Calculations of factors that affect thermal conductivity in epoxy composites with hybrid carbon nanotube and graphene nano platelet

Han Wang, Ercong Xiao, Taotao Fan, Xiaotuo Li and Wenkai Xiao

School of Power and Mechanical Engineering, Wuhan University, LuoJiaShan, Wuchang District, Wuhan, Hubei 430072, People’s Republic of China

E-mail: xiaowenkai@whu.edu.cn

Keywords: graphene, carbon nanotube, thermal conductivity, finite element, composites

Abstract
Carbon Nanotubes (CNTs) and Graphene Nano Platelets (GNPs) had been used to enhance the thermal conductivity of the epoxy composites and show a synergistic effect. Complex service conditions also put forward the requirements for the structural design of the composites to get better performance. Researches should be done to further understand the mechanism of enhancement in composites and find ways to assist the design and optimization of the structure. In this research, epoxy composites with CNTs, GNPs and hybrid CNTs-GNPs (5:2) were prepared, whose total content of fillers was kept constant at 0.4 vol%. Test of specific surface area show the hybrid fillers had less aggregation and the composites with hybrid fillers had the highest thermal conductivity. Observing the microstructure of the composites, CNTs were absorbed on the surface of GNPs, forming a cross-network which could improve aggregation and provide channels for the heat. A series of finite element models were established using scripts to find the factors that affect the forming of network and heat flow. A parameter was created to reflect the distribution of the fillers: distance of non-network (DNN). Positions, orientations, ratios, shapes, and sizes are all factors. The effect of angles depends on the relative positions of the fillers. A proper bending degree of CNTs would have better enhancement. The vertical-structure network was created manually and heat flux on the network was shown: GNPs expanded the area of network for the acceptance and release of heat. CNTs provide efficient channels for the multidirectional heat flow. The combination of the geometry expanded the influence region of the network.

1. Introduction

Epoxy is widely used to make composites because of its low shrinkage, strong mechanical properties, resistance to corrosion, and so on. Even so, multitudinous explorations are still being carried out to overcome some limitations faced by manufacturing industries. For instance, the effort of getting a smaller size and higher density in electronics has promoted the need for better heat dissipation [1, 2, 35, 37]. Carbon nanotubes (CNTs) have been widely pursued since its discovery, being applied in a variety of composites to improve the thermal performance. Because of its high aspect ratio and superior thermal conductivity (4000 W mK$^{-1}$), CNTs were expected to be the potential fillers for improving the thermal conductivity of epoxy composites [3, 4, 38]. So as the Graphene Nano Platelets (GNPs). Besides high aspect ratio and superior thermal conductivity (5300 W mK$^{-1}$), GNPNS have unique plane structure, which can provide a large area with epoxy matrix resulting in better enhancement of composite thermal conductivity than CNTs [5, 6]. However, direct experimental measurements of both fillers shew far lower enhancement on thermal conductivity than people had expected. Powerful Van der Waals forces between the CNTs and GNPs lead to serious agglomeration. It is a common problem that almost all the pony-size fillers have to face [7, 8]. Many methods have been put forward to improve
the agglomeration: controlling the preparation of fillers, adjusting the process of synthesis or modifying the surface of the fillers. These methods haven’t been widely used in consequence of the complex processes and the possibility of changing properties and structure. These years, some experimental research found that there is a surprising synergistic effect on the thermal conductivity when adding CNTs and GNPs together [9–13]. If the mechanism of the synergistic effect, the optimized proportion, and the efficient implementation method can all be known clearly, thermal conductivity could be enhanced with a slight amount of the hybrid fillers.

Heat conduction and heat dissipation are mainly reflected as vibration and scattering of the phonons. Molecular dynamics calculation can describe the behavior of phonons in detail but always cost high computational resources. To reduce the computational cost, a finite element method model can be established from a more macroscopic view. The finite element method (FEM) has been proposed to be a useful tool for the estimation of thermal conductivity [14, 15, 39–43]. Models could be established to show the heat flow in the fillers. A larger scale of simulation could reflect the internal situation of the composites more comprehensively. If the parameters of the models could be controlled precisely, accurate research could be carried out. The finite element method could be used to assist the structural design of the composites. If the mechanism of the enhancement especially the synergistic effect could be explained clearly, it can better instruct the design of the microstructure in the composite materials to achieve more expected properties [16–18].

In this research, epoxy composites with CNTs, GNPs, and hybrid CNTs-GNPs fillers have been made. Thermal conductivity and specific surface area had been tested. Morphology had been studied to show the microstructure of the composites. Based on the understanding of the composites, a series of program-controlled finite element models were established. We focused on the effect of position on thermal conductivity as well as orientations, ratios of CNTs and GNPs, angles between CNTs and GNPs, and the bending degrees of CNTs. The heat flow in the hybrid network has been shown in detail. Our results and method could provide references for the structural design of composites.

2. Materials and methods

2.1. Materials and specimen preparation

The matrix materials employed in the present study was an epoxy (E51) supplied by Shanghai Resin Factory Co., Ltd, as well as the hardener (MeTHPA) and accelerator (DMP30). Note that the epoxy used in this paper was only one representative, and the results of this research were applicable to most epoxy. The mixing ratio between the epoxy resin, hardener, and the accelerator is 10:8:0.09. The GNPs were supplied by XFNANO, Inc., Nanjing, China, the purity of which is larger than 99%. The diameter of the GNPs is 500 nm ~ 5 μm, and the thickness is 0.8 ~ 1.2 nm. Suzhou Carbon Technology Inc., Suzhou, China, supplied the CNTs, the purity of which is larger than 95%. The diameter of the CNTs is less than 2 nm, and the length is 0.5 ~ 2 μm.

Figure 1 shows the morphology of the GNPs and CNTs powder using a scanning electron microscope (SEM, FEI-Siron 200, FEI Co., Hillsboro, OH, USA). The agglomeration can be observed in both of the two nanomaterials. In figure 1(a), several pieces of platelets agglomerated to an adhering mass. The agglomeration happened in both horizontal and vertical directions of the GNPs, which made the size of the GNPs over 10 μm. In figure 1(b), CNTs gathered into balls with uneven sizes. Both of the fillers would form local weak areas in the matrix without any intentional treatments.

Three types of specimens with different fillers were prepared. One was filled with GNPs, one was filled with CNTs, another was filled with hybrid GNTs and CNTs. The total content of all the fillers was controlled at 0.4 vol%, and the CNT: GNP ratio of the hybrid fillers was 5:2. According to a series of researches in a low...
proportion of carbon nano-fillers epoxy, 0.4 vol% is an optimal ratio for several properties and the CNT: GNP ratio of 5:2 always performs an obvious synergistic effect [19]. These ratios can serve as a representative for further researches in the future. For each type, there were three specimens prepared to obtain consistent results.

Before the preparation of the epoxy resin, the original powder was treated by ultrasonic first to reduce agglomeration. The GNPs and CNTs were added in acetone separately with 10 min of mechanical stirring and 60 min ultra-sonication (KQ2200B, Kunshan Ultrasonic Instruments CO., Ltd, Kunshan, China). The solution was then stirred at 100 °C until the acetone is completely volatilized, which could be confirmed by waiting the weight of fillers to be the same as that before treatment. Figures 2(a), (b) shows the powder after ultra-sonication. The agglomeration was improved, and the fillers dispersed into a smaller size. Compared with figure 1(a), GNPs were separated into smaller lamella from large chunks. It is obvious that the nano platelets were getting thinner, which could provide larger contact areas with the epoxy matrix. Compared with figure 1(b), CNTs were spread out from spheres of different sizes. More independent nanotubes could be better dispersed and bond to the matrix.

Again, all the fillers were added in acetone at 50 °C with 10 min mechanical stirring and 30 min of ultra-sonication. For the hybrid fillers, GNPs and CNTs were added in acetone separately first with 5 min mechanical stirring, and then they were mixed with 5 min mechanical stirring 30 min of ultra-sonication. Next, the epoxy resin E51 was added in the solution with 5 min of mechanical stirring and 10 min of ultra-sonication. The solution was then stirred at 80 °C in the vacuum furnace (WF1330, SOTOR CO., Ltd, Anhui, China) until the weight didn’t decrease, proving the acetone is volatilized. The hardener and accelerator were added in the solution with 10 min of mechanical stirring and 20 min of ultra-sonication. Then the solution was poured into a mold in the vacuum furnace at 100 °C for 2 h. At last, the resin was heated at 50 °C for 24 h to solidify the epoxy nanocomposites. Also, a neat epoxy specimen with no fillers was prepared as a control group for comparison.

2.2. Experiments
In this study, to examine the morphology of the nanofillers, SEM was used to reveal the microstructure. Before adding the epoxy, the specific surface area of the fillers was tested by Quadrasorb Evo (Quanbachrome, FL, USA). The thermal conductivity (k) of the composite was characterized using the physical property measurement system (PPMS-9T, Quantum Design Inc., San Diego, USA). It measures the temperature drop along with the specimen when a known heat passed through it. Then the k was calculated according to the temperature drop and the length of the heat transfer. Each specimen had been tested three times, and the mean values of measurements for all three specimens of the same type were treated as the final k with a three-digit significant number.

3. Results and discussion

3.1. Specific surface area
The specific surface areas of the fillers are shown in table 1. Agglomeration can lead to a decrease in the specific surface area. Thus the specific surface area can reflect the degree of the agglomeration. It shows that the specific surface area of the hybrid fillers is about twice as much as the CNTs and GNPs. Thus, the improvement of dispersion can be verified. Compared with the difference of the specific surface area in theory: CNTs(1315 m² g⁻¹), GNPs(2630 m² g⁻¹), the results can be used to describe the degree of agglomeration for the CNTs and GNPs.
3.2. Thermal conductivity

The thermal conductivity \( k \) of the specimens are shown in Figure 3. All the nanocomposites had higher \( k \) than the neat epoxy. Compared with the \( k \) of the neat epoxy, \( k \) was improved by 5.95% because of adding 0.4 vol% CNTs, and GNPs improved by 3.1%. CNTs showed a better enhancement effect than the GNPs. Besides, the hybrid CNTs and GNPs fillers improved \( k \) by 9.5%, which shows a synergistic effect between GNPs and CNTs.

3.3. Morphology

The morphology of CNTs-GNPs/Epoxy had been carried out and was shown in Figure 4. From the figure, it can be seen that CNTs absorbed on the GNPs surface. It was a kind of physical interaction between CNTs and GNPs, which was formed by Van der Waals forces. Besides, when the contact length and orientations were appropriate, there emerged \( \pi-\pi \) interaction between CNTs and GNPs, leading to a closer bond [20, 21, 44, 45]. The large surface of the GNPs provided sufficient adsorption space for the CNTs to get sound dispersion. In the meantime, the CNTs on the surface of the GNPs prevented the further agglomeration of the GNPs. Besides, figures 4(b)–(d) shows that CNTs built bridges between the GNPs, which made the heat transfer more efficient. This virtuous circle improved the agglomeration that happened when only adding one kind of filler, and formed a 3D network for heat transfer. Thus, it can be concluded that due to the unique geometry of CNTs and GNPs, and the interactions between them, special microstructure (a 3D network) formed inside the epoxy matrix, as shown in figure 5. This structure can reduce the agglomeration, making the network formed by CNTs and GNPs distributed in the matrix more widely. Thus, the dispersion was improved. Besides, the networks provide efficient paths for heat transfer. All of these may be the reason for the synergistic effect of thermal conductivity. In a word, the network was the key to improve thermal conductivity.

3.4. Finite element analysis

From the experimental research, the importance of forming networks had been known for improving thermal conductivity. However, the understanding of the network was still superficial: the network would provide channels for the heat. What factors would change the formation of the network and how would the change of the network affect the thermal conductivity of the composites, which would be explored by using the finite element method.
3.4.1. Model established

Heat conduction and heat dissipation are mainly reflected as vibration and scattering of the phonons \[22, 23\]. Three important properties are reflecting the combination of micro-behaviors: thermal conductivity of matrix, the thermal conductivity of fillers, and interfacial thermal conductance. In this study, ANSYS Workbench was
used. The calculation model was established using scripts in SpaceClaim. Using a script will enable the model to be established quickly. Parameters can be adjusted accurately and the calculation will have good repeatability. To simplify the model and control variables to make the results clearer, the following settings were made:

3.4.1.1. CNTs were simplified as bent cylinder and GNP were simplified as round chips
As shown in figure 6, regular geometric parts were used to build the model. Considering the size of the fillers, the diameter of the GNP in models was 1 μm, and the thickness of GNP was 0.02 μm. The bent cylinder of CNTs was established by sweeping a round face along a spline and the spline was built from three feature points. The diameter of the CNTs was 0.09 μm, and the length of CNTs was 4 μm. The size of the matrix block was 5 × 5 × 5 μm³.

3.4.1.2. Each filler model has 6 parameters for location and orientation
Three for angles of rotation around x, y, z-axis and three for the spatial position: coordinates of x, y, z-axis. According to the parameters, every filler would be rotated and moved to a specific position after being created. All the parameters can be adjusted freely according to the need of research, which could provide conditions for careful researches. As shown in figure 6, GNP had four feature points, and CNT had three feature points. Knowing the parameters of movement and rotation, all the coordinates of the feature points can be calculated, which can be used in later analysis. As shown in figure 7, the network formed by the fillers was used to do the subtract operation from the matrix block. Then the fillers were translated into the gaps in the matrix formed by the subtract operation. The model of composites was created.

3.4.1.3. The thermal properties were assumed to be temperature independent
In fact, the thermal properties are dependent on temperature. However, the relationship between properties and temperature hadn’t been known clearly. Setting the properties to be temperature independent could reduce
interference factors, which was beneficial to explore the influence of network and interface thermal conductance [24, 25]. The thermal conductivity of the epoxy matrix was 0.2 W mK\(^{-1}\), the thermal conductivity of CNTs and GNP\(s\) were 4000 W mK\(^{-1}\) and 5300 W mK\(^{-1}\) [26–29]. These data were obtained from experiments by the manufacturers. The interfacial thermal conductance of CNT and CNT\((G_{cc})\) was set as 1.0E7 W/(m\(^2\)K), and the interfacial thermal conductance of GNP and GNP\((G_{gg})\) was set as 2.5E8 W/(m\(^2\)K). The interfacial thermal conductance of CNT and GNP\((G_{cg})\) was set as 1.3E9 W/(m\(^2\)K). Those were obtained from molecular dynamics simulations [30–33].

3.4.2. Calculation condition
In order to enable the changes of networks to be accurately captured, in this study, the heat flow and thermal conductivity were focused on the single-axis. As shown in figure 8, constant temperature and constant heat flux were set on the two opposite faces of the matrix. The thermal conductivity of the composites\((k)\) was calculated according to the Fourier equation [34]:

\[
k = \frac{q_z \Delta z}{T_{z+} - T_{z-}}
\]

Where \(q_z\) is the constant heat applied on the face, \(\Delta z\) is the size of the matrix, \(T_{z+}\) is the average temperature of the face where heat flux was imposed, \(T_{z-}\) is the average temperature of the face where the constant temperature was imposed.

3.4.3. Distance of non-network heat flow
The heat transmits fast through the network of fillers. However, discontinuity of the network would affect the heat transfer in the composites and reduce the thermal conductivity. A parameter was created in this research, which showed the distance between the network. In other words, it showed the distance of non-network (DNN) when heat transferred through the composites. Our calculation condition focused on the one-axis (y-axis), so the DNN also focused on the distance along the y-axis.

As shown in figure 9(b), the model of the entire composites was cut into 9 same-size pieces (along x, z-axis). As shown in figure 9(c), one piece was chosen as an example. On the top of the composites, there was a single GNP that didn’t connect with other fillers. Red lines show the distance between the GNP, the top surface of the matrix and network of fillers in the middle. In the middle part, there are some fillers: GNP and some incomplete CNTs. They can be seen as overlapped along the y-axis so there is no DNN between them. Add up the distances of every piece, the DNN of the composites can be got. All the calculation of DNN was done by a program using the coordinates of every feature points on the fillers, as shown in figure 10. Using the single-axis distance to reflect the distance of heat transfer rather than real spatial distance may bring some small errors, however, it can still generally reflect the distance of networks. Cutting the composites into pieces was to reduce error and the number of pieces could be changed according to the need for accuracy.

3.4.4. Random orientation and position
In some research, the calculation was carried out under random position and orientation. To verify the effect of random position and orientation on the accuracy of thermal conductivity, the total volume of fillers (0.4%) and the ratio of CNT: GNP (5:2) was controlled to be the same. The influence of CNT and GNP may be different, so they were explored separately. Figure 11(a) shows the thermal conductivity of five composites with random location and orientation parameters of CNT. Figure 11(b) shows the thermal conductivity of five composites with random location and orientation parameters of GNP. In each figure, the DNN was also shown. The thermal conductivity of both presents a distribution of fluctuations, which means changes in location and orientation would bring an
apparent influence on the thermal conductivity. Besides that, in both figures, DNN and thermal conductivity have the opposite trend. It verified that the distance of non-network heat flow (DNN) can reliably reflect the trend of thermal conductivity. It means the DNN can be used to guide rapid modeling. Calculating DNN first will provide a useful reference for modeling before long-time finite element calculation. It will be helpful for the design of composites network. As shown in figure 12, DNN of another 20 random models was calculated for GNP and CNTs respectively. It can be seen that whether change parameters of CNTs or GNP, violent fluctuations can be

![Figure 9](image9.png)

**Figure 9.** Distance of Non-Network Heat Flow: (a) model of composites; (b) cut the model into 9 pieces; (c) red line shows the DNN.

![Figure 10](image10.png)

**Figure 10.** Calculation process of DNN.

![Figure 11](image11.png)

**Figure 11.** Variation of thermal conductivity: (a) random CNT; (b) random GNP.
caused. So, in later research, the location and orientation must be controlled to be consistent. Random settings will bring errors in the results. Besides, from figures 11 and 12, the fluctuations caused by changing CNTs was more obvious than that of GNPs. It means that the change of CNTs was more likely to affect the thermal conductivity of the composites under the current combination of the fillers’ sizes and shape.

3.4.5. Effect of ratio (CNT: GNP)
Different ratios of CNTs and GNPs may form different networks. To explore the effect of ratio, 10 models of composites were established. The total volume was controlled at 0.4 vol%. Table 2 shows the details of the models. All the parameters of position and orientation for CNTs were chosen in order from the same parameters list, which can make the parameters consistent. So did the GNPs. Figure 13 shows some of the models. This method can eliminate the influence of position and orientation. Note that in this part of research, the interactions between the fillers were not considered. So, the results could not reflect the effect of agglomeration. As shown in figure 14, thermal conductivity decreased along with the decrease of the CNT ratio. It verified the judge above that in the current sizes of fillers, CNTs were more likely to affect the thermal conductivity. In this research, the aspect ratio of CNTs was larger than GNPs. The CNTs can span a more extensive area than the GNP in this research. If the aspect ratio was changed, the results may be different. However, there is an exception between 3:1 and 5:2 as circled in figure 14. The thermal conductivity of 5:2 is a little bigger than 3:1. These two models were very suitable for exploring the factors affecting thermal conductivity. As shown in figure a, b the two models were almost the same, except for one filler. In figure 15(a), it is a CNT, and in figure 15(b), it was changed into a GNP. The increase in thermal conductivity was caused by this change. In both models, the heat will transfer to the out-point, and flow out the composites. As shown in figures 15(e), (f) finite element calculation can give the value and direction of heat flux. For the CNT in the 3:1 model, the direction was

![Figure 12. Variation of thermal conductivity of 20 models for CNTs and GNPs respectively.](image)

**Table 2.** Details of the models with different ratios.

| Ratio  | Numbers of CNT | Numbers of GNP | Thermal conductivity (W/ (mK)) | DNN (mm) |
|--------|----------------|----------------|--------------------------------|----------|
| All CNTs | 20            | 0              | 0.2667                         | 26.948   |
| 4:1    | 16            | 6              | 0.2643                         | 27.047   |
| 3:1    | 15            | 8              | 0.2544                         | 27.363   |
| 5:2    | 14            | 9              | 0.2554                         | 27.645   |
| 2:1    | 13            | 11             | 0.2487                         | 28.02    |
| 1:1    | 10            | 16             | 0.2351                         | 28.057   |
| 1:2    | 7             | 21             | 0.2348                         | 28.102   |
| 2:5    | 6             | 23             | 0.2205                         | 28.521   |
| 1:3    | 5             | 24             | 0.2212                         | 28.424   |
| 1:4    | 4             | 25             | 0.2181                         | 28.591   |
| All GNPs | 0             | 32             | 0.2168                         | 28.768   |

**Figure 12.** Variation of thermal conductivity of 20 models for CNTs and GNPs respectively.
Figure 13. Some models of different ratios.

Figure 14. Variation of thermal conductivity of different ratios.

Figure 15. Comparison of 3:1 and 5:2 models: (a)(b) models; (c)(d) left view; (e)(f) heat flux.
downward but for GNP in 5:2 model the direction was rightward. It was caused by the difference of relative position between the filler and out-point. In figure 15(a), the CNT was directly above the out-point and the CNT was perpendicular to the total heat flux (y-axis). There was no obvious temperature difference on the CNT. Also, as shown in figure 15(c), there was some distance between the CNT and the fillers above, which caused the discontinuity of the network. In figure 15(b), the GNP was on the upper left of the out-point and the GNP was close to the surrounding fillers, as shown in figure 15(d). The GNP became part of the network. Thus the max heat flux on the GNP was 7330.8 W m$^{-2}$, bigger than that of the CNT (4765.7 W m$^{-2}$). All the reasons above caused the increase in thermal conductivity. It can be concluded that the relative position between the fillers and the out-point, and the angle between the fillers and the total heat flux (y-axis) may affect the network of heat flow.

3.4.6. Effect of angles between CNT and GNP

From the research above, it can be known that the orientation will affect the network. Models in figure 16 have the same number of CNTs and GNPs. To control the variables, all the CNTs in the models had the same parameters of orientation and positions. The orientation of the CNTs was set almost parallel to the y-axis and the orientation of the GNPs was changed from 0° to 90°. Figure 17 shows the results of thermal conductivity. In general, the thermal conductivity would increase along with the increase of the angle, such as from 15° to 90°. In this range of angles, GNPs played a direct role of heat transfer, like CNTs. When the angle between the fillers and the direction of total heat flux (y-axis) became smaller, the projection distance on the y-axis became bigger and it led to better enhancement on the thermal conductivity.

However, from 0° to 15° there was a drop in thermal conductivity. To explore why the thermal conductivity of 0° was a little bigger than 15°, the two models were compared. The same three fillers were chosen to compare the heat flux. From figure 18, all the max values of heat flux were improved. GNP A increased most, from
Was the vertical structure formed by CNT and GNP helpful for the heat transfer? To enlarge the effect of the vertical structure, the positions of the GNPs were changed manually. As shown in figure 19, some GNPs were moved to the end of CNT to create some vertical structures. Kept the position of GNPs, and changed the angle between CNT and GNP from $0^\circ$ to $90^\circ$. The thermal conductivity had significant improvement. Kept the position of GNPs, and changed the angle between CNT and GNP. The results were shown in figure 20(a), this time thermal conductivity decreased along with the increase of angle. Besides, from $0^\circ$ to $40^\circ$ the thermal conductivity dropped slowly, but from $40^\circ$ to $90^\circ$ it dropped fast. It can be inferred that the effect of angle between the CNTs and GNPs depends on the relative position of the fillers. There are different optimized angles for different positions. In the research above, when the ratio of CNT and GNP was changed, the model of all CNTs shew the best thermal conductivity. There was no
synergistic effect because the interaction was not considered. Knowing the effect of angle and position, the GNPs in the 5:2 model were moved manually to the end of CNTs, forming vertical structures. As shown in figure 20(b), the thermal conductivity of the 5:2 (design) model was much higher than that of all CNTs. Figure 21 shows the heat flux of the vertical structure. Soon after the heat entered the matrix, most of the heat was attracted by the large surface of GNPs. Then the heat was concentrated toward the center of the GNPs and transferred to the next disk of GNPs via the CNTs. The GNPs expanded the area of network for the acceptance and release of heat. According to the experimental results, when the composites are prepared by ordinary stirring, CNTs tend to absorb on the surface of GNPs, forming cross networks. The effect of the cross-network is similar to the vertical structure above and that’s the reason for a synergistic effect in hybrid CNTs and GNPs fillers. The conduction of heat in composites is not unidirectional. The optimal structure of the network should be a balance of distribution in multiple directions. When designing composites, angles between the fillers should be considered simultaneously with the positions, making the path of the heat flow as shorter as possible.

3.4.7. Effect of bending degrees of CNTs
In reality, due to the process of preparation or interaction between fillers, CNTs always have different bending degrees. To explore the effect of bending degrees, 5 kinds of CNTs was created. To change the bending degree, only the 3 initial feature points in scripts should be changed. CNTs in different composites shared the same parameters of location and orientation. Figure 22 shows the CNTs and the composites, and all the GNPs have the same parameters. As shown in figure 23, the thermal conductivity of the composites varied, which didn’t show linear rule along with the increase of the bending degree. The biggest bending degree (type 5) shew the worse enhancement. Nor did the no-bending CNTs (type 1) got well enhancement. CNTs with a bit of bending degree (type 4) got the best performance. A proper bending degree of CNTs may be more beneficial to the connection of different regions and adapt to more complicated directions of heat transfer.

3.4.8. Compare between CNTs and GNPs
For single GNP and CNT, GNP has large surface area for the acceptance and release of heat. When the graphene sheet is small, its influence is limited. While CNT has a large span of space, it can play the role of communication between
different temperature regions better. The disadvantages of GNP can be improved with the increase of sheet. From the point of contact with the matrix, according to the research before, the interfacial thermal conductance between GNP and epoxy matrix ($4.8 \times 10^8 \text{ W/(m}^2\text{K})$) is higher than that between CNT and epoxy matrix ($6.6 \times 10^7 \text{ W/(m}^2\text{K})$). It makes the GNP contacts better with the matrix, leading to more adequate heat transfer. However, for the composites, the fillers cannot be single. From the research above, it can be seen that the spatial network formed by fillers in composites has a greater influence on the improvement of thermal conductivity. From this point of view, it is not easy to form a wider spatial structure by adding only GNPs. GNPs tend to cluster into isolated islands and were unable to form an effective network for heat flow. While the CNTs are more easily connected to each other, so the thermal conductivity of CNTs/epoxy was higher than that of GNPs/epoxy in the experiments. Even so, enhancement of both fillers was limited by the aggregation. Fortunately, adding CNTs and GNPs can improve the aggregation. Appropriate structure formed by CNTs and GNPs could combine both strengths of the two fillers.

4. Conclusions

Program-controlled finite element models were established to explore the factors that could affect thermal conductivity in epoxy composites with hybrid CNTs and GNPs. It can be found that the positions and orientations of the fillers could have influence. Under the current combination of the fillers’ sizes and shape, changes of CNTs could have more influence on the thermal conductivity. The angles between the CNTs and GNPs can also make an influence, and the effect of angles would depend on the relative positions of the fillers. For the CNTs, a proper bending degree would have better enhancement. According to the experiments and calculation results, CNTs would be absorbed on the surface of GNPs, forming a cross-network, which could improve agglomeration. In the cross-network, GNPs expanded areas for the acceptance and release of heat. CNTs provide efficient channels for the multidirectional heat flow. The combination of the geometry expanded the influence region of the fillers. Thus a synergistic effect of thermal conductivity could be found in epoxy composites with hybrid CNTs and GNPs.

Funding

This research was funded by grants from National Natural Science Foundation of China (No. 51403223).

ORCID iDs

Wenkai Xiao @ https://orcid.org/0000-0003-0436-4445

Figure 23. Variation of thermal conductivity of different bending degrees.
References

[1] Park J S, An Y J and Shin K 2015 Enhanced thermal conductivity of epoxy/three-dimensional carbon hybrid filler composites for effective heat dissipation RSC Adv. 5 46898–96
[2] Das P, Ganguly S and Banerjee S 2019 Graphene based emergent nanolights: a short review on the synthesis, properties and application Res. Chem. Intermed. 45 3823–33
[3] Pradhan B and Srivastava S K 2014 Synergistic effect of three-dimensional multi-wall carbon nanotube–graphene nanofiller in enhancing the mechanical and thermal properties of high-performance silicone rubber Polym. Int. 63 1219–28
[4] Thostenson E T, Ren Z and Chou T W 2001 Advances in the science and technology of carbon nanotubes and their composites: a review Compos. Sci. Technol. 61 1899–912
[5] Balandin A A 2011 Thermal properties of graphene and nanostructured carbon materials Nat. Mater. 10 569–81
[6] Teng C C, Ma C M and Lu C H 2011 Thermal conductivity and structure of non-covalent functionalized graphene /epoxy composites Carbon 49 5107–16
[7] Tang Y and Gou J 2010 Synergistic effect on electrical conductivity of few-layer graphene /multi-wall carbon nanotube paper Mater. Lett. 64 2513–6
[8] Han S S, Meng Q S and Pan X 2019 Synergistic effect of graphene and carbon nanotube on lap shear strength and electrical conductivity of epoxy adhesives J. Appl. Polym. Sci. 136 48056
[9] Yu A, Ramesh P and Sun X 2008 Enhanced thermal conductivity in a hybrid graphite nanoplatelet–carbon nanotube filler for epoxy composites Adv. Mater. 20 4740–4
[10] Joyti J, Singh B P, Chockalingam S and Joshi A G 2018 Synergetic effect of graphene oxide–carbon nanotube on nanomechanical properties of acrylonitrile butadiene styrene nanocomposites Mater. Res. Express 5 045608
[11] Banal S A, Singh A P and Kumar S 2018 Synergistic effect of graphene and carbon nanotubes on mechanical and thermal performance of polysiloxene Mater. Res. Express 5 075602
[12] Machado B F, Marchioni A and Basca R R 2013 Synergistic effect between few layer graphene and carbon nanotube supports for palladium catalyzing electrochemical oxidation of alcohols Journal of Energy Chemistry 22 296–304
[13] Gedam S S, Chaudhary A K and Vijayakumar R P 2019 Thermal, mechanical and morphological study of carbon nanotubes–graphene oxide and silver nanoparticles based polystyrene composites Mater. Res. Express 6 085308
[14] Zain-ul-Abdein M, Azeem S and Shah S M 2012 Computational investigation of factors affecting thermal conductivity in a particulate filled composite using finite element method Int. J. Eng. Sci. 56 86–98
[15] Dede E M 2010 Simulation and optimization of heat flow via anisotropic material thermal conductivity Comput. Mater. Sci. 50 510–5
[16] Zhou E, Xi J, Guo Y and Liu Y 2017 Synergistic effect of graphene and carbon nanotube for high-performance electromagnetic interference shielding films Carbon 133 316–22
[17] Ivanov E, Kotsilkova R and Xia H 2019 PLA/Graphene /MWCNT composites with improved electrical and thermal properties suitable for FDM 3D printing applications Applied Sciences 9 1209
[18] Yu J, Choi H K and Kim H S 2016 Synergistic effect of hybrid graphene nanoplatelet and multi-wall carbon nanotube fillers on the thermal conductivity of polymer composites and theoretical modeling of the synergic effect Composites Part A: Applied Science and Manufacturing 88 79–85
[19] Min C, Liu D and Shen C 2018 Unique synergistic effects of graphene oxide and carbon nanotube hybrids on the tribological properties of polyaniline nanocomposites Tribol. Int. 117 217–24
[20] Seydou M, Marsaudon S and Buchoux J 2009 Molecular mechanics investigations of carbon nanotube and graphene sheet interaction Phys. Rev. B 80 245421
[21] Li Z, Fan G and Guo Q 2015 Synergistic strengthening effect of graphene–carbon nanotube hybrid structure in aluminum matrix composites Carbon 95 419–27
[22] Shenogina N, Shenogin S and Xue L 2005 On the lack of thermal percolation in carbon nanotube composite Appl. Phys. Lett. 87 133705
[23] Prasher R 2007 Thermal conductance of single-walled carbon nanotube embedded in an elastic half-space Appl. Phys. Lett. 90 143110
[24] Xu L, Wen N and Zheng Y 2012 Graphene–nanotube 3D networks: intriguing thermal and mechanical properties J. Mater. Chem. 22 1435–44
[25] Im H and Kim J 2012 Thermal conductivity of a graphene oxide–carbon nanotube hybrid /epoxy composite Carbon 50 5429–40
[26] Konatham D, Papavassiliou D V and Stroili A 2012 Thermal boundary resistance at the graphene–graphene interface estimated by molecular dynamics simulations Chem. Phys. Lett. 527 47–50
[27] Ghosh S, Bao W and Nika D L 2010 Dimensional crossover of thermal transport in few-layer graphene Nat. Mater. 9 555–8
[28] Balandin A A, Ghosh S and Bao W 2008 Superior thermal conductivity of single-layer graphene Nano Lett. 8 902–7
[29] Huxtable S T, Cahill D G and Shenogin S 2003 Interfacial heat flow in carbon nanotube suspensions Nat. Mater. 2 731–4
[30] Hu L, Desai T and Kehlinski P 2011 Thermal transport in graphene-based nanocomposite J. Appl. Phys. 110 033517
[31] Shinogina N, Shenogin S and Xue L 2005 On the lack of thermal percolation in carbon nanotube composite Appl. Phys. Lett. 87 133706
[32] Bao H, Shao C and Luo S 2014 Enhancement of interfacial thermal transport by carbon nanotube–graphene junction J. Appl. Phys. 115 035324
[33] Bui K, Duong H M and Stroili A 2011 Effective heat transfer properties of graphene sheet nanocomposites and comparison to carbon nanotube nanocomposites J. Phys. Chem. C 115 3872–80
[34] Li X, Fan X and Zhu Y 2012 Computational modeling and evaluation of the thermal behavior of randomly distributed single-walled carbon nanotube/polymer composites Comput. Mater. Sci. 63 207–13
[35] Qi Z, Tan Y and Zhang Z 2018 Synergistic effect of functionalized graphene oxide and carbon nanotube hybrids on mechanical properties of epoxy composites RSC Adv. 8 36689–700
[36] Lee S E, Choi O and Hahn H T 2008 Microwave properties of graphite nanoplatelet /epoxy composites J. Appl. Phys. 104 033507
[37] Kausar A, Rafaque I and Muhammad B 2016 Review of applications of polymer /carbon nanotubes and epoxy /CNT composites Polym.-Plast. Technol. Eng. 55 1167–91
[38] Decarlis A and Jaeger M 2001 Effective thermal conductivity of heterogeneous two-phase material using the self-consistent finite element method Scr. Mater. 44 1955–8
[39] Song Y S and Youn J R 2006 Evaluation of effective thermal conductivity for carbon nanotube /polymer composites using control volume finite element method Carbon 44 719–7
[40] Yamada R, Igawa N, Taguchi T and Jitsukawa S 2002 Highly thermal conductive, sintered sic fiber-reinforced 3d–sic /sic composites: experiments and finite–element analysis of the thermal diffusivity/conductivity J. Nucl. Mater. 307 1215–20
[41] Rocha R P A and Cru M A E 2001 Computation of the effective conductivity of unidirectional fibrous composites with an interfacial thermal resistance \textit{Numerical Heat Transfer, Part A: Applications} 39 179–203
[42] Bakker K 1997 Using the finite element method to compute the influence of complex porosity and inclusion structures on the thermal and electrical conductivity \textit{Int. J. Heat Mass Transfer} 40 3503–11
[43] Hu D, Gong W and Di J 2017 Strong graphene-interlayered carbon nanotube films with high thermal conductivity \textit{Carbon} 118 659–65
[44] Mondal S, Ganguly S, Das P and Bhawal P 2017 High-performance carbon nanofiber coated cellulose filter paper for electromagnetic interference shielding \textit{Cellulose} 24 5117–31
[45] Xu Z, Wei C and Gong Y 2016 Efficient dispersion of carbon nanotube by synergistic effects of sisal cellulose nano-fiber and graphene oxide \textit{Compos. Interfaces} 24 1–15