



Statistical multiscale homogenization approach for analyzing polymer nanocomposites that include model inherent uncertainties of molecular dynamics simulations



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ARTICLE INFO

Article history:

Received 7 May 2015

Received in revised form

16 August 2015

Accepted 21 September 2015

Available online 30 October 2015

Keywords:

- A. Polymer-matrix composites (PMCs)
- B. Interface/interphase
- C. Computational modelling
- C. Micro-mechanics
- C. Statistical properties/methods

ABSTRACT

A statistical multiscale homogenization strategy of polymer nanocomposites is proposed to account for the inherent uncertainties of molecular dynamics (MD) simulations. The proposed statistical multiscale homogenization scheme includes a discrete MD simulation system, a continuum theory of micro-mechanics of Eshelby's solution and two-scale homogenization, and Monte-Carlo simulations. The means and standard deviations of the elastic properties of the nanocomposites are quantified and discussed through statistical analyses that show the interphase effect. The elastic properties of the matrix, interphase, and composites are assumed to follow a lognormal distribution. An iterative inverse algorithm for obtaining the probability density distribution of the interphase is proposed and validated.

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1. Introduction

Polymer-based nanoparticulate composites have been widely developed owing to their extraordinary properties derived from the non-negligible contribution of the interphase zone formed between the polymer matrix and reinforcement [1,2]. Even with the same thickness of the interphase zone, the relative volume fraction of the interphase zone increases as the size of the embedded nanofillers increases because it strongly depends on the surface-to-volume ratio of the embedded fillers [3,4]. Therefore, understanding the link between the molecular structure and the macroscopic properties of polymer nanocomposites is crucial to providing useful guidelines and to accumulating knowledge on the design, analysis, synthesis, and manufacture of nanocomposites.

To assess the structure-to-properties or nanoparticle size-to-properties relationships through experimental measurement or atomistic simulations of nanocomposites, certain stochastic variations in microstructural parameters and their effect on the properties of nanocomposites must be clearly defined and

understood. For instance, fine control of the size of nanofillers for composites remains a challenge and there are mean and standard deviations in the size of nanoparticles inside a nanocomposite [5]. Moreover, the properties of the base polymer matrix, interfacial strength between the nanoparticle and matrix of concern, and spatial distribution of nanoparticles are neither deterministic nor homogeneous [6,7].

Full-atomistic molecular dynamics (MD) simulations have been widely employed to investigate the size-dependent properties of the embedded nanoparticles and to characterize the interphase zone of nanocomposites [3,4,8–13]. The concentration and properties of the interphase zone confirmed from the MD simulation are more easily identified in conjunction with continuum micro-mechanics than solely by MD simulations. For this reason, attempts to hierarchically bridge MD simulation results to composite micromechanics [3,8–12] or mathematical homogenization [4,14] have been proposed. In a series of successive studies, incorporation of the interphase zone as an additional phase within nanocomposite structures has been proposed to characterize the elastic, thermoelastic, and thermal transport properties—all of which depend on the size of the embedded filler [14,15]. In these computational studies, however, structural uncertainties that may affect the properties of nanocomposites have rarely been

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considered. In particular, for the dependencies of the physical properties of the nanocomposites on filler size, sufficient microstructural sampling of molecular structures is required to derive statistically convincing conclusions.

In addition to adequate sampling of initial molecular structures, MD simulations depend on the simulation setup, such as the initial random number seed to assign the starting kinetic energy of individual atoms to be further controlled to satisfy Boltzmann's distribution [16]. According to statistical mechanics, the ergodic hypothesis states that the average of sufficiently long simulations provides a reliable ensemble average of the same thermodynamic properties regardless of the initial velocity distribution. Despite the typical long relaxation time (3–5 ns) of the molecular unit cell through isothermal-isobaric ensemble simulations prior to the production runs, the average thermodynamic quantities of polymeric systems in MD simulations cannot avoid model-inherent uncertainties that stem from initial conditions. In MD simulations of polymeric nanostructures, a chaotic flow distribution of the polymer molecules is induced by the initial position and velocity of individual atoms as well as the chain conformation. However, such a chaotic flow distribution in an amorphous polymer is not homogeneous and can generate non-negligible local fluctuations in field quantities unless an enormous number of atoms is simulated. On the other hand, such uncertainties are not serious factors for simulating ordered crystalline structures. Moreover, the free volume in an amorphous polymer can lead to a local plasticizing effect, which in turn leads to non-negligible deviations in the properties of the same conformations depending on the initial velocity distributions of the atoms.

Minimizing the influence of conformation-dependent local field fluctuations caused by chaotic flows and free volume requires sufficiently long simulations and an enormous number of atoms to represent amorphous states. To reduce unavoidable model-inherent uncertainties, at least 10^7 ensemble frames should be considered [17]. However, MD simulations of polymeric structure cannot fulfill this requirement owing to the limitation of current computational power and memory. Therefore, a mean value-based statistical approach has been the preferred method to obtain reliable elastic properties, in which over 6–10 MD simulations are replicated on the same molecular structure while varying the initial velocity distributions of atoms in the system [3,4,18–22]. To reduce the errors originating from uncertain factors in predicting the properties of polymeric systems, for example, Yu et al. [21], Wei et al. [23], and others have typically demonstrated mean values of the properties of polymeric structures with standard deviations over 3 to 6 replications [18–22]. Despite the necessity of repeated calculations, however, there have been few attempts to explore the optimal number of repetitions to minimize the influence of model-inherent uncertainty on the properties of polymer nanocomposites obtained from MD simulations. Therefore, to increase the application of MD simulations to explore the multifunctional properties of nanocomposites, proper investigations should be performed to provide useful guidelines in assessing the inherent uncertainties in MD simulations. Moreover, uncertainties in the properties of interphases that surround embedded nanoparticles in nanocomposites have never been addressed in multiscale modeling approaches.

In this paper, we performed stochastic analysis of nanocomposites to provide useful guidelines in determining the elastic properties of epoxy-based SiC composites from MD simulations. To determine the proper number of trials, the cumulative average is calculated and discussed. By adopting an inverse analysis scheme that equates the MD simulation results to a three-phase micromechanics model, we propose a novel inverse statistical multiscale bridging method to obtain the probability density of the interphase

properties. Propagation of the model-inherent uncertainty described in Table 1 is addressed by the proposed statistical multiscale bridging method. To the best of our knowledge, this study is the first to quantify the influence of the model inherent uncertainty of MD simulations on the elastic modulus, and to construct a multiscale model that systematically includes this uncertainty. Based on a monoparticulate level multiscale model, an extension to the uncertainties in the size and spatial distribution of SiC nanoparticles inside the epoxy resin was realized by considering a large number of polydisperse representative volume elements (RVE) of nanocomposites.

2. Molecular modeling and simulation methodology

2.1. Preparation of unit cell

In this study, molecular models of epoxy nanocomposites with a single spherical SiC nanoparticle embedded at the center of the periodic unit cell were employed (Fig. 1a). To investigate the particle size dependency of elastic properties, four different epoxy/SiC nanocomposites unit cell systems (Particle radius: 5.18, 7.54, 9.00, or 10.00 Å) were modeled under the same volume fraction (5.8%). Details of the epoxy/SiC nanocomposite unit cell systems and pure epoxy systems are listed in Table 2. The epoxy resin is composed of triethylenetetramine (TETA[®]) and a diglycidyl ether of bisphenol F (EPON862[®]) as the curing agent and epoxy monomer, respectively. To describe crosslinking between the epoxy monomer and curing agent, a unit model of the representative crosslinked network is employed (Fig. 1b). This crosslinking method yields accurate results for the elastic properties [12,15], density [10,12,14,15], glass transition temperature [10], and thermal conductivity [14,15]. There are 2 and 6 curing sites in single molecules of EPON862[®] and TETA[®], respectively. In this study, the molecular ratio of epoxy monomer to curing agent was set to 3:1 to equate the number of curing sites between the two molecules. The curing ratio of the crosslinked epoxy was also set to 0.61 in line with a previous study [10].

All molecular modeling and MD simulations were conducted with Materials Studio 5.5.3. The COMPASS (ab initio Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies) [17] force field, which is built into Materials Studio 5.5.3, was used to describe the inter- and intra-atomic interaction forces. The target density of the neat epoxy and epoxy/SiC nanocomposite periodic unit cell systems was set to 1.20 g/cm³ in accordance with experimental results [24]. The Amorphous Cell module[®] was used to construct the amorphous unit cell system of neat epoxy and epoxy/SiC nanocomposites with the target density at 300 K and 1 atm. After constructing the initially defined unit cell system, the total potential energy of the unit cell was minimized, using the conjugate gradient method. Then, NVT (isothermal)-ensemble and NPT (isothermal and isobaric) simulations were performed to equilibrate the unit cell systems at 300 K and 1 atm for 500 and 2000 ps, respectively.

2.2. Production run for elastic properties

Here, the elastic stiffness tensor was calculated from the Parrinello-Rahman fluctuation method with an ensemble average of 10^4 strain fluctuated frames. This method [18] is based on the following equation:

$$C_{ijkl} = \frac{k_B T}{\langle V \rangle} \langle \delta \varepsilon_{ij} \delta \varepsilon_{kl} \rangle^{-1} \quad (1)$$

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