Effective thermal conductivity of two-phase composites containing highly conductive inclusions

Kamran A Khan¹, Sohaib Z Khan² and Muhammad A Khan²

Abstract

Thermal conductivity is one of the key material properties to understand the effective thermo-mechanical behavior of advanced composites. Experimental studies show that when highly conductive inclusions are embedded in a less thermally conductive matrix, the effective thermal conductivity of the composite changes drastically with the increase of volume fraction ($V_f$) of the inclusions. This study presents a theoretical model to predict the effective thermal conductivity of two-phase particulate composites containing highly conductive inclusions in a polymeric matrix. The probabilistic approach presented by Tsao (1961) has been modified and extended for predicting the effective thermal conductivity of two-phase composites. The expression for the effective thermal conductivity of a unit cube of two-phase composite is derived implicitly in terms of distribution function, $V_f$ and thermal conductivity of the constituents. Different distribution functions of the inclusions are proposed and the optimum function is obtained to describe the effective thermal conductivity of highly conductive particulate composites. Results of the effective thermal conductivity of a cubic unit cell obtained from different distributions of inclusions are compared with published experimental data, and other analytical and numerical models for particulate composites available in the literature. The results show a linear distribution of inclusions gives reasonable estimates of the effective thermal conductivity of the particulate composites. It is anticipated that the proposed approach can be used to develop models for the effective thermal conductivity of advanced composites containing highly conductive inclusions.

Keywords
Effective thermal conductivity, two-phase composites, particulate composites, the distribution of inclusions, highly conductive composites

Introduction

Polymeric composite materials have been utilized in various heat transfer-related applications, for example, thermal storage management and heat sink devices. The thermal performance of polymeric composites can be improved by varying microstructure and thermal properties of the constituents.¹² In recent years, the demand for polymeric composite materials with high thermal conductivity for applications in heat sinks in electronic packaging and other appliances is increasing in industrial sectors. A series of experimental studies shows that when highly conductive inclusions are embedded in a less thermally conductive matrix, the effective thermal conductivity (ETC) of the composite changes significantly with the increase of volume fraction ($V_f$) of the inclusions.³⁷ Therefore, a precise prediction of the ETC of the highly conductive
polymeric composites plays a significant role in evaluating the thermal performance of the composite.

The ETC of particulate composites depends on properties of the constituents such as shape, geometry, distribution, thermal conductivities, \( V_f \) and matrix-inclusion interfacial effects.\(^8\) It is almost impossible to estimate the ETC of a composite material unless details of the inclusion’s distribution and microstructures are known.\(^9\) The ETC of two-phase isotropic composites can vary in a wide range depending on the microstructural details and thermal conductivities of the constituents. The ETC of a composite material can simply be obtained by the rule of mixture which actually corresponds parallel (upper bound) and series (lower bound) configuration of the inclusions, respectively.\(^10\) More tighter bounds are also derived based on variational principle and statistical correlation functions.\(^11,12\) These bounds are used to define the thermodynamics limits of the ETC of two-phase composites. For a more detailed review, please see Torquato.\(^2\)

Many analytical models have been proposed to predict the ETC of a composite material based on simplified microstructures of the composites. Maxwell\(^13\) was one of the first persons to investigate the conduction of two-phase composites analytically by considering the dilute suspension of non-interacting spherical particles. An exact expression for the ETC of composites was obtained by solving the Laplace equation. Maxwell’s approach has been extended by many researchers. Fricke,\(^14\) Nielsen\(^15\) and Bruggeman\(^16\) derived the expressions for ellipsoidal inclusions, randomly oriented and long thin cylindrical dispersed particulate inclusions, respectively. Hamilton and Crosser\(^17\) studied the effect of various filler shapes; Benveniste\(^18\) and Hasselman and Johnson\(^19\) considered the effect of the interfacial thermal barrier resistance. These all modifications expanded the applicability of Maxwell’s approach for the variety of conditions. However, these models are not applicable to predict the ETC of composites having highly conductive inclusions.\(^3\)

Several micromechanical models have been proposed to predict the ETC of composites. Benveniste\(^20\) formulated the ETC for multiphase systems by determining the average flux in each constituent; the homogenization was performed using the Mori and Tanaka\(^21\) and a generalized self-consistent model.\(^2\) Verma et al.\(^22\) derived the ETC of two-phase composites containing spherical particles arranged in a three-dimensional cubic geometry. The arrangement was divided into multiple unit cells, each of which contained an equivalent sphere. The resistor model was used to determine the ETC of the unit cells. Recently, Khan and Muliana\(^1\) proposed a micromechanical model consists of four particles and a matrix sub cells to predict the ETC of particulate composites. The expression of ETC was formulated by imposing heat flux and temperature continuity at the sub cells’ interfaces. All the available models in literature offer good predictions of the overall ETC when the \( V_f \) is relatively small or when the conductivity of the particle \( (K_p) \) was comparable to the conductivity of the matrix \( (K_m) \).

Various experimental, computational and theoretical studies show that the ETC of a composite can significantly altered by the particle shape, size, interfacial thermal resistance aside from volume fraction and \( K_p/K_m \) ratio.\(^2,23\) Nan et al.\(^24\) developed a generalized effective medium approach (EMA) formulation to compute the ETC of arbitrary ellipsoidal particulate composites with interfacial thermal resistance. The formulation accounts for the effect of particle shape, size, orientation distribution, volume fraction and interfacial thermal resistance. With and without interfacial thermal resistance at large \( K_p/K_m \) ratio, the ETC significantly increases with the anisotropy of the inclusion shape. It was suggested that with large \( K_p/K_m \) ratio, the ETC of a composite can be significantly enhanced by reinforcing the matrix with prolate inclusion (e.g., whiskers) while for small \( K_p/K_m \), the spherical particle is good to enhance ETC.

Another reason that may enhance the ETC is the aggregation of nanoparticle which plays a significant role in the thermal transport in nanofluids.\(^25–27\) Putnam et al.\(^28\) demonstrated that good dispersion of inclusions in nonfluids do not lead to any unusual enhancement in ETC. Prasher et al.\(^27\) proposed a three-level homogenization theory to evaluate the ETC of colloids containing fractal clusters. They demonstrated that such fractal aggregates lead to thermal conductivity enhancement which was mainly attributed to the ability of the heat to move rapidly along the backbone of the clusters.

In nano-enhanced composites, the nanoparticles tend to agglomerate during the solid-liquid phase transition. Some studies showed enhancement in ETC with the formation of percolation networks\(^27\) while other showed reduction in ETC.\(^29\) The percolation threshold depends on the size and the shape of the nanoparticles.\(^30,31\) Nan et al., \(^24\) Gao et al.\(^32\) and Xie et al.\(^33\) studied the influence of the inclusions on ETC below the percolation threshold while recently Wemhoff\(^34\) developed a percolation threshold model for composite material containing uniformly distributed and oriented cylindrical or prolate inclusion. Along the same line, Wemhoff and Webb\(^35\) studied the influence of both spherical clustering and linear percolation network formation on the ETC of a composite. The EMA and percolation theories were employed for percolated and unpercolated areas. It was shown that both spherical clustering and linear agglomeration tend to reduce the ETC. However, the sensitivity analysis of the model
suggested that linear agglomeration can increase the 
bulk thermal conductivity. It was found that when the 
ratio of inclusion–matrix to inclusion–inclusion Kapitza 
resistance increases then the relative thermal resistance 
reduces through the percolation network compared to 
the unpercolated regions of the domain, which in turn 
leads to increase in the ETC of a composite.

Several empirical models are proposed to predict the 
ETC of highly thermally conductive composites. It has 
been experimentally shown by Agari and Uno\textsuperscript{3,4} and 
recently by Zhang et al.\textsuperscript{36} that at higher \( V_f \) and high 
ratios of particle to matrix thermal conductivity, i.e., 
\( V_f > 15\% \) and \( K_p/K_m > 100 \), there exists particle inter-
action in the form of a conductive chain mechanism.\textsuperscript{9} 
This mechanism accelerated the heat conduction pro-
cess, which was shown by an increase in the overall 
ETC of the composite. Agari and Uno\textsuperscript{3,4} used an empircal 
approach to account for the conductive chain mech-
anism. It was concluded that the \( V_f \) and the geometry of 
the particle were responsible for forming the conductive 
chain mechanism. Zhou et al.\textsuperscript{40} showed that at higher 
particle concentrations, some particles flocculated to 
form conductive chains. They introduced the heat trans-
fer passage which took the effect of local concentration 
fluctuation into account to evaluate the ETC of the com-
posites. Although Agari and Uno\textsuperscript{3} and Zhou et al.\textsuperscript{40} 
models are applicable to predict the ETC of highly con-
ductive composites, but the parameters involved in their 
models need to be determined from the experiments; 
therefore, these models are rarely used.

In this study, we have shown that the influence of 
conductive chain mechanism can be effectively captured 
by statistically representing the inclusions’ spatial dis-
tribution in a matrix. Tsao’s\textsuperscript{41} approach for predicting 
the ETC of two-phase composite is used, and Cheng 
and Vachon\textsuperscript{42} procedure has been extended to develop 
an analytical model. A probabilistic approach is used in 
deriving the expression for the ETC of the composite. 
Different distribution functions of the inclusions are 
assumed, and the parameters of the distributions are 
determined as a function of the inclusions’ \( V_f \). The 
ETC of a cubic unit cell of two-phase composite is 
derived implicitly in terms of distribution function, \( V_f \) 
and the thermal conductivity of the constituents.

**Theoretical analysis**

We consider an isotropic two-phase composite material 
consists of particle as inclusions embedded in a poly-
meric matrix. The thermal conductivity of the inclu-
sions (\( K_p \)) is much higher than the thermal 
conductivity of the matrix (\( K_m \)). An ideal contact 
between the inclusions and the matrix is assumed. We 
derived the ETC expression assuming a unidirectional 
heat flow, neglecting thermal convection, radiation and 
contact resistance between the matrix and the 
inclusions. It is assumed that there is no porosity in 
the composite, the inclusions are spatially distributed, 
thermally the mixture is isotropic, and during mechan-
cal mixing for manufacturing of the composite, no 
chemical reaction occurred.

A brief description of Tsao’s\textsuperscript{41} approach to deter-
mine the expression for the ETC of a two-phase com-
posite is provided here.

A unit cube (1 × 1 × 1) of a two-phase composite 
material is assumed to have inclusions dispersed in a 
matrix with some statistical spatial distribution as 
shown in Figure 1(a). Experimental observation for 
determining spatial distribution of inclusion in matrix 
is challenging although it can be done through advance 
materials characterization techniques such as X-ray 
tomography.\textsuperscript{43,44} As a solution of steering away from 
experimental observations, especially for statistical dis-
tribution, some form of continuous distribution of 
inclusions is usually assumed to determine the ETC of 
a composite.\textsuperscript{42} The outer surfaces of a cube parallel to 
\( xy \)- and \( xz \)-planes are perfectly insulated, i.e., the di-
erection of heat transfer is along \( x \)-axis. The two-phase 
composite is hypothetically sliced into numerous thin 
layers parallel to \( yz \)-plane as shown by the vertical lines 
in Figure 1(b). It is assumed that the driving potential 
(temperature gradient) for heat conduction in \( x \)-direc-
tion is uniform through each layer. Each composite 
layer consists of the inclusions and the matrix fractions 
Figure 1(c). Without changing the ETC of each indi-
vidual layer, both inclusions and matrix can equiva-
ently be represented by histograms of matrix and 
inclusions to compute the effective resistance of each 
slice which in turn gives the effective resistance (or 
ETC) of a unit cell. Alternatively, the sequence of the 
layers can be re-arranged into a continuous distribution 
function of the inclusions to compute the effective 
resistance of the unit cell Figure 1(d). The model 
obtained is geometrically invariant along \( z \)-axis.

The unidirectional effective heat flux (\( \bar{q}_e \)) in a unit 
cube can be expressed as

\[
\bar{q}_e = -k_e \frac{\partial \bar{T}}{\partial x_e}
\]

where \( k_e \) is the ETC of a composite and \( \partial \bar{T}/\partial x_e \) is the 
uniform temperature gradient through each layer. For 
a unit length along \( x \)-axis, the expression for effective 
resistance (\( R_e \)) of a unit cell is given by Cheng and 
Vachon\textsuperscript{42}

\[
R_e = \int_0^1 \frac{dx}{k_m + (k_p - k_m) \gamma(x)} + \frac{1 - 2x}{k_m}; \quad k_e = \frac{1}{R_e}
\]
The \( y(x) \) is a function that describes the variation in the collective volume of the inclusions (that may vary differently for different distributions) from one \( V_f \) to the other \( V_f \) of the inclusions. The volume under a surface formed by the curve projection on \( xy \)-plane represents the volume of all inclusions at a particular volume fraction. The ETC \( (k_e) \) can be obtained from equation (2) by taking the inverse of the equivalent overall resistance of the unit cell \( (R_e) \) obtained for different distributions. These calculations are only possible if one assumes that the driving potential (temperature gradient) for heat conduction along \( x \)-direction is uniform through each layer.

Tsao\(^{41}\) assumed a normal distribution with mean \( \mu \) and standard deviations \( \sigma \) of the inclusion that leads to the following expression for the effective resistance of the composite

\[
R_e = \int_0^1 \frac{d x}{k_m + (k_p - k_m) \int \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{(x-\mu)^2}{2\sigma^2} \right] d x}
\]

Unfortunately, it is impossible to get a close form solution of the integral equation and experimental data is necessary for a particular two-phase composite. Moreover, it is practically challenging to determine experimentally the distribution of the inclusions in a matrix. Cheng and Vachon\(^{42}\) modified Tsao's\(^{41}\) approach to obtain the ETC equation while eliminating the requirement of the experimental data.

**Cheng and Vachon model**

Cheng and Vachon\(^{42}\) model assumed that the sequence of the layers shown in Figure 1(c) can be represented by a continuous parabolic distribution of the inclusion material. Consider a unit area parallel to the \( xy \)-plane, as shown in Figure 2, in which shaded area reflects the collective area of the inclusions in a composite (following a specific distribution), while the rest shows the matrix.

Based on the additions of conductance and resistance in parallel and series, respectively, the equivalent thermal resistance can be expressed as

\[
R_e = 2 \int_0^x \frac{d x}{k_m + (k_p - k_m)y(x)} + \frac{1 - 2x}{k_m}
\]

Figure 1. A cubic unit cell for the study of the ETC of a two-phase composite material (after Putnam et al.\(^{28}\)). (a) Inclusions randomly distributed in the matrix, (b) hypothetically sliced thin layers, (c) histogram of the layers and (d) corresponding equivalent continuous distribution of the histogram.
and ETC can be obtained from equation (2). Cheng and Vachon\(^5\) assumed the function \(y(x) = B + Cx^2\) for unidirectional heat flow. There exists a set of coefficients \(B\) and \(C\) for each \(V_f\) and consequently for a given function \(y(x)\). Once the coefficients \(B\) and \(C\) are found as a function of \(V_f\) of inclusions, then the ETC expression for a composite can be determined as a function of \(V_f\) and the thermal conductivity of the constituents. For a given configuration and using the boundary conditions (BCs): \(y(0) = 1\) and \(y(1/2) = 0\), one can find the maximum \(V_f\) of the inclusions that can be represented by the parabolic distribution

\[
(V_f)_{\text{max}} = 2 \int_0^{1/2} y(x) \, dx
\]  

(5)

Substituting \(y(x)\) and using the BCs, the maximum inclusion \(V_f\) is found to be 0.667. For other distributions, the maximum \(V_f\) of the inclusions that can be imbedded in a matrix may be different. Assuming similar shrinkage of distribution along \(x\) (parallel to the heat propagation direction) and \(y\) (perpendicular to the heat propagation direction) from their absolute values, respectively, we can find \(B = -4/C.\)\(^4\)

Substituting this value in above integral gives

\[
B = \sqrt{\frac{3}{2}} V_f \quad \text{and} \quad C = -4 \sqrt{\frac{2}{3V_f}}
\]

(6)

It should be noted that the coefficients \(B\) and \(C\) are the bridge between the \(V_f\) of the inclusions and the distribution function. The resistance contributions of the inclusions are dictated by the values of these coefficients.

In terms of distribution function \(y(x) = B + Cx^2\), equation (2) can be written as

\[
R_c = 2 \int_0^{b/2} \frac{dx}{k_m + B(k_p - k_m) - C(k_p - k_m)x^2} + \frac{1 - B}{k_m}
\]

(7)

Equation (7) can be integrated resulting in for \(k_p \gg k_m\)

\[
R_c = \frac{1}{\sqrt{C(k_p - k_m)[k_m + B(k_p - k_m)]}} \times \ln \left( \frac{\sqrt{[k_m + B(k_p - k_m)] + \sqrt{2} \sqrt{C(k_p - k_m)}}}{\sqrt{[k_m + B(k_p - k_m)] - \sqrt{2} \sqrt{C(k_p - k_m)}}} + \frac{1 - B}{k_m} \right)
\]

(8)

Substituting \(B\) and \(C\) from equation (6), we get the following expression for the ETC of a two-phase composite as a function of \(V_f\) and the thermal conductivity of the constituents

\[
k_c = k_m \left\{ 1 - \sqrt{\frac{2}{3}} V_f \left[ 2 - \frac{\sqrt{2} \sqrt{3k_m}}{\sqrt{k_\gamma - k_m} + \sqrt{2} \sqrt{3k_m + (k_\gamma - k_m)}} \right] \right\}^{-1}
\]

(9)

### Proposed distribution-based models

#### Modified Cheng and Vachon I

In this work, various distributions are proposed to represent the inclusions \(V_f\). First, we modified the Cheng and Vachon model by introducing the parameter \(P\) which represents the maximum packing factor of a given shape of the inclusions. The packing factor \(P\) is an empirical parameter that characterizes the maximum \(V_f\) of the inclusions when randomly packed in a unit cube. For example, \(P = 0.75\) for spherical particles.\(^4\) We assumed the function \(y(x) = PB + Cx^2\) represents the continuous distribution function of the inclusions. Using the similar BCs discussed above, we obtained \(PB = 1\) and \(C = -4/PB\), which yield the maximum
inclusions $V_f$ to be 0.667. Using these relations and integrating above expression from 0 to $PB/2$ gives

$$B = \sqrt{\frac{3}{2PB}} V_f \quad \text{and} \quad C = -4\sqrt{2} V_f$$

(10)

The expression for overall thermal resistance can be written as

$$R_e = 2 \int_{0}^{\frac{PB}{2}} \frac{dx}{k_m + PB(k_p - k_m) - C(k_p - k_m)x^2 + \frac{1 - B}{k_m}}$$

(11)

Integrating (for kp $\gg$ km) and substituting B and C from equation (10) yields the following expression for the ETC of a two-phase composite

$$k_e = B = \sqrt{\frac{3}{PB}} V_f \quad \text{and} \quad C = -4\sqrt{2} V_f$$

(13)

$$\text{Modified Cheng and Vachon 2}$$

Next, we assumed that the function $y(x) = PB + Cx^2$ represents the continuous distribution function of the inclusions but the packing factor $P$ is now maximum at the origin. With BCs $y(0) = P$ and $y(1/2) = 0$, we found $B = 1$ and $C = -3$, which yield the maximum $V_f$ of the inclusions to be 0.75. Using these relations and integrating above expression from 0 to $B/2$ gives

$$B = \sqrt{\frac{4}{3} V_f} \quad \text{and} \quad C = -4P\sqrt{\frac{3}{4V_f}}$$

(14)

Integrating (for kp $\gg$ km) and substituting B and C from equation (13), we get the following expression for the ETC of a two-phase composite

$$k_e = \left[\frac{1}{\sqrt{k_m + PB(k_p - k_m) - C(k_p - k_m)x^2 + \frac{1 - B}{k_m}}}\right]^{-1}$$

(15)

$$\text{Linear distribution}$$

The evolution of parameters B and C (see Figure 3) and ETC with higher Kp/Km ratio shows the $B$ is the critical parameter that dictates the ETC behavior of two-phase composites. In previous two distributions, it was observed that the modified Cheng and Vachon I and II shows a range of $B$ values with increase of the $V_f$ of inclusions. Our goal is to obtain parameters $B$ and $C$ evolution equations for different distributions and find the optimum evolution functions that can predict the ETC of particulate composites. Next, we assumed that a linear function $y(x) = B + Cx$ represents the continuous distribution function of the inclusions. Using the BCs $y(0) = 1$ and $y(1/2) = 0$, we obtained $B = 1$ and $C = -2$, which yield the maximum inclusions’ $V_f$ to be 0.5. Using these relations and integrating above expression from 0 to $B/2$ gives

$$B = \sqrt{2V_f} \quad \text{and} \quad C = -2$$

(16)

The expression for overall thermal resistance can be obtained as

$$R_e = 2 \int_{0}^{\frac{B}{2}} \frac{dx}{k_m + PB(k_p - k_m) - C(k_p - k_m)x^2 + \frac{1 - B}{k_m}}$$

(17)

Integrating (for kp $\gg$ km) and substituting B and C from equation (16), we get the following expression for the ETC of a two-phase composite

$$k_e = \left[\frac{1}{\sqrt{\frac{k_m + PB(k_p - k_m) + \sqrt{2V_f(k_p - k_m)}}{k_m}} - \frac{1}{PB(k_p - k_m)}}\right]^{-1}$$

(18)
Quartic distribution

Next, we determined the evolution of parameters $B$ and $C$ when the inclusions distribution are represented by higher order functions behavior and analyzed it effects on the ETC of the composite. Using a quartic function, i.e., $y(x) = B + Cx^4$ yields the maximum inclusions $V_f$ to be 0.80 with $B = 1$ and $C = -16$. Using these relations and integrating quartic function from 0 to $B/2$ gives

$$B = \frac{5}{4} V_f \quad \text{and} \quad C = \frac{-16}{B^3} \quad (19)$$

The expression for overall thermal resistance can be obtained as

$$R_e = 2 \int_0^{B/2} \frac{dx}{k_m + B(k_p - k_m) - C(k_p - k_m)x^4} + \frac{1 - B}{k_m} \quad (20)$$

Integrating (for $k_p \gg k_m$) and substituting $B$ and $C$ from equation (19), we obtained

$$k_e = -\frac{\ln\left(\frac{2a}{\sqrt{a}} - \frac{\sqrt{c}}{2}\right)}{2(a)^{1/4} \sqrt{c}} + \frac{\ln\left(\frac{2a}{\sqrt{a}} + \frac{\sqrt{c}}{2}\right)}{2(a)^{1/4} \sqrt{c}} + \frac{1}{(a)^{1/4} \sqrt{c}} \tan\left(\frac{B \sqrt{c}}{2 \sqrt{a}}\right) \quad (21)$$

with

$$a = \left\{k_m + \frac{5}{4} V_f (k_p - k_m)\right\} \quad c = -16\left(\frac{4}{5V_f}\right)^2 (k_p - k_m) \quad (22)$$

Results and comparisons

Results obtained from the analytical solutions of ETC for different distributions presented above are compared with already published experimental data and other available analytical and numerical models in literature, specifically developed for highly conductive particulate composites. For modified Cheng and Vachon 1 and 2 models, the value of $P = 0.75$ is used for all analysis.

Comparison with experimental data

Wong and Bollampally$^7$ studied experimentally the ETC of epoxy filled with alumina ($K_p/K_m = 185$) and silica-coated aluminum nitride (SCAN, $K_p/K_m = 1128$) particulates. The comparison of the experimental and the predicted ETC with different models is shown in Figure 4. The thermal conductivities of all materials used in this study are given in Table 1.$^7$

For $K_p/K_m = 185$, Cheng-Vachon model, Cheng-Vachon modification 1 and quartic distribution gives reasonable estimation until $V_f < 20\%$ while underestimated the ETC at higher $V_f$. Though Cheng-Vachon modification 2 and linear distribution overestimated the ETC, but linear distribution gives reasonable trend of increase in the ETC with the increase of $V_f$.

For $K_p/K_m = 1128$, all the models deviated from the experimental data while linear distribution gives acceptable estimates.

Next, we compared the prediction of the model with the experimental data obtained by Sundstrom and Lee.$^5$ Figure 5 shows the comparison of the experimental data and the predicted ETC of polystyrene filled with CaO ($K_p/K_m = 97$) and MgO ($K_p/K_m = 354$)
particulates. Again Cheng-Vachon modification 2 and linear distribution overestimated the ETC at lower $V_f$, but linear distribution gives reasonable trend of increase in the ETC with the increase of $V_f$ as compared to all the other models.

Kumlutas et al.46 and Tavman6 experimentally studied the ETC of high-density polyethylene filled with aluminum ($K_p/K_m = 375$) and tin ($K_p/K_m = 120$) inclusions. The comparison of the experimental data and the predicted ETC is shown in Figure 6. For $K_p/K_m = 375$, Cheng-Vachon modification 2 gives the best estimates while all other models underestimated the predictions. However, for $K_p/K_m = 120$, linear distribution gives quite reasonable estimates of the trend in the increase of ETC with the increase of $V_f$ of the inclusions.

Graphite-based composites have also been studied experimentally by Agari and Uno.3,4 It was observed that at higher $V_f$ the graphite flakes agglomerated and formed the conductive chain and therefore ETC of the composite increases drastically.24 The comparison of the experimental data and the predicted ETC for polyvinyl chloride filled with graphite ($K_p/K_m = 1240$) particulate and polyethylene filled with graphite ($K_p/K_m = 718$) particulate is shown in Figure 7. For $K_p/K_m = 1240$, the linear distribution gives the best estimates until $V_f = 0.25$ while Cheng-Vachon modification 2 gives quite reasonable estimates when $V_f > 0.25$. For $K_p/K_m = 718$, the linear distribution gives reasonable estimates. The results in Figures 4 to 7 cover the commonly used range of the thermal conductivity ratio of matrix to the inclusions, i.e., $K_p/K_m = 100–1240$.

It can be realized that for all the available experimental data, the trend shows an increase of ETC with the increase of $V_f$ of the inclusions. All analytical models show good predictions of the overall ETC when the $V_f$ is relatively small, but the predictions tend to deviate as the $V_f$ increases. However, in most of the analyzed cases, linear distribution effectively predicts the trend in the increase of ETC with the increase of $V_f$ of the inclusions.

It should be noted that the information on the filler distribution uncertainty of the experimental data is not presented in the available experimental data. The increase of the $V_f$ of inclusions follows a specific distribution is just an assumption. Experiments should be performed to find the variation in the distribution of the inclusions as a function of $V_f$. We observed that the

Table 1. Thermal conductivity of materials.3–7,46

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity ($W m^{-1} K^{-1}$)</th>
<th>Material</th>
<th>Thermal conductivity ($W m^{-1} K^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>0.1549</td>
<td>Silica</td>
<td>1.5</td>
</tr>
<tr>
<td>Epoxy</td>
<td>0.195</td>
<td>Alumina</td>
<td>36</td>
</tr>
<tr>
<td>High-density polyethylene (HDPE)</td>
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<td>Aluminum</td>
<td>204</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>0.1687</td>
<td>Graphite</td>
<td>209.3</td>
</tr>
<tr>
<td>CaO (calcium oxide)</td>
<td>15.07</td>
<td>SCAN</td>
<td>220</td>
</tr>
<tr>
<td>MgO (magnesium oxide)</td>
<td>54.85</td>
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</table>
linear distribution worked very well for most of the particulate composites as shown by the validation of the model predictions with the experimental data performed by different researchers available in literature. However, the linear distribution might not be a true representation of other shapes and types of the inclusions. So, the model cannot be generalized for other composite systems. In case of other shapes and types of inclusions, we need to validate the model predictions with the experimental as well as the computational models. However, we have anticipated that the proposed approach can be used to develop an analytical model to predict the ETC of advanced composite materials.

For example, the model can be generalized by assuming that the inclusions in a composite are distributed according to a following generic polynomial function \( y(x) = B + Cx^n \), where the power “n” that best matches the experimental data can be obtained numerically for each composite system following the procedure discussed in Theoretical Analysis section.
Comparison with other models

Analytical models. To check the efficacy of the proposed model, the predictions are also compared with other models available in literature. For brevity, we have considered classical models relevant to our study. The Hashin and Shtrikman\textsuperscript{47} bounds are one of the most common bounds which are derived based on variational principle.\textsuperscript{48} These bounds are generally applicable to all isotropic composites, and it is well-known that the Hashin and Shtrikman\textsuperscript{47} bounds are tighter than those from the rule of mixtures.\textsuperscript{45} The value of $ETC_{ke}$ (ke) of a two-phase isotropic composite is bounded by these bounds\textsuperscript{2}

\begin{equation}
(k) = \frac{V_f(1 - V_f)(k_m - k_p)^2}{k_m V_f + k_p(1 - V_f) + 2k_m} \leq k_e \leq (k) \frac{V_f(1 - V_f)(k_m - k_p)^2}{k_m V_f + k_p(1 - V_f) + 2k_p} = k_m(1 - V_f) + k_p V_f
\end{equation}

Every et al.\textsuperscript{49} extended Bruggeman’s\textsuperscript{16} theory to account for the field of the neighboring particles and obtained the following expression for the ETC of composites when the inclusions are much more conductive than the matrix

\begin{equation}
k_e = k_m \frac{1}{(1 - V_f)^{3(1 - \alpha)/(1 + 2\alpha)}}
\end{equation}

$\alpha$ is a non-dimensional parameter accounting the microstructure and the interfacial resistance effect between particles and matrix. The other models used in this study are written as follows

Russell\textsuperscript{50}

\begin{equation}
k_e = k_m \frac{V_f^{2/3} + \frac{k_m}{k_p} \left(1 - V_f^{2/3}\right)}{V_f^{2/3} - V_f + \frac{k_m}{k_p} \left(1 - V_f^{2/3}\right)}
\end{equation}

Maxwell\textsuperscript{13}

\begin{equation}
k_e = k_m \frac{k_p + 2k_m + 2V_f(k_p - k_m)}{k_p + 2k_m - V_f(k_p - k_m)}
\end{equation}

Jeffrey\textsuperscript{51}

\begin{equation}
k_e = k_m + 3k_m V_f \left[1 + V_f \frac{\sigma_1(2k_m + k_p) + (k_p - k_m)}{2k_m + k_p}\right] \times \frac{(k_p - k_m)}{2k_m + k_p}
\end{equation}

$\sigma_1$ is parameter depending on the thermal conductivity ratio.

Numerical models. Several numerical models are also available to determine the ETC of particulate composites. For example, ETC of random two-phase composite materials was obtained by considering the shape, spatial distribution, thermal contact resistance and particles $V_f$(see literature\textsuperscript{23,52,53} and references therein). Experimental and numerical ETC of polymer matrix
filled with metallic spheres was presented by Karki et al.\textsuperscript{54} The effects of the filler concentrations, the ratio of thermal conductivities of filler to matrix material and the Kapitza resistance of the contact inclusion/matrix on the ETC were investigated. For more details and updated review/references on the numerical modeling of the ETC of particulate composites, please see Karki et al.\textsuperscript{54} To the best knowledge of the authors, there is only one model available in literature that considered the effect of the embedding highly conductive inclusions in less thermally conductive matrix on the ETC of particulate composites. Zhang et al.\textsuperscript{36} proposed a randomly mixed model to compute numerically the ETC of particulate composites with respect to the $V_f$ of the particles and the ratio of the thermal conductivity of the particle to that of the matrix. The cubic shape particles of uniform size are generated randomly using a computer program. The steady state heat equation was solved by the finite difference method directly for the composite with appropriate BCs.

**Comparison.** Figures 8 to 10 show the comparison of the ETC obtained from different distributions of inclusions with the experimental data, and other analytical and numerical models for particulate composites available in literature. It can be seen that all analytical models fall within the upper and lower bounds, but underestimates the ETC for almost all cases indicating that these models are not capable to predict the ETC and the trend in increase of ETC of the composite with high $K_p/K_m$ ratio. However, the linear distribution of inclusions predicts the ETC of the composite reasonably well. Moreover, the numerical model predicts the ETC of the composite reasonably well for some cases, while, in most of the cases, it is not very accurate. In comparison to numerical models, the proposed model is more efficient to provide a quick estimate of the ETC of two-phase composite.

It should be realized that the proposed models predict the ETC of composites and the discrepancies in predictions as compare with the experimental data are due to a number of reasons. Broadly four reasons can be considered (a) the proposed model does not account for the complex microstructure of the inclusions, (b) the interactions of the field variables among inclusions are ignored, (c) the geometry and the size effect of the inclusions are not considered and (d) the interfacial resistance between particle and matrix is not incorporated. The proposed approach leads to sensible predictions. However, the fundamental understanding about the effects of constituents’ properties and the microstructure geometries on the ETC of composites requires a comprehensive consideration of the mentioned reasons. Finding the analytical solution of such a model will be nearly impossible, and the numerical solution will be very complex and requires a huge computational cost.

Additionally, the proposed model mainly calculates the ETC of the unit cell based on the equivalent resistance model which requires the volume fraction and thermal conductivity of the constituents. This model does not account for the effect of particle shape, size, orientation distribution, interfacial thermal resistance

![Figure 8](image_url)

**Figure 8.** Comparison of experimental data with other models and predicted ETC for (a) Epoxy/alumina and (b) Epoxy/silica-coated aluminum nitride composites.
and the effect on particle agglomeration on the enhancement of the ETC of a composite. For such work, we refer to the work of Nan et al.,24 Hong et al.,25 Prasher et al.27 and more recently by Wemhoff34 and Wemhoff and Webb.35

**Conclusions**

In this study, we proposed a theoretical model to predict the ETC of two-phase composites containing inclusions which are highly conductive than the matrix. A probabilistic approach proposed by Tsao41 is used, and Cheng and Vachon42 procedure has been adopted to derive ETC expression for two-phase composite materials using different distributions of inclusions. The predictions obtained from the proposed equations were compared with the already published experimental data and other models available in literature. It has been found that the relation obtained from the linear distribution of the inclusions gives reasonable

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**Figure 9.** Comparison of experimental data with other models and predicted ETC for (a) Polystyrene/CaO and (b) Polystyrene/MgO composites.

**Figure 10.** Comparison of experimental data with other models and predicted ETC for (a) HDPE/aluminum and (b) Polyvinylchloride/graphite.
estimates and showed a rational trend in the increase of ETC for the high $K_p/K_m$ ratio as compared to the ones obtained from the other models. The advantage of the proposed model is that it does not require the detailed microstructure of the composite since the ETC of the two-phase composite was derived in terms of the $V_f$ and the thermal conductivity of the constituents. This feature allows using the proposed approach to develop an analytical model that can predict the ETC of highly conductive advanced particulate composites.

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Note

a. Here, the volume fraction ($V_f$) is the percolation threshold, which varies based on inclusion geometry. For example, according to the percolation theory given in Stauffer and Aharony, the value of the threshold for cubic particle percolation, $V_{fc}$, is 0.3117–0.3333. When $V_f < V_{fc}$, the conductive particles are mainly dispersed, so the effect of the particles’ conductivity on ETC is small. When $V_f$ goes up to $V_{fc}$, the connections of the particles increase and the formations of the conductive chains dominate the change of ETC. Yin et al. mentioned that the threshold limit of percolation can go as high as 0.78. More recently, Wang et al., Liang et al., Wemhoff, Gao and Li also observed the dependence of particle size and shape on the percolation threshold.

References