



Effect of defects on thermal conductivity of graphene/epoxy nanocomposites

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ABSTRACT

Owing to the super thermal conductivity of graphene, graphene/polymer nanocomposites have the potential as thermal management materials in many applications. Previous studies have proved that the defects in the graphene sheets can greatly reduce the thermal conductivity of suspended graphene. However, the effects of defects on the interfacial thermal conductance and thermal conductivity of graphene/epoxy nanocomposites have not been well understood. In this paper, the effect of four common types of defects, i.e., single-vacancy, double-vacancy, Stone-Wales and Multi-vacancy, on the interfacial thermal transport between the epoxy and graphene was systematically investigated by using molecular dynamic simulations. The simulation results showed that the interfacial thermal conductance between graphene-epoxy could be considerably enhanced with the existence of Stone-Wales and Multi-vacancy defects. The underlying mechanism was explicated by using the phonon vibration power spectrum. Additionally, based on the effective medium theory and the simulation results, the effect of defects on the thermal conductivity of graphene/epoxy nanocomposites was investigated concerning different graphene filler sizes and volume fractions. Although the inherent thermal conductivity of embedded graphene may be decreased by its defects, it was possible to increase the thermal conductivity of the nanocomposites when the graphene filler size was smaller than a critical value.

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1. Introduction

Epoxies exhibit excellent chemical corrosion resistance, good electrical insulation performance, considerable mechanical properties, and low cost which make them widely used in many engineering applications such as adhesive, coating and particularly in electrical packaging [1–3]. However, their rather low thermal conductivity (TC, ~0.2 W/mK) [4,5] limits their usage as thermal management since heat dissipation is one of the most critical issues [6]. The incorporation of high TC fillers in the epoxy matrix is the most common and useful way to improve the TC of epoxy-based composites [7,8]. Among various fillers, graphene [9] is expected as an ideal one due to its excellent TC (1000–5800 W/mK for freely

suspended samples), high aspect ratio and remarkable mechanical properties [10,11], and a low filler fraction of graphene results in a remarkable improvement in mechanical, thermal and electric properties of polymer composites. The characterizations of nanocomposites are difficult due to complexity and uncertainty of experimental characterizations techniques at the nanoscales, computation simulation approaches are now widely used as alternative characterization technique [12]. However, the TC values of graphene/polymer nanocomposites by experiments were far lower than those by the theoretical analysis and simulation [4,13,14]. These can be attributed to some impractical assumptions in the analysis and simulation, such as the dispersion, alignment of graphene, especially, the interfacial thermal conductance (ITC) between the graphene and polymer and ignoring the defects on the graphene [15].

Some works have been done to understand the ITC and TC of graphene filler modified polymer. Using molecular dynamic method, Luo et al. [16] found that the stronger interfacial interaction strength, the greater polymer density and the formation of

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covalent bonds between graphene/graphite edges and polymer molecules could obviously enhance the ITC. Wang et al. [17–19] showed that both non-covalent and covalent functionalization could dramatically improve the ITC. More recently, Shen et al. [13,20] found that the functionalization of graphene could enhance the ITC while it might decrease the TC of graphene/polymer nanocomposites when the graphene size exceeded a critical value.

These previous researches have improved our understanding of the interfacial thermal transport between polymer and graphene. But so far, most of the previous simulation studies focused on the graphene without any defect. Additionally, the defects [21,22] in the graphene such as single-vacancy (SV), Stone-Wales (SW), double-vacancy (DV) and Multi-vacancy (MV) are inevitable during the production process. Some of the previous simulation studies have proved that the defects have a significant impact on the mechanical properties [23–25] as well as thermal conductivity [26–28] of pristine suspended graphene. For example, Yeo et al. [27] showed that both kinds of Stone-Thrower-Wales and DV defects could decrease the TC by more than 80% as defect densities increased to 10% coverage through molecular dynamic. Mortazavi [26] et al. also found that elastic modulus decreased gradually by increasing the defect concentration, and their results suggested that only 0.25% concentration of defects in the graphene resulted in significant reduction of TC by around 50%.

However, the influences of the defects in the graphene on the ITC between graphene/epoxy and the TC of the graphene/epoxy nanocomposites have not been well understood [29–31]. It is of great significance to fully understand the underlying mechanisms of ITC between polymer and graphene with defects, that is, how the type and concentration of defects are related to the reduction or increase in ITC and how the defects in graphene are connected to TC of the graphene/epoxy nanocomposites.

In this study, we have conducted a series of non-equilibrium molecular dynamic simulations to provide a direct insight into the effect of defects on the ITC between the graphene and epoxy. Four major types of defects, i.e., SV, DV, SW defect and MV were randomly dispersed in graphene sheets, respectively. The phonon vibration power spectrums were analyzed and compared to clarify the mechanisms of the interfacial thermal transport between the epoxy and graphene. Finally, the TC of graphene/epoxy nanocomposites containing the graphene with or without defects were investigated based on the effective medium theory and the foregoing simulation results.

2. Modeling and simulation

2.1. Molecular model of graphene/epoxy nanocomposites

Molecular dynamics simulations were used to explore the interfacial thermal transport between graphene and cross-linked epoxy, and molecular models of nanocomposites were first constructed. The representative molecular method proposed by Yu et al. [32] was employed to construct the initial epoxy model, and this method has been successfully used to obtain mechanical [33] and thermal properties [34] of the cross-linked epoxy of which results were quite comparable to that by the in-situ crosslinking method [35] and experimental results. The epoxy model was composed of bisphenol A diglycidyl ether (DGEBA) as the resin matrix and triethylenetetramine (TETA) as the curing agent which has been widely used as the underfill materials in electronic packaging system, as shown in Fig. 1a. The size-dependent effect on the ITC across graphene-polymer has been investigated by replicating the basic model ($X \times Y \times Z = 8.5 \times 37 \times 155 \text{ \AA}^3$) in the x dimensions, it is found that the ITC increased with the increase of x -dimension, and then reaches a plateau of $\sim 135 \text{ MW/m}^2\text{K}$ (x -

dimension is $\sim 25.5 \text{ \AA}$, see detailed simulation results in Supplementary Information). Such phenomenon is consistent with the previous study conducted by Luo et al. [16]. Their results indicated that the ITC became insensitive to the size when the embedded graphene sheet's size was larger than $\sim 20 \text{ \AA}$, which might be attributed to the short mean free paths of heat carriers in polymers. The present work was focused on the effect of different defect, and the molecular model with single size was used in this study.

While investigating the effect of defects on the ITC and TC of graphene/epoxy nanocomposites, graphene with four common types of defects, including SV, DV, SW, and MV was constructed (as shown in Fig. 2), which have been observed in many studies by experimental methods [21,36]. The SV and DV defects were created by removing one carbon atom and two adjacent carbon atoms on the pristine graphene sheet, respectively. The SW defect was formed by rotating one of the C-C bonds by 90° . The MV was constructed by removing several carbon atoms resulting in forming a hole, and the removal of more than two atoms may be expected to result in larger and more complex defect configurations according to previous studies [21,37]. The four kinds of defects were randomly distributed on the graphene sheets, respectively. The concentration of SV, DV and SW defects varied from 0% to 13%. The defect concentrations of SV and DV were defined as the number density of atoms removed from the pristine graphene sheet; the concentration of SW was defined by considering two defected atoms for each defect. For the MV defect, the removed carbon atoms number varied from 0 to 56.

The nanocomposites model consisted of two graphene sheets with or without defects sandwiched between three epoxy blocks, as shown in Fig. 1c. The cross-section dimension of the composite model was $3.7 \text{ nm} \times 3.7 \text{ nm}$, and the length was around 15.5 nm . Periodic boundary conditions were applied in all directions. All the nanocomposites molecular models were first constructed by a commercially molecular simulation software Material Studio (Accelrys). An ab initio force field, polymer consistent force field (PCFF) [38] based on CFF91 with additional parameters was used to simulate inter-atomic interaction for the whole system as it has been successfully employed to model the interfacial atomistic interaction between graphene and various polymer, e.g., PE, epoxy resin [39]. The function form of the PCFF potential consists of bonded and non-bonded energy, the former includes the energy for bond stretching, angle bending, torsion, inversion, and the cross term of these function. The latter is expressed as the 9-6 Lennard-Jones (LJ) potentials, which can also be called as van der Waals interaction between graphene and epoxy matrix. The 9-6 LJ potential is described as $E_{ij} = \epsilon [2(\delta/r_{ij})^9 - 3(\delta/r_{ij})^6]$, where r_{ij} is the distance between atom i and j , ϵ and δ are the energy and distance constants, respectively. The LJ potential parameter between different types of atoms were calculated by using the sixth power mix rules (i.e., $\epsilon_{ij} = (2\sqrt{\epsilon_i\epsilon_j} \cdot \delta_i^3 \cdot \delta_j^3) / (\delta_i^6 + \delta_j^6)$; $\delta_{ij} = ((\delta_i^6 + \delta_j^6) / 2)^{1/6}$). A potential cutoff of 1.2 nm was used in calculation of nonbonded interactions. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [40] was used to conduct all the molecular dynamic simulation, and the velocity-Verlet method was used to integrate the equation of motion.

2.2. Calculation of ITC

After the initial model was established, the ITC between the graphene and cross-linked epoxy was investigated by using the Reverse Non-Equilibrium Molecular Dynamic (RNEMD) simulation based on Muller-Plathe's approach [41]. Before applying the method, the initial structure was relaxed to reach an equilibrium state, the relaxation involved five different steps. At the beginning, an energy minimization was performed using the conjugate

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