A New Theoretical Equation for Thermal Conductivity of Two-Phase Systems

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ABSTRACT: A new theoretical equation that describes the thermal conductivity of two-phase composite materials has been proposed. The Cheng-Vachon equation has been modified by introducing a new parameter named $P_{d \max}$, permitting the new equation to describe the thermal conductivity of composite materials for a wide variety of filler shapes and states of dispersion. The new equation can describe the thermal conductivity of two-phase materials more accurately than any of the previous equations. Furthermore, this new equation will make it possible to evaluate the dispersion state of the discontinuous phase by measuring the thermal conductivity of the filled polymers or the polymer blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1689–1697, 1999

Key words: thermal conductivity; composite; dispersion state; Cheng-Vachon equation; Nielsen equation

INTRODUCTION

Polymer materials have been used as thermal insulators for a long time because of their low thermal conductivity. However, they have also recently been used as composite materials in fields where highly thermally conductive materials are required. Such composite materials usually consist of polymers and highly thermally conductive inorganic fillers. In designing such filled polymers, it is essential to predict the thermal conductivity of the final products. Therefore, many theoretical or empirical equations have been proposed to describe the thermal conductivity of heterogeneous materials.¹⁻⁷ However, few equations consider the dispersion state of the filler, although this factor undoubtedly affects the thermal conductivity of the composite materials.

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Journal of Applied Polymer Science, Vol. 72, 1689–1697 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/131689-09 Cheng and Vachon proposed a theoretical equation that is regarded as one of the best fitting equations to the experimental data.^{4,8} The Cheng-Vachon equation is based on several assumptions: the filler is uniformly dispersed, no porosity exists in the composite material, the effect of the interface can be ignored, and thermal convection and radiation are negligible. In practice, however, real composite materials do not always exactly conform to these assumptions. Hence, the Cheng-Vachon equation does not provide an exact fit to such materials.

Nielsen applied equations for the elastic moduli of composite materials to the prediction of thermal conductivity of composite materials.^{5,9,10} This equation is provided by modifying the Halpin-Tsai equation¹¹ to include the effect of shape and orientation of the filler in two-phase materials. These factors are supposed to affect the dispersion state of the fillers. The Nielsen equation can provide very reasonable values to experimental results as long as such factors are known. In this study, the Cheng-Vachon equation is modified by introducing a new parameter named $P_{d \max}$. This new parameter includes information of the dispersion state of the fillers in the composite materials. This modified Cheng-Vachon equation is verified with experimental data and compared with both the Cheng-Vachon and Nielsen equations.

THEORY

Cheng and Vachon's Theory

The Cheng-Vachon equation is obtained from Tsao's theory. Tsao developed the relationship shown in eq. (1) for predicting the thermal conductivity of two-phase materials.³

 k_m

$$=\frac{1}{\int_{0}^{1}\frac{dP_{1}}{k_{c}+(k_{d}-k_{c})\int_{P_{1}}^{1}\frac{1}{\sigma\sqrt{2\pi}}e^{-1/2}\left(\frac{P_{1}-\mu}{\sigma}\right)^{2}dP_{1}},$$
(1)

where k_m , k_c , and k_d stand for the thermal conductivity of the two-phase material, the continuous phase, and the discontinuous phase, respectively. In this theory, the conductivity of the constituents is required. Values of μ and σ , which represent the mean and standard deviation of a "one-dimensional porosity," P_1 , are required to predict the thermal conductivity of the two-phase system. Tsao developed a relationship for "twodimensional porosity," P_2 in terms of P_1 using probabilistic theory. The effective thermal conductivity of the mixture was calculated with P_1 , μ , σ , and the thermal conductivity of the constituents. However, it is very difficult to obtain μ and σ in practice.

Cheng and Vachon extended Tsao's theory by assuming that the distribution function of the discontinuous phase is parabolic.⁴ This assumption circumvents the necessity of experimentally determining μ and σ , because these values are not required.

Cheng and Vachon used a unit cube, as shown in Figure 1(a), to predict the thermal conductivity of a two-phase mixture. This unit cube is sliced into many layers perpendicular to the heat flow



Figure 1 Model for the study of the thermal conductivity of two-phase materials.

direction, which is parallel to the *x*-axis. The arrangement of the discontinuous phase as shown in Figure 1(b) does not change the effective thermal conductivity of the unit cube because parallel conductivity is additive. Because each layer can be considered infinitesimally thin, the arrangement of the layers shown in Figure 1(c) does not affect the effective thermal conductivity of the unit cube.

The equivalent thermal resistance of the configuration, R_e , shown in Figure 1(c), is calculated by the following equation.

$$R_e = 2 \int_0^x \frac{dx}{k_c + (k_d - k_c)y} + \frac{1 - 2x}{k_c}.$$
 (2)

The thermal conductivity is obtained by definition as follows:

$$k_m = \frac{1}{R_e}.$$
 (3)

Cheng and Vachon's theory assumes that the distribution of the discontinuous phase, which represents the discontinuous volume fraction, is a normal distribution curve. Therefore,

$$y = C_1 \exp(-C_2 x^2),$$
 (4)

where C_1 and C_2 are constants. This equation can be expanded in a series.

$$y = C_1 \left(1 - C_2 x^2 + \frac{C_2^2 x^4}{2!} - \cdots \right).$$
 (5)

Because this series converges rapidly for all values of x between -0.5 and 0.5, all terms are eliminated except the first two.



Figure 2 Phase distribution for a two-phase material.

$$y = B + Cx^2. (6)$$

In this parabolic function, B and C are constants. The volume fraction of the discontinuous phase, P_d , is represented by the gray area surrounded by the parabolic curve and the *x*-axis in Figure 2. Therefore,

$$P_d = 2 \int_0^a y dx, \tag{7}$$

where

$$y = B + Cx^2$$
 at $|x| \le a < 0.5$,
 $y = 0$ at $a \le |x| \le 0.5$,

and a is the value of the *x*-intercept. As a boundary condition, it is assumed that this parabolic curve includes two points at the maximum point:

$$y = 1$$
 at $x = 0$

and

$$y = 0$$
 at $x = 0.5$.

This implies that the fillers will not fully agglomerate until they are in closest packing, and that thermal conductive paths through the composite materials are built when the fillers are in closest packing. From these boundary conditions, one obtains

$$B = 1$$

and

$$C = -4.$$

The maximum value of P_d is calculated to be 0.667 from eq. (7) and the boundary conditions. Assume as P_d decreases from its maximum value of 0.667, the absolute value of y at x = 0, corresponding to B in eq. (6), shrinks 2δ and the absolute value of x also shrinks 2δ at y = 0 in Figure 2. This assumption, substituting B/2 for x and 0 for y in eq. (6), leads to the following relationship between B and C:

$$B = -4/C.$$
 (8)

Because

$$P_{d} = 2 \int_{0}^{B/2} y dx = 2 \int_{0}^{B/2} (B + Cx^{2}) dx$$
$$= 2B^{2}/3,$$

B and C are obtained as a function of P_d as follows:

$$B = \left(\frac{3}{2} P_d\right)^{1/2} \tag{9a}$$

and

$$C = -4 \left/ \left(\frac{3}{2} P_d\right)^{1/2}$$
. (9b)

From eqs. (2) and (6), the effective thermal resistance of this composite material model is represented as follows:

$$R_{e} = 2 \int_{0}^{B/2} \frac{dx}{[k_{c} + B(k_{d} - k_{c})] - C'(k_{d} - k_{c})x^{2}} + \frac{1 - B}{k_{c}}, \quad (10)$$

where C' = -C.

When $k_d > k_e$, a normal condition for composite materials consisting of polymers and highly thermally conductive fillers,

$$\begin{aligned} R_e &= \left[C'(k_d - k_c)\{k_c + B(k_d - k_c)\}\right]^{-1/2} \\ &\times \ln \frac{\{k_c + B(k_d - k_c)\}^{1/2} + (B/2) \ C'(k_d - k_c)^{1/2}}{\{k_c + B(k_d - k_c)\}^{1/2} \ - \ (B/2) \ C'(k_d - k_c)^{1/2}} \end{aligned}$$

$$+\frac{1-B}{k_c}.$$
 (11)

When $k_d < k_c$, and R_e is represented as follows:

$$R_{e} = 2[-C'(k_{d} - k_{c})\{k_{c} + B(k_{d} - k_{c})\}]^{-1/2}$$

$$\times \tan^{-1} \frac{B}{2} \left\{ \frac{-C'(k_{d} - k_{c})}{k_{c} + B(k_{d} - k_{c})} \right\}^{1/2}$$

$$+ \frac{1 - B}{k_{c}}. \quad (12)$$

Finally, from eq. (11) or (12), the thermal conductivity of the composite material is predicted with k_c , k_d , and P_d .

New Theory

In Cheng and Vachon's theory, the dispersion state and the shape of the filler are not considered, although the thermal conductivity of composite materials is dependent on these factors. Therefore, in practice, the Cheng-Vachon equation does not provide an exact fit to some materials. For this reason, a new parameter, which includes such factors, has been introduced to the Cheng-Vachon equation to improve it.

Cheng and Vachon assumed that the parabolic distribution curve included (0,1) and (0.5,0) at the maximum filler content. Consequently, the maximum volume fraction of the discontinuous phase was inevitably fixed to be 0.667. However, this value should be dependent on the dispersion state and the shape of the filler as shown in Table I, in which ϕ_m , the maximum packing fraction, of typical fillers in selected packing orders is listed. ϕ_m is defined as the true volume of the particles divided by the volume they appear to occupy when packed to their maximum extent. For most fillers, ϕ_m has to be determined experimentally.

The maximum volume fraction of the discontinuous phase is defined as a new parameter named $P_{d \text{ max}}$, and is applied to the Cheng-Vachon equation. $P_{d \text{ max}}$ reflects the dispersion state and the shape of the filler and is defined as the area surrounded by the *x*-axis and the dispersion curve including points (0, 1) and (0.5, 0) in Figure 3.

 Table I Maximum Packing Fractions⁵

Shape of Particle Type of Packing	
Hexagonal close	0.7405
Face centered cubic	0.7405
Body centered cubic	0.60
Simple cubic	0.524
Random close	0.637
Random loose	0.601
Uniaxial hexagonal close	0.907
Uniaxial simple cubic	0.785
Uniaxial random	0.82
Three dimensional random	0.52
	Type of Packing Hexagonal close Face centered cubic Body centered cubic Simple cubic Random close Random loose Uniaxial hexagonal close Uniaxial simple cubic Uniaxial random Three dimensional random

Assuming the dispersion state of the discontinuous phase does not change substantially throughout the volume fraction of the discontinuous phase under examination, the shape of the distribution curve at a certain volume fraction, P_d , is supposed to be geometrically similar to that at $P_{d \max}$, as shown in Figure 3. Because the area is proportional to the square of the length, P_d and $P_{d \max}$ should have the following relationship:

$$P_d = B^2 P_{d \max}.$$
 (13)

Therefore, *B* and *C* are represented as a function of P_d and $P_{d \max}$ from eq. (8) and (13):

$$B = \left(\frac{P_d}{P_{d \max}}\right)^{1/2} \tag{14a}$$

$$C = -4 / \left(\frac{P_d}{P_{d \max}} \right)^{1/2}$$
. (14b)



Figure 3 Schematic diagram of $P_{d \max}$ and P_d .

From eqs. (6), (14a), and (14b), the distribution function of the discontinuous phase is

$$y = \left(\frac{P_d}{P_{d\max}}\right)^{1/2} - 4\left(\frac{P_{d\max}}{P_d}\right)^{1/2} x^2.$$
 (15)

To distinguish the constants B and C from the ones of the Cheng-Vachon equation, these are replaced by B'' and -C'', respectively. Thus,

$$B'' = B = \left(\frac{P_d}{P_{d \max}}\right)^{1/2}$$

and

$$C'' = -C = 4 \left(rac{P_{d \max}}{P_{d}}
ight)^{1/2}$$

When $k_d > k_c$, the effective thermal resistance of this composite material is represented as follows:

$$R_{e} = [C''(k_{d} - k_{c})\{k_{c} + B''(k_{d} - k_{c})\}]^{-1/2}$$

$$\times \ln \frac{\{k_{c} + B''(k_{d} - k_{c})^{1/2} + (B''/2) C''(k_{d} - k_{c})\}^{1/2}}{\{k_{c} + B''(k_{d} - k_{c})^{1/2} - (B''/2) C''(k_{d} - k_{c})\}^{1/2}} + \frac{1 - B''}{k_{c}}, \quad (16)$$

When $k_d < k_c$,

$$R_{e} = 2[-C''(k_{d} - k_{c})\{k_{c} + B''(k_{d} - k_{c})\}]^{-1/2}$$

$$\times \tan^{-1} \frac{B''}{2} \left\{ \frac{-C''(k_{d} - k_{c})}{k_{c} + B''(k_{d} - k_{c})} \right\}^{1/2}$$

$$+ \frac{1 - B''}{k_{c}}. \quad (17)$$

The thermal conductivity of this composite material is obtained as a reciprocal of R_e by definition. If $P_{d \max} = 0.667$, this new theoretical equation is identical to the Cheng-Vachon equation.

Nielsen's Theory

Nielsen proposed the following equation to predict the thermal conductivity of composite materials.

$$k_m = \frac{1 + ADP_d}{1 - D\psi P_d} k_c \tag{18}$$

where

$$D = \frac{k_{d}/k_{c} - 1}{k_{d}/k_{c} + A}$$
(19)

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right) P_d \tag{20}$$

The constant A depends on the shape and the orientation of the filler in the composite material; the constant A is related to the generalized Einstein coefficient k_E .

$$A = k_E - 1. \tag{21}$$

Table II lists the values of *A* for typical fillers.

Nielsen initially applied this equation to describe the modulus and viscosity of composite materials. Nonetheless, it is confirmed that the Nielsen equation fits the experimentally obtained thermal conductivity data quite well for the wide range of fillers.⁷

RESULTS AND DISCUSSION

Effect of Filler Shape

Figure 4 shows the relationship between the thermal conductivity of spherical glass-filled polystyrene and the volume fraction of the filler. The experimental data used here are values reported by Sundstrom et al.¹² In this case, the three theoretical equations fit the experimental data very well.

The values used for the parameters A and ϕ_m in the Nielsen equation are 1.5 and 0.64, respectively. These values are reasonable values for the spherical fillers in random packing. Fitting the calculated values given by eq. (16) to the experimental data provides 0.69 as the value of $P_{d \text{ max}}$. The average deviations of the calculated values from the experimental data for eq. (16), the Cheng-Vachon equation, and the Nielsen equation are 1.9, 2.4, and 5.0%, respectively. This indicates that the new equation would be able to describe the thermal conductivity of two-phase composite materials consisting of spherical particles more accurately than the other two equations.

Although Cheng and Vachon's theory does not consider the effect of the shape and the dispersion state of the filler, it gives reasonable values for

Type of Dispersed Phase	Direction of Heat Flow	A	
Spheres	Any	1.50	
Randomly oriented rods, Aspect ratio $= 2$	Any	1.58	
Randomly oriented rods, Aspect ratio $= 4$	Any	2.08	
Randomly oriented rods, Aspect ratio = 6	Any	2.8	
Randomly oriented rods, Aspect ratio = 10	Any	4.93	
Randomly oriented rods, Aspect ratio = 15	Any	8.38	
Uniaxially oriented fibers Uniaxially oriented fibers	Parallel to fibers Perpendicular to fibers	$2 L/D^{*}$ 0.5	

Table II Value of A for Various Two-Phase Systems⁵

^a L and D represent length and diameter of the filler, respectively.

composite materials consisting of spherical particles due to the lack of orientation factor and agglomeration. This implies that the spherical particles would not make effective thermal conductive paths until the fillers are maximally packed, and that the filler content at the maximum packing would be close to 0.667, as Cheng and Vachon assumed.

However, it is difficult for the Cheng-Vachon equation to accurately describe the thermal conductivity of composite materials produced from fillers having a larger aspect ratio. The thermal conductivity of polyethylene–carbon short-fiber composite materials is shown in Figure 5. The experimental data used are from Agari et al.¹³ The aspect ratio of this milled carbon fiber is 13.4. Figure 5 clearly shows that eq. (16) and the Nielsen equation can represent the thermal conductivity more accurately than the Cheng-Vachon equation when the filler has a large aspect ratio. In this case, $P_{d \text{ max}}$ is determined to be 0.45 by fitting the calculated values to the experimental data. For the Nielsen equation, A and ϕ_m are selected to be 6.5 and 0.48, respectively. These values are reasonable values for a random packing system of short fibers whose aspect ratio is 13.4.^{5,14} The average deviations of the calculated values from the experimental data are 3.5% for eq. (16), 5.0% for the Nielsen equation, and 10.7% for the Cheng-Vachon equation. These results prove that the introduction of $P_{d \text{ max}}$ as a new



Figure 4 Effect of volume content of the filler on the thermal conductivity of the spherical glass filled polystyrene. Experimental data from ref. 12. \Box Experimental; — eq. (16); — Nielsen equation; ----- Cheng-Vachon equation.



Figure 5 Effect of volume content of the filler on the thermal conductivity of the carbon short fiber-filled polyethylene. Aspect ratio of the carbon short fiber is 13.4. Experimental data from ref. 13. □ Experimental; ______ eq. (16); ______ Nielsen equation; ----- Cheng-Vachon equation.



Figure 6 Effect of volume content of the filler on the thermal conductivity of the graphite filled polyethylene: Experimental data from ref. 15. \Box Experimental; — eq. (16); — Nielsen equation; ----- Cheng-Vachon equation. (a) powder mixture; (b) solution mixture; (c) roll-milled mixture; and (d) melt mixture.

parameter improves the Cheng-Vachon equation, and the new equation can describe the thermal conductivity of composite materials consisting of nonspherical fillers.

The values of $P_{d \max}$ and ϕ_m are very close in each composite system. This trend has also been seen in many other composite systems, which are not detailed in this article. Although $P_{d \max}$ is obtained from experimental data and ϕ_m is determined from theoretical calculation, they would theoretically represent the same content of the filler in the composite materials. Therefore, it is consistent for these values to be close to each other. However, the processes by which eq. (16) and the Nielsen equation are deduced are completely different. Nevertheless, it is interesting that these equations provide very similar values of thermal conductivity of composite materials.

The Nielsen equation needs two parameters to describe the thermal conductivity of compos-

ite materials. If, at least, either the shape and orientation or the maximum packing fraction of the filler in the composite materials, i.e., A or ϕ_m , is known, it would be valuable to apply the fitting data technique to the Nielsen equation. However, in practice, it is difficult to determine these parameters when the filler shape is unknown. It is also difficult for those systems with mixed shapes. Meanwhile, the new equation needs only one parameter to describe the thermal conductivity of composite materials. Even if the filler shape is unknown, the new equation can provide precise values for any kind of composite material. This implies that the new equation has the potential to be applied to polymer blend systems.

Effect of Dispersion State of the Filler

Agari et al. reported the effect of the filler dispersion state on the thermal conductivity of the com-

	$P_{d \max}$			Average Deviation (%)		
		Equation (16)	Nielsen Equation	Cheng-Vachon Equation		
Powder mixture	0.28	7.6	37.0	25.9		
Solution mixture	0.41	8.8	36.8	27.1		
Roll-milled mixture	0.43	8.4	33.7	23.2		
Melt mixture	0.47	13.9	24.5	17.7		

Table IIIAverage Deviation of the Theoretical Values from the Experimental Dataof Polyethylene-Graphite Composite Materials in Different Dispersion Systems

posite materials by using four dispersion systems: powder mixture, solution mixture, roll-milled mixture, and melt mixture.¹⁵ According to Agari et al., the number of particles touching each other decreases in the order of powder mixture > solution mixture = roll-milled mixture > melt mixture. In this order, the dispersion state of the filler becomes better if a state in which the filler particles scarcely touch each other is defined as good dispersion state.

Agari et al. used a polyethylene–graphite composite to investigate the filler dispersion effect. Figure 6(a)–(d) shows the thermal conductivity of the composite materials for each dispersion system. The Cheng-Vachon and Nielsen equations are compared with eq. (16) in Figure 6(a)–(d). The assigned parameter values for the Nielsen equation are 1.5 for A and 0.64 for ϕ_m . Nonetheless, because it is impossible to know the exact values of A and ϕ_m for each dispersion system, applying the Nielsen equation to these systems might be inappropriate.

The average deviation of the theoretical values from the experimental data of the polyethylene–graphite composite materials for these four different dispersion systems are listed in Table III. $P_{d \max}$ values, which are obtained by the fitting process, are also listed in this table. Table III shows that no matter what dispersion system is used, the thermal conductivity values obtained from the new equation are closer to the experimental data than the ones obtained from the other equations.

The higher $P_{d \max}$ corresponds to the better dispersion state of the filler. This, in turn, implies that $P_{d\max}$ will make it possible for the thermal conductivity measurement to evaluate the dispersion state of the filler in composite materials.

CONCLUSIONS

The new theoretical equation including $P_{d \max}$ can describe the thermal conductivity of twophase composite materials more accurately than both the Cheng-Vachon and Nielsen equations. Even if the composite materials consist of fillers having a larger aspect ratio, the new equation is applicable to such composite materials. Because the new equation needs only one parameter, it is more practical in describing the thermal conductivity of two-phase materials than the Nielsen equation. The new equation does not even need the information of the filler shape. Therefore, the new equation could be applied to polymer blends.

Several composite materials that have different filler dispersion systems have been investigated with the new equation. This investigation has shown that the new equation can describe the thermal conductivity of any dispersion system more accurately than both the Cheng-Vachon and Nielsen equations. The higher $P_{d \max}$ values correspond to the better dispersion state of the filler in the composite materials. Therefore, $P_{d \max}$ can potentially determine the dispersion state of the filler in composite materials.

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