



Atomistic to coarse grained simulations of diffusion of small molecules into polymeric matrix



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ABSTRACT

The diffusion of small molecules into a polymeric matrix often occurs on a wide range of length- and time-scales that are not easily accessible by standard atomistic simulations. It has limited applications of atomistic simulations for evaluating barrier properties of a polymeric film associated with the diffusion of small molecules into the film. Here, we present a multiscale scheme that combines atomistic and coarse-grained (CG) simulations for predicting the diffusion of small molecules into a polymeric film. The atomistic simulations are used to parameterize the CG MARTINI force field and to interpret time scales of the resulting CG models. As a case study, the developed scheme is applied to investigate the diffusion of the Octanal (C8) molecules into a polymeric film composed of four different components. Based on the atomistic simulations, the CG parameters for each polymer component in the film are optimized, and their ability to describe the mixed C8-polymer systems and predict the corresponding dynamic properties are tested. The diffusion results from the CG simulations are validated by analyzing effects of the concentration, the temperature, the water and the polymer components' weight ratio changes. It is shown that the CG simulations are much faster than the atomistic simulations and can describe the diffusion of C8 molecules into the polymeric film. This provides an effective way for studying the diffusion of small molecules into a complex polymeric matrix and evaluate its barrier properties.

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1. Introduction

The accurate knowledge of transport properties of small molecules in a polymeric matrix is needed in various technological applications. These properties have been predicted through theoretical, experimental and numerical approaches over the last few decades [1–24].

At the macroscopic (continuum) level, the diffusion of small molecules into a polymer film can often be satisfactorily described by Fick's laws [1]. At the molecular level, the classical free volume theory [2–4], the dual-mode sorption model [5,6] and the activation energy model [7,8] have been used to describe the diffusion of small molecules into polymers. These phenomenological models extend our understanding of the diffusion mechanisms and are useful for correlating the measured diffusivities. However, they lack predictive capability since the model parameters are not directly related to the polymer structures.

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Various experimental techniques such as the gravimetric [9], isostatic permeation measurement [10], Fourier transform infrared (FT-IR) spectroscopy [11] and nuclear magnetic resonance (NMR) [12] have been developed to study the transport of small molecules through polymeric films. These techniques are mainly based on the sorption and permeation kinetic determinations, and have greatly expanded our ability to measure a wide range of diffusion rates. However, they are expensive, time consuming and labor intensive. The accurate determination of the diffusion properties also is quite challenging since there is no standard method available for measuring them. Depending upon the test method used, large variations in the measured transport coefficients are found. For example, using different permeation methods, the diffusion coefficient of D-limonene was found to vary between $3.7 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and $17 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ (by a factor of 4.6) in high-density polyethylene films, and between $3.7 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ and $32 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ (by a factor of 8.6) in polypropylene films [13–15].

Atomistic simulations are a powerful research tool for studying the diffusion of small molecules into polymers. They are widely used to characterize the molecular-level structural and dynamics

details of penetrator-polymer systems that usually are not accessible with experimental techniques, and have been applied to compute the diffusion coefficients of small molecules into various polymer films [16–21]. For example, Karlsson et al. [16] found that the simulated diffusivity and the activation energy of D-limonene in molten polyethylene were within 30% and 16% of their experimental values. They also observed that the penetration of D-limonene molecules occurred via the tumbling process. Wang et al. [17] assessed the diffusion coefficients of 13 small molecules (e.g., limonene, linalool and citral) in amorphous polyethylene terephthalate (PET) using atomistic simulations. Their simulated results were found to be very close to the experimental values, which suggested the effectiveness of the molecular dynamics (MD) method to estimate the diffusion coefficients. Despite the extensive use of atomistic simulations in predicting the diffusion properties, due to their inherent limitations of length and time scales, they can only model the penetrator-polymer systems made of hundreds of thousands of atoms and the corresponding diffusion trajectories are computed from simulation results for a few nanoseconds. Since the normal diffusive regime might still be far away, it has hindered the use of atomistic simulations for assessing more accurate values of the diffusion coefficients and consequently evaluate barrier properties of the polymer film [22]. This limitation has been overcome, at least partially, by adopting the coarse-grained (CG) simulations.

The CG simulations extend the accessible size and time duration by lumping a group of atoms into a pseudo-atom or bead to reduce system's degrees of freedom and by using a larger time step size as a result of the smoother interparticle interactions than those in the MD simulations. Various CG models such as the structure-based [23,24] and the thermodynamics-based [25–28] have been developed for this purpose. Here, we use the thermodynamics-based MARTINI force field developed by Marrink et al. [27,28]. In the MARTINI force field, the interaction parameters are determined by reproducing system's mass density and the free energy partitioning between polar and apolar phases of a number of chemical building blocks. Compared to other CG methods, this parameterization process has made the CG modeling of new molecules relatively easy, and hence suitable for modeling complex polymer matrix systems. Though the MARTINI force field was originally developed for lipid bilayers and subsequently extended to proteins, there are no theoretical impediments for applying it to polymer systems [29].

In this work, we present a multiscale simulation method that combines the atomistic and the MARTINI force field modeling to study the diffusion of small molecules into polymeric films. The atomistic simulations are used to parameterize the MARTINI force field and to calculate the self-diffusion coefficients of the small molecules for interpreting the CG time scales. As a case study, we investigate the diffusion of Octanal (C8) molecules into a polymeric film composed of four different components. The C8-polymer system is selected for its wide application in the food industry where the C8 molecules are usually used as fragrance agents to provide orange-like taste to the product. During storage of these products, the diffusion of C8 molecules into the protective polymeric film lining often occurs, which results in a loss of concentration balance in the food and affects the taste. The rate of C8 diffusion into the polymer film plays an important role in determining the concentration loss rate and hence the shelf life of the food. This work focuses on (i) exploiting a multi-scale scheme to determine the self-diffusion coefficients of C8 molecules and (ii) evaluating the barrier properties of the protective polymer film. Even though the diffusion of only C8 molecules has been investigated, the proposed multiscale simulation scheme can be readily extended to other small molecules (i.e., eugenol and D-limonene) and polymer systems.

The remainder of the paper is organized as follows. In Section 2, we describe the CG force field parameterization and the optimization for the C8-polymer film system. In Section 3, the multiscale approach that combines the atomistic and the CG modeling is used to study the diffusion of C8 molecules into the polymeric film. The performance of the developed CG model at different temperatures and in the presence of water molecules is also discussed. The findings of our work are summarized in Section 4.

2. Development of models for the C8-polymer

2.1. Atomistic models

The preparation of the polymer film model is based on its four components: methyl acrylate, poly(ethylene-co-acrylic acid) (EAA), hydrogen peroxide (H_2O_2) and poly(ethyleneimine) solution 50% (w/v) in H_2O . Their weight percentages are listed in Table 1. In applications, the methyl acrylate and the EAA serve as primary components due to their excellent water barrier properties while H_2O_2 and the poly(ethyleneimine) solution are used as the polymerization initiator and the crosslinking agent to link the two main components to form the final network of the polymer film. Based on the analysis of possible polymerization and curing mechanisms occurring in the mixture of the four components, it is assumed that the final heterogeneous polymer film is mainly made of poly(methyl acrylate) (PMA), EAA, and linear and branched poly(ethyleneimine) (LPEI and BPEI) polymers. Their chemical structures are illustrated in Fig. 1. Due to the complex polymerization process of preparing the film, it is very challenging to construct an atomistic model that accurately describes the connected film system. Thus, in the current study, the simulated film is prepared by directly mixing the four polymers without modeling crosslinking. Based on the weight proportions listed in Table 1, 20 PMA chains with 20 repeating units ($n = 20$), 87 EAA chains with 3 repeating monomers ($n = 3$) of 14 mers ethylene ($x = 14$) and 1 mer acrylic ($y = 1$), 5 LPEI chains with 10 repeating units ($n = 10$) and 5 BPEI chains with only 1 repeating unit ($n = 1$) are chosen to represent the polymer film. By investigating this uncured film, deep insights into the diffusion of small molecules into this polymeric film can still be gained.

2.2. Coarse-grained modeling

The CG modeling of the polymeric film involves two fundamental steps: mapping of atoms into CG beads and the parameterization of the interaction potentials among the CG beads. The choice of atoms to be mapped is often arbitrary in CG modeling. In the MARTINI force field, the original mapping scheme is based on the 4-to-1 rule. That is, on average four heavy atoms (non-hydrogen) are mapped into one CG bead. However, considering the structural symmetries of the four components in the polymer film and to minimize the number of CG bead types, this unified 4-to-1 scheme is not always the best strategy for the current polymer system with four chemical components. Here, the finer rules (e.g., 2-to-1 and 3-to-1) are also applied in modeling the four polymer components, as shown in Fig. 2, with the objective of keeping as many structural characteristics of these polymer chains as possible. For the CG beads interaction potentials, we choose both the structural and the thermodynamic properties as the target properties for the parameterization. Distributions of the distances and the angles from the atomistic simulations are used to parameterize the bonded interactions. The non-bonded interactions are characterized by following conventions in the MARTINI force field to reproduce the mass density and the radius of gyration of the polymer chains from the atomistic simulations.

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