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Effects of covalent functionalization on the thermal transport in carbon nanotube/polymer composites: A multi-scale investigation

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ABSTRACT

A multi-scale approach, including large-scale molecular dynamics simulations, finite element simulations and analytical effective media modeling, has been adopted to investigate the effects of covalent functionalization on the thermal transport in carbon nanotube (CNT)/polymer composites. It is shown that the cross-links between the polymer and CNTs can further remarkably suppress thermal conductivities of embedded functionalized CNTs by up to 50%, compared with free-standing functionalized CNTs. The cross-links can enhance the thermal coupling between the polymer and CNTs but they also cause density variation in near-interface polymer layers and induce secondary interfacial resistances in the polymer. The thermal coupling between CNTs and polymers mainly occurs on the sidewall of the CNTs and the functionalization will actually shrink the coupling zones. By considering all these effects, an analytical thermal transport model has been developed for the prediction of the effective thermal conductivity of CNT/polymer composites and it shows that overall the functionalization leads to an adverse effect on the thermal transport in the composites. Compared with single-walled CNTs, multi-walled CNTs are less sensitive to these effects, rendering them more suitable as fillers. This study may shed light on the fundamental understanding of the thermal transport in composites with carbon-based fillers such as graphene or graphene oxide.

1. Introduction

Polymers are widely used in numerous engineering areas because of their light weight, low cost, corrosion resistance and ease of processing. Due to the weak van der Waals (vdWs) interactions among molecule chains and the randomness in molecular arrangement, bulk polymers typically have an intrinsic thermal conductivity k below 1.0 W/m-K near room temperature [1,2]. It is desirable to improve k of polymer-based materials for various industry applications requiring thermal management, such as circuit boards in power electronics, electronic packaging, thermal interface materials and heat exchangers [3–5]. A conventional approach to enhance thermal transport in polymers is to add fillers with a high k, including graphite lamellae [6,7], carbon nanotubes (CNTs) [1], carbon fibers [8], and ceramic [9] or metal particles [10], into the polymers to form thermally conductive composites. Among various fillers, CNTs are regarded as the most promising candidates owing to their high mechanical strength, high chemical stability and unusually high intrinsic k (up to ~3000 W/m-K near 300 K [11]). Therefore, thermally conductive CNT/polymer composites have attracted great attentions [1,5,6,12–16] in recent decades.

Despite the superior thermal conductivities of CNTs, many experimental studies [12–15] reported that the enhancement ratio of thermal conductivity was often less than two for polymers filled with randomly orientated CNTs. High interfacial thermal resistance (~10^{-8} m^{2}K/W) on the vdWs-interaction-dominated CNT/polymer interface is widely believed to be one of the main causes [17,18] for such a low enhancement ratio. Covalent functionalization [19–21] is expected to be an efficient approach to significantly reduce the interfacial thermal resistance and achieve good CNT dispersions by strengthening the coupling between CNTs and polymer matrix [22,23]. However, the chemical functionalization introduces sp^3-carbon defects onto CNT surface, which can remarkably reduce k of free-standing CNTs [24]. Up until now, the net effect of covalent functionalization on the thermal transport properties of CNT/polymer composites is still unclear [2]. There is a large scatter in the reported experimental data of k of CNT/polymer composites, even including some contradictory results. Yang et al. [25] reported that the enhancement ratio of epoxy resin with multi-walled CNTs

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(MWCNT) could be improved by 44% through the functionalization of CNTs. However, Gojny et al. [26] and Gulotty et al. [27] found that non-functionalized CNTs led to a larger improvement of k of CNT/polymer composites. Since numerous factors such as CNT dispersion, bond strength, and processing conditions might affect k of CNT/polymer composites [2], which are difficult to control in experiments, numerical simulations and theoretical modeling may help to clarify these issues and develop the fundamental understanding of the thermal transport in these composites. By combining equilibrium molecular dynamics simulations (EMD) and a micro model with effective medium approximations (EMA) [28], Clancy and Gates [29] reported a positive effect of functionalization for single-walled CNT (SWCNT) composites, in contrast to the results from Shenogin et al. [22] using the same methodology. The major difference between these two studies is that the latter considered the reduction in k of free-standing SWCNTs by sp^3-carbon defects. However, the vibration states of functionalized CNTs might be influenced further by polymer through the strong covalent bonding when they are embedded into polymer matrix, leading to possible change in their thermal transport properties. The coupling between CNTs and polymer may also modify the molecular arrangement and in turn the resistance in polymer. These two effects have been rarely explored before. Meanwhile, a multi-scale investigation is desirable for better understanding how these microscale effects influence the macroscale thermal transport in bulk CNT/polymer composites.

In this work, we have explored the functionalization effect on the thermal transport properties of CNT/polyethylene composites using a multi-scale approach. The influence of cross-link on the intrinsic k of both SWCNTs and MWCNTs embedded in polymer and the interfacial thermal resistance was investigated by non-equilibrium and equilibrium MD (NEMD and EMD) simulations. It is found that cross-links can further disturb the phonon transport in CNTs and they also induce density variation and limit the interfacial conductance. By considering the functionalization dependence of k and interfacial resistance, the thermal transport in composites with entirely embedded CNTs was investigated using the finite element method (FEM) and modeled by the EMA approach. Various factors such as the CNT length, the functionalization degree, the random orientation of CNT distribution and the CNT sidewall thermal coupling with polymer, were considered in the modeling. The net effects of covalent functionalization of CNTs on the thermal transport in the composites were then discussed.

2. MD simulations for CNT/polyethylene composites

Three types of SWCNTs including (5,5), (10,10) and (15,15) SWCNTs and the corresponding (5,5)@(10,10)@(15,15) MWCNT were considered in this work. The methyl ($-CH_3$) groups were taken as the functional group. The functionalization degree x is defined as the ratio of the number of functional groups to the number of carbon atoms in the SWCNT or the outermost layer of the MWCNT. The functional groups were uniformly distributed onto the surface of CNTs according to the designed functionalization degree. Then the covalent bond between a selected C atom of the CNT and its nearest methyl group neighbor was created. The polymer considered is the amorphous polyethylene. The adaptive intermolecular reactive empirical bond-order potential (AIREBO) [30], which is derived from the second-generation Brenner potential [31] and offers the capability of modeling both chemical reactions and intermolecular interactions in condensed-phase hydrocarbon systems, was adopted to describe the interatomic interactions in pristine and functionalized CNTs as well as in polymers. This potential can well reproduce the elastic properties [32] and the phonon density of states (DOS) [33] of CNTs and has been widely used to calculate k of pristine or functionalized CNTs [24,34]. The vdWs interactions between adjacent layers of MWCNTs or between CNTs and polymer were modeled by the Lennard-Jones (LJ) potential with parameters from Ref. [30]. The cross-link C–C bonds between the functionalized CNT and the surrounding polymer were described by the Morse potential $U_{ij} = U_0((1 - e^{(-\alpha(r_{ij}-\delta))})^2 - 1)$ with parameters $U_0 = 70$ kcal/mol, $\alpha = 2.236$ Å^{-1}, $\delta = 1.53$ Å [35]. Here U_{ij} and r_{ij} are the potential energy and the distance between the atoms i and j.

Fig. 1(a) shows the representative simulation domain for a CNT/polymer sample. The system was divided into bins of approximately 10 Å along the axis. To form CNT composites, a fully optimized periodical polyethylene cell with a density of 0.95 g/cm^3 was first constructed. Each polymer chain contains 398 $-CH_2$ units and two $-CH_3$ units as tips. Then, a cylindrical hole with the radius equal to the radius of the (15,15) SWCNT plus the vdWs equilibrium distance 0.34 nm between C atoms was created in the middle of the cell to embed pristine or functionalized CNTs, and H atoms were added to saturate the broken bonds in the polymer chains. To obtain the stable structure of the periodical polyethylene cell with such a hole, a pristine (15,15) SWCNT was inserted into the hole to form a nanocomposite. After the full optimization of this nanocomposite by molecular mechanics (at 0 K), the SWCNT was removed. The resulted polymer matrix was then used to embed pristine or functionalized CNTs to ensure almost the same surrounding environment. The obtained nanocomposites were optimized again using molecular mechanics before the MD simulations. Thereafter, using LAMMPS package [36], the CNT nanocomposite was equilibrated in the *NVT* (fixed number of atoms, volume and temperature) ensemble with Noose-hoover thermostat at 300 K for 5–40 ns until the potential energy of the system remains constant and then in the *NVE* (fixed number of atoms, volume and energy) ensemble for 300 ps. It should be noted that, for nanocomposites with pristine CNTs, the relaxation time within 2–3 ns is enough in the *NVT* ensemble. However, for nanocomposites with functionalized CNTs, the relaxation time strongly depends on the functionalization degree. For example, it took ~40 ns to relax the functionalized nanocomposite with the functionalization degree 25% in the *NVT* ensemble at 300 K because of the covalent bonds between the functionalized CNT and the matrix. After reaching the equilibrium state, a temperature difference of 30 K was thereafter introduced by contacting the two end bins of the system with Langevin thermostats in the *NVE* ensemble. In all simulations, a timestep of 0.25 fs was adopted. The exchanged energy between the system and the thermal reservoirs was used to calculate the heat flux J. After getting a stable temperature gradient ∇T, k was calculated according to Fourier's law $k = -J/\nabla T$. Similar simulation procedures were also applied for free-standing CNTs. For pristine or functionalized SWCNTs, the cross section A is defined as $A = 2\pi rh$, wherein r is the radius, h is the wall thickness and is taken as 0.34 nm [37], while for MWCNTs, A is defined as the summation of the cross-section area of each layer. To eliminate the finite-size effects, a series of simulations were performed with different simulation domain lengths L_i ranging from 40 to 600 nm for pristine CNTs and 40 to 60 nm for functionalized CNTs and nanocomposites embedded with CNTs. The thermal conductivity k of an infinite system was obtained by fitting to $1/k_i{\sim}1/L_i$ relation under gray approximation and extrapolating $L_i \rightarrow \infty$, where a good linear correlation was found.

2.1. Thermal conductivities of functionalized CNTs in vacuum

The influence of the functionalization seems to be well captured by the AIREBO potential. As shown in Fig. 1(b), sp^2 carbon atoms attached with functional groups in the SWCNT or MWCNT change