EVALUATION OF THERMAL CONDUCTIVITY OF CNT COMPOSITES USING A MODIFIED REPRESENTATIVE VOLUME ELEMENT (RVE) APPROACH

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Keywords: Carbon nanotube; nanocomposites; thermal conductivity; finite element

Abstract
Thermal conductivity is considered to be an important property in selecting heat transfer devices. In composite materials, the thermal properties can be improved substantially by changing process parameters, type and orientation of the reinforcing materials. One of the best candidate as a reinforcing material is carbon nanotubes (CNT). Utilizing the superior properties of CNTs offers exciting opportunities for new composites. Based on the reported values of CNT, 10% is enough to produce a composite product with heat conductivity coefficient comparable to many metallic counterparts. In the proposed work, the main focus will be on the numerical modeling of nanocomposites using a modified RVE approach. In this approach the CNT is modeled as FE line elements instead of the traditional way of modeling the CNT as a cylindrical volume. The air trapped inside the CNT is accounted for using the rule of mixture. The proposed approach is more effective and allows the simulation of more complex components by reducing the number of FE elements while maintaining the same level of accuracy. The modified RVE approach is validated and used to predict the thermal conductivity of various cases with different dispersions and number of CNTs.

1 Introduction
Nanoparticles, such as carbon nanotubes (CNT), carbon nanofibers (CNF), nanoclay, and exfoliated graphite, are of great interest due to their nanoscale dimensions and remarkable prospect for improvement of mechanical, thermal, electrical, and chemical properties when introduced in small quantities in polymer matrix composites. Thermally conductive thermoplastics have many applications in the aerospace, electronics, and energy storage industries [1].
While a number of advances have been made in the development of polymer nanocomposites, it is clear that significant research and development still need to be done. For example, the role of processing of these nanocomposite materials cannot be underestimated, as often a slight change in base polymer material, nanoparticle type, and/or processing conditions can drastically alter the dispersion, orientation, and/or microstructure of the nanocomposite, with corresponding changes in the resulting nanocomposite properties [2]. There is also a need for enhanced, and more quantitative, techniques to characterize the distributions and orientations of nanoparticles, as well as to experimentally assess the properties of the interface between the polymer and the nanoparticles.

Due to the limitation in the analytical work that can be done to analyze CNTs and the difference between the analytical results and the experimental observations, researches started to focus on computational models to study CNTs and nanocomposites. Once a computational model is tested and proved to be reliable, it can be used to study the behavior and predict the mechanical and thermal properties for a wide class of nanocomposites instead of experiments which are expensive and difficult to perform within controlled conditions. The purpose of this work is to present a new way of modeling CNTs which is computationally more efficient than current models in the literature, and easier to implement with different orientations and dispersions. The proposed model has the potential to be extended and implemented in large scale applications rather than just a single CNT as it is common in the literature.

2 Literature Review

One of the common approaches in modeling CNTs in a FE frame of work is through the use of Representative Volume Element (RVE) [3]. In this approach a controlled volume, representing the matrix material, encloses a cylindrical tube that represents the CNT. A two scale modeling approach was proposed by Harkin-Jones *et al*. [4] that depends on the RVE concept. Their method is based on the assumption that, to some extent, the theory of continuum mechanics/micromechanics can still be used at the nanometer length scale. The two scales are linked to predict the effective elastic properties of the nanocomposite and the stress-strain curves at the macroscale level. Liu and Chen [5] evaluated the effective mechanical properties of CNT-based composites using RVE with FEM. Three loading cases were applied and the material constants were extracted suing the theory of elasticity. An extended rule of mixtures that can be used to estimate the Young's Modulus in the axial direction of RVE was derived based on the strength of material theory. Karimzadeh*et al*. [6] used the RVE approach to study the interaction between the CNT and the matrix material. Several examples were carried out to investigate the stress distribution and to demonstrate the load carrying capacity of CNTs. From the stress and strain distribution, the material properties of the CNT are then calculated using the standard theory of elasticity. Two different RVEs were used in their work, an axisymmetric and a 3D square RVE models.

A meshless element-free Galerkin approach was proposed by Singh *et al.* [7-9] to perform thermal analysis on CNT-based nanocomposites with the use of cylindrical RVE to evaluate the thermal properties using a multiscale simplified approach in which only the matrix domain is modeled since CNT is assumed to have a constant unknown temperature. The temperature values in their approach are calculated at different points in the domain and then plotted against RVE length and radius. The study showed that thermal conductivity is a function of the lengths and radiuses of CNT and RVE. A hybrid boundary node method (HdBNM) was implemented by Zhang *et al*. [10, 11] in a FE work frame with the use of RVE for heat conduction analysis with focus on the thermal conductivity of CNTs. The temperature distributions and heat flux concentrations were studied. The equivalent thermal conductivity of the RVE as a function of the nanotube length was calculated and discussed. The HdBNM was also proposed to overcome difficulties associated with the discretization of the geometry and the computational cost. The first issue is alleviated by default since the HdBNM is a boundary-type meshless method. A simplified mathematical model for thermal analysis of CNT was proposed to overcome the second difficulty which reduces the size of the linear system by nearly half. A variety of RVEs containing different number of CNTs were studied. Different cases were carried out with different orientations and CNTs distribution.Another RVE FE model was used by Basavanahalli [12] to evaluate the thermal conductivity of carbon nanotube reinforced polymer composites based on the theory of continuum mechanics and consists of an RVE with a single multi-walled nanotube (MWNT) inclusion. In this model, thermal contact elements are used to model the interface resistance between the nanotube and the matrix material. The FE analysis was performed by keeping the volume fraction of the MWCT fibers constant and varying influential parameters, such as the length and the diameter, that control the thermal conductivity. Then the study was performed by varying the volume fractions of CNT fibers to examine its effect. A heterogeneous material with discontinuous properties was assumed to be a homogenous material that gives the same (averaged) response for a given input at the macroscale. The process of homogenizing the material was applied in finding the thermal conductivity of effective solid fibers, which replaces the MWCT as the inclusion phase in RVE.

3 Modeling

In this paper we present a new FE approach for modeling RVEs that is based on modifying the classical approach that was introduced by Hill [3]. In this approach the CNT is modeled as a series of line elements rather than a cylindrical volume. This modification allows for a better handling of the RVE in terms of the number of CNTs and their orientation. In addition to that, the number of elements can be significantly reduced, which allows this approach to be used in modeling large composite materials or mechanical/electrical components with large number of CNTs. The matrix is modeled as a set of sub-volumes sharing a line between them which represents the CNT. A general representation of an RVE containing one CNT in the matrix is shown in Figure 1.

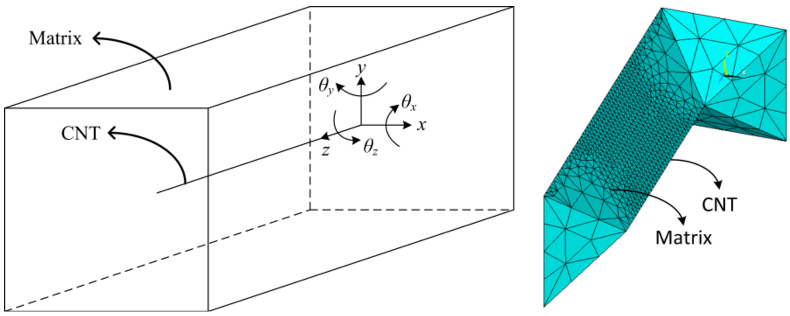

Figure 1. Geometrical setup and FE mesh of an RVE with a single CNT.

3.1 Finite Element Model

In the current proposed approach, CNTs are modeled using line elements rather than the traditional cylindrical shaped volume. This allows for better handling of the CNT dispersion in terms of the angle and orientation. To derive the heat conduction equations for the CNT and the matrix we start with the 1st law of thermodynamics considering only heat conduction:

$$\nabla \cdot \{q\} = Q \tag{1}$$

where q is the heat flux vector and Q is the heat generated per unit time per unit volume. Using Fourier’s law, we can relate the heat flux to the thermal gradient:

$$\{q\} = -[D]\nabla T \tag{2}$$

where D is the conductivity matrix consisting of the thermal conductivity coefficients and T is the temperature vector. Re-writing (1) we end up with the steady state heat conduction equation having the following form:

$$\nabla \cdot \left([D] \nabla T \right) = -Q \tag{3}$$

Expanding (3) into the FE form, we get the following:

$$\begin{aligned} [K_c]\{T\} &= \{f_Q\}, \qquad [K_c] = \int_{Vol} [B]^T [D][B] dV \\ \{f_Q\} &= \int_{Vol} [N]^T Q dV, \qquad [B] = \nabla [N]^T \end{aligned} \tag{4}$$

where N is the element shape functions, K_c is the element conductivity matrix and f_Q is the element heat generation load. A uniaxial 2-noded heat conduction element is used for the CNT with temperature being the single DOF. Element length, cross sectional area and longitudinal thermal conductivity are required in the FE model of the CNT. For the matrix, a 3D 8-noded solid element with heat conduction capabilities and temperature being the single DOF is used. Geometry and material properties are required in the FE model of the matrix. A rectangular volume is used as the RVE in this work where the volume of the represents the matrix material. The RVE is constructed such that it divided into volumes which share a line or a node that is used to model the CNT elements. The geometrical setup and the interior FE mesh of a general RVE with a single CNT is shown in Figure 1.

3.2 Thermal Conductivity of CNT with Air

In the common RVEs in the literature, air is either ignored or modeled as a volume inside the CNT. For more accurate computational modeling, air will be included in this approach. Since we are modeling the CNT as line elements then we no longer can model it as a volume, so an alternative is required. We compute an equivalent thermal conductivity for the CNT with air by applying Fourier's law to the CNT and air similar to the rule of mixtures.

$$\begin{gathered} Q_{CNT} + Q_{Air} = Q_{Eq} \\ k_{CNT} A_{CNT} \frac{\Delta T}{\Delta x} + k_{Air} A_{Air} \frac{\Delta T}{\Delta x} = k_{Eq} A_{Eq} \frac{\Delta T}{\Delta x} \end{gathered} \tag{5}$$

where Q represents the heat flow and k is the thermal conductivity of the CNT, Air and the equivalent CNT, respectively. Having the same temperature difference and the same length leads to (3.1) being reduced to the rule of mixtures.

4 Cases and Discussion

4.1 Single CNT

To validate the proposed approach and ensure its reliability we present a case study consisting of two sets; an RVE with single CNT using different aspect ratios between varying length and fixed radius of the CNT, and an RVE with single CNT using different volume fractions between a fixed volume of the CNT and a varying volume of the RVE while keeping the length of the CNT fixed, which is consistent with the physical process where the increase in the volume fraction is obtained by increasing the number of CNT particles in the matrix and therefore reducing the gap between the neighboring CNTs. The properties of the CNT and the matrix will be fixed and the results of different aspect ratios will be validated using numerical homogenization approach by Song and Youn [13]. In their approach the traditional modeling of RVEs is used where the CNT is modeled as a volume. The thermal conductivity of the Air, CNT and the polymer matrix are 0.026, 100 and 0.122 W/m.K, respectively. The diameter of the CNT is fixed to be 13nm. In the first set, the CNT length varies between 400 and 12000 nm where the length of the RVE is taken as the length of the CNT plus 200 nm with a width and height of 213 nm. In the second set, the length of the CNT is fixed as 12000 nm and the RVE as 12200 nm, where the volume of the RVE is not fixed. The temperature boundary conditions are taken as 303 and 333 K on both ends of the RVE.

Figure 2 compares the plot of the thermal conductivity obtained from our approach and Song and Youn [13] against the aspect ratio and volume fraction. It can be seen that the results obtained from the two models are very close and they follow the same behavior. The results show that as the aspect ratio reaches a higher value, the gain in the thermal conductivity becomes asymptotically constant. This can be physically explained by the fact that as we increase the length of the RVE, the ratio of the affected volume to the total volume becomes almost constant. Higher volume fraction values mean that more of the matrix material is affected by CNT and hence a better value for the thermal conductivity. Basically from these results we can confidently say that this modified RVE approach is validated and shows good results in comparison with other numerically validated methods. The results are logical since the increase on the aspect ratio as we increase the length with respect to the radius of the CNT leads to a higher effective thermal conductivity. The increase in the volume fraction (and hence decreasing the cross sectional area of the RVE) leads to higher thermal conductivity since we are increasing the presence of the CNT in the material.

4.2 Multiple CNTs

A more comprehensive study is presented in this section covering more cases with multiple CNTs. The results obtained our approach are compared to analytical results that are based on the equations presented by Clancy and Gates [14]. The analytical model for computing the effective thermal conductivity of CNT composites is presented as follows:

$$K_e = K_m \frac{3 + f\left(\beta_x + \beta_z\right)}{2 - f\beta_x} \tag{6}$$

$$\beta_x = \frac{2\left(K_{11}^c - K_m\right)}{K_{11}^c + K_m}, \quad \beta_z = \frac{K_{33}^c}{K_m} - 1 \tag{7}$$

$$K_{11}^c = \frac{K_c}{1 + \frac{2a_{\mathrm{K}}}{d}\frac{K_c}{K_m}}, \quad K_{11}^c = \frac{K_c}{1 + \frac{2a_{\mathrm{K}}}{L}\frac{K_c}{K_m}} \tag{8}$$

$$a_{\mathrm{K}} = R_{\mathrm{K}} K_m \tag{9}$$

where K_e, K_c *and* K_m are the thermal conductivities of the nanocomposite, CNT and polymer matrix, respectively. f is the volume fraction, d is the CNT diameter and L is the CNT length. a_{K} is the Kapitza radius and is calculated using the matrix thermal conductivity and the interfacial thermal resistance R_{K}. Four cases are discussed in this study, all using parallel alignment of straight CNTs in an RVE. The four cases consist of 1, 3, 5 and 7 CNTs with a radius of 5 nm and a length of 195 nm. The width and height of the RVE are taken as 120 and 20 nm, respectively, with a total length of 200 nm. Uniform temperatures of 200 and 300 K are imposed on both ends of the RVE. The thermal conductivity is taken as 0.37 W/m.K for the polymer and 1750 W/m.K for the CNT. Using 0.026 W/m.K as the thermal conductivity of the air, the equivalent conductivity of the CNT is calculated using equation (5) to be 268.82 W/m.K. The interfacial thermal resistances are taken as $1.17\text{x}10^{-9}$, $1.42\text{x}10^{-9}$, $1.67\text{x}10^{-9}$ and $1.92\text{x}10^{-9}$ m^2K/W

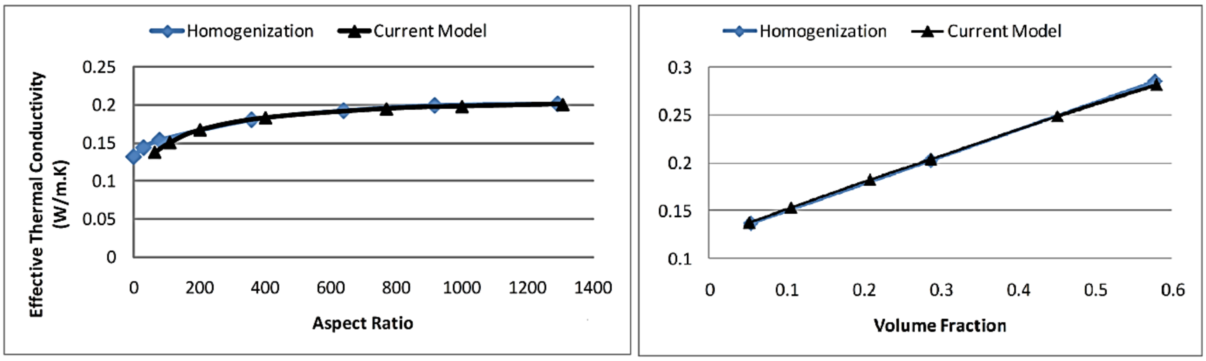

Figure 2. Comparison of the thermal conductivity with respect to different aspect ratios and volume fractions

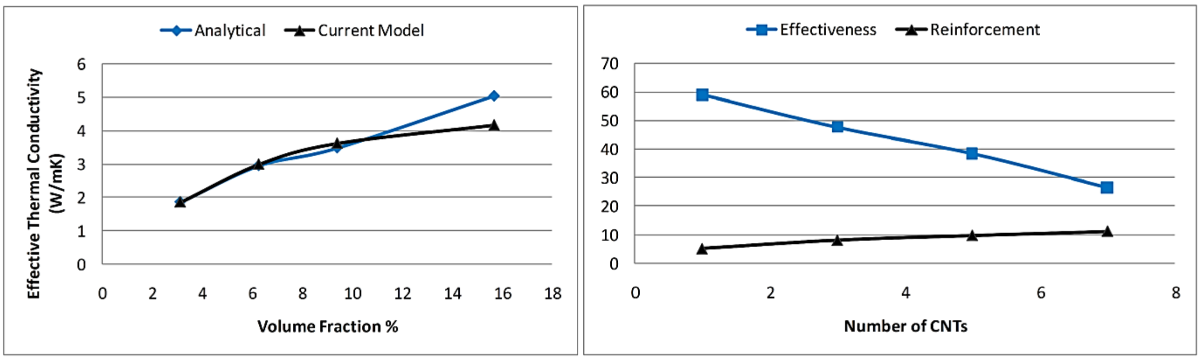

Figure 3. (a) Comparison of the thermal conductivity with respect to different volume fractions, (b) Effect of increasing the number of CNTs on the reinforcement and effectiveness

Case	Volume Fraction (%)	Analytical Thermal Conductivity (W/m.K)	Numerical Thermal Conductivity (W/m.K)	Reinforcement K_e/ K_m	Effectiveness K_e / f
1	3.136	1.853	1.852	5.005	59.056
2	6.272	2.945	2.986	8.070	47.608
3	9.408	3.477	3.612	9.772	38.430
4	15.68	5.031	4.1624	11.249	26.546

Table 1. Effective thermal conductivities from analytical and numerical results

The results for the four cases are summarized in Table 1 based on the values we obtained using our modified RVE approach and the analytical model. The thermal conductivity is compared in Figure 3 between our numerical results and the analytical model. The results are in good agreement especially for lower volume fractions values. Many factors are not included in the analytical model which could cause the difference in the results compared to the numerical one. The spacing between the CNTs and their alignment is not fully integrated in the analytical equations and this was one of the main factors that explain the change in the results for higher volume fraction values. This explanation is logical if we look at Figure 3(a) where the change in the volume fraction was achieved by increasing the volume of the RVE and not by increasing the number of CNTs (and hence introduce the effect of spacing). Figure 3(b) shows the reinforcement and effectiveness results as the number of CNTs increases. It is clear from the figure that as the number of CNTs increases in an RVE, their enhancement increases (because of the increase in the volume fraction), although the increase in the reinforcement is less at higher number of CNTs and that is due to the fact that the RVE might be thermally improved fully by a certain number of CNTs (optimum) and any additional CNTs would not introduce any improvement. This can be clearly visualized by looking at the effectiveness curve which decreases dramatically as we increase the number of CNTs used in the same RVE.

4.3 Multiple CNTs with Different Orientation

In this section, we provide an extension to the analysis done in the previous section involving the multiple CNTs. The same four cases have been simulated with 4 different orientations with respect to the coordinate system shown in Figure 1. For the θ_x we will use 2^o and 4^o for each of the CNTs, and then the same will be done for the θ_y. It is clear from Fig. 4 that cases having a straight alignment for the CNTs give better results in terms of the thermal conductivity. The same observation can be seen from either the change in θ_x or the θ_y cases. It can also be seen that at higher volume fraction, the effect of the orientation becomes more prominent since the effect gets repeated for each CNT. Since it is difficult to control the CNTs dispersion when manufacturing the CNT composites, it is therefore important to understand and be able to study the effect of the orientation and dispersion of a huge number of CNTs in real components. The proposed modified approach provides the first step into that direction since we can eliminate the need for a large number of elements to model the CNTs in addition to the great advantage of being able to model many different cases including real mechanical/electrical components easily.

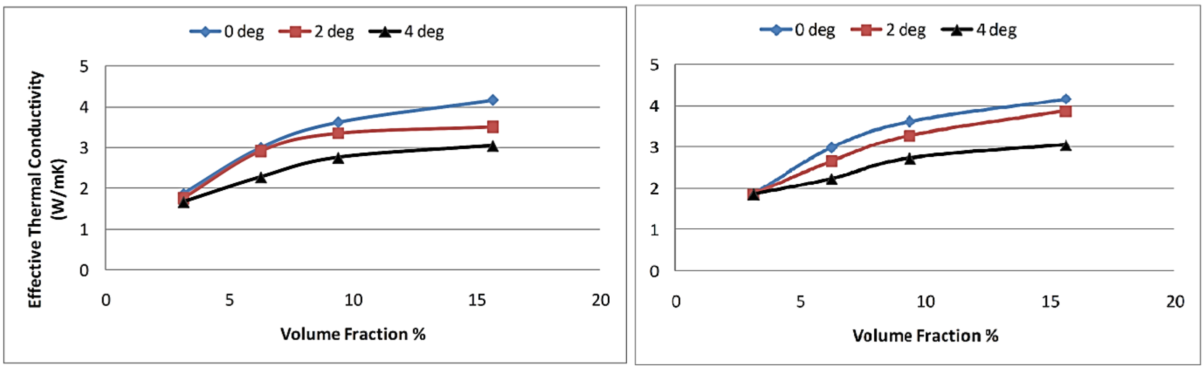

Figure 4. Effect of the CNT orientation in the x and y-axis on the thermal conductivity

5 Conclusion

This paper presented an approach for modeling CNT composites by modifying the traditional RVE into an easier to handle model. The matrix is modeled as volume whereas CNT as line elements having equivalent thermal conductivity to incorporate the effect of air inside the tube. Based on the results of various studies conducted, the following conclusions are drawn:

- This simplified approach allows to model with much smaller number of elements making simulation more efficient.
- Change and manipulation of the CNT orientation and dispersion can be easily done.
- The current model agrees well with the thermal conductivity estimation for RVE with 1, 3, 5 and 7 CNTs with available results in the literature.

The proposed technique clearly shows improvements in terms of simplifying CNT modeling while maintaining the same level of accuracy achieved through the traditional RVE approach. The next step would be to continue from here and take advantage of this approach and move into larger scale models since most studies in the literature stop at this stage due to the difficulties in modeling larger models using the traditional RVE models.

Acknowledgments
The authors acknowledge the support provided by King Fahd University of Petroleum & Minerals to conduct this work.

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