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Investigating thermal conductivities of functionalized graphene and graphene/epoxy nanocomposites

Tai-Yuan Wang *, Jia-Lin Tsai

Department of Mechanical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

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ABSTRACT

This research investigated the thermal conductivities of functionalized graphene (FG) and FG/epoxy nanocomposites by using molecular dynamics simulation. The functional groups considered in FG are carboxyl and amine groups. The results indicated that the thermal conductivity of FG is markedly reduced compared with that of pristine graphene. However, the FG/epoxy nanocomposites demonstrated higher thermal conductivity than did the pristine graphene nanocomposites. To understand the enhancement mechanism, the interfacial thermal conductance (ITC) between the FG and the surrounding epoxy matrix was examined. The effects of the FG on ITC were explicated using vibrational density of state and normalized interaction energy. The improvement of the thermal conductivity of FG/epoxy nanocomposites was attributable to the enhancement of the ITC resulting from the functional groups grafted on the graphene surface. In addition, establishing the functional groups facilitates atomistic interaction between the graphene and epoxy, which can reduce the phonon mismatch and enhance the thermal transport efficiency in the nanocomposite. The enhanced thermal conductivity in the FG/epoxy nanocomposites was validated by experimental observation.

1. Introduction

With superior mechanical and thermal properties, Young's modulus of 1 TPa, tensile strength of 130 GPa, and a thermal conductivity of 600–5000 W/m K [1–4], graphene has become a candidate for use in polymeric nanocomposites to achieve exceptional properties [5]. However, when graphene is applied for improving thermal conductivity, its superior thermal properties may not guarantee that graphene/epoxy nanocomposites possess prominent properties, except that the heat can be transferred without obstacles at the interface. Therefore, modifying the interfacial thermal properties is essential for attaining nanocomposites with high thermal conductivity. Many researchers have functionalized graphene to improve the thermal conductivity of nanocomposites [6–8]. Hung et al. [6] indicated that the nitric acid treatment of graphite nanoplatelets could effectively increase the thermal conductivity of nanocomposites. Ganguli et al. [7] demonstrated that functionalized graphite platelets considerably increased the thermal conductivity of nanocomposites by diminishing interfacial phonon scattering. Song et al. [8] illustrated that the noncovalent functionalization of graphene flakes could also increase the thermal conductivity of nanocomposites through π–π stacking. These experimental results have suggested that functionalization could effectively enhance the interaction and interfacial thermal conductance (ITC) at the interface. In addition, direct characterization of the ITC of the graphene/matrix interface is essential for understanding the mechanism of interfacial thermal transport and the enhancement of nanocomposite thermal conductivity. Therefore, the influences of functional groups on the ITC have been investigated using molecular dynamics (MD) simulation [9–13]. Wang et al. [9] examined the ITC in graphene/polyethylene (PE) nanocomposites and indicated that grafting PE chains to the graphene surface can effectively improve the ITC as well as the vibrational coupling between the graphene and polymer. Luo and Lloyd [10] examined thermal energy transport across the graphene polymer interface and demonstrated that forming covalent bonds at the interface can improve the thermal transport properties of nanocomposites. Wang et al. [11] characterized the effect of the grafting density of functional groups on the ITC of graphene nanocomposites and indicated that increasing the grafting density of functionalization can enhance the interfacial thermal transport properties. Shen et al. [12] evaluated the vibrational power spectrum of functionalized graphene (FG) and epoxy and demonstrated that the extent of vibrational coupling between the graphene and epoxy can be improved by the functional groups. Liu et al. [13]

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* Corresponding author.
E-mail address: voidfoe.me99g@nctu.edu.tw (T.-Y. Wang).

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studied the effects of the hydrogenation of a graphene surface and the interfacial bonding strength on the ITC in a silicene/graphene bilayer structure. When the hydrogen coverage on the graphene surface attained 50%, the ITC reached a peak value. These studies have reported that the functionalization of graphene effectively increases the thermal conductivity of nanocomposites by enhancing the ITC; however, few studies have discussed the connection between the thermal conductivity of graphene and the corresponding thermal conductivity of graphene/epoxy nanocomposites. Grafting functional groups alters the hybridization of pristine graphene while markedly reducing the associated thermal conductivity [14,15]. Nevertheless, the thermal conductivity of nanocomposites is still effectively increased because of the FG, a notion that deviates from the general rule of mixtures. Therefore, the objective of the present study was to understand the mechanism of the effective enhancement in the thermal conductivity of nanocomposites caused by FG. According to our previous experimental work [16], FG with carboxyl and amine groups enhanced the thermal conductivity of graphene/epoxy nanocomposites. Hence, the molecular structure of FG in the current study was constructed on the basis of our previous experimental measurement. We performed heat flux simulations using pristine graphene, FG, and the corresponding graphene/epoxy nanocomposites to evaluate the associated thermal conductivities as well as interfacial properties including ITCs, normalized interaction energy, and the phonon mismatch. Our results could clarify the mechanism of thermal conductivity enhancement caused by graphene in polymeric nanocomposites.

2. Computational methodology

2.1. Thermal conductivity of graphene and FG

2.1.1. Atomistic model of graphene and FG

To explore the thermal conductivity by using MD simulations, the atomistic structures of pristine graphene and FG were constructed. A typical model of pristine graphene is composed of carbon atoms arranged in hexagonal patterns with 50 Å in-plane sizes, as shown in Fig. 1. However, because the thermal conductivity of graphene may be affected by the size [17], graphene with lengths of 10, 20, 40, 80, and 160 nm in the *x* direction was considered with the heat flow assumed in the same direction. In addition, to avoid the boundary effect, the periodic boundary condition was imposed in the boundary of the simulation model along the *y* direction.

Moreover, the functionalization effects on the thermal conductivity as well as the vibrational characteristics of graphene were of concern in this study. Thus, two functional groups—carboxyl (COOH) and amine (NH_2)—as shown in Fig. 2(a and b), were randomly distributed for the smallest length (50 Å) and then repeated to generate the desired simulation cells of FG. These two functional groups were considered because they are commonly observed in FG [11]. In addition, to graft the functional groups to the graphene surface, the hybridization was changed from sp^2 to sp^3. The functionalization ratio (FR), which is defined as the number of functional groups divided by the number of carbon atoms in pristine graphene, was designated as 0%, 5%, or 15% in the FG. The MD simulations were conducted using a large-scale atomic/molecular massively parallel simulator (LAMMPS) [18], and the interatomistic behaviors were described according to the polymer consistent force field (PCFF) potential [19]. Because the PCFF potential has been employed to model the mechanical properties of graphene and epoxy resin accurately [11,20,21], in this study, the PCFF potential was utilized to characterize the properties of graphene and graphene/epoxy nanocomposites. The functional form of the PCFF potential is expressed according to the summation of bonded and nonbonded energy. The bonded energy includes the energy for bond stretching, angle bending, torsion, inversion, and the cross term of these functions. Conversely, the nonbonded energy is a combination of Coulomb and 9-6 Lennard-Jones contributions with a cutoff distance of 10 Å, which relates to pairwise electrostatic and van der Waals interactions, respectively. An equilibrated molecular structure of graphene with minimized energy was attained by performing NPT ensembles in the MD simulation for 0.1 μs with an integration time step of 1 fs. The NPT ensembles were performed at 0 atm to achieve a stress-free state, and the corresponding temperature was maintained at 300 K. Afterward, the atomistic graphene was subjected to a heat flux along the *x* direction for evaluating the corresponding thermal conductivity in an NVE ensemble. The term "NPT ensemble" signifies the number of atoms (*N*), pressure (*P*), and temperature (*T*) being fixed during the MD simulation, and "NVE ensemble" indicates that the number of atoms (*N*), volume (*V*), and energy (*E*) remain constant during the simulation.

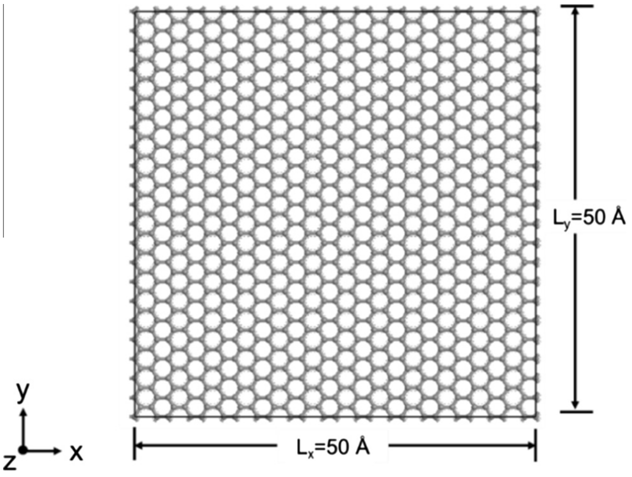

Fig. 1. Atomistic model of pristine graphene.

2.1.2. Calculations of thermal conductivity for graphene and FG

The thermal conductivity of graphene is calculated through nonequilibrium molecular dynamics (NEMD) [22]. To create a temperature difference between the two sides of the graphene, the heat source was deployed on the right side and the heat sink was deployed on the left side; the size of the heat source and heat sink was 10 Å in width, as shown in Fig. 3. The energy supplied from the heat source was then removed through the heat sink continually.

In the NEMD simulation, the steady-state temperature profiles of graphene along the heat flux were obtained from the NVE ensemble, and the thermal conductivity of graphene was determined on the basis of Fourier's law [23] as

$$K_x = \frac{q}{\Delta t \cdot A \cdot (\partial T/\partial x)} \quad (1)$$

where K_x is the thermal conductivity of graphene, *q* is the applied/removed energy (0.02 Kcal/mol) per step, Δt denotes the time step (1 fs), *A* is the cross-sectional area (the graphene thickness is assumed to be 3.4 Å), and $\partial T/\partial x$ is the temperature gradient along the heat flux.

2.2. Thermal conductivity of graphene/epoxy nanocomposites

2.2.1. Construction of models of ideal graphene/epoxy nanocomposites

In addition to the graphene, the thermal conductivity of graphene/epoxy nanocomposites was examined. The graphene/epoxy nanocomposites were composed of cross-linked epoxy and graphene with or without functionalization. We focused on the effect