Estimation of thermal conductivities of a novel fuzzy fiber reinforced composite

S.I. Kundalwal, M.C. Ray*

Department of Mechanical Engineering, Indian Institute of Technology, Kharagpur, 721302, India

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ABSTRACT

The effective thermal conductivities of a novel fuzzy fiber reinforced composite (FFRC) have been determined by employing the effective medium approach in conjunction with the composite cylinder assemblage approach. The novel constructional feature of this FFRC is that the uniformly spaced carbon nanotubes (CNTs) are radially grown on the circumferential surfaces of the unidirectional carbon fiber reinforcements. The present study reveals that the transverse thermal conductivities of the FFRC are improved up to ~1040% and ~400% over those of the composite without CNTs when the values of CNT volume factions present in the FFRC are 6.88% and 4.27%, respectively. It is also found that the CNT/polymer matrix interfacial thermal resistance does affect the effective thermal conductivities of the FFRC, and the effective values of thermal conductivities of the FFRC are improved with the increase in the values of carbon fiber volume fraction and temperature.

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1. Introduction

The research on the synthesis of molecular carbon structure by an arc-discharge method for evaporation of carbon led to the discovery of an extremely thin needle-like graphitic carbon nanotube [1]. Researchers probably thought that carbon nanotubes (CNTs) may be useful as nanoscale fibers for developing novel nano-composites and this conjecture motivated them to accurately predict their physical properties (mechanical, thermal and electrical properties). Ruoff and Lorents [2] examined some aspects of the mechanical and the thermal properties of multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) in terms of the known elastic properties of graphite. Many research investigations revealed that the axial Young’s modulus of SWCNTs is in the terapascal range [3–6], and the thermal conductivities of SWCNTs and MWCNTs are more than 2500 W/mK [7–10]. The quest for utilizing such exceptional mechanical and thermal properties of CNTs, and their high aspect ratio and low density led to the opening of an emerging area of research on the development of CNT-reinforced nanocomposites.

In order to exploit the exceptional mechanical and thermal properties of CNTs for increasing the heat transport in CNT-reinforced nanocomposites, a great number of experimental studies have been carried out for investigating the thermal conductivities of CNT-reinforced composites. For example, Choi et al. [11] produced nanotube-in-oil suspensions in a two-step process and measured their thermal conductivities. They found that the measured thermal conductivity is greater than theoretical predictions and is nonlinear with CNTs loading. Single-walled CNTs were used to augment the thermal transport properties of industrial epoxy by Biercuk et al. [12]. In their experiment, samples loaded with 1 wt% unpurified SWCNTs showed a 125% increase in the value of thermal conductivity at room temperature. Their test results suggest that the thermal and the mechanical properties of CNT-reinforced composites can be improved without the chemical functionalization of CNTs. Bryning et al. [13] reported thermal conductivity measurements of purified CNT-reinforced composites prepared by using suspensions of SWCNTs in N-N-Dimethylformamide and surfactant stabilized aqueous SWCNT suspensions. Thermal conductivity enhancement is observed as 80% and 8% for N-N-Dimethylformamide processed composites and surfactant processed samples, respectively, at 1 wt% SWCNT loading. The difference in the enhancement of the thermal conductivity is attributed to a ten-fold larger SWCNT/matrix interfacial thermal resistance in surfactant processed composites compared to N-N-
Dimethylformamide processed composites. Guthy et al. [14] fabricated SWCNT/PMMA composites by employing the coagulation method with 6% CNT loading and found 240% enhancement in the thermal conductivity of SWCNT/PMMA composites. Further increase in SWCNT loading does not result in significant increase in the thermal conductivity. Haggenmueller et al. [15] investigated the thermal conductivities of SWCNT/polystyrene nanocomposites in terms of SWCNT loading, polystyrene crystallinity and polystyrene alignment. They reported that the thermal conductivity of SWCNT/high density polyethylene is higher than that of SWCNT/low density polyethylene. They attributed this effect primarily due to the aligned polyethylene matrix which eventually reduces the interfacial thermal resistance between CNTs and high density polyethylene. The thermal conductivity of SWCNT/PMMA nanocomposites is determined by Pradhan and Lannacchione [16]. A large enhancement of the thermal conductivity is observed by them as the mass fraction of SWCNTs increases from 0.014 to 0.083. Chu and coworkers [17,18] synthesized CNT/copper nanocomposite by means of the particles-compositing process. They reported that the addition of CNTs in the pure copper matrix showed no enhancement in the overall effective thermal conductivity of CNT/copper composites due to the interfacial thermal resistance associated with the low phase contrast of CNTs to copper and the random orientations of reinforced CNTs. Chai and Chen [19] characterized the thermal conductivities of CNT/copper nanocomposite by using a novel electrochemical co-deposition process aiming to reduce the interfacial thermal resistance between CNTs and copper matrix. They reported that the effective thermal conductivity of CNT-reinforced copper nanocomposite is 180% greater than that of the pure copper. Cho et al. [20] fabricated the uniformly dispersed CNT/copper nanocomposite by using wet mixing and spark plasma sintering. Their results indicate that CNTs can be used as primary reinforcements in the copper matrix for improving the thermal conductivity of the resulting composite. Marconnet et al. [21] reported the experimental data for the thermal conductivity of densified, aligned MWNTs arrays infiltrated with an unmodified aerospace-grade epoxy with maximum loading of CNT up to 20%. In their study, the axial thermal conductivity of the aligned CNT-epoxy composite is improved by a factor of 18.5 at 16.7% volume fraction of CNT.

The review of literature on the measurements of the thermal conductivities of two-phase CNT-reinforced composites reveals that the degree of enhancement of the thermal conductivity of nanocomposites varies substantially with the dispersion quality of CNTs and the CNT/matrix interfacial thermal resistance. The interfacial thermal resistance is also known as Kaptiza resistance. Wilson et al. [22] reported that the magnitude of the interfacial thermal resistance of carbon nanotubes and different matrices ranges from $0.77 \times 10^{-8}$ m^2 K/W to $20 \times 10^{-8}$ m^2 K/W. The CNT-matrix interfacial thermal resistance reported by Huxtable et al. [23] is about $8.3 \times 10^{-8}$ m^2 K/W. In addition to their experimental endeavors, theoretical evaluations of the thermal conductivities of CNT-reinforced composites have also been reported by researchers incorporating such CNT/polymer interfacial thermal resistance. A simple equation has been derived by Nan et al. [24] for predicting the effective thermal conductivity of CNT-reinforced nanocomposite by implementing an effective medium (EM) approach. In particular, their model shows that the thermal conductivity enhancement in the nanocomposite is limited by the CNT/matrix interfacial thermal resistance. Subsequently, the effective thermal conductivities of CNT-reinforced nanocomposites are computed by several researchers [25–28] incorporating the CNT/matrix interfacial thermal resistance.

For structural applications, the manufacturing of two-phase unidirectional continuous CNT-reinforced composites in large scale has to encounter some manufacturing difficulties. In case of three-phase hybrid CNT-reinforced composite, short CNTs are grown on the circumferential surfaces of the advanced fiber reinforcements such as carbon fibers and alumina fibers. It seems that in comparison to the manufacturing of long CNTs and the dispersion of long CNTs in the polymer matrix, direct growth of short CNTs on the circumferential surfaces of the advanced fibers for achieving uniform distribution of CNTs throughout the composite is practically more feasible and advantageous. For example, Bower et al. [29] have grown aligned CNTs on the substrate surface using high-frequency microwave plasma-enhanced chemical vapor deposition technique. They have found that the growth rate of CNTs are approximately 100 nm/s with entire growth of 12 μm and such CNT growth always occurs perpendicular to the substrate surface regardless of the substrate shape. Qian et al. [30] experimentally investigated that the enhancement in the fiber/matrix interfacial shear strength can be achieved by growing CNTs on the circumferential surface of the fiber. Veedu et al. [31] demonstrated that the remarkable improvements in the interlaminar fracture toughness, hardness, delamination resistance, in-plane mechanical properties, damping and thermal behavior of laminated composite can be obtained by growing MWNTs about 60 μm long on the circumferential surfaces of the fibers. Their test results suggest that the presence of CNTs in the transverse (i.e., thickness) direction of the composite enhances the effective thermal conductivity up to 51%.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$a_k$</td>
<td>Kaptiza radius m</td>
</tr>
<tr>
<td>D</td>
<td>Diameter of the RVE of the FFRC μm</td>
</tr>
<tr>
<td>d</td>
<td>Diameter of the carbon fiber μm</td>
</tr>
<tr>
<td>$d_{nt}$</td>
<td>Diameter of the CNT nm</td>
</tr>
<tr>
<td>$K_{ij}$</td>
<td>Effective thermal conductivities of the FFRC W/mK</td>
</tr>
<tr>
<td>$K^{CEF}$</td>
<td>Effective thermal conductivities of the CFF W/mK</td>
</tr>
<tr>
<td>$K$</td>
<td>Thermal conductivity of the carbon fiber W/mK</td>
</tr>
<tr>
<td>$K^\sigma$</td>
<td>Thermal conductivity of the CNT W/mK</td>
</tr>
<tr>
<td>$K^{PMNC}$</td>
<td>Effective thermal conductivities of the unwound lamina of the PMNC W/mK</td>
</tr>
<tr>
<td>$K^{PMNC}$</td>
<td>Effective thermal conductivity matrix of the unwound lamina of the PMNC W/mK</td>
</tr>
<tr>
<td>$K_P$</td>
<td>Thermal conductivity of the polymer W/mK</td>
</tr>
<tr>
<td>$K^{PMNC}_{ij}$</td>
<td>Effective thermal conductivities of the PMNC W/mK</td>
</tr>
<tr>
<td>L</td>
<td>Length of the RVE of the FFRC μm</td>
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<tr>
<td>$L_n$</td>
<td>Length of the straight CNT nm</td>
</tr>
<tr>
<td>$(N_{CNT})_{\text{max}}$</td>
<td>Maximum number of radially grown aligned CNTs on the circumferential surface of the carbon fiber</td>
</tr>
<tr>
<td>R</td>
<td>Radius of the RVE of the FFRC μm</td>
</tr>
<tr>
<td>$R_k$</td>
<td>Interfacial thermal resistance between the CNT and the polymer m² K/W</td>
</tr>
<tr>
<td>$[T]$</td>
<td>Transformation matrix</td>
</tr>
<tr>
<td>V</td>
<td>Volume of the RVE of the FFRC μm³</td>
</tr>
<tr>
<td>$V^i$</td>
<td>Volume of the i-th phase μm³</td>
</tr>
<tr>
<td>$(V_{CNT})_{\text{max}}$</td>
<td>Maximum volume fraction of the CNT in the FFRC</td>
</tr>
<tr>
<td>$V_{CEF}$</td>
<td>Volume fraction of the CFF in the FFRC</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Volume fraction of the carbon fiber in the FFRC</td>
</tr>
<tr>
<td>$\phi_f$</td>
<td>Volume fraction of the carbon fiber in the CFF</td>
</tr>
<tr>
<td>$\phi_n$</td>
<td>Volume fraction of the CNT in the PMNC</td>
</tr>
<tr>
<td>$\phi_p$</td>
<td>Volume fraction of the polymer in the PMNC</td>
</tr>
<tr>
<td>$\phi_{PMNC}$</td>
<td>Volume fraction of the PMNC in the CFF</td>
</tr>
<tr>
<td>$\phi_f$</td>
<td>Volume fraction of the polymer in the FFRC</td>
</tr>
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</table>

compared to that of the base composite. Electrospinning technique has been utilized for the selective deposition of \textit{MWCNTs} and \textit{SWCNTs} on the circumferential surfaces of the carbon fibers by Bekyarova et al. [32]. For \textit{SWCNT}/carbon fiber reinforced composites they demonstrated \textasciitilde{} 30\% enhancement in the interlaminar shear strength and 2-fold improvement of the out-of-plane electrical conductivity as compared to that of the composite without CNTs. Garcia et al. [33] fabricated a hybrid laminate in which the reinforcements are a woven cloth of alumina fibers with \textit{in situ} grown CNTs on the circumferential surfaces of the fibers. With the use of modified chemical vapor deposition process the growth rate for CNTs achieved as 10--100 \textmu m for 0.5--5 min. They demonstrated that the electro-mechanical properties of such a laminate are enhanced because of CNTs grown on the circumferential surfaces of the alumina fibers. Multifunctional properties of a hybrid composite comprised of aligned CNTs grown \textit{in situ} on the woven fibers and a thermoset polymer matrix have been characterized by Yamamoto et al. [34] and found that the loading of 2.2\% CNT volume fraction in a hybrid composite enhances its effective thermal conductivity by two times over that of the base composite. Chen et al. [35] augmented the carbon/carbon composite by growing CNTs on the circumferential surface of the carbon fiber. The thermal conductivities of this composite becomes greater than that of the composite without CNTs. Such a fiber augmented with radially grown CNTs on its circumferential surface is being called as “fuzzy fiber” [33,34] and the resulting composite may be called as fuzzy fiber reinforced composite (FFRC) [34,36,37].

Recently, a novel FFRC reinforced with the continuous fuzzy fiber reinforcements is independently studied by Kundalwal and Ray [36], and Chatzigeorgiou et al. [37]. The distinct constructional feature of such FFRC is that the uniformly aligned CNTs are radially grown on the circumferential surfaces of the unidirectional carbon fiber reinforcements. Kundalwal and Ray [36] predicted that the transverse effective elastic properties of this novel FFRC are significantly enhanced over their values without CNTs. Most recently, the effective thermoelastic properties of the continuous FFRC and the load transfer analysis of the short FFRC have been extensively studied by Kundalwal [38] using several analytical and numerical micromechanics models. This study authenticate that the novel FFRC with improved multifunctional properties can be used for fabricating different FFRC laminated structures having a wide range of unexplored applications in numerous technological areas such as aerospace, automobile, medicine, defence, energy etc. The thermal conductivity is one of the most important properties to characterize the heat transport phenomena of the FFRC structures to avoid excessive temperature buildup along its thickness direction. However, the thermal conductivities of such nanocomposites being composed of the fuzzy fiber reinforcements have not yet been reported. In this paper, authors intend to estimate the thermal conductivities of the FFRC and investigate the effect of CNT/polymer matrix interfacial thermal resistance on the effective thermal conductivities of the FFRC.

2. Effective thermal conductivities of the FFRC

Fig. 1 shows a schematic sketch of a lamina of the FFRC. The constructional feature of such a continuous unidirectional carbon fiber reinforced composite is that CNTs of equal length are uniformly spaced and radially grown on the circumferential surfaces of the carbon fiber reinforcements. Such a resulting fuzzy fiber is shown in Fig. 2. When this fuzzy fiber is embedded into the polymer matrix, the gaps between the adjacent CNTs are filled with the polymer. Consequently, radially aligned CNTs reinforce the polymer matrix surrounding the carbon fiber along the transverse direction of the length of the carbon fiber. Thus the augmented fuzzy fiber can be viewed as a circular cylindrical composite fuzzy fiber (CFF) in which a carbon fiber is embedded in the CNT-reinforced polymer matrix nanocomposite (PMNC) and the radius of the CFF equals the sum of the radius of the carbon fiber and the length of a CNT. Such a CFF is schematically demonstrated in Fig. 3. Therefore, the representative volume element (RVE) of the FFRC can be treated as being composed of two phases wherein the reinforcement is the CFF and the matrix is the monolithic polymer material. Thus the analytical procedure for estimating the effective thermal conductivities of the FFRC starts with the estimation of the effective thermal conductivities of the PMNC material a priori. Subsequently, considering the PMNC material as the matrix phase and the carbon fiber as the reinforcement, the effective thermal conductivities of the CFF are to be computed. Finally, using the thermal conductivities of the CFF and the monolithic polymer matrix, the effective thermal conductivities of the FFRC can be estimated. The CFFs are assumed to be uniformly spaced over the volume of a lamina of the FFRC in such a way that three orthogonal principal material coordinate (1--2--3) axes exist in the composite as shown in Fig. 1.

2.1. Modeling approaches

This Section deals with the procedures of employing two modeling approaches, namely, the effective medium (EM) approach and the composite cylinder assemblage (CCA) approach to predict the effective thermal conductivities of the FFRC. It is well known fact that the randomly distributed reinforcements in the matrix results isotropic thermal conductivities of the resulting composite whereas the aligned reinforcements in the matrix results highly anisotropic thermal conductivities of the resulting composite. The PMNC, the CFF and the FFRC are being studied here.

Fig. 1. Schematic diagram of a lamina made of the FFRC.

Fig. 2. Fuzzy fiber coated with CNTs on its circumferential surface.
are made of the aligned CNT reinforcements, aligned carbon fiber reinforcement and the aligned CFF reinforcement, respectively. In the literature, the EM and CCA approaches have been reported to be the efficient analytical models for predicting the effective anisotropic thermal conductivities of the aligned fiber reinforced composites [21,39,40]. Thus EM and the CCA models have been employed herein to determine the effective anisotropic thermal conductivities of the FFRC and its phases. The results predicted by the EM approach are also found to be in good agreement with those of the experimental results with small volume fraction of CNT (2%–20%) [15,21,25,27]. Hence, the EM approach has been utilized for estimating the effective thermal conductivities of the PMNC incorporating the CNT/polymer matrix interfacial thermal resistance. Subsequently, the CCA approach has been utilized for estimating the effective conductivities of the CFF and the FFRC since the CCA approach estimates the effective conductivities of the resulting composite by incorporating the anisotropic thermal conductivities of the constituent phases with high volume fraction of reinforcement (10%–90%) [40,41]. It should be noted that the perfect bonding between the reinforcement and the matrix is assumed in the CCA approach. Schematic diagram shown in Fig. 4 illustrates the various steps involved in the computation of the thermal conductivities of the FFRC and are also outlined as follows:

- First, the effective thermal conductivities of the PMNC have been determined by using either the EM approach (Rk ≠ 0) or the CCA approach (Rk = 0) where Rk is the CNT/polymer matrix interfacial thermal resistance.
- Utilizing the effective anisotropic thermal conductivities of the PMNC material and the isotropic thermal conductivity of the carbon fiber, the effective thermal conductivities of the CFF have been determined by using the CCA approach.
- Finally, using the effective anisotropic thermal conductivities of the CFF and the isotropic thermal conductivity of the polymer matrix, the effective thermal conductivities of the FFRC have been estimated by employing the CCA approach.

2.1.1. Effective medium (EM) approach

This Section presents the Maxwell–Garnett type EM approach to estimate the effective thermal conductivities of the PMNC incorporating the CNT/polymer matrix interfacial thermal resistance. Assuming CNTs as solid fibers [13,24,25,27], the EM approach by Nan et al. [39] can be modified to predict the effective thermal conductivities (K^{nc}_p) of the unwound PMNC material with straight CNTs. From the constructional feature of the CFF, it may be viewed that the carbon fiber is wrapped by a lamina of the PMNC material. Such an unwound lamina of the PMNC is reinforced by CNTs along its thickness direction (i.e., along the 3-direction) shown in Fig. 5. The average effective thermal conductivities of the PMNC material surrounding the carbon fiber may be approximated by estimating the effective thermal conductivities of this unwound lamina. The effective thermal conductivities of the unwound lamina of the PMNC (K^{nc}_p) are given by Ref. [39]:

\[
K^{nc}_{11} = K^{nc}_{22} = K_p K^{0}_{11} (1 + \alpha) + K^{0} + v_n K^{0} (1 - \alpha) - K^{0} \\
K^{nc}_{33} = v_n K^{0} + v_p K^{0}
\]  

In Eq. (1), a dimensionless parameter \( \alpha = 2a_k/d_n \) in which the interfacial thermal property is concentrated on a surface of zero thickness and characterized by Kaptiza radius, \( a_k = R_k K_p \) where \( d_n \) and \( R_k \) represent the diameter of the CNT and the CNT/polymer matrix interfacial thermal resistance, respectively. In Eqs. (1) and (2), the superscripts \( nc \), \( n \) and \( p \) represent the unwound PMNC material with straight CNTs, the CNT fiber and the monolithic polymer matrix, respectively; the subscripts \( v_n \) and \( v_p \) represent the volume fractions of the CNT fiber and the monolithic polymer material, respectively, present in the RVE of the PMNC. The effective thermal conductivity matrix for the unwound lamina of the PMNC [K^{nc}] can be represented as follows:

\[
[K^{nc}] = \begin{bmatrix}
K^{nc}_{11} & 0 & 0 \\
0 & K^{nc}_{22} & 0 \\
0 & 0 & K^{nc}_{33}
\end{bmatrix}
\]
It may be noted that the effective thermal conductivity matrix \([\mathbf{K}^{nc}]\) directly provides the effective thermal conductivities at a point in the portion of the PMNC surrounding the carbon fiber where the CNT is aligned with the 3-axis. But for the point located in the PMNC where the CNT is oriented at an angle \(\theta\) with the 3-axis in the \(2-3\) plane, \([\mathbf{K}^{nc}]\) also provides the effective thermal conductivities with respect to the local material coordinate \((1', 2', 3')\) system. Thus the location dependent effective thermal conductivity matrix \([\mathbf{K}^{nc}]\) at any point of the PMNC with respect to the \(1-2-3\) coordinate system can be obtained by the following transformations [42]:

\[
[\mathbf{K}^{PMNC}] = [\mathbf{T}]^{-1} [\mathbf{K}^{nc}] [\mathbf{T}]^{-1}
\]

where, 
\[
[\mathbf{T}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{bmatrix}.
\]

Therefore, the effective thermal conductivities of the PMNC surrounding the carbon fiber with respect to the principle material coordinate axes of the FFRC varies over an annular cross section of the PMNC phase of the RVE of the CFF. A simple homogenization process can be carried out on the RVE of an annular cross section of the PMNC phase to compute its effective properties [42,43]. Thus without loss of generality, it may be considered that the volume average of these effective thermal conductivities over the volume of the PMNC can be treated as the constant effective thermal conductivities of the PMNC material surrounding the carbon fiber with respect to the \(1-2-3\) coordinate axes of the FFRC and are given by Ref. [43]:

\[
[\mathbf{K}^{PMNC}] = \frac{1}{\pi (R^2 - a^2)} \int_0^{2\pi} \int_a^R [\mathbf{K}^{PMNC}] r dr d\theta
\]

If the CNT volume fraction is homogenized in the annular portion of the RVE of the PMNC then the homogenized effective thermal conductivities of the PMNC will not be radially dependant and the same has been proved in Appendix A. It is worthwhile to note that the thermal conductivity matrix of the PMNC \([\mathbf{K}^{PMNC}]\) is transversely isotropic. Next, utilizing the transversely isotropic thermal conductivities of the PMNC as the matrix phase and the carbon fiber being aligned along the 1-direction as the reinforcement, the CCA model is suitably augmented to compute the effective thermal conductivities of the CFF. Finally, the CCA model for the CFF is used in a straightforward manner to estimate the effective thermal conductivities of the FFRC in which the monolithic polymer is the matrix material and the CFF is the reinforcement aligned along the 1-direction.

### 2.1.2. Composite cylinder assemblage (CCA) approach

This Section presents the CCA approach to estimate the effective thermal conductivities of the PMNC material, the CFF and the FFRC. The effective thermal conductivities of the unwound lamina of the PMNC \((K_{ij}^{PMNC})\) are given by Ref. [40]:

\[
K_{11}^{nc} = K_{22}^{nc} = K^P \left( \frac{g_i (1 + v_n) + 1 - v_n}{g_i (1 - v_n) + 1 + v_n} \right)
\]

\[
K_{33}^{nc} = v_n K^P (1 - v_n) K^P
\]

where, \(g_i = K^P / K^P\).

Once \([\mathbf{K}^{nc}]\) is computed, Eqs. (4) and (5) are used to estimate the average effective thermal conductivities of the PMNC material surrounding the carbon fiber.

Since the CFF is a composite in which the carbon fiber is the reinforcement and the matrix phase is the PMNC material, the CCA approach can be employed to estimate its effective thermal conductivities. Thus according to the CCA approach [40], the effective thermal conductivities of the CFF are given by

\[
K_{33}^{FF} = K_{22}^{FF} = K_{22}^{PMNC} \left( \frac{g_2 (1 + v_f) + 1 - v_f}{g_2 (1 - v_f) + 1 + v_f} \right)
\]

\[
K_{11}^{FF} = \frac{v_f}{v_f} K_{11}^{11} + v_{PMNC} K^{PMNC}
\]

where, \(g_2 = \sqrt{K_{22}^{PMNC} K_{33}^{PMNC} / K_{22}^{PMNC} K_{33}^{PMNC}}\).

In Eqs. (8) and (9), \(v_f\) and \(v_{PMNC}\) are the volume fractions of the carbon fiber and the PMNC material, respectively, with respect to the volume of the RVE of the CFF. Finally, considering the CFF as the cylindrical inclusion embedded in the isotropic polymer matrix, the effective thermal conductivities of the FFRC can be obtained by using the CCA approach [40] as follows.
\[ K_{33} = K_{22} = K^0 \left[ g_s \left( 1 + V_{\text{FF}} \right) + 1 - V_{\text{FF}} \right] \]
\[ K_{11} = V_{\text{FF}} K_{11}^{\text{FF}} + \nabla_p K^p \]

where, \( g_s = \sqrt{K_{33}^{\text{FF}} K_{11}^{\text{FF}} / K^0} \), \( V_{\text{FF}} \) and \( \nabla_p \) are the volume fractions of the CFF and the polymer material, respectively, with respect to the volume of the RVE of the FFRC.

3. Results and discussion

In this Section, numerical values of effective thermal conductivities of the FFRC are evaluated by using the models presented in Section 2.1. Armchair SWCNTs, carbon fiber and polymer matrix are considered for evaluating the numerical results. In the numerical calculation, the thermal conductivities of the armchair (10, 10) CNT, the carbon fiber and the polymer are taken as 3.8 × 10^4 – 3.1 × 10^3 W/mK [8], 222 – 912 W/mK [44] and 0.16 – 0.205 W/mK [45], respectively, for the temperature range 100 – 400 K. The relationships between the thermal conductivities of the constituent phases of the FFRC and the temperature are given by Ref. [8,44,45]:

\[ K^0 = -2.3476 \times 10^{-10} T^{10} + 5.1847 \times 10^{-15} T^9 - 4.9368 \times 10^{-12} T^8 \]
\[ + 2.6466 \times 10^{-9} T^7 - 8.744 \times 10^{-8} T^6 + 1.8296 \times 10^{-4} T^5 \]
\[ - 0.02398 T^4 + 1.8888 T^3 - 85.366 T^2 + 2256.4 T \text{ W/mK} \]

\[ K' = 1.4235 \times 10^{-7} T^4 - 1.0199 \times 10^{-4} T^3 + 0.0214499 T^2 \]
\[ + 0.8331 T \text{ W/mK} \]

\[ K^0 = -1.2805 \times 10^{-15} T^6 + 1.8231 \times 10^{-12} T^5 - 1.0343 \times 10^{-9} T^4 \]
\[ + 2.9748 \times 10^{-7} T^3 - 4.6272 \times 10^{-5} T^2 - 0.0040278 T \text{ W/mK} \]

The value of diameter of the carbon fiber is taken as 2a = 10 \( \mu \)m. The volume fraction of CNT (\( V_{\text{CNT}} \)) in the FFRC depends on the CNT diameter, the carbon fiber diameter and the surface to surface distance between two adjacent radially aligned CNTs at their roots. The surface to surface distance between the two adjacent CNTs at their roots is considered as 1.7 nm [36]. Recall that the FFRC lamina can be viewed as being comprised of the CFFs and the polymer matrix. For fibers with circular cross section, it is well known fact that hexagonal array of packing is the optimal packing of fibers with the corresponding maximum fiber volume fraction is 0.9069.

Recently, Sihn and Roy [46] determined the transverse thermal conductivities of composites with hexagonal packing array of uniformly distributed fibers for wide ranges of fiber volume fractions and fiber-to-matrix conductivities ratios by employing both analytical and numerical models. Their study reveals that the effective inclusion method yields a reasonably agreeable solution with the finite element solution using a hexagonal array regular fiber distribution for wide ranges of the fiber volume fractions. Hence, it is reasonable to assume that the FFRC is made of hexagonal packing array of the CFFs and the polymer as shown in Fig. 6 for evaluating the numerical results of the FFRC.

The determination of \( V_{\text{CNT}} \) in the FFRC is an important issue. It is obvious that the constructional feature of the FFRC imposes a constraint on the maximum value of \( V_{\text{CNT}} \). Based on the surface to surface distance at the roots of two adjacent CNTs and the CNT diameter, the maximum number of CNTs grown on the circumferential surface of a carbon fiber of particular diameter can be determined. Then based on the carbon fiber volume fraction (\( V_f \)) in the FFRC, the maximum value of \( V_{\text{CNT}} \) can be determined as

\[ V_{\text{CNT}}^{\text{max}} = \frac{V_{\text{CNT}}}{V_{\text{FFRC}}} = \frac{\pi d_n^2}{2(d_n + 1.7)^2} \left( \frac{\pi V_f}{2\sqrt{3} - V_f} \right) \]

The value of diameter of the armchair (10, 10) CNT is taken as \( d_n = 1.36 \text{ nm} [5] \) to evaluate the numerical results. The derivation of Eq. (15) has been presented in Appendix B. It is evident from Eq. (15) that when \( V_f = 0 \), \( V_{\text{CNT}} \) is zero. Also, when \( V_f = \pi/2/3 \) i.e., there is no PMNC, the value of \( V_{\text{CNT}} \) is zero. Thus the maximum value of \( V_{\text{CNT}} \) will be maximum at a particular value of \( V_f \). Fig. 7 illustrates the variation of the maximum value of CNT volume fraction \( (V_{\text{CNT}})^{\text{max}} \) present in the FFRC with the carbon fiber volume fraction while the values of \( V_f \) varies from 0.1 to \( \pi/2/3 \). It may be observed from this figure that the maximum value of \( V_{\text{CNT}} \) is 0.07 when the value of \( V_f \) is 0.24. In what follows, unless otherwise mentioned, the effective thermal conductivities of the FFRC are computed for a particular value of \( V_f \) while the maximum value of \( V_{\text{CNT}} \) corresponding to this value of \( V_f \) is used for computing the numerical results.
3.1. Comparisons with the experimental results

The predictions by the EM and the CCA approaches utilized herein are first compared against those from the experimental results by Marconnet et al. [21]. Marconnet et al. [21] fabricated the aligned CNT-polymer nanocomposites consisting of MWNTs arrays infiltrated with an aerospace-grade thermoset epoxy. In their study, the axial and the transverse conductivities of the aligned CNT-polymer nanocomposites are found to be in good agreement against the predictions from the EM approach. For the comparison purpose, the values of thermal conductivities of the MWNT and the polymer matrix are taken as $K_{\text{p}} = 22.1$ W/mK and $K_{\text{m}} = 0.26$ W/mK, respectively, as considered by Marconnet et al. [21]. The comparisons of the axial ($K_A$) and the transverse ($K_T$) conductivities of the aligned CNT-polymer nanocomposites estimated by the EM and CCA approaches with those of the experimental results [21] are illustrated in Fig. 8(a) and (b), respectively. In these figures, dotted blue line represents best fits obtained from the EM approach for the experimental results considering an alignment factor (AF) of CNTs as 0.77 observed from the scanning electron microscopy (SEM) (in the web version). Fig. 8 (a) reveal that the axial thermal conductivity ($K_A$) of the aligned CNT-polymer nanocomposite predicted by the EM and CCA approaches overestimate the values of $K_A$ by 20% and 25% when the values of CNT volume fractions are 0.07 and 0.16, respectively. On the other hand, the EM and CCA approaches underestimate the values of $K_T$ by 40% and 58% when the values of CNT volume fractions are 0.07 and 0.16, respectively. These differences between the results are attributed to the fact that the perfect alignments of CNTs (i.e., AF = 1) are considered while computing the results by the EM and CCA approaches whereas the value of AF is 0.77 in Ref. [21]. Other possible reasons for the disparity between the analytical and the experimental results include the CNT/matrix interfacial thermal resistance [21,24–28,39,47], lattice defects within CNTs [48,49], modification of the phonon conduction within CNTs due to interactions with the matrix [50] and the formation of voids in CNT-reinforced composite [51,52]. In the present study, only the effect of CNT/matrix interfacial thermal resistance on the thermal conductivities of the FFRC is investigated since the CNT/matrix interfacial thermal resistance may significantly affect the thermal conductivities of the PMNC. Investigation of the effect of all other factors is beyond the scope of the present study. It can be inferred from the comparisons shown in Fig. 8(a) and (b) that the EM and the CCA approaches can be reasonably applied to predict the thermal conductivities of the FFRC and its phases.

3.2. Analytical modeling results

First, the effective thermal conductivities of the PMNC material surrounded the carbon fiber are computed by the models presented in Section 2.1. Unless otherwise mentioned, the effective thermal conductivities of the PMNC are computed considering the perfect CNT/polymer matrix interface without any interfacial thermal resistance. It should be noted that the value of CNT volume fraction in the PMNC varies with the variation of the carbon fiber volume fraction in the FFRC as shown in Fig. 7. The CNT volume fraction in the PMNC ($\nu_{\text{m,}\text{max}}$) given by Eq. B (8) has been used to determine the effective thermal conductivities of the PMNC. The maximum value of $\nu_{\text{m,}\text{max}}$ in the PMNC reaches up to 0.1551 when the value of carbon fiber volume fraction ($\nu_f$) is 0.0069. Figs. 9 and 10 illustrate the variation of the axial ($K_{\text{p,}\text{PMNC}}$) and the transverse ($K_{\text{t,PMNC}}$) thermal conductivities of the PMNC, respectively, with the carbon fiber volume fraction. These figures reveal that the thermal conductivities predicted by the EM approach excellently agree with those predicted by the CCA approach for both the values of temperature. This is attributed to the fact that CNTs are considered to be perfectly aligned in the PMNC (i.e., AF = 1) and the value of CNT/polymer matrix interfacial thermal resistance is considered as zero ($R_k = 0$). The value of $K_{\text{t,PMNC}}$ shows ~9% enhancement with the increase in the value of temperature irrespective to the values of $\nu_f$. On the other hand, the effective values of $K_{\text{t,PMNC}}$ are decreased up to ~82% with the increase in temperature when the values of $\nu_f$ are 0.3 and 0.6. This is attributed to the fact that the thermal conductivity of CNTs ($K_{\text{CNT}}$) grown on the circumferential surfaces of the carbon fibers are decreased with the increase in temperature which eventually lowers the effective value of $K_{\text{t,PMNC}}$. Since the PMNC is transversely isotropic with 1-axis as the axis of symmetry, the effective values of thermal conductivity $K_{\text{p,PMNC}}$ and $K_{\text{t,PMNC}}$ of the PMNC are found to be identical to those of $K_{\text{p,PMNC}}$ and $K_{\text{t,PMNC}}$ of the FFRC but are not presented here. Since the effective thermal conductivities of the PMNC predicted by the EM approach and the CCA approach are transversely isotropic, the CCA approach is suitably augmented to estimate the thermal conductivities of the CFF and the FFRC. However, for the sake of
It may also be noted that radial growing of fibers does not in the effective thermal conductivities of the CFF material. Practically the carbon fiber volume fraction in the composites can vary typically from 0.3 to 0.6. Hence, to analyze the effect of CNT/polymer matrix interfacial thermal resistance on the effective thermal conductivities of the FFRC, these two permissible values of carbon fiber volume fractions are considered while the value of CNT/polymer matrix interfacial thermal resistance is varied up to $20 \times 10^{-8}$ m$^2$ K/W [22,23]. Fig. 13 illustrates the variation of the effective axial thermal conductivity ($K_{11}^{PMNC}$) of the PMNC incorporating the CNT/polymer matrix interfacial thermal resistance. It is observed from this figure that the value of $K_{11}^{PMNC}$ decreases rapidly with the increase in the value of $R_k$ up to $5 \times 10^{-8}$ m$^2$ K/W and beyond a value of $R_k = 5 \times 10^{-8}$ m$^2$ K/W, the value of $K_{11}^{PMNC}$ stabilizes. It may also be observed that the value of $K_{11}^{PMNC}$ does not vary much with temperature. Although not presented here, the values of $K_{33}^{PMNC}$, $K_{15}$, $K_{22}$ and $K_{33}$ are found to be independent of the values of $R_k$.  

![Fig. 9. Variation of the axial thermal conductivity ($K_{11}^{PMNC}$) of the PMNC with the carbon fiber volume fraction in the FFRC ($R_k = 0$).](image)

![Fig. 10. Variation of the transverse thermal conductivity ($K_{33}^{PMNC}$) of the PMNC with the carbon fiber volume fraction in the FFRC ($R_k = 0$).](image)

![Fig. 11. Variation of the axial thermal conductivity ($K_{11}$) of the FFRC with the carbon fiber volume fraction in the FFRC ($R_k = 0$).](image)

![Fig. 12. Variation of the transverse thermal conductivity ($K_{33}$) of the FFRC with the carbon fiber volume fraction in the FFRC ($R_k = 0$).](image)
So far the effect of CNT/polymer matrix interfacial thermal resistance on the effective thermal conductivities of the FFRC has been studied considering the values of \( v_f \) as 0.3 and 0.6. However, the variation of the carbon fiber volume fraction for the maximum value of \( R_k = 20 \times 10^{-8} \text{ m}^2\text{ K/W} \) would be an important study. For this the discrete values of \( v_f \) are considered as 0.2, 0.4, 0.5 and 0.7. Figs. 14 and 15 illustrate the variation of the effective thermal conductivities \( K_{11} \) and \( K_{33} \) of the FFRC, respectively, with temperature variation. Fig. 14 depicts that the effective value of \( K_{11} \) increases with the increase in the values of carbon fiber volume fraction and temperature. Fig. 15 reveals that the effective value of \( K_{33} \) of the FFRC increases with the increase in temperature and is independent of the value of \( v_f \).

### 4. Conclusions

Thermal conductivities of the novel FFRC have been estimated in the present study by employing the EM approach in conjunction with the CCA approach. The distinctive constructional feature of this FFRC is that the uniformly spaced CNTs are radially grown on the circumferential surfaces of the carbon fiber reinforcements. The following main conclusions are drawn from the investigations carried out in this study:

1. Since the CNTs are radially grown on the circumferential surface of the carbon fiber with their axes normal to this surface, the effective transverse thermal conductivities of the FFRC are improved up to \( \sim 1040\% \) and \( \sim 400\% \) compared to those of the composite without CNTs when the values of carbon fiber volume factions in the FFRC are 0.3 and 0.6, respectively, and the corresponding values of CNT volume fractions present in the FFRC are 6.88\% and 4.27\%. On the other hand, the effective axial thermal conductivities of the FFRC are independent of the value of CNT volume fraction in the FFRC.

2. The CNT/polymer matrix interfacial thermal resistance does affect the effective axial and transverse thermal conductivities of the FFRC.

3. The effective axial conductivities of the FFRC are increased with the increase in the values of carbon fiber volume fraction and temperature. The effective transverse conductivities of the FFRC are increased with the increase in temperature and are independent of the values of carbon fiber volume fractions.

Since the transverse thermal conductivities of the FFRC are significantly enhanced, the FFRC will have better thermal management in the transverse direction to avoid temperature buildup. The present analysis may motivate the researchers for constructing this novel composite and serve the purpose of verifying the experimental estimates.

### Appendix A

If the CNT volume fraction is homogenized then the homogenized effective thermal conductivities of the PMNC will not be radially dependent and the same can be proved as follows: Fig. A.1 illustrates an RVE of the PMNC surrounding the carbon fiber containing one CNT.

The volume fraction of the CNT at any location \( r \) of the RVE of the PMNC is given by
The maximum number of radially grown aligned CNTs \( (N_{\text{CNT}})_{\text{max}} \) on the circumferential surface of the carbon fiber is given by

\[
(N_{\text{CNT}})_{\text{max}} = \frac{\pi d_n^2}{2(d_n + 1.7)^2} \quad \text{B (5)}
\]

Therefore, the volume of the CNTs \( (V_{\text{CNT}}) \) is

\[
V_{\text{CNT}} = \frac{\pi}{4} d_n^2 (R - a) (N_{\text{CNT}})_{\text{max}} \quad \text{B (6)}
\]

Thus the maximum volume fraction of the CNT with respect to the volume of the FFRC \( (V_{\text{CNT}})_{\text{max}} \) can be determined as

\[
(V_{\text{CNT}})_{\text{max}} = \frac{V_{\text{CNT}}}{V_{\text{FFRC}}} = \frac{\pi d_n^2}{2(d_n + 1.7)^2} \left( \sqrt{\frac{d_n}{2\sqrt{3}} - \frac{V_f}{\rho}} \right) \quad \text{B (7)}
\]

Finally, the maximum volume fraction of the CNTs with respect to the volume of the PMNC \( (V_n)_{\text{max}} \) and with respect to the volume of the CFF \( (V_f)_{\text{max}} \) can be determined in terms of \( (V_{\text{CNT}})_{\text{max}} \) as follows:

\[
(V_n)_{\text{max}} = \frac{V_{\text{CNT}}}{V_{\text{PMNC}}} = \frac{2\sqrt{3}}{\pi} (D^2 - d^2) (V_{\text{CNT}})_{\text{max}} \quad \text{B (8)}
\]

\[
(V_f)_{\text{max}} = \frac{V_{\text{CNT}}}{V_{\text{CF}}} = \frac{2\sqrt{3}}{\pi} (V_{\text{CNT}})_{\text{max}} \quad \text{B (9)}
\]

Appendix B

Equation (15) as shown in the results and discussion Section can be derived as follows:

Referring to Fig. 6, the RVE of the FFRC can be considered as an equilateral triangle. Thus the volume of the RVE of the FFRC \( (V_{\text{FFRC}}) \) is given by

\[
V_{\text{FFRC}} = \frac{\sqrt{3}}{4} D^2 L \quad \text{B (1)}
\]

where \( D = 2R \). The volume of the carbon fiber \( (V_f) \) is

\[
V_f = \frac{\pi}{8} d^2 L \quad \text{B (2)}
\]

where \( d = 2a \). Thus the carbon fiber volume fraction in the FFRC \( (V_f) \) can be expressed as

\[
V_f = \frac{V_f}{V_{\text{FFRC}}} = \frac{\pi d^2}{2\sqrt{3} D^2} \quad \text{B (3)}
\]

Using B (3), the carbon fiber volume fraction in the CFF \( (V_f) \) can be derived as

\[
V_f = \frac{2d^2 L}{3D^2} = \frac{2\sqrt{3}}{\pi} V_f \quad \text{B (4)}
\]

References


