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A study on the homogenization modeling for thermal conductivity of polymer nanocomposites

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ABSTRACT

In this study, a sequential multiscale homogenization method to characterize the effective thermal conductivity of nano particulate polymer nanocomposites is proposed through a molecular dynamics (MD) simulations and a finite element-based homogenization method. The thermal conductivity of the nanocomposites embedding different-sized nanoparticles at a fixed volume fraction of 5.8% is obtained from MD simulations. Due to the Kapitza thermal resistance, the thermal conductivity of the nanocomposites decreases as the size of the embedded nanoparticle decreases. In order to describe the nanoparticle size effect using the homogenization method with accuracy, the Kapitza interface in which the temperature discontinuity condition appears and the effective interphase zone formed by highly densified matrix polymer are modeled as independent phases that constitutes the nanocomposites microstructure, thus, the overall nanocomposites domain is modeled as a four-phase structure consists of the nanoparticle, Kapitza interface, effective interphase, and polymer matrix. The thermal conductivity of the effective interphase is inversely predicted from the thermal conductivity of the nanocomposites through the multiscale homogenization method, then, exponentially fitted to a function of the particle radius. Using the multiscale homogenization method, the thermal conductivities of the nanocomposites at various particle radii and volume fractions are obtained, and parametric studies are conducted to examine the effect of the effective interphase on the overall thermal conductivity of the nanocomposites.

1. INTRODUCTION

Polymer nanocomposites have been widely employed due to their weight advantage and multifunctionality. Especially, if carbon materials are employed as reinforced filler, the polymer nanocomposites has an enhanced thermal characteristic by overcoming

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low thermal characteristics of polymer matrix.

In order to reflect filler size effect, molecular dynamics (MD) simulation is widely employed. However, MD approach needs high computational time and memory. Therefore, MD simulation is not appropriate for analyzing the reliability based design approach and optimal design. Therefore, a sequential multiscale bridging method was proposed.

In thermal transport problem, temperature discontinuity zone exists due to scattering and reflection of phonon at interface. Kapitza thermal resistance zone is introduced in order to describe the temperature discontinuity. Meanwhile, condensed phase near the reinforced filler takes positive effect on the overall thermal characteristics. Therefore, 4 phase continuum model is constructed with effective interphase and Kapitza thermal resistance in this study.

In this study, the multiscale homogenization model is proposed and the results are compared with those of previous micromechanics model (Yu 2011). In order to investigate filler size effect, the 5 unit cell models are constructed at same filler volume fraction. An iterative inverse algorithm is proposed to compute thermal characteristics of effective interphase. Thermal conductivities of polymer nanocomposites with various radii and volume fraction are investigated.

2. Multiscale homogenization method for thermal conductivity

Multiscale homogenization method has been widely used to estimate the homogenized physical properties of periodic microstructures. The principle of virtual temperature is given by Eq. (1).

$$\int_V \nabla_X \bar{\theta} : \mathbf{k} : \nabla_X \theta dV = \int_V \bar{\theta} q^B dV + \int_A \bar{\theta}^S q^S dS + \sum_i \bar{\theta}^i Q^i \ , \tag{1}$$

where Q^i is the concentrated heat flow inputs, q^B and q^S are the internal heat generation and surface heat flow inputs on *A*, respectively, and $\bar{\theta}$ and θ denote an arbitrary virtual temperature distribution and real temperature distribution inside of the nanocomposites, respectively. In order to describe macroscopic and microscopic mechanical behavior all together, the two scale coordinates, microscopic coordinate y and macroscopic coordinate x, are introduced. The real temperature distribution θ could be expanded about ε asymptotically as Eq. (2).

$$\theta(\vec{X}) = \theta^0(\vec{x},\vec{y}) + \varepsilon\theta^1(\vec{x},\vec{y}) + \varepsilon^2\theta^2(\vec{x},\vec{y}) + \cdots . \tag{2}$$

By applying Eq. (2) to Eq. (1), Eq. (1) could be arranged in order of ε as follows:

$$\frac{1}{\varepsilon^2} O(\varepsilon^{-2}) + \frac{1}{\varepsilon} O(\varepsilon^{-1}) + O(\varepsilon^0) + \cdots = 0 . \tag{3}$$

From $O(\varepsilon^{-2})$ and $O(\varepsilon^{-1})$ of Eq. (3), the relationship between microscopic and macroscopic temperature fields could be determined as follows:

$$\theta^0(\vec{x},\vec{y}) = \theta^0(\vec{x}), \ \theta^1(\vec{x},\vec{y}) = -\boldsymbol{\chi}(x,y) : \nabla_x \theta^0(\vec{x}) . \tag{4}$$

where

$$\int_{\bar{Y}} \nabla_y \bar{\theta} : \mathbf{k} : \nabla_y \boldsymbol{\chi} dV_y = \int_{\bar{Y}} \nabla_y \bar{\theta} : \mathbf{k} dV_y . \tag{5}$$

By rearranging $O(\varepsilon^0)$ of Eq. (3), the homogenized thermal conductivity could be computed as follows:

$$\int_Y \nabla_x \overline{\theta} : \mathbf{k}^H : \nabla_x \theta^0 dV_x = \int_A \overline{\theta}^S q^S dV_y . \tag{6}$$

where

$$\mathbf{k}^H = \frac{1}{|Y|}\int_A \mathbf{k} - \mathbf{k} : \nabla_y \boldsymbol{\chi} dV_y . \tag{7}$$

3. Characterization of interphase thermal conductivity

Thermal transport problem of nanocomposites is analogous to the elastic problem with weakened interface. In this study, Kapitza thermal resistance is introduced in order to reflect the weakened interface effect. In order to define Kapitza thermal resistance, bilayer molecular model is constructed. Non-equilibrium molecular dynamics(NEMD) simulation is conducted for this bilayer molecular model and the thickness and thermal conductivity of Kapitza thermal resistance are quantified explicitly. In order to characterize the effective interphase thermal conductivity, iterative inverse algorithm is proposed in this study as shown in Fig. 1.

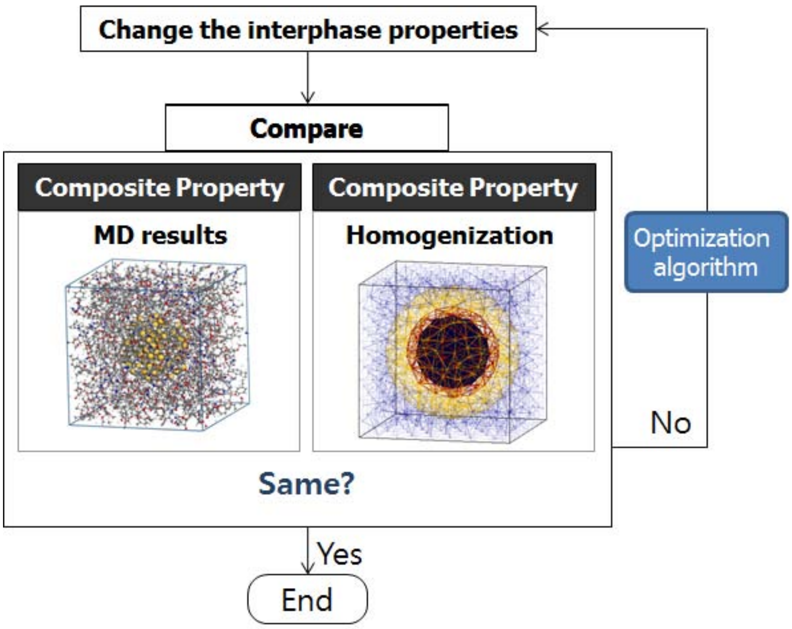

Fig. 1 Iterative inverse algorithm for characterization of effective interphase thermal conductivity

Thickness and thermal conductivity of Kapitza thermal resistance are 2.18 Å and 0.0199 W/mK. Thickness of effective interphase is 5 Å determined from radial density distribution. Thermal conductivities of pure epoxy and spherical SiC filler are 0.1416 W/mK and 120 W/mK, respectively. Table 1 shows the unit cell configuration employed in this study..

Table 1. Unit cell composition of nanocomposites. The number of chains in bracket: in duplicated geometry.

SiC particle		Epoxy	Nanocomposites	
Radius	Volume fraction(%)	Chain No.	X=Z(Å)	Y(Å)
7.54		6 (12)	31.40	62.80
9.00		10 (20)	37.32	74.64
10.9	5.8	18 (36)	45.38	90.76
11.6		22 (44)	48.41	96.82
13.0		31 (62)	54.29	108.58

4. Results and discussion

4.1. Characterization of effective interphase

Thermal conductivities of effective interphase and nanocomposites are computed from multiscale homogenization method. The results are compared with those of micromechanics-based bridging method as shown in Fig. 2. The computed thermal conductivities of effective interphase from multiscale homogenization approach are higher than those of micromechanics as shown in Fig. 2 (a). In previous study, the estimated thermal conductivities from micromechanics approach are lower than the molecular simulation results as shown in Fig. 2 (b). Therefore, the results from present study are more accurate than those of previous study.

(a) (b)

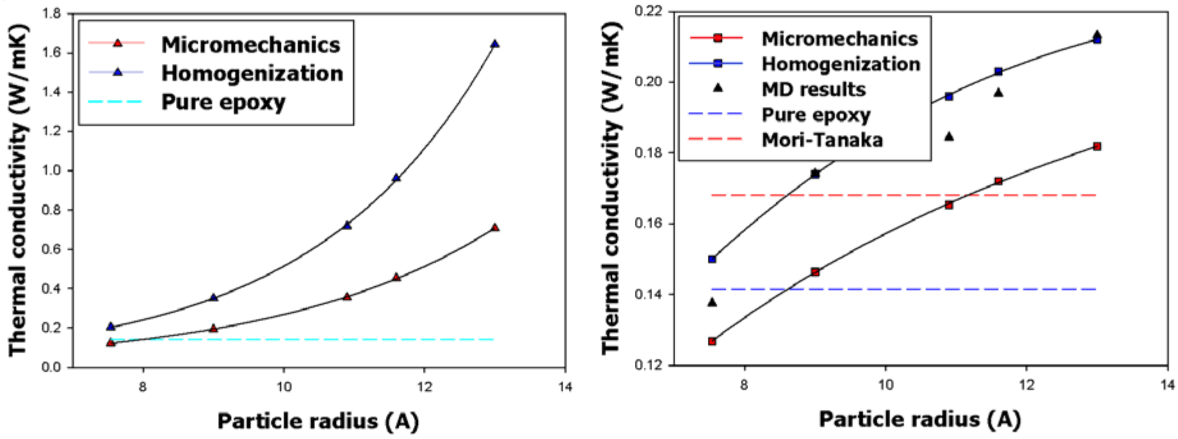

Fig. 2 Thermal characteristics with respect to particle radii: (a) Effective interphase and (b) Nanocomposites

Kapitza thermal resistance degrades the overall thermal conductivities of nanocomposites, however, the effective interphase influences positive effect on the overall thermal conductivities of nanocomposites. Micromechanics-based approach needs feedback of thermal conductivities of infinite medium in order to reflect the filler concentration effect. Meanwhile, multiscale homogenization approach is based on the rigorous numerical formulation. Therefore, multiscale homogenization approach is more accurate and reliable than the micromechanics-based approach.

4.2. Estimation of thermal conductivities of polymer nanocomposites with respect to various particle radii and volume fractions

Thermal characteristics of effective interphase could be fitted by exponential function as follows:

$$\lambda_{\text{int}} = -0.0021 + 0.0108\exp\left(0.3856 r_p\right) \tag{8}$$

where r_p is particle radius.

As shown in Fig. 3 (a), Kapitza thermal resistance is more dominant than effective interphase. When particle size increases over 1.6 nm, effective interphase is more dominant than Kapitza thermal resistance. As the particle size increases to micro size, the homogenized thermal conductivity converges to Mori-Tanaka solution. Fig. 3 (b) shows thermal characteristics about various particle radii and volume fractions. As the volume fraction of particles increases, the homogenized thermal characteristics increases as shown in Fig. 3 (b).

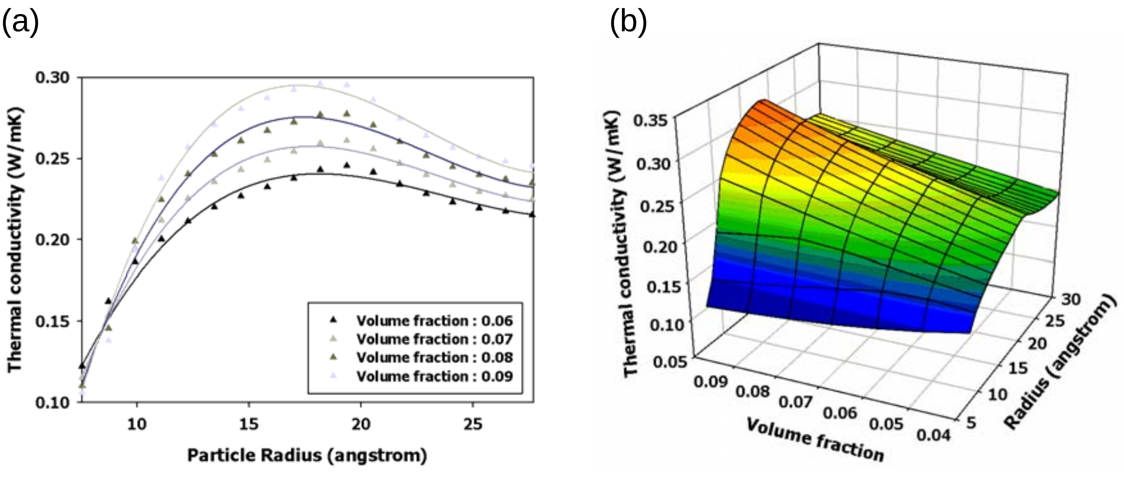

Fig. 3 Thermal conductivities of polymer nanocompsites: (a) about only particle radii and (b) about particle radii and volume fractions.

5. Conclusion

In thermal transport problem of nanocomposites, multiscale homogenization method is more accurate than micromechanics-based approach. However, multiscale homogenization method needs finite element analysis which needs more computational time and memory than the micromechanics-based approach. Micromechanics-based approach and the proposed multiscale homogenization method are applied to analyze the homogenized thermal conductivities complementarily. In real manufacture and characterization of nanocomposites, it is still a challenging issue to distribute filler uniformly without filler agglomeration and growth in size. The stochastic multiscale homogenization which considers filler geometric uncertainty and model inherent uncertainty from molecular dynamics simulation is ongoing research.

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