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A new heat transfer model of inorganic particulate-filled polymer composites

J. Z. Liang · G. S. Liu

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Abstract Thermal conductivity is an important parameter for characterization of thermal properties of materials. Various complicated factors affect the thermal conductivity of inorganic particulate-filled polymer composites. The heat transfer process and mechanisms in an inorganic particulate-filled polymer composite were analyzed in this article. A new theoretical model of heat transfer in these composites was established based on the law of minimal thermal resistance and the equal law of the specific equivalent thermal conductivity, and an relevant equation of effective thermal conductivity (K_{eff}) for describing a relationship between K_{eff} and filler volume fraction as well as other thermal parameters were derived based on this model. The values of K_{eff} of aluminum powder-filled phenol–aldehyde composites and graphite powder-filled phenol–aldehyde composites were estimated by using this equation, and the calculations were compared with the experimental measured data from these composites with filler volume fraction from 0 to 50% in temperature range of 50–60 °C and the predictions by Maxwell–Eucken equation and Russell equation. The results showed that the predictions of the K_{eff} by this equation were closer to the measured data of these composites than the other equations proposed in literature.

Introduction

Thermal conductive polymeric materials are used more and more extensively in industry, such as chemical process and exchangers in seawater treatment. The heat transfer process in polymer composite materials is very complicated. Bose and Mahanwar [1] investigated the effects of particle size and particle size distribution on the mechanical and thermal properties of mica-filled nylon-6, and found that the composite showed improved mechanical, thermal, and dielectric properties on addition of filler. Dong et al. [2] studied influence of the filler on the thermal characteristics of high-density polyethylene filled with graphite, such as the melting and crystallization temperatures and enthalpy of crystallization by differential scanning calorimetry. They found that the dispersion of filler particles altered the morphology/structure of the composites and resulted in the changes of properties of the polymer matrix, especially when the particle-percolated structure was formed. Zulfiqar et al. [3] measured the thermal and mechanical properties of SEBS-g-MA-based inorganic composite materials. The results indicated a shift in T_g values with the addition of silica in the matrix, which suggested an increased interfacial interaction between organic and inorganic phases while this effect was less pronounced in polymer–clay system.

It is quite important, therefore, to understand the heat transfer mechanisms in polymer composites. Recently, Hill and Supancic [4] proposed an indirect method to determine this interfacial boundary resistance by preparing large-scale "macromodel" simulations of the polymer–ceramic interface. They also investigated the effects of similar size and shape of platelet-shaped particles on the thermal conductivity of polymer/ceramic composite materials [5]. Yu et al. [6] measured the thermal conductivity of polystyrene–aluminum nitride (AIN) composite, and found that the thermal conductivity of composites was higher for a polystyrene particle size of 2 mm than that for a particle size of 0.15 turn. The thermal conductivity of the composite was five

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J. Z. Liang (✉) · G. S. Liu
College of Industrial Equipment and Control Engineering,
South China University of Technology, Guangzhou 510640,
People's Republic of China
e-mail: liangjz@scut.edu.cn; scutjzl@sohu.com

times that of pure polystyrene at about 20% volume fraction of AIN for the composite containing 2 mm polystyrene particles. More recently, Liang and Li [7] simulated the heat transfer in hollow glass bead-filled polypropylene composites by using a finite element method. On the basis of experimental and simulation studies, there have been few theoretical models for describing the heat transfer in polymer composites [8], such as Nielsen model [9], Cheng–Vochon model [10], and Agari–Nagai model [11]. Recently, Liang and Li [12] studied the heat transfer mechanisms in hollow sphere-filled polymer composites, and proposed a new heat transfer model.

Effective thermal conductivity is an important characteristic of heat transfer properties of materials. Similarly, there are some equations for prediction of the effective thermal conductivity for polymer composites, such as Maxwell–Eucken equation [13], Bruggeman equation [14], Russell equation [15], Nielsen–Lewis equation [16], and Baschirow–Selenew equation [17]. Liang and Li [12] derived a new effective thermal conductivity equation based on the law of minimal thermal resistance and the equal law of the specific equivalent thermal conductivity for hollow sphere-filled polymer composites.

As stated above, the factors affecting the effective thermal conductivity and heat transfer in polymer composites are relatively more, such as the nature of resin, the shape, size, and content of particles as well as the dispersion and distribution of the fillers in the matrix. Therefore, it is necessary to make a thorough research into the heat transfer process and mechanisms in inorganic particulate-filled polymer composites and their quantitative description. The objectives of this article are to investigate the main factors affecting the heat transfer process and its mechanisms in inorganic particulate-filled polymer composites, so as to establish a relevant mathematical model for estimating the effective thermal conductivity of these composites with a wide content range of filler particles.

Theory

Heat transfer elements

From the law of minimal thermal resistance and the equal law of the specific equivalent thermal conductivity, when the specific equivalent thermal resistance of the element of composites is equal to that of the total and heat conduction is only considered, then the equivalent thermal conductivity of the element is equal to that of the total, while the size of the element may not be considered [18]. Therefore, the calculation of the equivalent thermal conductivity for composites can be attributed to the determination of the equivalent thermal conductivity of the element with the same specific equivalent thermal resistance. If one supposes that an overall composite consists of a number of small squared elements, and each element only contains a spherical particle in the center, the heat flow enters into the element from the top of the square, as shown in Fig. 1. Suppose the side length of the square and the particle diameter is H and $2r$, respectively, then one can get the expression among the particle volume fraction (ϕ_f), H, and r as follows:

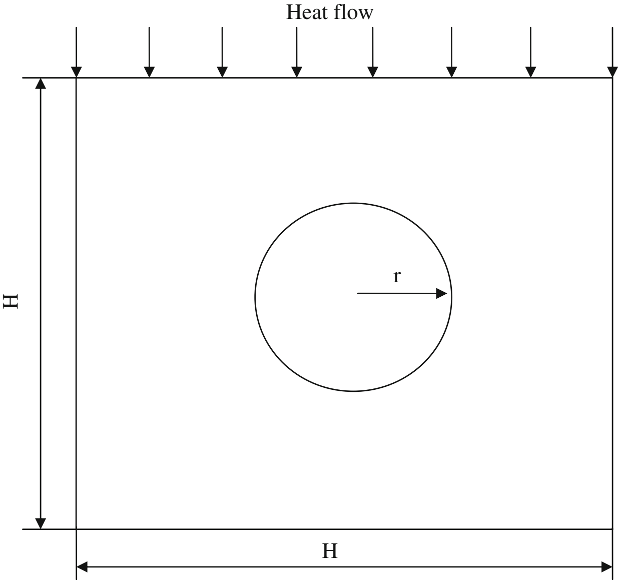

Fig. 1 A heat transfer model in particulate-filled polymer composite

$$\phi_f = \frac{4\pi r^3}{3H^3}. \tag{1}$$

Modeling

In general, the heat quantity through a body depends, to a greater extent, upon the heat transfer route in the materials. In this article, a series model as a heat transfer model in particulate-filled polymer composites is considered.

Figure 2 shows a series model of heat transfer elements in an inorganic particle-filled polymer composite, named as model I. For convenience, only the case of a spherical particle located in the center of an element is considered, and the element is divided into three parts: part one, part two, and part three. K_1, K_2, and K_3 are, respectively, the mean conductivity coefficients of the three parts. K_p and K_f are the conductivity coefficient of the resin matrix and the filler, respectively. A_p and A_f, respectively, are the cross-sectional areas of the matrix and the filler, and Q_p and Q_f are the heat quantities through the cross-sectional area of matrix and the filler in this element, respectively.

From the Fourier's law, the heat quantity (Q) can be expressed as

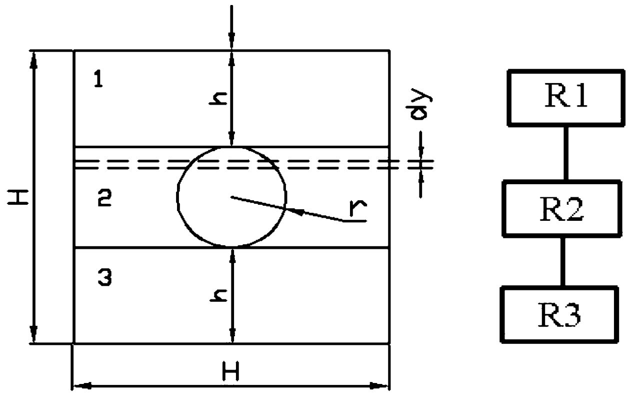

Fig. 2 Diagram of heat transfer series model

$$Q = KA\frac{dT}{dx} = KA\frac{\Delta T}{d} = \frac{\Delta T}{d/KA}. \tag{2}$$

And the thermal resistant (R) is

$$R = \frac{d}{KA}, \tag{3}$$

where d represents the element geometry dimension.

For parts one and three,

$$K_1 = K_3 = K_p. \tag{4}$$

For part two, taking a thin piece with thickness (dy) as shown in Fig. 1 and according to the Fourier law, we have

$$Q_f = K_f A_f \frac{dT}{dy}, \tag{5}$$

$$Q_p = K_p A_p \frac{dT}{dy}. \tag{6}$$

From Fig. 2,

$$Q = Q_p + Q_f = (K_p A_p + K_f A_f)\frac{dT}{dy} = K_2' A \frac{dT}{dy} \tag{7}$$

and

$$K_2' = K_p \frac{A_p}{A} + K_f \frac{A_n}{A}. \tag{8}$$

On the basis of the above equations, the mean conductivity coefficient and the corresponding equivalent thermal resistant of these three parts can be obtained. For part one,

$$K_1 = K_3 = \int_h K_p dy/h = K_p \tag{9}$$

and

$$R_1 = R_3 = \frac{h}{K_p A}. \tag{10}$$

For part two,

$$K_2 = \int_{2r} K_2' dy/2r = \int_0^{2r} \left(K_p \frac{A_p}{A} + K_f \frac{A_f}{A}\right) dy/2r = K_p \frac{V_p}{2Ar} + K_f \frac{V_f}{2Ar} \tag{11}$$

and

$$R_2 = \frac{2r}{\left(K_p \frac{V_p}{2Ar} + K_f \frac{V_f}{2Ar}\right)A} = \frac{4r^2}{(K_p V_p + K_f V_f)}, \tag{12}$$

where V_p and V_f are the volume of polymer and filler, respectively.

The total equivalent thermal resistant is

$$R = R_1 + R_2 + R_3. \tag{13}$$

Substituting Eqs. 10 and 12 into Eq. 13 as well as according to the definition of effective thermal conductivity, we have an effective thermal conductivity equation of inorganic particulate-filled polymer composites as follows:

$$K_{eff} = \frac{1}{\frac{1}{K_p} - \frac{1}{K_p}\left(\frac{6\phi_f}{\pi}\right)^{\frac{1}{3}} + \frac{2}{K_p\left(\frac{4\pi}{3\phi_f}\right)^{\frac{1}{3}} + \left(\frac{2\phi_f}{9\pi}\right)^{\frac{1}{3}}\pi(K_f - K_p)}}. \tag{14}$$

Results and discussion

Raw materials

The raw materials included mainly a phenol–aldehyde resin and two fillers, aluminum powder, and graphite powder, and the partial physical and thermal properties of the raw materials were as follows [19]:

Phenol–aldehyde resin—density: 1248 kg/m^3 and thermal conductivity: 0.111 W/m K.
Aluminum powder—density: 2670 kg/m^3, thermal conductivity: 203.5 W/m K, and particle mean diameter: 112 μm.
Graphite powder—density: 2250 kg/m^3, thermal conductivity: 120 W/m K, and particle mean diameter: 46 μm.

Instrument and methodology

After the phenol–aldehyde resin was mixed respectively with aluminum powder and graphite powder, the blends were molded by using a molding machine to fabricate the specimens. The temperature was 155 °C and the solidification time was 10 min. The specimens were plates with length of 50 mm, width of 50 mm, and thickness of 2–4 mm. In these filled phenol–aldehyde composites, the filler weight fraction varied from 10 to 60%.

The thermal conductivity of aluminum powder-filled phenol–aldehyde composites and graphite-filled phenol–aldehyde composites was measured by means of a protecting heat plate method, and the main apparatus was a protecting heat flow type of thermal conductivity instrument (model NF-7) supplied by Huagong Chemical Machine Factory, China. The environmental temperature for the test was 25 °C and the test temperature was 50–60 °C. Four measuring points were setup equally on a plate, and the average was reported for each specimen.

Measurement results

The measured thermal conductivities of phenol–aldehyde/aluminum composites and phenol–aldehyde/graphite composites are listed, respectively, in Tables 1 and 2. It can be seen that the thermal conductivity increases with an increase of the filler weight fraction W_f.

Primary verification

In this article, Eq. 14 will be primarily verified by quoting these experimental data. Substituting the above physical and thermal property parameters of phenol–aldehyde and aluminum powder into Eq. 14, one can calculate the effective thermal conductivities of the aluminum powder-filled phenol–aldehyde composites, and compare these calculations with the measured data listed in Table 1, as shown in Fig. 3. Here, the relationship between volume fraction and weight fraction may be expressed by following equation [20]:

$$\phi_f = \frac{W_f}{W_f(1-\chi)+\chi}, \tag{15}$$

where $\chi = \rho_f/\rho_m$, ρ_f and ρ_m are the density of filler and resin matrix, respectively.

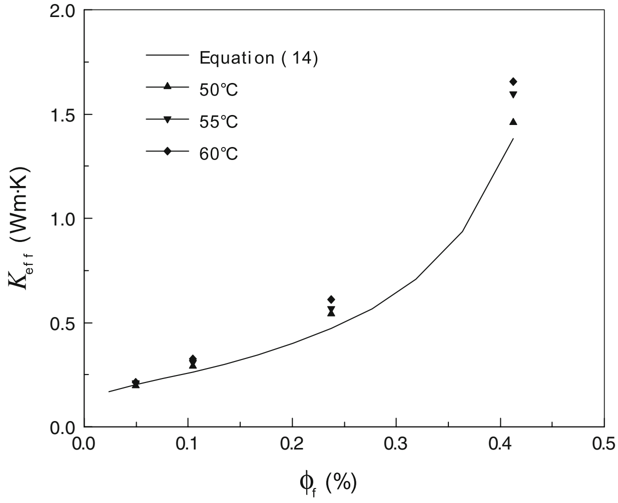

Fig. 3 Relationship between effective thermal conductivity and filler volume fraction of phenol–aldehyde/aluminum composites

Table 1 Measured conductivity values of aluminum powder-filled phenol–aldehyde composites

W_f (wt%)	Specimen thickness (mm)	K_{eff} (W/m K)		
		50 °C	55 °C	60 °C
0	3	0.110	0.110	0.111
10	3.5	0.195	0.209	0.215
20	4	0.289	0.306	0.324
40	2.5	0.539	0.565	0.612
60	2	1.457	1.594	1.654

Table 2 Measured conductivity values of graphite powder-filled phenol–aldehyde composites

W_f (wt%)	Specimen thickness (mm)	K_{eff} (W/m K)		
		50 °C	55 °C	60 °C
0	3	0.110	0.110	0.111
10	2.5	0.229	0.235	0.242
20	2.5	0.306	0.316	0.332
40	3.5	0.523	0.541	0.573
60	2	2.228	2.385	2.654

It can be observed that the thermal conductivity of both the predictions and measured data of the phenol–aldehyde/aluminum composites increases nonlinearly with an increase of the filler volume fraction, and the estimations of the thermal conductivity are roughly consistent with the measured data under the experimental conditions, especially at test temperature of 50 °C and the volume fraction of aluminum powder being less than 40%. When the volume fraction is more than 40%, the difference between the predictions and measured data of the thermal conductivity of these composite systems is relatively obvious. In general, the measured values of thermal conductivity are roughly around the theoretical prediction curve.

Similarly, by substituting the above physical and thermal property parameters of phenol–aldehyde and graphite powder into Eq. 14, one can calculate the effective thermal conductivities of the graphite powder-filled phenol–aldehyde composites, and compare these calculations with the measured data listed in Table 2, as shown in Fig. 4. It can also be seen that the thermal conductivity of both the predictions and measured data of the phenol–aldehyde/graphite composites increases nonlinearly with an increase of the filler volume fraction, and the estimations of the thermal conductivity are roughly consistent with the measured data under the experimental conditions. Although

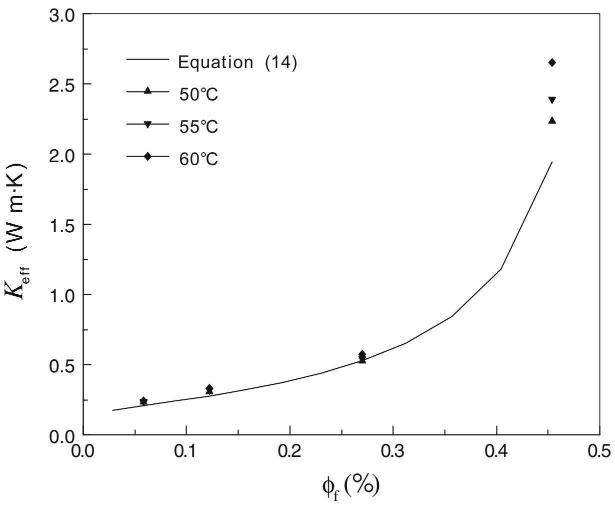

Fig. 4 Relationship between effective thermal conductivity and filler volume fraction of phenol–aldehyde/graphite composites

there is some difference between them, the variation tendency is consistent; the measured data is basically near the theoretical prediction curve.

In the case of high concentration of both aluminum powder and graphite powder, the difference between the predictions and measured data of the thermal conductivity of these composite systems is relatively obvious. It might be that the aluminum and graphite particles produce heat transfer links in the matrix due to the small distance between neighboring particles in the case of high concentration. Thus, the conductive capacity of the composite system is quickly enhanced, leading to increased difference between the predictions and measured data of the thermal conductivity of these composite systems.

Discussion

As stated above, there have been several mathematical models for predicting the thermal conductivity of filled polymer composites since 1970s, such as Maxwell–Eucken model [13]

$$K_{\mathrm{eff}} = \frac{2K_{\mathrm{p}} + K_{\mathrm{f}} + 2\phi_{\mathrm{f}}(K_{\mathrm{f}} - K_{\mathrm{p}})}{2K_{\mathrm{p}} + K_{\mathrm{f}} - 2\phi_{\mathrm{f}}(K_{\mathrm{f}} - K_{\mathrm{p}})} K_{\mathrm{p}}, \tag{16}$$

Bruggeman model [14]

$$1 - \phi_{\mathrm{f}} = \frac{K_{\mathrm{p}} - K_{\mathrm{eff}}}{K_{\mathrm{f}} - K_{\mathrm{p}}} \left(\frac{K_{\mathrm{f}}}{K_{\mathrm{eff}}} \right)^{\frac{1}{3}}, \tag{17}$$

Russell model [15],

$$K_{\mathrm{eff}} = K_{\mathrm{p}} \left[\frac{\phi_{\mathrm{f}}^{2/3} + \frac{K_{\mathrm{p}}}{K_{\mathrm{f}}}(1 - \phi_{\mathrm{f}}^{2/3})}{\phi_{\mathrm{f}}^{2/3} - \phi_{\mathrm{f}} + \frac{K_{\mathrm{p}}}{K_{\mathrm{f}}}(1 - \phi_{\mathrm{f}}^{2/3})} \right], \tag{18}$$

Nielsen–Lewis model [16],

$$K_{\mathrm{eff}} = \frac{1 + AB\phi_{\mathrm{f}}}{1 - B\psi\phi_{\mathrm{f}}}, \tag{19a}$$

$$B = \frac{(K_{\mathrm{f}}/K_{\mathrm{p}}) - 1}{(K_{\mathrm{f}}/K_{\mathrm{p}}) + A}, \tag{19b}$$

$$\psi = 1 + \frac{\phi_{\mathrm{f}}^2(1 - \varsigma)}{\varsigma^2}, \tag{19c}$$

and Baschirow–Selenew model [17],

$$K_{\mathrm{eff}} = K_{\mathrm{p}} \left\{ 1 - \frac{a^2\pi}{4} + \frac{a\pi P}{a} \left[1 - \frac{P}{a} \ln\left(1 + \frac{a}{P} \right) \right] \right\}, \tag{20a}$$

$$P = \frac{K_{\mathrm{f}}}{K_{\mathrm{p}} - K_{\mathrm{f}}}, \tag{20b}$$

$$a = \left(\frac{6\phi_{\mathrm{f}}}{\pi} \right)^{\frac{1}{3}}, \tag{20c}$$

where A and ς are the constants related to the shape and size of filler particles.

Agari et al. [21] introduce vertical and horizontal heat transfer mechanisms, and proposed a new expression as follows:

$$\log K_{\mathrm{eff}} = \phi_{\mathrm{f}} C_2 \log K_{\mathrm{f}} + (1 - \phi_{\mathrm{f}}) \log(C_1 K_{\mathrm{p}}), \tag{21}$$

where C_1 is the factor affecting crystallinity and crystalline size and C_2 is the free factor for formation of thermal conductive link, $0 \leq C_2 \leq 1$. The more C_2 is close to 1, the particles are easier to form thermal conductive links in the matrix, especially in the case of high filler concentrations.

Under general conditions, parameters A, ς, C_1, and C_2 are not easy to be determined. Relatively, Maxwell–Eucken equation and Russell equation are simple and convenient to estimate thermal conductivity. In this article, therefore, the thermal conductivities of the phenol–aldehyde/aluminum composites and phenol–aldehyde/graphite composites are estimated by using Eqs. 16 and 18, respectively, and compare the predictions with the measured data, as well as the calculations by Eq. 14. Figure 5 displays the comparison between the predictions and the measured data of the thermal conductivity of the phenol–aldehyde/aluminum composite systems. It can be seen that the difference between the estimations by Eq. 18 increases with an addition of the filler volume fraction, whereas the predictions by Eq. 14 are more close to the measured data than those by Eqs. 16 and 18. Figure 6 displays the comparison between the predictions and the measured data of the thermal conductivity of the phenol–aldehyde/graphite composite systems. Similarly, the difference between the estimations by Eq. 18 increases with an addition of the filler volume fraction, whereas there is some difference between the predictions by Eqs. 16 and the measured data

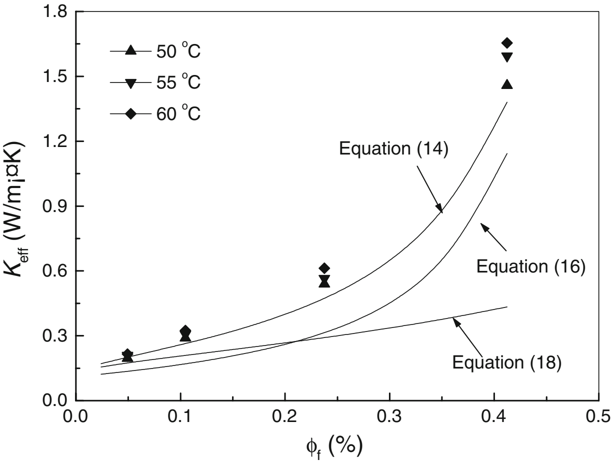

Fig. 5 Comparison between estimations and measurement of effective thermal conductivity of phenol–aldehyde/aluminum composites

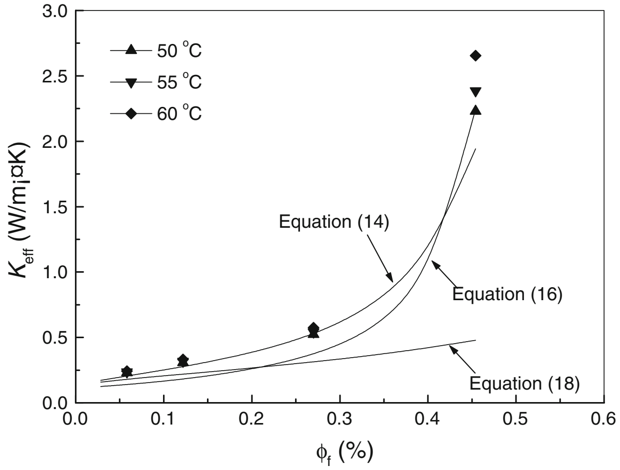

Fig. 6 Comparison between estimations and measurement of effective thermal conductivity of phenol–aldehyde/graphite composites

when ϕ_f is less than 40%, and then they are close to each other. In general, the predictions by Eq. 14 are closer to the measured data.

Summing-up the above results, Eq. 14 describes the relationship between the effective thermal conductivity of inorganic particle-filled polymer composites and the physical parameters, such as conductivity coefficient of polymer and inorganic particle and the volume fraction of the fillers when inorganic filler volume fraction is less than 60% and polymer composites are in solid state. Aluminum and graphite are, respectively, a metal material and an inorganic material, and the experimental measured data of the thermal conductivity for both the two filled phenol–aldehyde composite systems is close to the theoretical estimations, thus Eq. 14 is primarily verified.

Conclusions

A new theoretical model of heat transfer in these composites was established based on the law of minimal thermal resistance and the equal law of the specific equivalent thermal conductivity. Equation 14 describes the relationship between the effective thermal conductivity (K_{eff}) of inorganic particulate-filled polymer composites and inclusion volume fraction as well as other physical parameters of matrix resin and fillers when inorganic filler volume fraction is less than 60% and polymer composites are in solid state.

The values of K_{eff} of both aluminum powder-filled phenol–aldehyde composites and graphite powder-filled phenol–aldehyde composites were estimated by using Eq. 14 and the predictions were compared with the experimental measured data from these two filled composite systems. Good agreement was shown between the theoretical estimations and measured data of the K_{eff} under the experimental conditions. Furthermore, the calculations by Eq. 14 are closer to the experimental measured data from these two filled composite systems than those by Russell equation and Maxwell–Eucken equation.

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