Dependence of equivalent thermal conductivity coefficients of single-wall carbon nanotubes on their chirality

V S Zarubin\textsuperscript{1*} and E S Sergeeva\textsuperscript{2}

\textsuperscript{1}Bauman Moscow State Technical University, Moscow, Russia
\textsuperscript{2}JSC “Kompozit”, Korolev, Moscow Region, Russia
E-mail: *zarubin@bmstu.ru

Abstract. Composite materials (composites) composed of a matrix and reinforcing components are currently widely used as structural materials for various engineering devices designed to operate under extreme thermal and mechanical loads. By modifying a composite with structure-sensitive inclusions such as single-wall carbon nanotubes, one can significantly improve the thermomechanical properties of the resulting material. The paper presents relationships obtained for the equivalent thermal conductivity coefficients of single-wall carbon nanotubes versus their chirality using a simulation model developed to simulate the heat transfer process through thermal conductivity in a transversely isotropic environment. With these coefficients, one can conventionally substitute a single-wall carbon nanotube with a continuous anisotropic fiber, thus allowing one to estimate the thermal properties of composites reinforced with objects of this sort by using the well-known models developed for fibered composites. The results presented here can be used to estimate the thermal properties of carbon nanotube-reinforced composites.

1. Introduction

Given their high thermoelastic performance, the nanoscale objects such as graphene flakes, fibers, single- and multi-wall carbon nanotubes (SWCNT / MWCNT) \cite{1–9} have increasingly been used nowadays as modifying elements for composite materials. These objects are capable of aggregating into nanoclusters; however, the uniformly-dispersed reinforcement can also be attained. It is commonly known that the nanoscale graphene objects, even in a small proportion, can significantly improve the thermoelastic characteristics of a composite reinforced with them \cite{10–13}. The development of a composite-based structure designed to operate under extreme mechanical and thermal loads requires correct estimates of the material elastic and thermal properties that are mainly governed by the corresponding characteristics of the reinforcing elements, which in turn depend on their geometry. There are plenty of publications addressing the dependence of the elastic properties of nanoscale elements on their geometry. However, the dependence of the thermal properties of these objects on their characteristic dimensions has not yet been studied in detail.

To construct a simulation model representing the SWCNT-reinforced composite thermal properties, a nanotube can be represented as an anisotropic circular cylinder, its length being...
Figure 1. Several ways of rolling the graphene plane into a tube and their corresponding SWCNT configurations.

much larger than its radius. With such a representation, one can use the well-known models developed for estimating the thermal conductivity coefficient of fibered composites [14].

This paper focuses on the dependence of the equivalent thermal conductivity coefficients, both in the axial direction and in the cross-sectional plane, on the SWCNT diameter and configuration type determined by the chirality index [15].

2. Main relationships
A single-wall carbon nanotube (SWCNT) is a cylinder, up to several tens nanometer in diameter, representing a single graphene plane rolled in a seamless tube, namely, a surface composed of regular hexagons, with carbon atoms residing at their vertices [15]. The result of this rolling procedure depends on the graphene plane orientation angle as related to the nanotube axis. The orientation angle, in turn, governs the nanotube chirality, thus determining the nanotube characteristics. For the nanotube chirality, the notation \((\mathbf{m,n})\) is used, indicating the coordinates of the hexagon to be aligned with the one residing at the origin point after the graphene plane is rolled into a tube (see figure 1). The chirality indices \((m,n)\) of a single-wall carbon nanotube uniquely determine its diameter \(D\) [15]

\[
D = \frac{\sqrt{3}d_0}{\pi} \sqrt{m^2 + n^2 + mn}. \tag{1}
\]

Of all possible ways of rolling the graphene plane into a tube, we set aside those for which the alignment of hexagon \((m,n)\) with the origin point does not distort its structure. This condition is met, particularly, with angles \(\alpha = 0^\circ\) (Armchair-type configuration) and \(\alpha = 30^\circ\) (Zigzag-type configuration). These configurations correspond to chiralities \((n,n)\) and \((m,0)\), correspondingly. The remaining combinations of indices refer to the Chiral-type configuration.

For our simulation model, the nanotube is represented as a circular cylindrical shell formed by rolling a polyatomic graphene layer into a tube, with halves of fullerene molecules on the edges [10]. Assume that the thermal conductivity coefficient of graphene in its isotropy plane is equal to \(\lambda_0\). In this case, the thermal conductivity coefficient is equal to \(\lambda_0\) along any direction tangent to the middle surface of the shell [16]. However, given the conventional substitution of SWCNT with a continuous circular cylinder, the equivalent thermal conductivity coefficients \(\lambda_//\) and \(\lambda_\perp\) along the longitudinal axis and in the plane perpendicular to it are, correspondingly, different. Since the SWCNT length is assumed to be much larger than its outer radius, the effect of the shell semispherical parts on the values of \(\lambda_//\) and \(\lambda_\perp\) may be neglected.
3. Equivalent thermal conductivity coefficient

The dependence of the effective SWCNT thermal conductivity coefficient on the SWCNT diameter and configuration can be obtained using the simulation model representing the heat transfer through thermal conductivity in a nanotube [16].

The equivalent thermal conductivity coefficient \( \lambda_{\parallel} \) along the SWCNT axis can be determined from the axial heat resistance equality between the circular cylindrical shell, its thermal conductivity coefficient equal to \( \lambda_0 \) in any tangential direction, and the continuous circular cylinder substituting the shell:

\[
\frac{L}{2\pi R_0 h_0 \lambda_0} = \frac{L}{\pi (R_0 + h_0/2)^2 \lambda_{\parallel}},
\]

where \( L \) is shell/cylinder length; \( R_0 \) and \( h_0 \) are the middle surface radius and the shell thickness, correspondingly. The latter value is assumed to be equal to 0.34 nm, i.e., the distance between two neighboring atomic planes in the graphite crystal [18]. From the above equality follows that

\[
\lambda_{\parallel} = \frac{2R_0 h_0 \lambda_0}{\tilde{R}^2}, \tag{2}
\]

where \( \tilde{R} = R_0 + h_0/2 \). This relation is meaningful for \( R_0 \geq h/2 \), which, given equation (1), for the Zigzag-type SWCNT corresponds to the condition \( n \geq 5 \), while for Armchair-type SWCNT, to the condition \( n = m \geq 3 \). For other chirality index combinations (Chiral-type SWCNT), the condition \( n + m \geq 5 \) shall be satisfied. Depending on the chirality indices or, more precisely, the their sum, the polygon, namely, the SWCNT cross section, tends to a circle. To obtain a first-order estimate, we assume that SWCNT can be represented by a cylinder satisfying the condition \( n + m \geq 5 \).

To find the equivalent thermal conductivity coefficient \( \lambda_{\perp} \), we use the model simulating the interaction between a sufficiently long circular cylindrical shell and its environment of unlimited volume with thermal conductivity coefficient \( \lambda \) [16]. The temperature distribution established in the area \( L/\tilde{R} \gg 1 \) can be represented as a function \( T(r, \varphi) \) under the assumption that it remains unchanged along the shell axis and satisfies the Laplace equation

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \varphi^2} = 0
\]

in the polar coordinate system, with origin on shell axis.

If we assume that the temperature field gradient vector is equal to \( G \) in the environment at a distance \( r \) greater than \( \tilde{R} \) in the direction of the polar angle \( \varphi \), then the obtained temperature distribution in this environment, with regard to the temperature field distortion induced by the cylindrical shell, is described by the formula [16]

\[
T(r, \varphi) = Gr \cos \varphi + \frac{B_0}{r} \cos \varphi, \quad r \geq \tilde{R}, \quad 0 \leq \varphi < 2\pi, \tag{3}
\]

where \( B_0 \) is a constant coefficient which can be determined from the condition of thermal interaction between the environment and the cylindrical shell.

The temperature \( T_0 \) is assumed uniform through the shell thickness, depending on the polar angle \( \varphi \) alone. Under the assumption that the thermal contact between the shell and the environment to be perfect, from formula (3) for the temperature the cylindrical surface at \( r = \tilde{R} \) we obtain

\[
T_0(\varphi) = \left( G\tilde{R} + \frac{B_0}{\tilde{R}} \right) \cos \varphi. \tag{4}
\]
Table 1. Chirality index for various SWCNT configurations.

|        | Armchair | Zigzag | Chiral |
|--------|----------|--------|--------|
| m      | m        | n      | n      |
| 5      | 5        | 5      | 0      |
| 10     | 10       | 10     | 0      |
| 20     | 20       | 20     | 0      |
| 50     | 50       | 50     | 0      |
| 100    | 100      | 100    | 0      |
| 200    | 200      | 200    | 0      |

From (3) and (4), given the thermal balance in the shell, we have

\[
\frac{B_0}{R^2} = G \frac{1 - \beta_0}{1 + \beta_0}, \quad \beta_0 = \frac{\lambda_0 h_0}{\lambda R_0}.
\]  

(5)

The replacement of the cylindrical shell by a continuous cylinder of radius \( \tilde{R} \) and with thermal conductivity coefficient \( \lambda_\perp \) will also distort the temperature field in the environment, which is described by the term \( (\tilde{B}/r^2) \cos \varphi \) [17], where

\[
\tilde{B} = G \tilde{R}^2 \lambda - \lambda_\perp \lambda + \lambda_\perp.
\]  

(6)

Assuming that the temperature distribution over the outer surface of the cylindrical shell is similar to that over the surface of the continuous cylinder substituting the shell, we have \( B_0 = \tilde{B} \), from which, considering (5) and (6), we obtain the second SWCNT equivalent thermal conductivity coefficient:

\[
\lambda_\perp = \frac{\lambda_0 h_0}{R_0}.
\]  

(7)

4. Analysis of the results

As the input data for SWCNT thermal conductivity coefficient \( \lambda_0 \), we use the value 3500 W/(m·K) [18]. The values of the chirality index chosen for various SWCNT configurations are given in table 1.

Using formula (1), the SWCNT diameter values were found for different chirality index combinations (see the Table below), with the previously established limits for these values taken into account.

From (2) and (7), we find the values of \( \lambda_\parallel \) and \( \lambda_\perp \), correspondingly. Thus we have determined the dependence of the SWCNT equivalent thermal conductivity coefficient on the nanotube diameter, and hence, on the chirality type. The dependence is shown in figure 2.

In figure 2, one can see that the values of the SWCNT equivalent thermal conductivity coefficient decrease as the nanotube diameter increases. Figure 3 shows the dependence of \( \tilde{\lambda} = (\lambda_\parallel/\lambda_\perp)/(\lambda'_\parallel/\lambda'_\perp) \) on the ratio \( \tilde{d} = d/d' \), where \( \lambda'_\parallel \), \( \lambda'_\perp \), and \( d' \) are maximum values of the equivalent thermal conductivity coefficient and the diameter for each SWCNT type.

It is clear from figure 3 that for a certain chirality index, the corresponding values of \( \tilde{\lambda} \) are greater for the Armchair-type SWCNT than those obtained for the Zigzag-/Thiral-type SWCNT; however, when the dimensionless coefficient \( \tilde{d} \) becomes equal to or larger than 0.5, the difference becomes almost unnoticeable. It should also be noted that the Chiral-type SWCNT and Zigzag-type SWCNT are almost identical by their values of \( \tilde{\lambda} \) obtained with the selected chirality indices.
Figure 2. Dependence of the SWCNT equivalent thermal conductivity coefficient \((W/(m\cdot K))\) on the diameter and chirality type.

Figure 3. Dependence of \(\tilde{\lambda}\) on \(\tilde{d}\).

Conclusion
The relationships outlined above can be used to estimate the equivalent thermal conductivity coefficient of single-wall carbon nanotubes that are currently widely used as reinforcing inclusions for advanced structural materials in devices designed to operate under extreme loads of different nature. Based on these coefficients and the nanotube representation as an anisotropic continuous circular cylinder, one can predict the thermal properties of materials on the basis of simulation models developed for fibered composites.

Acknowledgments
The work was performed in the framework of implementation of the basic part of the governmental task of the Ministry of Education and Science of the Russian Federation (Project 9.7784.2017/BP).

References
[1] Palermo P 2015 Structural ceramic nanocomposites: A review of properties and powders’ synthesis methods *Nanomater.* 5 656–96
[2] Casati R and Vedani M 2014 Metal matrix composites reinforced by nano-particles — A review *Metals* 4 65–83
[3] Alibeigloo A and Liew K M 2013 Thermoelastic analysis of functionally graded carbon nanotube-reinforced composite plate using theory of elasticity *Compos. Struct.* 106 873–81
[4] Ayatollahi M R, Shadlou S, and Shokrieh M M 2011 Multiscale modeling for mechanical properties of carbon nanotube reinforced nanocomposites subjected to different types of loading *Compos. Struct.* 93 2250–9
[5] Liew K M, Lei Z X, Zhang L W, et al. 2014 Mechanical analysis of functionally graded carbon nanotube reinforced composites: A review *Compos. Struct.* 120 90–7
[6] Montinaro N and Pantano A 2014 Parameters influencing the stiffness of composites reinforced by carbon nanotubes — A numerical–analytical approach Compos. Struct. 109 246–52
[7] Ürk D, Demir E, Bulut O, et al. 2016 Understanding the polymer type and CNT orientation effect on the dynamic mechanical properties of high volume fraction CNT polymer nanocomposites Compos. Struct. 155 255–62
[8] Konstantinos G and Costas G 2012 Polymer–nanotube interaction in MWCNT/poly(vinyl alcohol) composite mats Carbon 50 4291–301
[9] Jin G P, Qunfeng Ch, Jun L, et al. 2012 Thermal conductivity of MWCNT/epoxy composites: The effects of length, alignment and functionalization Carbon 50 2083–90
[10] Katz A E 2008 Fullerenes, Carbon Nanotubes And Nanostructures: Genealogy of Forms and Ideas (Moscow: LKI Publishers) p 296
[11] Zarubin V S, Sergeeva E S, and Shishkina S I 2016 Estimating the elastic properties of the carbon nanotube-reinforced composite matrix Nauka Obraz. Nauchn. Izdanie 9 155–70
[12] Sergeeva E S 2016 Investigations of elastic properties of a composite containing ellipsoidal inclusions Molodezhn. Nauchn.-Techn. Vestnik 5 URL http://sntbul.bstu.ru/doc/839933.html
[13] Sergeeva E S 2016 Investigations of elastic properties of nanocomposites Molodezhn. Nauchn.-Techn. Vestnik 8 URL http://sntbul.bstu.ru/doc/846958.html
[14] Zarubin V S, Kuvyrkin G N, and Savelieva I Yu 2013 Thermal Conductivity of Fiber Reinforced Composites: Derivation, Verification and Parametric Analysis of Calculation Formula (Saarbrücken: LAP LAMBERT Academic Publishing) p 121
[15] Yeletski A V 2002 Carbon nanotubes and their emission properties Usp. Fiz. Nauk 172 (4) 401–38
[16] Zarubin V S 2013 Estimates for the equivalent thermal conductivity coefficients of fullerenes and single-wall carbon nanotubes Inzh. Zh. Nauka Innovats. 4(16) URL http://engjournal.ru/catalog/mathmodel/hidden/669.html
[17] Carslaw H S and Jaeger J C 1964 Conduction of Heat in Solids (Moscow: Nauka) p 488
[18] Yelets A V, Iskandarova I M, Knizhnik A A, and Krasikov D N 2011 Graphene: fabrication methods and thermophysical properties Usp. Fiz. Nauk 181 (3) 233–268