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Multiscale homogenization modeling for thermal transport properties of polymer nanocomposites with Kapitza thermal resistance

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ABSTRACT

In this study, multiscale homogenization modeling to characterize the thermal conductivity of polymer nanocomposites is proposed to account for the Kapitza thermal resistance at the interface and the polymer immobilized interphase. Molecular dynamics simulations revealed that the thermal conductivity dependent on the embedded particle size originated from the structurally altered interphase zone of surrounding matrix polymer in the vicinity of nanoparticles, and clearly indicate strong dominance of interfacial phonon scattering and dispersion. To account for both the thermal resistance and the immobilized interphase, a four-phase equivalent continuum model composed of spherical nanoparticles, Kapitza thermal interface, effective interphase, and bulk matrix phase is introduced in a finite element-based homogenization method. From the given thermal conductivity of the nanocomposites obtained from MD simulations, the thermal conductivity of the interphase is inversely and numerically obtained. Compared with the micromechanics-based multiscale model, the thermal conductivity of the interphase can be obtained more accurately from the proposed homogenization method. Using the thermal conductivity of the interphase, the random distribution and radius of nanoparticles to describe real nanocomposite microstructure are considered, and the results confirm the applicability of the proposed multiscale homogenization model for further stochastic approaches to account for geometric uncertainties in nanocomposites.

1. Introduction

Recent development of nanoscale fabrication techniques has prompted synthesis and manufacture of a variety of nano-structured materials over the last few decades [1–3]. Among the many kinds of nano-structured materials, polymer nanocomposites that utilize nano-sized fillers to tailor various properties of base polymer have been applied to both academic and industrial fields, such as aerospace systems [4], energy storage and conversion systems [5], biomedical industry [6] and electrochemical sensors [7], due to their potential multi-functionality and weight advantage. The addition of highly conductive functional nano-sized fillers with high thermal conductivity such as graphite, carbon nanotubes, nanoclays, ceramic/metal particles and carbon black, can enhance the poor thermal conductivity of amorphous base polymers to show exceptional heat dissipation [8]. Polymer nanocomposites with highly conductive nanofillers embedded can substitute for metallic and metal alloy parts in various applications, such as heat exchangers, power electronics, thermally conductive tapes and pads, and epoxy molding compound for heat sinking [8,9].

When the size of fillers is on the nanometer scale, due to increased surface-area-to-volume ratio, the physical properties of nanocomposites show a prominent filler-size dependency. The molecular arrangement of polymer matrix near the nanoparticles is known to be a densified and crystallized form of a unique phase called the 'interphase.' As the surface-to-volume ratio of the nanoparticles surrounded by the interphase increases, more portions of the atoms in nanoparticles can actively interact with the atoms at the interphase to generate stronger interfacial adhesion, which is desirable for efficient load transfer under mechanical loading and efficient phonon transfer for thermal energy dissipation. As such, the filler-size effect on the physical properties of the nanocomposites such as mechanical, thermal, electromagnetic and optical properties has been examined diversely. One of the most preferred computational tools to characterize the effective properties of nanocomposites with the filler-size effect is molecular dynamics (MD)

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simulation. Due to high computational costs, however, efficient multiscale modeling approaches that combine MD simulation and conventional continuum mechanics have been proposed [10–12]. In order to obtain an equivalent continuum model using multiscale bridging method, the interphase has been considered via three-phase continuum micromechanics model consisting of particle, matrix, and interphase in elasticity problems. Yang and Cho [10,11], and Yu et al. [12] investigated the filler-size effect on the elastic stiffness of nanocomposites using MD simulations, and introduced a sequential multiscale bridging method by utilizing the multi-inclusion model based on the Eshelby's solution [13].

In case of the thermal conductivity problem of nanocomposites in which the material interface between filler and host material is naturally formed, there exists a temperature jump at the interface as a result of phonon scattering and reflection [14], which is often referred to as the 'Kapitza thermal resistance effect.' The overall thermal transport properties are critically affected by the thermal resistance. The importance of the Kapitza thermal resistance of CNT nanocomposites in the equivalent continuum model prediction of the thermal conductivity of CNT-reinforced nanocomposites was demonstrated by Seidel and Lagoudas [15]. Prasher developed a framework for the calculation of the thermal resistance at the interface, and showed that the thermal boundary resistance of the Si/Ge nanocomposites depends on the temperature and particle size [16]. Additionally, Hao et al. investigated the Kapitza thermal resistance effect of crystalline Si/Ge nanocomposites in NEMD simulation, and the temperature discontinuity at interface was verified [17]. They discussed that the temperature discontinuity occurs due to phonon scattering at the interface. Konatham et al. estimated the Kapitza thermal resistance at the graphene sheet-liquid octane interface using classical molecular dynamics simulations, and demonstrated that it is possible to reduce the Kapitza thermal resistance by appropriately functionalizing the graphene sheets [18]. The dominance of the Kapitza thermal resistance becomes more prominent when the particle size decreases, especially on the nanoscale, because the relative volume concentration of the finite Kapitza interface zone increases as the particle size decreases. A more rigorous consideration by Yu et al. of the embedded filler-size effect on the overall thermal conductivity of Silicon carbide/epoxy nanocomposites has been investigated through MD simulation by considering different sizes of SiC nanoparticles [19]. In their approach, the Kapitza thermal resistance was described by defining an additional phase with finite thickness, and with extremely small thermal conductance in the immediate vicinity of nanoparticles [20] for the equivalent continuum modeling of nanocomposites.

While the Kapitza thermal resistance degrades the overall thermal energy transport, the aforementioned interphase zone that has higher density than bulk polymer plays a positive role in enhancing the thermal conductivity of polymer nanocomposites, because the reduced free volume inside the interphase zone results in efficient thermal energy transport. Thus, the local temperature gradient inside of the nanocomposites becomes rather complicated, with both positive and negative effects contributing to the overall thermal properties differently with crystalline composites including negative effect only [17]. However, it is difficult to calculate the thermal conductivity of the interphase zone because of the unique and sophisticated crystalline molecular structure of the interphase.

For the analysis of the thermal characteristics of nanocomposites, a four-phase micromechanics-based multiscale model that consists of a particle, matrix, Kapitza interface and the interphase has been proposed, and an inverse estimation scheme to predict the thermal conductivity of the interphase zone has been demonstrated [19]. Efficiency and accuracy have been achieved by the micromechanics approaches based on Eshelby's equivalent inclusion model, which describes the interaction of the local field via a mean field approach [21], or a fictitious phase that surrounds the overall composites domain [13]. However, there still exist limitations in considering the non-dilute particle-concentration effect, especially for nanocomposites [11]. Thus, Cho et al. [22] proposed a new approach to describe the particle size effect of nanocomposites by employing a finite element-based homogenization method. In our previous study [22], a two-scale homogenization method was proposed to predict the equivalent material properties of heterogeneous structures referring to the basic formula presented by Bendsøe and Kikuchi [23] and Guedes and Kikuchi [24]. In case of thermal transport problem where the two conflicting local field fluctuations each of them are the result of the Kapitza thermal resistance and the higher density interphase should be considered simultaneously, the description of the local field fluctuation and their relative concentration effect become more serious. As a complementary problem, a mathematical homogenization method [25] can be effectively applied to the same problem without losing the rigorousness in describing the local field fluctuations.

In the present study, a two-scale homogenization-based multiscale bridging model is proposed to characterize the effective thermal conductivity of SiC/Epoxy nanocomposites that undergo interfacial thermal resistance and polymer immobilization at the interphase zone. All the thermal transport properties required for the present homogenization-based multiscale model such as the effective thermal conductivity of SiC nanoparticles, Kapitza thermal interface, epoxy matrix, and nanocomposites, were obtained from non-equilibrium molecular dynamics (NEMD) simulation. A numerical iteration scheme is proposed to predict the thermal conductivity of the interphase zone in nanocomposites. The thermal conductivity of the interphase obtained from the proposed numerical scheme and the conductivity of the nanocomposites reproduced from the present model are compared with the results obtained from the previous micromechanics-based multiscale model [19], and the advantages of each bridging method to model polymer nanocomposites are discussed. Based on the thermal conductivity of the interphase obtained from the present multiscale homogenization method, randomly distributed microstructure of nanoparticles having different radii observed in real nanocomposite microstructures was considered, and the effective thermal conductivity of the nanocomposites is compared with the possible upper and lower bounds.

2. Molecular modeling and simulation

2.1. Model construction

The nanocomposite molecular structure used to predict the effective thermal conductivity consists of a cross-linked epoxy matrix and a spherical SiC nanoparticle. Different from thermoplastic polymer, molecular modeling of thermoset polymer and their nanocomposites has gained remarkable attention in the field of molecular modeling and simulations, for their unique material properties that strongly depend on the cross-linked network structure and conversion ratio. There have been several methodologies proposed to mimic the real cross-linked network of epoxy in molecular dynamics [26–29]. The existing methodologies can be categorized as the Monte Carlo method [26], the close contact method [27,28], and the representative molecule method [12,29,30]. Among them, we adopt here the representative molecule method that employs several identically cross-linked molecules to model an amorphous unit cell structure. As one cross-linked molecule represents detailed cross-link density and cross-linked network structure, this method is referred as a 'representative