Inter-Carbon Nanotube Contact and Thermal Resistances in Heat Transport of Three-Phase Composites

Feng Gong,† Hai M. Duong,*† and Dimitrios V. Papavassiliou‡

†Department of Mechanical Engineering, National University of Singapore, Singapore, 117576 Singapore
‡School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, Oklahoma 73019, United States

ABSTRACT: Single-walled carbon nanotubes (SWNTs) tend to aggregate into bundles due to van der Waals forces during the fabrication of the composite. A computational model using an off-lattice Monte Carlo method is developed to systematically investigate the effects of SWNT bundles, the number of SWNTs per bundle and the thermal boundary resistance (TBR) at the SWNT—SWNT interfaces on the effective thermal conductivity ($K_{eff}$) of three-phase composites. It is found that the aggregation of the SWNTs in bundles can reduce significantly the $K_{eff}$ of the composites with SWNTs oriented parallel or randomly to the heat flux direction, but it enhances slightly the $K_{eff}$ of those with SWNTs perpendicular to the heat flux direction. The $K_{eff}$ of the composites also decreases when more individual SWNTs aggregate in each bundle and with larger SWNT—SWNT TBR values. The thermal transport mechanism within the composites is dominated by a critical SWNT—SWNT TBR of $0.155 \times 10^{-8}$ m$^2$K/W.

1. INTRODUCTION

Carbon nanotubes (CNTs) have been used as fillers to improve advanced multifunctional properties of polymer composites. Due to intrinsic van der Waals forces, CNTs dispersed in a polymer matrix tend to aggregate into bundles. For heat transfer applications, the bundles limit the heat conduction for CNT-polymer composites. Moreover, the thermal conductivity of an aggregated CNT bundle is usually lower than that of an individual CNT within the bundle due to the thermal boundary resistance (TBR) between adjacent CNTs. This TBR may be incurred by the gaps between the adjacent CNTs and the weak van der Waals interaction, much weaker than the strong sp$^2$ interaction between carbon atoms in the CNTs for phonon transport. Therefore, polymer composites with dispersed CNT bundles inherit lower thermal conductivity than expected.

In order to achieve uniform dispersion of the CNTs and avoid inter-CNT contact points in polymer composites, cost-ineffective treatments, such as covalent or noncovalent functionalization of CNTs, and long-time sonication, are commonly employed. It has been recently reported that a mixture of solid lubricant nanoparticles added with CNTs into a polymer matrix can improve the homogeneous distribution of CNTs. In addition to the enhanced homogeneity of the CNT dispersions, the obtained three-phase composites can combine the properties and advantages of all components (i.e., CNTs, lubricant nanoparticles, and polymer matrix). Other novel three-phase composites have also been fabricated and studied for their multifunctional properties, such as CNT/graphene/polymer composites, CNT/nanoparticle/polymer composites, CNT/fiber/polymer composites, and CNT-stabilized polymer blends. Compared to two-phase composites, three-phase or multiphase composites can integrate the merits of all fillers and polymer into a hybrid system, resulting in more advanced properties of the composite materials. In these three-phase composites, the effective thermal properties may be influenced by the thermal properties and morphologies of both fillers, as well as their interactions. However, there are few comprehensive studies on the effect of the fillers and their interactions on the effective thermal conductivity of three-phase composites.

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Effective medium theory (EMT) and its modifications can be applied to predict the effective thermal conductivity ($K_{\text{eff}}$) of CNT-dispersed polymer composites. While such predictions take into account the diameter and length of CNTs, they assume a perfect dispersion of single CNTs and ignore the CNT bundles and the effect of CNT orientation. However, in three-phase composites, scanning electron microscopy (SEM) images show that CNT bundles, individual CNTs, and lubricant nanoparticles coexist in the polymer matrix. Common EMT-based calculations cannot predict accurately the $K_{\text{eff}}$ of complex CNT-polymer composites where individual CNTs and CNT bundles coexist. The inter-CNT contact within the CNT bundles may cause smaller $K_{\text{eff}}$ for the composites than when the TBR is only between CNTs and the polymer matrix. The CNT-CNT TBRs may dominate heat transfer and limit heat conduction in the complex CNT-polymer composites.

The random walker model developed by Duong et al. can take into account the CNT bundle configuration and can be used to explore the effect of CNT-CNT TBR in two-phase composites. But prior studies did not investigate the composites with CNT bundles having random orientations and complex morphology (e.g., different number of CNTs in a bundle). Moreover, their model may fail to represent accurately the three-phase composites when considering the interaction between the fillers. In order to overcome the limitations of the previous models, appropriate simulation approaches are desired to predict more accurately the $K_{\text{eff}}$ of composites with complex morphology, CNT local agglomeration, CNT bundles, and TBRs at all interfaces.

We have developed an advanced mesoscopic model using an off-lattice Monte Carlo method to study the thermal transport phenomena and limitations in three-phase poly(ether ether ketone) (PEEK) composites having single-walled carbon nanotubes (SWNTs) and tungsten disulphide (WS2) nanoparticles. Our model predicted more accurately the $K_{\text{eff}}$ of three-phase composites than previous models, such as EMTs, by taking into account: (i) various aspect ratios and orientations of the SWNTs, (ii) the nanoscale interface between the SWNTs and WS2 nanoparticles, and (iii) the TBRs between the nano-fillers (SWNTs and WS2) and the PEEK matrix. But our previous model ignored the effects of SWNT bundles and SWNT inter-contact, which cannot be avoided in the composite fabrication procedures. To replicate practical three-phase composites and predict more accurately their $K_{\text{eff}}$ in this work we eliminate the assumptions of the previous three-phase model and investigate comprehensively the effects of the number of SWNT bundles, the SWNT number per bundle, and the SWNT-SWNT TBRs on the $K_{\text{eff}}$ of the three-phase composites. The simulation results of our present work and our previous works can provide quantitative perspectives about the thermal transport mechanisms and limitations of complex multiphase systems, including two- and three-phase polymer composites, metal composites, nano-fluids, and biological systems having CNTs. The developed model promises to bridge the atomistic approaches (e.g., molecular dynamic simulations) and the continuum approaches (e.g., rule of mixture and Halpin–Tsai models) by taking into account the interfacial thermal resistances and the complex configurations of composites (e.g., random-oriented SWNTs, SWNT bundles, larger aspect ratio, and number of SWNTs).

### 2. SIMULATION METHODOLOGY

More details of the algorithm development can be found in our previous works. In brief, thermal energy is quantified through a large quantity of discrete thermal walkers having the same energy. The transfer of heat is considered as the result of the Brownian motion of the thermal walkers in the polymer matrix, which is described by the random motion of the thermal walkers in each space direction. The random movement occurs in jumps that take values from a normal distribution with a zero mean and a standard deviation $\sigma$, expressed as:

$$\sigma = \sqrt{2D_m \Delta t} \quad (1)$$

where $D_m$ is the PEEK thermal diffusivity and $\Delta t$ is the time increment of the simulation. When a walker jumps to the SWNT–PEEK interface, it may jump into the SWNT with a probability $f_{\text{m-SWNT}}$ or remain within the PEEK matrix with a probability $(1 - f_{\text{m-SWNT}})$. The probability is a function of the TBR between PEEK and SWNT, $R_{\text{m-SWNT}}$, obtained using the acoustic mismatch theory (AMT),:

$$f_{\text{m-SWNT}} = \frac{4}{(\rho C_p v R_{\text{m-SWNT}})} \quad (2)$$

where $\rho$ is the PEEK density, $C_p$ is the PEEK specific heat, and $v$ is the sound velocity in PEEK. Due to the ballistic phonon transport and ultrahigh thermal conductivity in the SWNT, thermal walkers are assumed to travel at an infinite speed inside the SWNT. The walker is allowed to exit from a SWNT to the matrix by using another probability $f_{\text{CNT-m}}$ which is related to $f_{\text{m-SWNT}}$ in a way that satisfies the second thermodynamic theorem.
\[
V_{\text{CNT}} f_{\text{m-CNT}} = C_{f-CNT} \sigma_{m-CNT} f_{\text{m-CNT}}
\]

where \( V_{\text{CNT}} \) and \( A_{\text{CNT}} \) are the volume and surface area of a SWNT and \( \sigma_m \) is the standard deviation of Brownian motion in the PEEK matrix. \( C_{f-CNT} \) is a coefficient that can be called the thermal equilibrium factor at the PEEK–SWNT interface, which is dependent on the geometry of the SWNTs and the interfacial area between the SWNT and the matrix.

Similar to the motion within the PEEK matrix, the thermal walkers inside a WS\(_2\) nanoparticle also jump randomly in three directions but with a different thermal diffusivity (that of the WS\(_2\)). The governing probability for the thermal walker entering the WS\(_2\) nanoparticles, \( f_{\text{m-WS}_2} \), is also determined by the AMT as expressed in eq 2. At the WS\(_2\)–PEEK interface, thermal walkers from either the WS\(_2\) side or the PEEK side behave similarly to the walkers crossing the PEEK-SWNT interface from the PEEK matrix. However, due to the different motion of walkers inside WS\(_2\) nanoparticles and inside the SWNTs, the relation between the two probabilities governing the thermal walkers’ movements crossing the WS\(_2\)–PEEK interface, \( f_{\text{m-WS}_2} \) and \( f_{\text{WS}_2-\text{m}} \), is different from eq 3, and is as follows:

\[
F_{\text{WS}_2-\text{m}} = C_{f-\text{WS}_2} \frac{(r + \sigma_{m})^3 - r^3}{r^3} f_{\text{m-WS}_2}
\]

where \( \sigma_{WS_2} \) is the standard deviation of the Brownian motion inside the WS\(_2\) nanoparticle, \( r \) is the radius of WS\(_2\) nanoparticles, and \( C_{f-\text{WS}_2} \) is the thermal equilibrium factor at the WS\(_2\)–PEEK interface. All the parameters used in the simulations can be found in Table 1.

The assumptions of the model described in this paper are:

1. Collisions between thermal walkers are not considered: walker–walker collisions reflect the phonon–phonon scattering in the composites, which is much weaker than the phonon scattering by the disordered matrix materials. We ignore this nonlinear collision between thermal walkers in the current work.
2. Thermal properties of all components do not change with temperature over the modeled range.
3. TBRs are identical at the same interface for thermal walkers entering or exiting from a component.
4. WS\(_2\) nanoparticles are assumed to disperse well without aggregating into clusters due to their lubrication properties.
5. The bulk properties of the polymer are used in the current model, while the crystallinity of the polymer is not taken into account.
6. Walkers bounce back
when jumping outside the computational box in the x direction. This boundary condition is used to avoid walkers entering and immediately leaving, thus to fix the constant heat flux in the x direction. Periodic boundary conditions are applied in the y- and z-directions to achieve the energy conservation. And (7) Computational domain has the same initial temperature.

The individual SWNTs are parallel to each other to form SWNT bundles, and then the SWNT bundles and the unbundled individual SWNTs are randomly distributed in the PEEK matrix as shown in Figure 1a. Both the bundled SWNTs and the individual SWNTs have the same length (500 nm) and diameter (2 nm).9a When a thermal walker travels inside a SWNT bundle, it may jump among the bundled SWNTs, the SWNT bundles and the SWNT/WS2/PEEK composites. The developed model can be determined by the SWNT/WS2/PEEK composites can be determined by releasing 40000 hot walkers (carrying positive energy) from the opposite side, as seen in Figure 1. When reaching steady state, the temperature at every position of the computational box can be determined by using a 300 × 300 grid mesh in the computational box and counting the number of hot and cold walkers in each grid cell.20 The K_eff of the SWNT/WS2/PEEK composites can be determined by the ratio of the temperature gradients along the heat flux in the composite and the pure matrix without fillers, as expressed as

\[ \frac{q''}{ \frac{dT}{dx}} = - \frac{dT_{\text{m}}}{dx} \]

where \( T_{\text{c}} \) and \( T_{\text{m}} \) are the temperatures along the heat flux direction in the composites and in the neat PEEK model, respectively. \( q'' \) is the heat flux and \( K_{\text{m}} \) is the thermal conductivity of PEEK (0.23 W/m K). So the K_eff can be obtained as

\[ K_{\text{eff}} = K_{\text{m}} \frac{dT_{\text{m}}}{dx} / \frac{dT_{\text{c}}}{dx} \]

This paper focuses on the effects of the inter-SWNT contact, various SWNT orientations, the number of SWNT bundles, and the individual SWNT number per bundle on the K_eff of SWNT/WS2/PEEK composites. The developed model can be applied to double-walled CNTs, multiwalled CNTs, and even graphene nanosheets.15,33 The effects of TBRs between the nanofillers (SWNT and WS2) and the PEEK matrix, nanofiller weight fractions, and the individual SWNT morphologies can be found in our previous work.22 A 0.3/0.5/99.2 SWNT/WS2/PEEK composite, in which weight fractions of the SWNTs, the WS2 nanoparticles, and the PEEK matrix are 0.3%, 0.5%, and 99.2%, respectively, is chosen as the study case.20 At this mass fraction of SWNTs (0.3 wt %), 960 SWNTs are involved to construct the composite.19

3. RESULTS AND DISCUSSIONS

3.1. Effects of the Number of SWNT Bundles on the K_eff of the Three-Phase Composites. We present in Figure 2, the effect of the number of SWNT bundles (0–48) on the K_eff of the SWNT/WS2/PEEK composites having different SWNT bundle orientations (parallel, perpendicular, and random to the heat flux direction), as shown in Figure 1.

While the number of SWNTs is kept at 960 and each bundle has 20 individual SWNTs, the extent by which SWNTs are in contact with each other varies from no SWNTs in contact (0 bundles) to all SWNTs in contact (48 bundles). Compared to the pure PEEK matrix, the K_eff of the composites having 48 SWNT bundles oriented parallel or randomly to the heat flux can be enhanced by ~2.3 or ~1.7 times, respectively. The K_eff decreases with increasing the number of SWNT bundles because (i) more SWNT bundles cause more local SWNT agglomeration and reduce the uniform distribution of the individual SWNTs in the PEEK matrix;14 and (ii) the SWNT–PEEK TBRs within the bundles inhibit heat transfer along the heat flux direction. When the SWNT bundles are perpendicular to the heat flux, K_eff slightly increases, approximately by 40% when the number of SWNT bundles increases to 48.
Figure 4. Effect of the SWNT–SWNT TBR on the $K_{\text{eff}}$ of the SWNT/WS$_2$/PEEK composites having 12–48 SWNT bundles. The individual SWNT number in each bundle is kept at 20. The TBRs between nanofilbers (SWNT and WS$_2$) and PEEK matrix are kept constant as Figure 3. The critical TBR (dash line) is estimated to be $R_c = 0.155 \times 10^{-8} \, \text{mK/W}$ by intersecting the $K_{\text{eff}}$ curves of different SWNT bundles.

happens as the bundles formed from 20 individual SWNTs have bigger diameter and can allow the heat to transfer more easily in the direction of their radius.

3.2. Effects of the Number of Individual SWNTs Per Bundle on the $K_{\text{eff}}$ of the Three-Phase Composites. The effect of the number of individual SWNTs in each bundle on the $K_{\text{eff}}$ of the composites is presented in Figure 3. While a total of 960 SWNTs and 36 bundles are kept constant as Figure 3, the number of individual SWNTs in each bundle is varied from 10 to 25 with an interval of 5. For composites having the SWNTs oriented parallel or randomly to the heat flux direction, the $K_{\text{eff}}$ decreases with increasing the number of individual SWNTs in each bundle. With the same number of bundles, more individual SWNTs aggregated in each bundle cause the distribution of the SWNTs in the composites to be nonuniform. A bundle with more aggregated SWNTs has a larger diameter and a lower aspect ratio (length/diameter), which may also decrease the $K_{\text{eff}}$. The finding is consistent with previous works. The phonon coupling between the SWNTs and the PEEK occurs only via low-frequency vibrations. The lower aspect ratio may enhance the SWNT bundle stiffness and weaken the low-frequency vibrations in the SWNT bundles. This leads to a larger SWNT-PEEK TBR and then a reduction of the composite $K_{\text{eff}}$.

The number of individual SWNTs in each bundle seems to have no significant effect on the $K_{\text{eff}}$ when the SWNTs are perpendicular to the heat flux. This may be explained as follows: when SWNTs are oriented perpendicular to the heat flux, individual SWNTs cannot enhance the $K_{\text{eff}}$ of the composites. Since the addition of few CNTs does not much alter the bundle diameter, and only SWNT bundles may slightly improve the $K_{\text{eff}}$ of the composites, when the number of SWNT bundles is fixed, the $K_{\text{eff}}$ of the composites is also expected to remain nearly constant.

3.3. Effects of the SWNT–SWNT TBR on the $K_{\text{eff}}$ of the Three-Phase Composites. In Figure 4, we present the effect of the SWNT–SWNT TBR on the $K_{\text{eff}}$ of the three-phase composites. Results for composites with different degree of SWNT aggregation and with random dispersion in the composites are presented. Composites having randomly oriented SWNTs are chosen for further study as they replicate most of the practical SWNT-dispersed composites fabricated in the experiments. The SWNT–SWNT TBR in the bundles, $R_{\text{CNT–CNT}}$, was varied in the range from $0.0615 \times 10^{-8}$ to $6.1530 \times 10^{-8} \, \text{mK/W}$. The simulation results are summarized in Table 2. When the number of SWNT bundles is constant, the $K_{\text{eff}}$ of the composites decreases as the $R_{\text{CNT–CNT}}$ increases. A larger $R_{\text{CNT–CNT}}$ more significantly impedes the transfer of heat between bundled SWNTs, inducing a lower $K_{\text{eff}}$ of the composites. Surprisingly, the heat

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<th>Table 2. Effects of the SWNT Bundle Number, the Individual SWNT Number Per Bundle, and the $R_{\text{CNT–CNT}}$ on the $(K_{\text{eff}}/K_m)$ of the SWNT/WS$_2$/PEEK Composites$^*$</th>
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<td>$K_{\text{eff}}/K_m$</td>
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<td>$R_{\text{CNT–CNT}} \times 10^{-8} , \text{mK/W}$ ($\mu_{\text{CNT–CNT}}$)</td>
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<td>individual SWNT number in each bundle</td>
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<td>0.0615 (1.0)</td>
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<td>Bundled and Unbundled SWNTs are Parallel to the Heat Flux</td>
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<td>Bundled and Unbundled SWNTs are Random to the Heat Flux</td>
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<td>Bundled and Unbundled SWNTs are Perpendicular to the Heat Flux</td>
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$^*$The result in each case is averaged from the results of three simulations with the different spatial distributions of the individual SWNTs and the SWNT bundles. TBRs of SWNT-PEEK ($1.158 \times 10^{-8} \, \text{mK/W}$) and WS$_2$–PEEK ($0.0116 \times 10^{-8} \, \text{mK/W}$) are kept constant in all the simulations.
transfer mechanism is dominated by a critical SWNT–SWNT TBR, $R_c$, which is estimated to be $0.155 \times 10^{-8}$ m$^2$K/W. This value is obtained based on the data shown in Figure 4, by choosing as the critical point the point at which the lines intersect (see the inset figure). When the $R_{\text{CNT-CNT}}$ is lower than the $R_c$, more bundles lead to significant increase of the $K_{\text{eff}}$ of the composite. This can be explained physically, since at very low $R_{\text{CNT-CNT}}$, more contact between SWNTs may allow more heat transport between individual SWNTs in a bundle. However, when the $R_{\text{CNT-CNT}}$ is larger than the $R_c$ the $K_{\text{eff}}$ of the composites with more bundles increases dramatically because the individual SWNTs may dominate the heat transfer. A large SWNT–SWNT TBR in the bundles may arise from the weak van der Waals interactions for phonon coupling and the strong phonon–phonon scattering at interfaces. Covalent functionalization can be applied to shift the van der Waals interactions into the strong sp$^2$/sp$^3$ interactions for phonon coupling and to weaken the phonon–phonon scattering at interfaces to reduce the SWNT–SWNT TBRs.

4. CONCLUSIONS

In summary, the effects of SWNT bundle configurations on the $K_{\text{eff}}$ of the SWNT/WS$_2$/PEEK composites having different SWNT orientations are investigated by the off-Lattice Monte Carlo method. Except for the cases of heat flux perpendicular to the SWNTs, the simulation results show that the more SWNT bundles and the more individual SWNTs in each bundle can reduce the $K_{\text{eff}}$ of the SWNT/WS$_2$/PEEK composites. The same is true when the TBR at the SWNT–SWNT contact increases. A critical SWNT–SWNT TBR, which may dominate the heat transfer mechanism in the three-phase composites, is estimated to be $R_c = 0.155 \times 10^{-8}$ m$^2$K/W. We can speculate that the $K_{\text{eff}}$ of the three-phase composites can be enhanced by proper covalent functionalization of the SWNTs. The functionalization of SWNTs can uniformly disperse SWNTs in the composites and reduce the TBRs at the SWNT–SWNT contact and at the SWNT–polymer interfaces.

AUTHOR INFORMATION

Corresponding Author
E-mail: mpedhm@nus.edu.sg.

Notes
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