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Thermal conductivity of functionalized graphene-polymer nanocomposite: A non-equilibrium molecular dynamics study

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Abstract

Heat transfer across thermal interface material, such as graphene-polymer composite, is a critical issue for microelectronics thermal management. To improve its thermal performance, we use chemical functionalization on the graphene with hydrocarbon chains in this work. Molecular dynamics simulations are used to identify the thermal conductivity of monolayer graphene and graphene-polymer nanocomposites with and without grafted hydrocarbon chain. The influence of functionalization with hydrocarbon chains on the interfacial thermal conductance of graphene-polyethylene nanocomposites was investigated using a non-equilibrium molecular dynamics (NEMD) simulation. We also study the effects of the graft density (number of hydrocarbon chain) on the thermal conductivity of graphene and the nanocomposite.

Keywords: Functionalized graphene; Nanocomposite; Thermal conductivity; Non-equilibrium molecular dynamics

1. Introduction

Polymeric nanocomposite materials have been widely used to enhance the mechanical, electrical, and thermal properties of pure polymers [1-5]. They have potential application such as in aerospace[6], automotive[7], electronics[8], energy systems[9], etc. Among the various polymeric composites of current engineering interest, Graphene-based composite materials have received significant attention due to their exceptional thermal conductivity (~3000 W/mK)[10], mechanical stiffness (1060 GPa)[11] and electronic transport properties[12, 13]. Since pure polymers usually have very low thermal conductivities (~0.1-0.5 W/m·K), researchers attempted to enhance its thermal conductivity by adding a small percentage of carbon nanotube (CNT), graphite, graphene to the polymer matrix, and reached to 3-6 W/m·K[14-16] .

Though the thermal conductivity enhancement in such nanocomposite is limited to within one order of magnitude, which is induced by the large barrier to the thermal transport between fillers and polymer matrix. Recently, the thermal interface conductance of graphene-liquid oil ranges from 25-270 MW/m^{2}Kdepending on the functionalization of the graphene edge[17]; and of 30 MW/m^{2}K between graphene and phenolic resin [18]. Chemical functionalization of graphene by introducing atoms and atomic groups has been served as an effective routine to enhance the thermal performance of nanocomposites[19-22]. Owing to the molecule vibrations of thermal transport inside polymers, covalent bond between the matrix and the filler can reduce phonon scattering at graphene-polymer interface, leading to better interfacial conductance[20, 23]. Compared with neat epoxy, the thermal conductivity of graphene nanosheets (GNS) filler epoxy composites through functionalization of pyrene molecules increased more than 800% with low GNS loading[15]. It was superior to the epoxy composites with individual CNTs or GNS. However, the thermal energy transport across the graphene-polymer interface has not been well understood through physical experiment due to its nanosized structure. Numerical simulation such as molecular dynamics (MD) modeling provides an alternative approach to study the interfacial thermal transport.

In this study, we have conducted non-equilibrium molecular dynamics (NEMD) simulations to study the thermal transport across graphene-polymer interface. The effect of functionalization, i.e., grafting hydrocarbon chains to graphene layer with covalent bonds, on the interfacial thermal conductance was also investigated. The effect of model size and thermal conductivity of graphene was taken into account. We then predicted the thermal conductivity of nanocomposite based on a theoretical model. We also study the effects of the filler length and the filler volume fraction on the thermal conductivity of graphene and the nanocomposite.

2. Molecular modeling and simulation

The polymer simulated in this study is polyethylene ((C2H4)n, n=30) which has been widely used as thermal interface material. The polyethylene model was prepared with the dimensions of 30 × 30 × 38 Å, with an initial density of 0.85 g/cc, which agrees well with experimental data of 0.85-0.93 g/cc[24]. To build the graphene-polyethylene nanocomposite model, a sandwich structure with graphene placed in the middle of polyethylene matrix was prepared first, with dimensions of 30 × 30 × 70 Å. All of the models were constructed using Amorphous cell module of Material Studio 7.0 (Accerlys Inc.)[25], and optimized by smart mininizer, as shown in Figure 1. Graphene layers grafted with linear hydrocarbon

chains ($-C_nH_{2n+1}$, n=15) were established in order to explore the effect of functionalization on interfacial thermal conductance (Figure 2). Such covalent end-grafting with a weight ratio (wt%) of 11.65%, 20.87%, and 28.35% corresponds to six, twelve and eighteen respectively.

MD simulations are employed within the LAMMPS package to compute thermal conductivities for all of the systems considered in this work. The adaptive intermolecular reactive empirical bond order (AIREBO) potential[26], which has been widely used in simulations of carbon systems and their thermal energy transport[41]. An ab initio force field, polymer consistent force field (PCFF)[27], is used to model the polymer molecules and the interactions between the graphene and polymers.
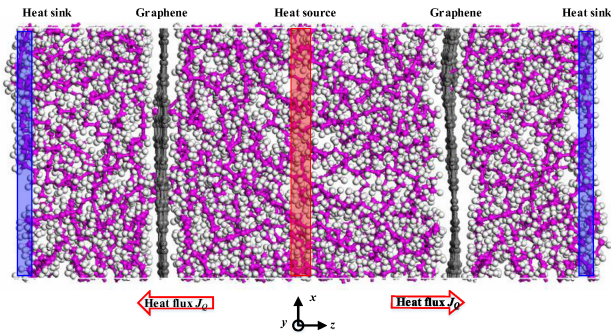

Figure 1. Definition of the heat sink, source to calculate the thermal conductivity of graphene-polymer nanocomposite via NEMD.

Here, we adopt the NEMD to calculate the thermal conductivity via Fourier's law. Before applying the NEMD method to calculate the thermal conductivity of nanocomposites, graphene, and polyethylene, cell equilibration process at finite temperature of 300 K is implemented from 300 ps via Müller-Plathe method [28] for isothermal-isobaric NPT simulations. Periodic boundary conditions are applied to all three spatial directions. Then a rectangular unit cell which has been replicated in the heat flux direction, it is divided into 40 slabs to calculate the local temperature field, and the central and two edge slabs are defined as the heat source and sink region, respectively, as shown in Figure 1. A finite amount of heat energy is simultaneously added into the heat source region at every time step of 1 fs during a 500 ps of NVE ensemble simulation.

In general, the total potential energy of a simulation system contains the following terms:

$$E_{total} = E_{bond} + E_{over} + E_{val} + E_{tors} + E_{vdW} + E_{Coulomb} \quad (1)$$

where E_{bond}, E_{over}, E_{val}, E_{tors}, E_{vdW}, and $E_{Coulomb}$ are the energies corresponding to bond, over-coordination, angle, torsion, van der Waals (vdW), and Coulomb interactions, respectively.

During the continuous energy scaling process of the NEMD method, the heat flux J_Q can be calculated as:

$$J_Q = E/2A \quad (2)$$

where E is the energy added into the heat source, and A is the cross-sectional area through which the heat energy passes. As the heat flux is split into two heat sink regions from the heat source region, the amount in Eq.(2) is divided into 2. Then, the thermal conductivity is calculated on the basis of Fourier's law,

$$J_Q = -k \ (\Delta T/\Delta z) \quad (3)$$

where k is the thermal conductivity, and $\Delta T/\Delta z$ is the temperature gradient. As for the interfacial thermal conductance, it is calculated using the expression

$$J_Q = -G_k\Delta T \quad (4)$$

where J_Q is the heat flux across the interface, G_k is the interfacial thermal conductance, and ΔT is the temperature variation across the interface.
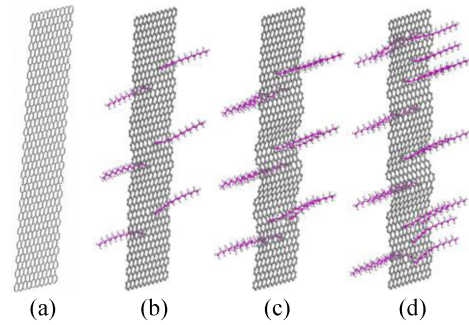

Figure 2. Simulation models of (a) pristine graphene and graphene functionalized with (b) six, (c) twelve, (d) eighteen linear grafted hydrocarbon chains.

3. Result and Discussion

3.1. Model validation

To validate the PCFF potential for thermal transport simulation in graphene-polyethylene nanocomposite, the thermal conductivity of pure polyethylene was calculated using NEMD method. The thermal conductivity of the polyethylene model is calculated as k= 0.36 W/mK. This value is in agreement with the previous experimental values[29]. As shown in Figure 3, the temperature gradient of polyethylene is linear, indicating the regime of linear response in heat source/sink simulation.
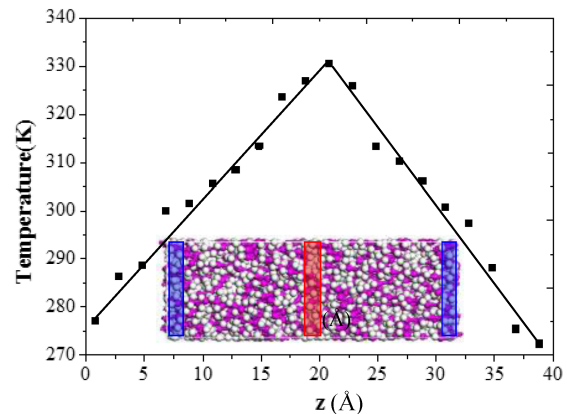

Figure 3. Steady-state temperature profile along the entire length of the polyethylene model.

3.2. Effect of functionalization on the thermal conductivity of graphene

The length of graphene is crucial to its thermal conductivity owing to the fact that small model size can omit some significant modes of long wavelengths[22]. Thus we discuss the influence of functionalized graphene with different graphene length and grafting number, as shown in Figure 2. Figure 4 shows the normalized thermal conductivity of functionalized graphene k with pure monolayer graphene k_0. Functionalization at a very small wt% of 11.32% leads to the sharp drop of k around 95%. With the increase of grafting density, the drop of k becomes slower and gets saturated at a value of 98%. It is induced by the formation of sp3 bonds between graphene and hydrocarbon chains, soften the high-frequency phonon modes and weaken the in-plane energy transfer[22, 30]. Besides, the falling thermal conductivity of graphene lies in the grafted hydrocarbon but less relies on the length of graphene.
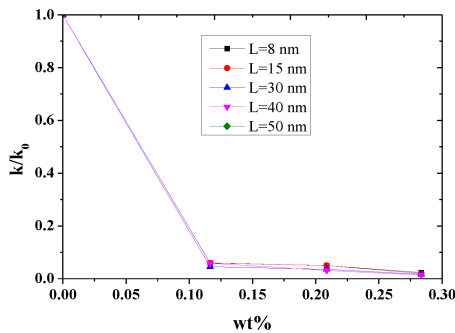

Figure 4. Normalized thermal conductivity of functionalized graphene k/k_0 versus wt% of hydrocarbon. L and k_0 denote the length of graphene and the thermal conductivity of pure graphene, respectively.

3.3. Effect of functionalization on the thermal conductivity of graphene-polyethylene nanocomposite

The thermal transport across the interface between pristine graphene and polyethylene was investigated. After NEMD simulations were performed, the corresponding interfacial thermal conductance can be calculated in terms of Equation (4). Figure 5 shows the steady state temperature profile of pristine graphene-polyethylene nanocomposite, where the temperature changes linearly along the heat flux direction with a sudden temperature jump at the interface due to the different thermal properties of the graphene and the polyethylene. The temperature drop leads to the value of interfacial thermal conductance to be G_k=77.89 MW/m²K, which is close to the value obtained in Wang's work[22].

The effect of functionalization on the graphene-polyethylene interfacial thermal conductance can be established by using the interfacial thermal conductance between pristine graphene and polyethylene as a reference. The functionalization effect was examined through simulating the graphene with different functional hydrocarbon, as shown in Figure 6. It is clearly that the interfacial thermal conductance are largely enhanced by grafting hydrocarbon chains to graphene. When the wt%

of hydrocarbon chains up to 11.32%, the G_k is remarkably improved to 141.62 MW/m²K by 183.9%. With number of hydrocarbon chains increasing, the G_k is increased smaller and reached saturation. At last, using the interfacial thermal conductance evaluated before, we can calculate the thermal conductivity of graphene-polyethylene nanocomposite by an analytical formula according to Nan's work[18]. The results are listed in Table 1. Similar to the interfacial thermal conductance, the k of graphene-polyethylene is improved obviously by grafting 11.32% hydrocarbon chain, while k increases slow as the wt% is up to 28.07%. Hence, functionalization on the graphene can enhance the thermal performance of graphene-polyethylene nanocomposite efficiently, owing to the hydrocarbon chain can widen the overlap in low-frequency vibration modes. Nevertheless, the simulation results are higher some experimental results[31], which may be induced by aggregation of nanofillers, wrinkles, and bad graphene-polymer interfaces during the experiment.
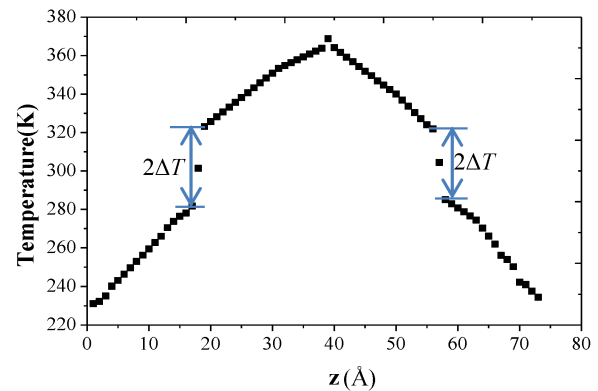

Figure 5. Steady state temperature profile of pristine graphene- polyethylene nanocomposite
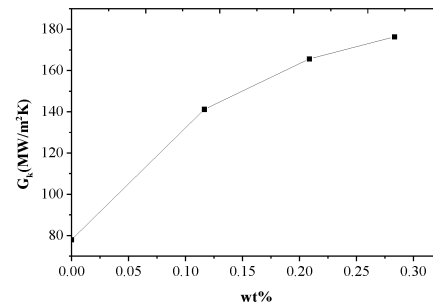
Figure 6. Interfacial thermal conductance G_k as a function of the weight ratio of grafted hydrocarbon

Table 1. Thermal conductivity of nanocomposite k with different number of hydrocarbon chain

Number of hydrocarbon chain	Weight ration of grafted filler (wt%)	k of grafted graphene (W/mK)	k of functionalized graphene-polyethylene (W/mK)
0	0	2247.5	3.42
6	11.32%	119.56	10.85
12	20.87%	99.91	11.84
18	28.35%	46.51	12.54

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4. Conclusion

In this paper, we used steady-state NEMD to investigate the thermal transport in graphene–polymer nanocomposite. The effects of the functionalization on the thermal conductivity of graphene and graphene-polymer nanocomposite are analyzed systemically. We found that functionalized graphene has lower thermal conductivity than pristine graphene. The more grafted hydrocarbon chain the lower thermal property of functionalized graphene. It is induced by the formation of sp3 bonds between graphene and hydrocarbon chains, soften the high-frequency phonon modes and weaken the in-plane energy transfer. Conversely, with the increase wt% of hydrocarbon chain, the interface thermal conductance between graphene and polymer, and the thermal conductivity of functionalized graphene-polymer composite are enhanced increasingly. While the improvement will reach to saturation as the wt% is up to 28%. It is attributed to that grafted hydrocarbon chains can widen the overlap in low-frequency vibration modes and consequently enhance the interfacial thermal conductance. The approaches explored in this study to enhance interfacial thermal transport provide practical guidance to the thermal conductivity improvement of polymeric composite.

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