J Mater Sci (2007) 42:6749–6754
DOI 10.1007/s10853-006-1480-y

# Thermal conductivity of ceramic particle filled polymer composites and theoretical predictions

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Received: 31 August 2006 / Accepted: 21 December 2006 / Published online: 27 April 2007


**Abstract** Models and theories for predicting the thermal conductivity of polymer composites were discussed. Effective Medium Theory (EMT), Agari model and Nielsen model respectively are introduced and are applied as predictions for the thermal conductivity of ceramic particle filled polymer composites. Thermal conductivity of experimentally prepared $Si_3N_4$/epoxy composite and some data cited from the literature are discussed using the above theories. Feasibility of the three methods as a prediction in the whole volume fraction region of the filler from 0 to 1 was evaluated for a comparison. As a conclusion: both EMT and Nielsen model can give a well prediction for the thermal conductivity at a low volume fraction of the filler; Agari model give a better prediction in the whole range, but with larger error percentage.

## Introduction

Thermally conductive but electrically insulating, also for their cost-effectiveness and design flexibility, ceramic particle reinforced epoxy composites are largely used as electronic packaging and/or substrate materials [1–3]. During the last few decades, however, in the microelectronic systems, great effect has been contributed to improving higher integration density, faster performance, miniaturization of electronic devices and lower cost [4, 5]. Therefore, the power density in the electronic devices is becoming larger and larger. That turns the researchers' focus to be placed on the thermal conductivity in order to get heat-dissipating composites.

The prediction of thermal conductivity of composites comprises a significant portion of the heat transfer literature. Many reports concerning about the thermal conductivity of polymer composites, associated with various thermal conductive models or equations for predicting the thermal conductivity, have been published. They are either theoretically based or are empirical which means to include one or more experimentally determined (or empirical) parameters. A good overview has been given by Progelhof [6]. Procter and Solc [7] used Nielsen model as a prediction to investigate the thermal conductivity of several types of polymer composites filled with different fillers, and confirmed its applicability. Nagai [8] found Bruggeman model for $Al_2O_3$/epoxy system and a modified form of Bruggeman model for AlN/epoxy system are both good prediction theories for thermal conductivity. Wong [2] found that Agari model predicts better than Maxwell model for thermal conductivity of $SiO_2$/epoxy composite at high percentage of filler.

However, polymer composites are always not treated as different despite the volume fraction of the filler are not the same when their thermally conductivity are treated employing theoretical models mentioned above. At different volume fraction, the ''filler'' in the composite can be regarded to be either phase, for example: the dilute system when the polymer phase is regarded to be the matrix or the heavily loaded system when the filler can be considered to be the matrix. At the medial concentration, the fillers start to contact which is called the percolation phenomenon [9, 10], then both phase can be treated as the matrix. In this study, we select the Effective Medium Theory (EMT), Nielsen model and Agari model, (models which take into

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consideration of the above conditions), for a comparative discussion. Application feasibility of the three methods as a prediction through the whole volume fraction range of the filler from 0 to 1 was evaluated.

### Effective medium theory

Starting with the potential theory and the concept of mean-field (effective medium), Bruggeman pioneered the effective-medium theory (EMT) for consideration of several physical properties of composites, such as electrical conductivity, and dielectric constant [11]. That attempt achieved great success. And then the EMT was extended in application of other physical properties such as elastic [12, 13], and thermal conductivity [14–17]. An excellent overview was given by Landauer [18].

The EMT supposes that the composite system is a homogeneous medium that has the same macroscopic properties and physical constants, including elastic modulus, and dielectric constant, and thermal or electrical conductivity, etc. as the composite system itself. And when a portion of the effective medium is replaced by one of the component materials, which make up the composite, the relevant fields, stress, strain, electric field, thermal field for example, in the whole medium are changed. Then the physical properties or constants of the composites can be considered. Through the Laplace equation for thermal transfer, the EMT equation for thermal conductivity can be derived and expressed as follows [15–18]:

$$v_1 \frac{\lambda_1 - \lambda_e}{\lambda_1 + 2\lambda_e} + v_2 \frac{\lambda_2 - \lambda_e}{\lambda_2 + 2\lambda_e} = 0 \tag{1}$$

where, $\lambda$ is thermal conductivity, V is volume fraction, subscription 1, 2, e is the matrix, filler and the composite respectively.

### Agari experimental model

Agari developed a model based on the generalization of models of series and parallel conduction in composites [19].

Supposing that the filler in the composite is arranged in blocks parallel to the direction of the thermal flux, the thermal conductivity can be expressed by parallel conduction equation:

$$\lambda_e = (1 - V_2) \cdot \lambda_1 + V_2 \lambda_2 \tag{2}$$

Then on the contrary, the series conduction equation can be expressed as following:

$$1/\lambda_e = (1 - V_2)/\lambda_1 + V_2/\lambda_2 \tag{3}$$

where the meaning of the symbols and the subscriptions are the same as mentioned in EMT.

The agari model is expressed as following:

$$\begin{gathered} \log \lambda_e = A v_2 + B \\ A = C_f \cdot \log\left[\lambda_2/(C_p \cdot \lambda_1)\right] B \ = \ \log(C_p \cdot \lambda_c) \end{gathered} \tag{4}$$

In composites, each constitute phase cannot be restrictedly arranged in a block but only clusters or discontinuous network. Then the constant $C_f$ is introduced to define the ability of forming continuous network of filler in the matrix. That's also to say, to take into consideration of percolation. Considering that the preparation procedure of the composites can affect the crystalline of the polymer thus affects thermal conductivity of the matrix, the constant $C_p$ is introduced. In Eq. 4, logarithms of the thermal conductivity of the composite increases linearly with the volume fraction of the filler, constants $C_f$ and $C_p$ are experimentally determined.

### Nielsen semi-empirical model

Nielsen modified Halpin-Tsai equation by introducing two factors namely: $A$, a constant related to the generalized Einstein coefficient $k_E$; $B$, a constant related to the relative conductivity of the components; $\psi$, a function related to the maximum packing fraction $\phi_m$ of the filler [6, 20–22]. The modified equations for thermal conductivity are:

$$\frac{\lambda_e}{\lambda_1} = \frac{1 + AB\phi}{1 - B\phi\psi} \tag{5}$$

$$A = k_E - 1; B = \frac{\lambda_2/\lambda_1 - 1}{\lambda_2/\lambda_1 + A}; \psi \approx 1 + \left[(1 - \phi_m)/\phi_m^2\right] v_2 \tag{6}$$

The value of the Einstein constant $k_E$, constants $A$ and $\phi_m$ can be obtained in Ref. [6] and Ref. [17].

## Thermal conductivity of ceramic particles filled polymer composites and a comparison with theoretical models

### Thermal conductivity of experimentally prepared $Si_3N_4$/epoxy composite

To prepare testing specimens, we used both liquid and solid form of high performance thermosetting epoxy resin (linear-phenolic aldehyde used as solidification resin, supplied by Lanxing Chemical New Materials Co. Ltd., Wuxi China), for a comparison, as the matrix, and $Si_3N_4$ powder (with a particle size of 5–10 μm and rod-like morphology) as filler. The original materials were first mixed in a glass container and stirred by a mechanical blender. Then the mixture was hot pressed at 180 °C and 30 MPa and cured to get samples for measurement. Thermal conductivity measurement of the composites was performed on a self-assembled instrument bases on the steady-state method. Full details can be picked up in Curran's papers [23, 24]. In the measuring process, the sample was heated and the heat flux through cross section was determined, then the thermal conductivity was calculated.

Thermal conductivity of samples as a function of the volume fraction of the filler is shown in Fig. 1, every point of thermal conductivity is an average of three samples. And the thermal conductivity calculated by EMT and Nielsen model is also plotted against the volume fraction of the $Si_3N_4$ filler.

From Fig. 1, we can see that thermal conductivity of the Epoxy/$Si_3N_4$ composite increases with the volume fraction of the filler with increasing slope. At a low concentration, the values calculated by both EMT and Nielsen model fit the experimental data very well. However, the lines for EMT and Nielsen begin to deviate from the experimental data at volume fraction of 15–20% and 25–30% respectively. At higher concentration exceeding that, the values calculated by the two models are much higher than the experimental values. That means both EMT and Nielsen model cannot give good prediction for the thermal conductivity of the composites at high concentration.

## Data of thermal conductivity of composites cited from the literature

To exclude chance coincidence, we achieve data from Wong' experiment (Ref. 2) for a confirmation. They also prepared composite samples using a method similar to ours. We get the plot in Fig. 2. From Fig. 2, we find the same phenomenon. The values calculated by both EMT and Nielsen model start to deviate from experimental data at the filler volume fraction of 15–20%, 25–30% respectively. As both shown in Figs. 1 and 2, the values

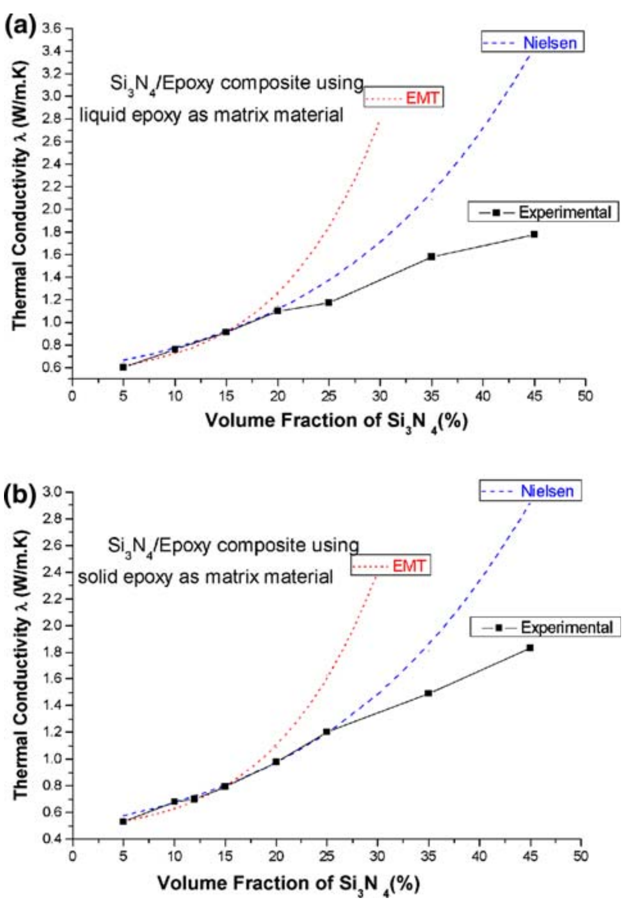


**Fig. 1** Experimental and model values of thermal conductivity of $Si_3N_4$/epoxy composite (**a**) $Si_3N_4$/epoxy composite using liquid epoxy as matrix material; (**b**) $Si_3N_4$/Epoxy composite using solid epoxy as matrix material)

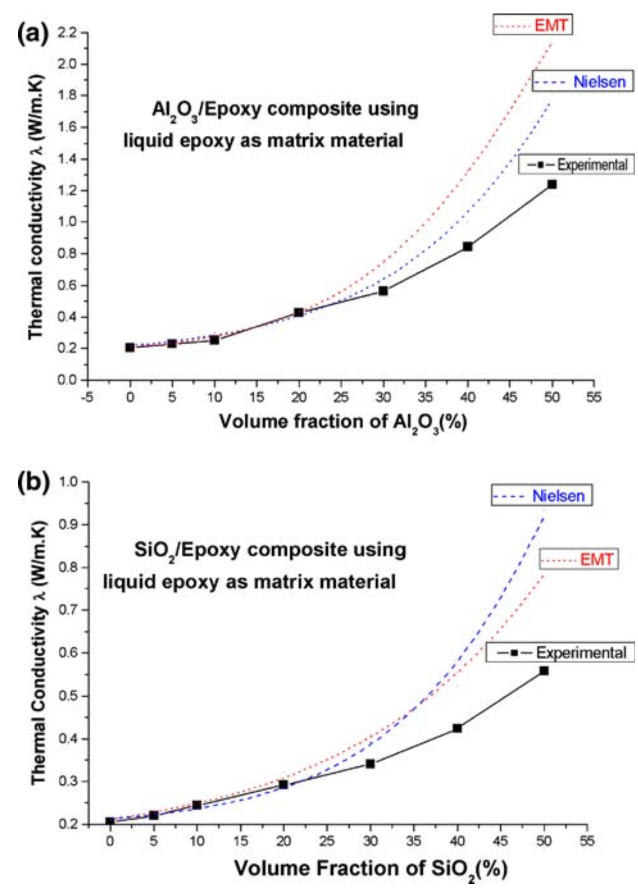


**Fig. 2** Thermal conductivity of $Al_2O_3$/epoxy and $SiO_2$/epoxy composites. (Data from Ref. 2) (**a**) $Al_2O_3$/epoxy composite using liquid epoxy as matrix material; (**b**) $SiO_2$/Epoxy composite using liquid epoxy as matrix material)

calculated by Nielsen model have a better applicability through a wider range than EMT.

Concerning about EMT equation, however, it was demonstrated by Björn Håkansson [14, 15] that their thermal conductivity data for AgCl/LDPE and NaCl/LDPE composites have good agreement with the EMT model in the full concentration range from 0 to 1, as shown in Fig. 3.

## Evaluation of EMT, Nielsen and Agari models

### Application of EMT and Nielsen model at not high percentage of the filler

The EMT begins with the potential theory and is on the assumption that the filler particles are surrounded with a continuous matrix medium, which does not consider the percolation effect. As research about the electrically conductive composites has demonstrated, the percolation phenomenon performs a pronounced effect when the filler concentration reaches the percolation threshold value, which means the conductive clusters become to form conductive chains [9, 10]. The electrical resistance drops rapidly as the volume fraction of the filler reaches the percolation threshold (or critical volume fraction $V_c$). Helsing and Helte have given an excellent demonstration on the values of percolation threshold for different systems [25]. In Björn Håkansson's experiment, the polymer matrix particles and filler particles were just compacted under pressure. The polymer matrix did not undergo a phase transformation or distortion, so, it was in good accordance with EMT assumption. At very high percentage of AgCl or NaCl, the matrix is considered to be AgCl or NaCl. The polymer is considered to be the filler. Thus, EMT gives good prediction for the experimental thermal conductivity data. Unfortunately, in epoxy composites filled with ceramic particles, the epoxy resin formed the bulk, and the filler clusters connected to form continues chains after percolation. That's the reason EMT fails.

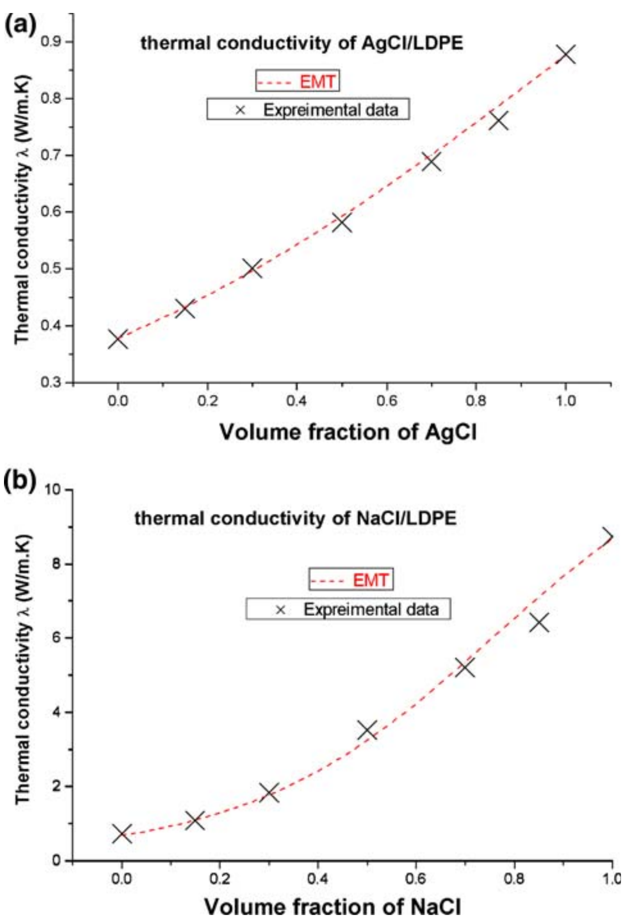


**Fig. 3** Thermal conductivity of AgCl/LDPE and NaCl/LDPE composites (Ref. 14, 15) (**a**) AlCl/LDPE composites; (**b**) NaCl/LDPE composites)

With a careful scanning of the literature, we found that the Nielsen model works only at a not high volume fraction of filler [11]. We also found that many similar researches were only done at a relatively low volume fraction of filler [22]. At the volume fraction of above 30%, the values calculated by Nielsen model starts to deviate from the experimental data. The same as the EMT does, the Nielsen model does not consider the percolation effect. What's more, the constants $A$ and $B$ are empirical and they always vary in different systems, and are difficult to extract an exact value.

Hasselman and Johnson [26] early developed a theory for the effective thermal conductivity of composites consisting of a continuous matrix phase with dilute concentrations of filler with a thermal barrier resistance at the interface. They claim that the thermal barrier resistance (Kapitza resistance), which may arises from poor mechanical or chemical adherence at the interface in the manufacture process or thermal expansion, is a very important. Their theory can also be applied here for am explanation. The EMT and Nielsen model both consider the composites system to be homogenous with an ideal interface. However, with the volume fraction of the filler increasing, the mismatch between the matrix and the filler in the form of interfacial gap becomes to be more serious, that's bad for heat conducting. Thus modification of the two models with an interfacial thermal resistance consideration should be applied.

### Agari model for prediction at the whole concentration and it's precision

In Agari model, logarithm of the thermal conductivity of polymer composites increases linearly with the volume fraction of the filler. We plot logarithm of thermal conductivity data of our epoxy composites in Fig. 4. We fit the logarithm data to a line using the least squares techniques. In Fig. 4, we can see that the experimental data cannot exactly stay on the line with a largest error percentage about 10%. Get the slope coefficient and intercept of the linearly fitted line in Fig. 4, and using Eq. 4, we plot the thermal conductivity values predicted by Agari model in Fig. 5. Also, the experimental data cannot agree exactly with the prediction, and the largest error percentage is in the limitation of 10%. However, the Agari model still gives a relatively better prediction than the other two equations in the whole experimental volume fraction range.

At very low volume fraction of filler, Agari model always gives a thermal conductivity value a litter higher than the experimental data, also seen in Ref. [2] and in our study. Agari model starts with the idea that the filler particles in the matrix body form chains. However, at a very

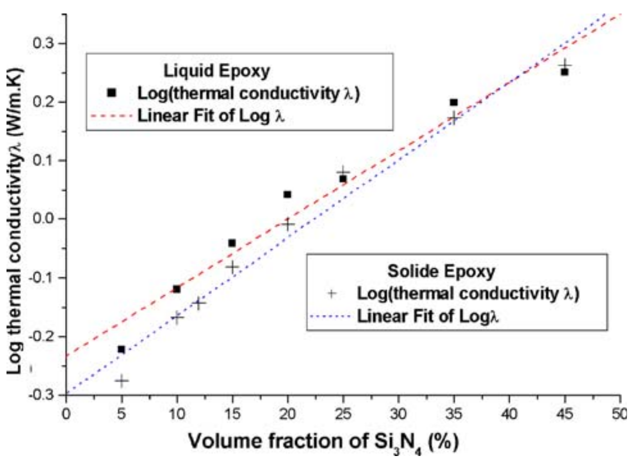


**Fig. 4** Logarithm thermal conductivity of epoxy/$Si_3N_4$ composites

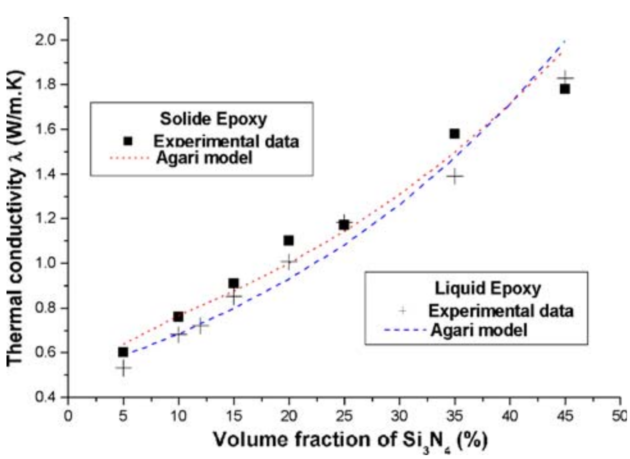


**Fig. 5** Experimental data and Agari model value for thermal conductivity

**Table 1** $C_p$ and $C_f$ for Agari model for epoxy/ $Si_3N_4$ composites

| $C_p$ | $C_f$ | Constitution |
|---|---|---|
| 1.120 | 0.7075 | Solid epoxy resin filled with $Si_3N_4$ |
| 1.168 | 0.6010 | Liquid epoxy resin filled with $Si_3N_4$ |

low concentration, the particle only contact to form clusters, and cannot form continuous chains [12, 27, 28]. So, as indicated in Agari' paper [19], the ease of forming thermally conductive chains of filler, namely the value of $C_f$, increases with the volume fraction of filler increasing. We calculated the values of $C_p$ and $C_f$ by Eq. 4 as shown in Table 1. The values of $C_p$ and $C_f$ in the table are in good accordance with those proposed by Agari which are speculated to be around 1.0 and 0.75 respectively. The $C_f$ value for composite using solid epoxy is a litter larger than that of liquid epoxy, that's because during the pressing process, the filler clusters in solid matrix are easier to contact with each other. However, the two values themselves are all experimentally determined, and may vary in different experimental situation.

## Summary

Thermal conductivity of polymer composites filled with ceramic particles was discussed applying three types of methods including Effective Medium Theory (EMT), Agari model and Nielsen model. Thermal conductivity of experimentally prepared $Si_3N_4$/epoxy composite and some data cited from the literature were discussed for a discussion. EMT and Nielsen model both give a well prediction for the thermal conductivity at the volume fraction not higher than the range of 15–20%, 25–30% respectively. As the EMT is based on the assumption that the filler particles are homogeneously dispersed in the matrix, and does not consider the percolation effect of the filler, it fails to give a good prediction of the thermal conductivity at high volume fraction of the filler. Nielsen model also does not consider the percolation effect and the equations of Nielsen model include empirical constants $A$ and $B$, which will vary in different dispersion system. At high volume fraction of the filler, it also fails to predict. Agari model gives a better prediction in the whole volume fraction range than the former two theories. However it is also not an exact prediction, the largest error percentage is as high as 10%. The constants related $C_p$ and $C_f$ are experimentally determined and cannot be precisely predicted.

**Acknowledgements** This work was supported by a grant from the National Nature Science Foundation of China (Grant No. 50472019).

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