in a real nanocomposite formation process.

Macrosopic Modeling and Simulation. As stated, in silico testing of the PNCs coating is accomplished by macroscopic modeling and simulation. To determine the barrier property, the permeation of gases through a nanocoating sample is investigated.

Representative Volume Element Construction. Construction of a representative volume element (RVE) that can precisely reflect the underlying multiscale hierarchical structure of a nanocoating sample is critical for a reliable property prediction. A good RVE should have the following two features. First, all major geometric and material characteristics are fully taken into account. The geometric features include features of nanoparticles; in particular, particle shape, size, dispersion, and orientation distribution. The material features can be described in terms of particle volume fraction, polymer–particle interface behavior, and polymer morphology. Second, the size of a RVE is considerably larger than the characteristic size of nanoparticles and the number of nanoparticles included in the RVE is large enough (e.g., 50–100) to obtain an accurate statistical representation of the structure.

In many cases, a RVE can be constructed on the basis of quantitative structural parameters (such as interlayer spacing, distance between stacks of clay sheets, and the number of layers in one stack) extracted from experimental measurements (e.g., large and small-angle X-ray diffraction (XRD) patterns and transmission electron microscopy (TEM) micrographs). A typical RVE constructed for an ideal case of polymer–clay nanocomposites is shown in Figure 5. In this case, the nanoparticles demonstrate a fully exfoliated morphology and are randomly dispersed in the polymer matrix. They have exactly the same orientation, i.e., perpendicular to the gas diffusion direction as shown in Figure 5. There are 80 nanoparticles included in this RVE, and each nanoparticle has an aspect ratio of 100. The structures are periodic in the direction of particle alignment. Three phases are involved in this case: bulk polymer phase \( \Omega_1 \), interfacial region \( \Omega_2 \) (see the areas in the vicinity of the nanoparticle surface enclosed by dashed lines), and nanoparticle phase \( \Omega_3 \).

**Gas Diffusion Model.** Gas diffusion through the thin film sample follows Fick’s second law, i.e.,

\[
\frac{\partial C(z,t)}{\partial t} = \nabla \cdot (D(z) \nabla C(z,t))
\]  

(9)

where \( C \) is the concentration of the penetrant gas and \( D \) is the diffusion coefficient or diffusivity. As discussed earlier, different phases in the sample may demonstrate distinctively different structures, which can result in different properties. Thus, the diffusivity is location dependent, i.e.,

\[
D(z) = D(\Omega_j) \quad \text{if} \quad z \in \Omega_j
\]  

(10)

The diffusivity of the phase \( j \) material, \( D(\Omega_j) \), is derived on the basis of its microstructure through a micro–macro coupling approach (the details will be described in a following section). When the diffusion process reaches a steady state, eq 9 can be simplified as

\[
\nabla \cdot (D(z) \nabla C(z)) = 0
\]  

(11)

The solution of eq 11 is the steady-state gas concentration contour in the thin film, from which the overall permeability can be calculated.

**Numerical Solution.** Solution derivation is accomplished using Fluent, a commercial computational fluid dynamics (CFD) software.

The geometry of a RVE (see an example in Figure 5) is first constructed and meshed. Since the nanoparticle can be safely assumed to be impermeable (i.e., \( D(\Omega_3) = 0 \)), the gas concentration in phase \( \Omega_3 \) must be zero. The computational domain consists of two subdomains only, i.e., bulk polymer phase \( \Omega_1 \) and interfacial region \( \Omega_2 \). Proper meshes for the
computational domain \( \Omega_1 \cup \Omega_2 \) should be generated to ensure reliable prediction and efficient computation. Compared with the grid size for \( \Omega_1 \), finer grids are used for \( \Omega_2 \) to better capture the mass transfer behavior in the interface region, which will be critical for the evaluation of the interfacial effect on the macroscopic material property. At the same time, the grid size should be carefully selected so that the prediction results are mesh-independent and the solution time can be minimized.

The well-established finite volume method is then utilized to solve the steady-state Fick’s second law (eq 11) under the following boundary conditions. (1) The inlet and outlet gas concentrations are \( C_\text{in} \) and \( C_\text{out} \) (\( C_\text{in} > C_\text{out} \)), respectively. The inlet and outlet boundaries are, respectively, the bottom and the top faces of the simulation box (see Figure 5). (2) Periodic boundary conditions are applied on the remaining four faces of the simulation box. (3) Zero mass flux is applied on the nanoparticle surface \( \partial \Omega_i \), i.e., the boundary of the nanoparticle phase.

**Property Evaluation.** The barrier property is quantitatively evaluated using the permeability coefficient \( K \), which is the product of diffusivity \( D \) and solubility \( S \):

\[
K_e = D_e S_e
\]

where the subscript “e” indicates the effective property of the overall composite material. The diffusivity is derived on the basis of Fick’s first law, which gives

\[
D_e = -\frac{J}{C_\text{out} - C_\text{in}} L
\]

where \( L \) is the thickness of the thin film (see Figure 5) and \( J \) is the gas diffusion flux at the steady state, which can be calculated as

\[
J = -\int_0^1 D(z) \nabla C(z) \, dA
\]

where the integration (i.e., the numerator in eq 14) gives the gas flow rate across a surface perpendicular to the diffusion direction (e.g., the top surface of the simulation box in Figure 5), whose area is \( A \).

Calculation of the overall solubility is much simpler, as compared with the diffusivity calculation. The effective solubility is a linear function of the solubility of each phase, i.e.,

\[
S_e = \sum_{i=1}^N S(\Omega_i) \phi_i
\]

where \( \phi_i \) is the volume fraction of the \( i \)th phase.

**Micromacro Information Coupling.** As presented in the previous sections, MC simulations generate the 3D polymer chain morphology in the microscopic subdomains \( \Omega_1 \) (bulk polymer), \( \Omega_2 \) (interfacial region), and if applicable, \( \Omega_3 \) (interlayer gallery). On the other hand, the properties of each phase \( \bar{Y}_{\text{ar}}(\Omega_i) \) are the essential inputs for the macroscopic CFD model and the property evaluation task. Consequently, an efficient scale-coupling approach needs to be developed to quantitatively correlate the microstructure to macroscopic property of each phase. This correlation can be derived by resorting to the following free volume models:

\[
D(\Omega_i) = B_1 \exp\left(-\frac{B_2}{f''(\Omega_i)}\right)
\]

where \( B_1 \) is a constant depending on the size and shape of gas molecules and system temperature; \( B_2 \) is a constant, determined by the gas molecule kinetic diameter; and \( B_3 \) is a constant relying on the system pressure and gas molecular weight. As indicated in eqs 16 and 17, both the diffusivity and the solubility are directly determined by the fractional free volume \( f'' \), i.e.,

\[
f''(\Omega_i) = 1 - \frac{v_i(\Omega_i)}{V(\Omega_i)}
\]

where \( v(\Omega_i) \) is the volume of domain \( \Omega_i \) and \( v_i(\Omega_i) \) is the volume occupied by the polymer beads in domain \( \Omega_i \), which can be readily calculated on the basis of the microstructure.

To obtain the macroscopic properties of each phase, property values derived from eqs 16–18 should be further averaged over a set of independent microscopic configurations, which gives

\[
D(\Omega_i) = \langle D(\Omega_i) \rangle
\]

\[
S(\Omega_i) = \langle S(\Omega_i) \rangle
\]

**Case Study**

The generic methodologies introduced in this work are applicable to the design of a range of polymer nanocomposite materials containing nanoparticles of any shape or size embedded in a thermoplastic or a thermoset polymer. In this section, a thermoplastic nanocomposite material, which is a mixture of polyethylene and montmorillonite (MMT) clay, is investigated to demonstrate the attractiveness of our methods. The diffusive gas studied is \( \Omega_2 \).

A total of 13 cases, including a base case, are designed to study three key material parameters: polymer–nanoparticle interaction strength (\( \phi^{pn} \)), nanoparticle aspect ratio (\( \alpha \)), and nanoparticle volume fraction (\( \phi^p \)). The detailed material parameters in each case are listed in Table 1. Two major assumptions are made on nanoparticle dispersion: (i) the nanoparticles demonstrate a fully exfoliated morphology and (ii) the nanoparticles have the same orientation (i.e., they are perpendicular to the gas diffusion direction).

**Base Case Analysis.** In the base case, a relatively strong polymer–nanoparticle interaction is applied. Since a fully exfoliated system is assumed, a representative volume for microscopic MC simulation is designed to contain one clay sheet placed in the middle of the simulation box. The polymer chains are placed randomly surrounding the nanoparticle sheet. Due
to the application of periodic boundary condition, only part of the clay sheet needs to be involved in the simulation, which leads to a significant reduction in the computational time and makes possible the simulation of a large-aspect-ratio nanoparticle contained system. Figure 6 shows initial and equilibrated microstructures, which are plotted using the visual molecular dynamics (VMD) software. The partial clay sheet has an aspect ratio of 10. It is surrounded by 185 polymer chains, each of which has a length of 10. The silver beads are nanoparticle beads and the green ones are polymer beads. Some polymer beads have bond connections to those outside the simulation box boundary; such polymer beads are shown in blue in the figure. The rectangular simulation box has a size of $10\sigma \times 10\sigma \times 16.68\sigma$. To have a clear view of the polymer chain morphology, the size of the polymer beads is reduced in the display.

It is found that, in the initial configuration (Figure 6a), the polymer beads are uniformly distributed in the simulation box. The polymer bead number density slightly fluctuates around 1.18, i.e., the preset bulk polymer number density. Through an equilibration process in an $NVT$ ensemble at a reduced temperature of 1, the polymer chains tend to self-organize themselves to form an ordered structure in the vicinity of the nanoparticle surface (see the ordered structures enclosed by the two white boxes in Figure 6b). This ordered structure leads to the formation of a high density layer, in which polymer bead number density shows prominent peaks. The highest peak is almost 7 times bigger than the bulk density. This high-density layer plays a significant role in affecting the overall material properties. In this special case, there are three phases: the bulk matrix ($\Omega_1$), the interfacial layer ($\Omega_2$), and the nanoparticle phase ($\Omega_3$).

The microstructure is then sent to the coupling block to determine the thickness of the interfacial layer, the free fractional volume in the interfacial layer and bulk matrix, and the diffusivity and solubility of phases $\Omega_1$ and $\Omega_2$. The results are listed in Figure 7. Note that property values are obtained by averaging over four independent microscopic configurations. All properties are expressed in a reduced form, i.e., the ratio between the property of a specific phase or the overall material and the property of the bulk matrix, which is equivalent to the property of a pure polymeric material. In this way, the effect of adding nanoparticles into a pure polymer can be clearly demonstrated.

The results generated by the coupling block are further transmitted into the macroscopic modeling block. A 2D RVE is constructed for illustration (see Figure 7), which contains 80 nanoparticles and each of them has an aspect ratio of 80. The size of the simulation box $(230\sigma \times 460\sigma)$ is determined on the basis of the nanoparticle volume fraction (6%). The diffusivity at any location within the simulation box is given by the coupling block (see Figure 7). With this information, a gas concentration contour is derived through solving the steady-state Fick’s second law. Two adjacent RVEs are plotted in Figure 7 to show how the gas molecules diffuse across the

\[ \text{Property evaluation:} \quad \frac{D_c}{D_m} = 8.54\%, \quad \frac{S_c}{S_m} = 88.58\%, \quad \frac{K_c}{K_m} = 7.57\% \]
boundary of the simulation box (due to the application of periodic boundary condition).

The material properties in terms of diffusivity, solubility, and permeability are finally quantified on the basis of the macroscopic simulation results. The results listed in Figure 7 show that the permeability of the nanocomposite coating in this case is reduced by 92.43% when compared with a pure polymeric coating. As a result, adding 6% MMT clay nanoparticles with an aspect ratio of 80 can significantly improve the coating barrier performance, if a fully exfoliated morphology can be achieved and favorable interactions can be realized between polymers and nanoparticles.

**Parametric Analysis.** A thorough parametric analysis gives quantitative correlations between the coating property and material parameters. Figure 8a–c shows the permeability as a function of polymer–nanoparticle interaction, aspect ratio, and volume fraction, respectively. Each of them contains two sets of results. The solid line is derived from the multiscale modeling method introduced in this work that takes into account three phases (bulk matrix, interfacial region, and nanoparticles), while the dashed line is obtained using the macroscopic finite volume method only that neglects the interfacial region. The significant difference between two sets of results demonstrates that the overall barrier property of the nanocomposites is affected greatly by the interfacial region. Thus, neglecting the interfacial region effect in permeability calculation will lead to considerable errors. The multiscale computational methods offer a unique opportunity to quantitatively take this effect into account. Most importantly, they can shed light on the fundamental understanding of the structural origin of this effect. It has been shown that adding nanoparticles into a polymer matrix can lead to a considerable morphological change of the polymer chains in the vicinity of the nanoparticle surface (Figure 6). Favorable interactions result in a well-ordered polymer structure, which, consequently, leads to the formation of a high-density layer adjacent to the nanoparticle surface. This high-density layer occupies a considerable amount of volume and its permeability is much less than the bulk matrix. As a result, neglecting the high-density layer (i.e., the interfacial region) can generate a significant error in permeability prediction.

As shown in Figure 8a, a higher interaction leads to a lower permeability (i.e., better barrier performance). This is because a more prominent high-density layer will be formed when the interaction strength is increased (see Figure 9). It is also found that increasing the aspect ratio or volume fraction of the nanoparticles will result in a negligible effect on the polymer distribution, but better barrier performance (Figure 8b,c). These results are qualitatively consistent with experimental measurements.7

**Model-Based Permeability Prediction.** One of the attractive features of the modeling and simulation methods developed in this work is that it allows the development of quantitative correlations between the overall property and the key material parameters. The following empirical model is derived on the basis of the simulation results.

\[
\frac{K_s}{K_m} = \exp \left( -\left( \frac{\alpha \phi}{1.33} \right)^{0.68} \times \left( \frac{\varepsilon^{\text{pn}}}{1.72} \right)^{0.08} \right) \tag{21}
\]

![Figure 8. Effects of material parameters on the coating permeability: (a) interaction effect, (b) aspect ratio effect, and (c) volume fraction effect.](image)

![Figure 9. Polymer number density distribution: (a) \(\varepsilon^{\text{pn}} = 2\), (b) \(\varepsilon^{\text{pn}} = 6\), and (c) \(\varepsilon^{\text{pn}} = 10\).](image)
With this model, the permeability of a nanocoating with any combination of material parameter values can be easily obtained, as long as they are within the range where the model is validated. Note that the gas—polymer interaction strength may affect the permeability coefficients (i.e., $K_m$ and $K_e$). It is assumed that, however, such an interaction effect can be canceled out in the permeability ratio ($K_e/K_m$). Figure 10 shows the detailed model predictions. It is worthwhile to point out that this model is capable of providing a quick estimation of barrier performance for a large number of polymer nanocomposite coatings. It can greatly facilitate experimentalists in rational design of nanocomposite coatings through offering opportunities to accomplish a quick screen of candidate formulations, identify the most promising design spaces, and develop the best possible experimental plans.

Gusev and Lusti derived a similar empirical model for permeability prediction:\(^\text{(11)}\)

$$
\frac{K_e}{K_m} = \exp\left(-\left(\frac{\alpha \phi^n}{3.47}\right)^{0.71}\right)
$$  \hspace{1cm} (22)

A major disadvantage of their model is that the contribution of polymer molecular level transformation (in the interfacial region) to the overall barrier property is neglected. Thus, eq 22 is essentially a two-phase model and it has been shown that such a model will give rise to considerable errors in permeability prediction (see the results discussed in the preceding section). The model developed in this paper (eq 21), on the other hand, takes the interfacial layer effect into account by incorporating an interaction strength parameter into the model. In this way, different interactions between polymer and nanoparticles can be effectively captured and the model prediction should be more reliable.

**Concluding Remarks**

A reliable property prediction of PNCs is critical for the rational design of this type of nanostructured material. It is a very challenging task, however, due to the intrinsic multiscale hierarchical structure of PNCs that has to be fully taken into account in property calculation. This requirement disqualifies all existing monoscale modeling and simulation methods.

In this work, a generic multiscale modeling and simulation method is developed to fulfill this challenging task. The method is applicable to the design of a wide range of PNCs containing any-shaped nanoparticles dispersed in a thermoplastic or thermoset polymer matrix. A case study on polyethylene—montmorillonite clay nanocomposites demonstrates that the method introduced in this paper can generate reliable predictions on the overall permeability by effectively accounting for the effect of the interfacial region. Most importantly, the multiscale approach can offer deep insights into the structural origin of the performance improvement resulting from nanoparticle incorporation. Although an ideal case of PNCs with perfectly oriented nanoparticles is investigated in the case study, the methodology is applicable to most PNCs with randomly oriented nanoparticles. Although the barrier property is mainly discussed in this paper, applications of the multiscale computational framework to other properties should be straightforward. This framework is being applied for mechanical property prediction, whose results will be presented in an upcoming paper.

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**Literature Cited**


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