Numerical study on the thermal behavior of polymer nano-composites

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Abstract. In this work, Mori-Tanaka (MT) scheme has been implemented to predict effective thermal properties of polymer nano-composites composed of high-density polyethylene (HDPE) and single-walled carbon nano-tubes (SWCNTs) as matrix and nano-fillers, respectively. The technique uses the fourth order tensor to effectively determine the thermal conductivities, specific heat and global density of the composites. Effect of constituent’s volume fraction and orientation have been investigated for effective thermal conductivities of composites. The composite fillers are numerically simulated as aligned, 2-D and 3-D random orientation in the polymer matrix. Numerical results show that in-plane and out-of-plane thermal conductivities have a linear relation with increasing volume fraction. The specific heat capacity of a composite decrease as the volume fraction of SWCNTs increases. The randomly distributed SWCNTs decreases the heat flux whereas the alignment of SWCNTs has shown a maximum heat flux.

1. Introduction
Polymers are known for their easy processability. They have a low glass transition temperature compared to metals. This makes them favorable to be chosen as a matrix in polymer composites. Research has been going on to study the mechanical, thermal and electrical properties of polymer composites. Although a need to find a suitable polymer composite for a particular application is still a hunt. Polymer composites have gained popularity due to their low weight, resistance to corrosion, wear and remarkable mechanical and thermal properties.

Polymer composites have gained popularity in electronic devices for heat dissipation due to their low-cost fabrication, easy miniaturization and resistive nature against moisture [1]. Thus, to take advantage of their properties, polymers are used as a matrix in polymer composites. But polymers have low thermal conductivity. To enhance the thermal conductivity of polymers, highly thermally conductive fillers are used as reinforcements. Various reviews are available on the applications of graphene, graphite, and carbon-nano-tubes in aerospace, automotive, medical and electronics industries [1–3]. These excellent reinforcements help the matrix to achieve thermal stability. Applications like capacitors to solar cells focus on the thermal and electrical conductivity of the reinforcements. Also, from the viewpoint of mass saving in aerospace applications, polymer composites are replacing the metals. The requirement of low weight, high thermal conductivity, easy processing and resistance to moisture leads us to study the polymer composites.

It had been confirmed experimentally that volume fraction up-to or more than 50% fillers increase the thermal conductivity but degrade the mechanical and physical properties which are also not desired.
for many applications [4]. Thus, to find out the appropriate volume fraction in order to obtain the desired thermal conductivity is necessary. This led to predict the thermal conductivity of polymer composites computationally first and then for experimental validations. The time-consuming and bulky specimen is required to measure thermal conductivity when conventional steady-state methods are employed [3]. Therefore, a model was required in the past to evaluate the transport properties such as thermal and electrical of a two-phase composite.

A lot of literature is available from 1935 to 1970 to calculate the transport properties mathematically [5–10]. These mathematical expressions were lacking in many factors like shape, aspect ratio, distribution, and orientation. Transport properties depend on these factors. Thus, a need to consider these factors and study their simultaneous effect is important. Using a mean-field homogenization (MFH) scheme, many research had been carried out to determine the elastic properties of the polymer nanocomposites [11–16]. According to Nielsen [17], conductivity is analogous to an elastic stiffness of the composites and heat flux distribution in a thermally conductive composite is analogous to the stress field distribution due to a second phase present in the composite. Following are the major leading features of this work:

- MFH has been implemented to predict in-plane and out of plane thermal conductivity of polymer nano-composites.
- The effect of volume fraction and orientation of SWCNTs fillers have been analyzed for effective thermal properties of composites.
- To study the effect of networked SWCNTs on the thermal conductivities of considered composite material.

In all the above-mentioned aims, the nano-filler size and aspect ratio were kept constant. Although, many theories fail to include the nano-filler size, aspect ratio, and orientation effect. MFH employed in this article has included all factors to compute the thermal conductivities, specific heat constant and density of the composites. MFH scheme computes the properties by using the averaging theorem. It averages the strains and the stresses and then relates them to compute the effective property of a composite.

2. Modeling

In this section, the details of MT scheme for the evaluation of thermal conductivity of a composite containing SWCNT as nano-filler and HDPE as the matrix is discussed. The various properties as illustrated in table 1 are used as material input. The size, shape, orientation and volume fraction of nanofiller plays an important role in predicting the thermal conductivity. However, in this article, the effect of orientation and volume fraction are studied only. Other factors were kept constant during the simulation.

| Phase                  | SWCNT (nano-filler) | HDPE (matrix) |
|------------------------|---------------------|---------------|
| Density (Kg/m³)        | 2100                | 950           |
| Specific heat[18],[19] (J/kg-K at 25°C) | 0.71                | 1555          |
| Thermal conductivity[20],[21] (W/m-K at 25°C) | 2000                | 0.44          |
| Aspect ratio           | 10                  | ---           |
| Nano-filler radius (nm) | 0.5                 | ---           |

2.1 Mori-Tanaka (MT) Method: Mean Field Homogenization Scheme

In this sub-section of the article, authors want to focus on the mathematical theory of the homogenization scheme employed to obtain the effective transport properties. The scheme is one of the simplest and efficient micromechanics methods to estimate the thermal and elastic properties of a composite material. The scheme usually works in the manner defined by Benveniste [12]. The averaged strains and stresses
are related to each other by fourth order strain and stress concentration tensors. The MT analogous form for thermal analysis is represented in equation 1 & 2 [12].

\[
\langle VT_{nf}\rangle = \langle G_{nl}\rangle_{nf} \langle V \rangle T = \langle G_{nl}\rangle_{nf} \langle G_{MT}\rangle_p \langle VT \rangle
\]

(1)

\[
\langle q_{nf}\rangle = \langle H_{nl}\rangle_{nf} \langle q \rangle = \langle H_{nl}\rangle_{nf} \langle H_{MT}\rangle_p \langle q \rangle
\]

(2)

where \(\nabla T\) represents temperature gradient vector, \(q\) represents heat flux vector, \(G\) and \(H\) denotes the second order tensors of temperature gradient and heat flux concentration.

The MT stress concentration tensors for nano-fillers and polymer can be expressed as:

\[
\langle G_{MT}\rangle_p = \left[\left(1 - v_{nf}\right)I + v_{nf}\langle G_{nl}\rangle_{nf}\right]^{-1}
\]

(3)

\[
\langle G_{MT}\rangle_{nf} = \langle G_{nl}\rangle_{nf} \left[\left(1 - v_{nf}\right)I + v_{nf}\langle G_{nl}\rangle_{nf}\right]^{-1}
\]

(4)

where \(I\) define the identity tensor of fourth order and \(v_{nf}\) is the volume fraction of the nano-fillers. Hill’s expression can be used to find out the dilute concentration tensor [22]. In Hill’s expression replace the \(I\) by the second order identity tensor, stiffness tensor for the constituents by the conductivity tensors and Eshelby tensor of second order for diffusion problem can be considered from Hiroshi and Minoru [23]. MT macroscopic effective conductivity tensor (\(K_c\)) for the composite can be expressed as [24]:

\[
K_c = \left[\left(1 - v_{nf}\right)K_p + v_{nf}\left\langle K_{nf}\langle G_{nl}\rangle_{nf}\right\rangle\right]\left[\left(1 - v_{nf}\right)I + v_{nf}\langle G_{nl}\rangle_{nf}\right]^{-1}
\]

(5)

3. Results and discussions

The heat flux is transferred in a two-phase polymer nano-composite through the interface of the constituents. A perfect bonding between the nano-filler and the matrix is assumed. The conductivity of the nano-filler is high compared to the matrix. Thus, the orientation of the nano-filler is an important criterion to obtain the desired heat flux in the desired direction. Hence, four cases were studied in this article to justify the effect of orientation.

3.1 Nano-fillers are aligned i.e. \(\theta = 90^\circ\) and \(\phi = 0^\circ\)

The cylindrical SWCNTs as shown in figure 1 aligned along the x-axis are considered. It is evident from table 2 that the in-plane and out-of-plane conductivity increases with an increase in the volume fraction of the nano-fillers. The effect of aligned SWCNTs is more in out-of-plane as compared to in-plane conductivity. This is due to the large surface area in the perpendicular direction. The specific heat of a composite is decreasing with an increase in the content of the nano-filler. The density of a composite varies linearly with the volume fraction of the nano-fillers.
Figure 1. Aligned SWCNTs in the matrix.

Table 2. Effect of volume fraction on the thermal conductivities in an aligned nano-filler composite.

| Parameter                             | Units       | $V_f = 2\%$ | $V_f = 4\%$ | $V_f = 6\%$ | $V_f = 8\%$ | $V_f = 10\%$ |
|---------------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Thermal conductivity (out-of-plane)   | W/m-K       | 0.87781     | 1.3337      | 1.8087      | 2.3041      | 2.8213      |
| Thermal conductivity (in-plane)       | W/m-K       | 0.45832     | 0.47741     | 0.49731     | 0.51807     | 0.53975     |
| Composite specific heat               | J/kg-K      | 1487.9      | 1423.9      | 1362.8      | 1304.4      | 1248.5      |
| Global density                        | Kg/m$^3$    | 973         | 996         | 1019        | 1042        | 1065        |

3.2 Nano-fillers are embedded in a 2-D random manner

The randomness of the SWCNTs in a 2-D manner can be seen in figure 2. It is evident from table 3 that the in-plane and out-of-plane conductivity increases with an increase in the volume fraction of the nano-fillers. The effect of 2-D random nano-fillers is more in in-plane conductivity compared to out-of-plane conductivity. This is due to the formation of the network in a plane at some local sites. The networking help in increasing the thermal conductivity along the longitudinal direction. The effect of networking has decreased thermal conductivity in the perpendicular direction. The specific heat and density have shown the usual behavior with increasing volume fraction as defined in subsection 3.1.

Table 3. Effect of volume fraction on the thermal conductivities in a 2-D random nano-filler composite.

| Parameter                             | Units       | $V_f = 2\%$ | $V_f = 4\%$ | $V_f = 6\%$ | $V_f = 8\%$ | $V_f = 10\%$ |
|---------------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Thermal conductivity (out-of-plane)   | W/m-K       | 0.45832     | 0.47741     | 0.49731     | 0.51807     | 0.53975     |
| Thermal conductivity (in-plane)       | W/m-K       | 0.66806     | 0.90553     | 1.153       | 1.4111      | 1.6805      |
| Composite specific heat               | J/kg-K      | 1487.9      | 1423.9      | 1362.8      | 1304.4      | 1248.5      |
| Global density                        | Kg/m$^3$    | 973         | 996         | 1019        | 1042        | 1065        |
Figure 2. 2-D random SWCNTs in the matrix.

3.3 Nano-fillers are embedded in a 3-D random manner

The 3-D randomly oriented SWCNTs can be seen in figure 3. The effect of the random distribution of SWCNTs is such that the MT scheme predicted the thermal conductivity as isotropic. The composites with a random distribution of SWCNTs can be used for the applications where the transfer of heat flux of 6 W/m² is required. The conductivity will not vary with direction as predicted isotropic through MFH simulation as illustrated in table 4. The specific heat and density have shown the usual behavior as predicted in sub-section 3.1 and 3.2.

Table 4. Effect of volume fraction on the thermal conductivities in a 3-D random nano-filler composite.

| Parameter                     | Units  | $V_f = 2\%$ | $V_f = 4\%$ | $V_f = 6\%$ | $V_f = 8\%$ | $V_f = 10\%$ |
|-------------------------------|--------|-------------|-------------|-------------|-------------|-------------|
| Thermal conductivity (isotropic) | W/m-K   | 0.59815     | 0.76282     | 0.93443     | 1.1134      | 1.3003      |
| Composite specific heat       | J/kg-K | 1487.9      | 1423.9      | 1362.8      | 1304.4      | 1248.5      |
| Global density                | Kg/m³  | 973         | 996         | 1019        | 1042        | 1065        |

Figure 3. 3-D random SWCNTs in the matrix.
3.4 Basic yarn structured nano-filler (Warp/weft = 90°)

The networked SWCNTs as figure 4 has shown a dramatic increase in in-plane thermal conductivity with the increasing volume fraction of the nano-fillers. The networked SWCNTs has also shown the change in composite specific heat and density. The decreasing trend and increasing trend of specific heat and density as illustrated in table 5 is usual, respectively. The networked structure is easy to produce nowadays with the help of a chemical vapor deposition method. Transfer of high heat flux in the applications like heat exchanger can use the SWCNTs array. A comparison of in-plane and out-of-plane thermal conductivities is shown for the four cases discussed above in figure 5 and 6. The in-plane thermal conductivity is dominating in case of basic yarn structure whereas out-of-plane is higher is dominating in aligned SWCNTs.

Table 5. Effect of volume fraction on the thermal conductivities in basic yarn (warp/weft = 90°) nano-filler composite.

| Parameter                     | Units | V_f =2% | V_f =4% | V_f =6% | V_f =8% | V_f =10% |
|-------------------------------|-------|---------|---------|---------|---------|----------|
| Thermal conductivity (out-of-plane) | W/m-K | 0.47665 | 0.51649 | 0.55994 | 0.60753 | 0.65988  |
| Thermal conductivity (in-plane) | W/m-K | 40.45   | 80.461  | 120.47  | 160.49  | 200.51   |
| Composite specific heat       | J/kg-K | 1423.9  | 1304.4  | 1195    | 1094.5  | 1001.8   |
| Global density                | Kg/m³  | 996     | 1042    | 1088    | 1134    | 1180     |

Figure 4. Basic yarn structure of SWCNTs.
4. Conclusions
In this article, thermal properties have been evaluated and compared for four different cases of SWCNTs distribution in the HDPE matrix. The assumption of isotropic nature of matrix and nano-filler has been employed in the presented simulation results. The maximum volume fraction of the nano-fillers is restricted to 10%. The obtained numerical results can be summarised as:

(i) The filler orientation has a prominent effect on the thermal conductivity of the composites.
(ii) The increase in volume fraction has shown a positive effect on the thermal conductivity but the orientation effect cannot be neglected.
(iii) An array of nano-fillers can increase the in-plane thermal conductivity drastically compared to randomly distributed nano-fillers.
(iv) The specific heat has shown an inverse nature with an increase in the volume fraction of the SWCNTs.
(v) 3-D random distribution has given a result for isotropic thermal conductivity of the composite.

References
[1] Balandin A A 2011 Thermal properties of graphene and nanostructured carbon materials Nat. Mater. 10 569–81
[2] Sadasivuni K K, Ponnamma D, Thomas S and Grohens Y 2014 Evolution from graphite to graphene elastomer composites Prog. Polym. Sci. 39 749–80
[3] Han Z and Fina A 2011 Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review Prog. Polym. Sci. 36 914–44
[4] Eksik O, Bartolucci S F, Gupta T, Fard H, Borca-Tasciuc T and Koratkar N 2016 A novel approach to enhance the thermal conductivity of epoxy nanocomposites using graphene core–shell additives Carbon N. Y. 101 239–44

[5] Bruggeman D A G 1935 Calculation of different physical constants of heterogeneous substances. I. Dielectric constants and conductivities of the mixed bodies of isotropic substances Ann. Phys. (N. Y). 416 636–64

[6] Kerner E H and H. E 1956 The Elastic and Thermo-elastic Properties of Composite Media Proc. Phys. Soc. Sect. B 69 808–13

[7] Tsao G T-N 1961 Thermal Conductivity of Two-Phase Materials Ind. Eng. Chem. 53 395–7

[8] Springer G and Tsai S 1967 Journal of composite materials. (Technomic Pub. Co)

[9] Halpin J C 1969 Stiffness and Expansion Estimates for Oriented Short Fiber Composites J. Compos. Mater. 3 732–4

[10] Sundstrom D W and Lee Y-D 1972 Thermal conductivity of polymers filled with particulate solids J. Appl. Polym. Sci. 16 3159–67

[11] Kroner E 1958 Calculation of the elastic constants of the multi-crystal from the constants of the single crystal Mag. Phys. 151 504–18

[12] Benveniste Y 1987 A new approach to the application of Mori-Tanaka’s theory in composite materials Mech. Mater. 6 147–57

[13] Jia Z, Wang Z, Xu C, Liang J, Wei B, Wu D and Zhu S 1999 Study on poly(methyl methacrylate)/carbon nanotube composites Mater. Sci. Eng. A 271 395–400

[14] Mercier S and Molinari A 2009 Homogenization of elastic–viscoplastic heterogeneous materials: Self-consistent and Mori-Tanaka schemes Int. J. Plast. 25 1024–48

[15] Chwal M and Muc A 2015 Transversely isotropic properties of carbon nanotube/polymer composites Compos. Part B Eng. 88

[16] Sokolowski D and Kami M 2018 Homogenization of carbon/polymer composites with anisotropic distribution of particles and stochastic interface defects Acta Mech.

[17] Nielsen L E 1968 The thermal and electrical conductivity of two phase systems vol 76 (McGraw-Hill)

[18] Pradhan N R, Duan H, Liang J and Iannacchione G S 2009 The specific heat and effective thermal conductivity of composites containing single-wall and multi-wall carbon nanotubes 245705

[19] Mark J E 2006 Physical properties of polymers handbook

[20] Han Z and Fina A 2011 Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review Prog. Polym. Sci. 36 914–44

[21] Chiu, Jen and Fair P G 1979 Determination of thermal conductivity by differential scanning calorimetry Thermochim. Acta 34 267–73

[22] Hill R 1965 A self-consistent mechanics of composite materials J. Mech. Phys. Solids 13 213–22

[23] Hiroshi H and Minoru T 1986 Equivalent inclusion method for steady state heat conduction in composites Int. J. Eng. Sci. 24 1159–72

[24] Weng G J 1990 The theoretical connection between Mori-Tanaka’s theory and the Hashin Shtrikman-Walpole bounds Int. J. Eng. Sci. 28 1111–20