Composites Science and Technology 168 (2018) 145–151

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Analysis of the influence of interphase characteristics on thermal conduction in surface-modified carbon nanotube-reinforced composites using an analytical model

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ARTICLE INFO

Keywords:
A. Carbon nanotubes (CNTs)
A. Polymer-matrix composites (PMCs)
B. Interphase
B. Thermal properties
C. Multiscale modeling

ABSTRACT

In this study, the influence of interphase characteristics on thermal conductivity of carbon nanotube (CNT)-reinforced polymer composites was investigated using a thermal resistance theory-based analytical model. Pristine, nitrogen doped, and carboxyl functionalized CNTs were used to verify the effect of surface modifications. Interfacial thermal conductivities of nanocomposites containing three different CNTs were calculated from non-equilibrium molecular dynamics (NEMD) simulations, to analyze the influence of functionalization on the interphase characteristics. Equilibrium molecular dynamics (EMD) simulations of three different CNTs and epoxy matrix were performed to estimate their effective thermal conductivities. The thermal conductivities of the nanocomposites were predicted by applying the results obtained from the MD simulations in the analytical model. The results predicted by the analytical model show that while thermal conduction in the longitudinal direction of the nanocomposites depends on thermal conductive performance of the CNTs, transverse thermal conductivity could be significantly influenced by the interphase characteristics.

1. Introduction

Carbon nanotubes (CNTs) firstly discovered in 1976 by Oberlin and colleagues [1] are nano-sized carbon fillers having beneficial mechanical, thermal, and electrical properties [2,3]. They have been widely used to improve the performance of polymer matrix-based composites [4,5]. Interphase region in the nanocomposites is formed by various interactions (e.g. van der Waals, Coulombic, and long-range interactions) between CNTs and a polymer matrix. These interactions affect the thermal conductivity of the nanocomposites as well as thermal resistance in the interphase region [6,7]. Thus, interphase characteristics such as interaction energy and interfacial thermal resistance can provide important information for design of thermally conductive nanocomposites.

One of these characteristics, interfacial thermal resistance, is associated with heat flow across the interface between two solids [8,9]. However, experimental investigations on interfacial thermal resistance are difficult to specify the tiny interphase region and to control environmental variables that are insignificant in the study [10,11]. A non-equilibrium molecular dynamics (NEMD) simulation [12] has been used to calculate the interfacial thermal resistance between nanofillers and a matrix [13–15]. As a specific case, modified thermal boundary condition was introduced for a hollow interphase between a CNT and polymer [16]. Hida et al. calculated the thermal boundary conductance between a CNT and polyethylene by applying the thermal boundary condition in the NEMD simulation [17]. However, the NEMD simulation is not appropriate for calculating the thermal conductivity of the overall nanocomposites containing CNTs of high aspect ratio due to very long simulation time required for large systems. Thus, the simulation method is not adequate to analyze the relations between the interphase characteristics and the thermal conductivity of the nanocomposites.

An alternative approach, continuum-based analytical models of the CNT-reinforced nanocomposites that consider the interphase characteristics, has been proposed in several studies. For example, Nan et al. presented a simple formula to describe the enhancement of thermal conductivity in CNT composites by incorporating the interfacial thermal resistance with an effective medium approach [18]. Seidel et al. developed a micromechanics approach for assessing the impact of interfacial thermal resistance on the effective thermal conductivity of

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https://doi.org/10.1016/j.compscitech.2018.09.014
Received 25 June 2018; Received in revised form 13 September 2018; Accepted 15 September 2018
Available online 18 September 2018
0266-3538/

CNT-polymer nanocomposites [19]. The analytical models in these studies did not satisfy the important consideration, such as specifying an effective region and a property of the interphase in the nanocomposites, when analyzing thermal conduction in nanocomposites. The parameter study for the effective region and property had been performed using the analytical model considering functionally graded interphase [20,21]. The parameter study showed that the interphase parameters such as the effective region and the property were the important parameters in determining thermal conductivities of the nanocomposites. However, the interphase characteristics are the parameters determined by the type of a CNT in conjunction with a matrix. Thus, the changes of the type of a CNT and a matrix should be critically considered to determine the interphase characteristic parameters. In addition, a presence of void inside the CNTs has a significant impact on the effective thermal conductivities of nanocomposites [19]. The CNT formed by rolling up the graphene has complex thermal conductive mechanism in its transverse direction due to its configuration. An effective region for thermal conduction in the radial direction of the CNT is also limited. Therefore, the structural characteristics of the CNTs should be significantly considered as geometrical parameters for analyzing thermal conduction in the CNT-reinforced composites in the analytical model.

Above-mentioned MD simulations can be useful for obtaining the reasonable interphase characteristics that are very difficult to experimentally measure. The combination of the analytical model and the MD simulations can be an effective approach for analyzing the relations between the interphase characteristics and the thermal conductivities of nanocomposites. For this study, an analytical model considering the interphase characteristics and a thermal conductive mechanism of CNT-reinforced nanocomposites was proposed. The conditions of CNT surface modification included pristine, nitrogen doping, and carboxyl functionalization. The interphase characteristics in the nanocomposites containing three different CNTs were calculated from NEMD simulation. Thermal conductivities of an infinite epoxy matrix and infinitely long CNTs were estimated by curve fitting to the EMD simulation results for each constituent. The thermal conductivity of the nanocomposites was predicted by applying the results obtained from the MD simulations in the analytical model. Then, a comparative study of the predicted results was performed to analyze the relation between the interphase characteristics and the thermal conductivity of the nanocomposites.

2. All atom-based molecular dynamics simulation

2.1. Non-equilibrium molecular dynamics simulation

A local interphase region may occur between the CNTs and matrix in the nanocomposites. A simulation method that can obtain the temperature in this local region is needed to calculate a thermal conductivity of the interphase. The NEMD simulation imposes a constant heat flux using the energy variation between the heat source and sink in the simulation model to give the temperature distribution within thermal boundary. We chose this simulation method to analyze thermal conduction in the interphase region. The thermal conductivity (k_i) between the heat source and sink is expressed as [22,23].

$$k_i = \frac{\Delta E_{kinetic}}{A_i \Delta t (\Delta T / \Delta x_i)}, \quad (1)$$

where $\Delta E_{kinetic}$ is the kinetic energy transferred from the heat source to sink during simulation time step Δt. Here, A_i is a cross sectional area in the heat flow direction x_i, and $\Delta T/\Delta x_i$ is the temperature gradient in the heat flow direction. In this work, Shenogin's thermal boundary condition [16] was applied in the NEMD simulation for the case of nanocomposites containing the CNTs. Fig. 1 shows a concept of the NEMD simulation for radial thermal conduction in the nanocomposites and its interphase.

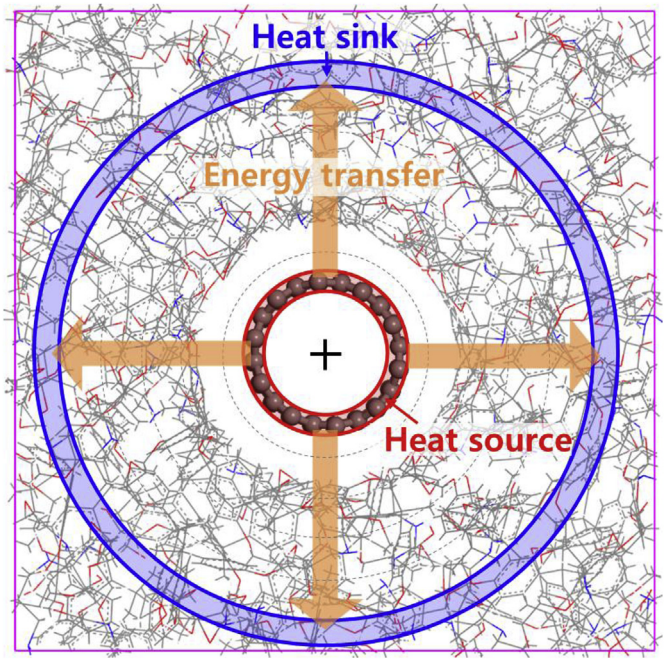

Fig. 1. Concept of the NEMD simulation for radial thermal conduction in the nanocomposites and its interphase.

2.2. Simulation details

The CNT molecular model was a single-walled chiral structure (10, 0) with diameter of 0.79 nm. It was modified using two different functionalization methods for nitrogen doping and carboxyl functionalization. A small portion (4%) of the total number of carbon atoms on the CNT was removed to create defects. The carboxyl functionalized CNT included −H, −O, −OH, −COH, and −COOH functional groups on the defects. The nitrogen doped CNT consisted of quaternary, pyridinic, and pyrrolic doping groups on the defects. Every kind of functional group was randomly located on the CNT surface. The molecular models of the nanocomposites containing pristine, nitrogen doped, or carboxyl functionalized CNTs were constructed by dispersing cross-linked epoxy chains around the CNTs. The constructed models carried out the energy minimization using a conjugate method with the tolerance of 10^{-8} kcal/mol. The NPT (isobaric-isothermal state, N: constant number of atoms, P: constant pressure, T: constant temperature) ensemble of the minimized models was performed for relaxation at room temperature and under atmospheric pressure for 1 ns with time steps of 1 fs.

The NEMD simulation was performed to calculate the interfacial thermal conductivities of the three different nanocomposite models. The thickness of the heat source and sink was 0.2 nm (that is thicker than the diameter of carbon atom: 0.142 nm). The region between the heat source and sink was divided into 48 layers with thickness of 0.025 nm. The kinetic energy of 0.01 kcal/mol was added to the heat source and removed from the heat sink at each 1 fs time step. The NVE (microcanonical state, N: constant number of atoms, V: constant volume, E: constant potential energy) ensemble was simulated for 2 ns to generate a temperature gradient. Heating up simulations of the nanocomposite models were performed to calculate the interfacial heat capacity. The initial and final temperature were 298 and 373 K, respectively. Total simulation time was 2 ns. The interaction energy ($U_{int} = U_{comp} - U_{CNT} - U_{matrix}$), which was defined as the difference in the total potential energy between a nanocomposite and its constituents, and the interphase volume were calculated at each temperature. The interfacial heat capacity was determined by a change in the density of interaction energy with respect to the temperature. Every MD simulation was performed using the software LAMMPS (Large-scale Atomic/