

# Effective Thermal Conductivity Behavior of Filled Vulcanized Perfluoromethyl Vinyl Ether Rubber

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Received 5 June 2007; accepted 2 November 2007

DOI 10.1002/app.27612

Published online 27 February 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The effective thermal conductivity behavior of vulcanized perfluoromethyl vinyl ether (PMVE) rubber filled with various inorganic fillers was investigated and analyzed with thermal conductivity models. Experimental results showed that there was no significant improvement in the thermal conductivity of PMVE rubber if the intrinsic thermal conductivity of the fillers was greater than 100 times that of the rubber matrix, and this agreed with the prediction of Maxwell's equation. The thermal conductivity of PMVE rubber filled with larger size silicon carbide

(SiC) particles was greater than that of PMVE filled with smaller size SiC because of the lower interfacial thermal resistance, and there existed a transition filler loading at about 60 vol %. It was also found that flocculent graphite was the most effective thermally conductive filler among the fillers studied. A modified form of Agari's equation with a parameter independent on the units used was proposed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2968–2974, 2008

**Key words:** composites; fillers; rubber; thermal properties

## INTRODUCTION

Perfluoromethyl vinyl ether (PMVE) rubber is well known for its outstanding comprehensive performance, such as high thermal and hydrolytic stability, resistance to aging and oxidation, chemical inertness, and low-temperature flexibility.<sup>1–3</sup> A rubber lip seal working in hostile environments is one of the applications of PMVE rubber. For lip seals, most energy spent to overcome frictional losses during operation is converted into heat. The area density of the heat flux in contemporary lip seals for crankshafts normally varies within 8–12 W/mm<sup>2</sup> at a linear shaft speed exceeding 20 m/s and at a fluid temperature above 110°C. Because of insufficient heat conduction and the Joule effect, the temperature under the lip can reach up to 185°C.<sup>4</sup> The thermal aging and reduction of mechanical properties caused by the increasing temperature at the lip–shaft interface result in leakage and shorten the durability of seals. Increasing the thermal conductivity of the rubber is one way to solve this problem.

Heat transportation in nonmetals occurs through the flow of phonons and/or lattice vibration energy. Generally, the thermal conductivity of polymers is very low, ranging from 0.14 to 0.60 W/mK.<sup>5</sup> Most conductive fillers, such as ceramic and carbon-containing fillers, have thermal conductivity 2 or 3

orders of magnitude higher than that of polymers. By the addition of conductive fillers, polymers could be modified to have high thermal conductivity. Until now, lots of researchers have reported on the improvement of the thermal conductivity of polymer–matrix composites filled with various types of fillers. However, the polymer–matrix composites in most of these reports were used for making electronic packaging and substrate materials, and most of these polymers were thermoplastics and resins such as polyethylene,<sup>5–9</sup> polystyrene,<sup>10</sup> epoxy resin,<sup>11,12</sup> poly(vinylidene fluoride),<sup>13</sup> and polyimide.<sup>14</sup>

Numerous models and equations have been reported to predict the effective thermal conductivity of organic matrix composites, such as Maxwell's equation, Bruggeman's equation, Nielsen's equation, Cheng and Vochon's equation, Russell's equation, and Agari's equation.<sup>5</sup> All these equations can be divided into two types: the rigorous equations that contain no empirical parameters and the empirical equations containing one or more parameters whose values must be estimated or determined by fitting to the experimental data. Maxwell's equation predicts fairly well for randomly distributed and noninteracting homogeneous spheres in a continuous medium and is expressed as follows:<sup>5</sup>

$$k_c = k_m \frac{k_f + 2k_m + 2v(k_f - k_m)}{k_f + 2k_m - v(k_f - k_m)} \quad (1)$$

where  $k_c$ ,  $k_f$ , and  $k_m$  are the thermal conductivities of the composite, filler, and matrix, respectively, and  $v$  is the volume content of the filler.

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TABLE I  
Physical Properties of the Matrix and Conductive Fillers

	Material	Density (g/cm <sup>3</sup> )	Diameter (μm)	Particle shape	Thermal conductivity (W/mK) <sup>6,7,15</sup>
Matrix	PL455	1.78	—	—	0.21
	SiC	3.20	0.5, 74	Irregular	85
	Al <sub>2</sub> O <sub>3</sub>	3.90	0.5	Irregular	30
	AlN	3.26	0.5	Irregular	160
Filler	Wollastonite	2.80	3.5–10 <sup>a</sup>	Acicular	2.50
	Graphite	2.26	5	Flocculent	200
	Mica power	2.76	44	Flakelike	10

<sup>a</sup> Aspect ratio: 3/1–20/1.

Among empirical equations, Agari's model shows the closest approximation to the experimental data over a wide range of filler contents, and it can be applied to many different systems.<sup>7</sup> The equation is

$$\log k_c = v c_2 \log k_f + (1 - v) \log(c_1 k_m) \quad (2)$$

where  $C_1$  is the coefficient of the effect of the filler on the secondary structure of the polymer and  $C_2$  is the coefficient of ease in forming conductive chains of the filler.

In this study, the effective thermal conductivity behavior of vulcanized PMVE rubber filled with various inorganic fillers was investigated. These fillers included silicon carbide (SiC), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), aluminum nitride (AlN), wollastonite, graphite, and mica power. Effects of the intrinsic thermal conductivity of the filler, filler content, and filler size and shape on the thermal conductivity of the composites were investigated and analyzed with Maxwell's equation and Agari's equation. For a noncrystal elastomer, a modified form of Agari's equation neglecting the effect of the filler on the secondary structure of the polymer is proposed.

## EXPERIMENTAL

### Materials

The PMVE gum in this study was Tecnoflon PL455 (Solvay Solexis, Bollate, Italy). SiC with two different particle sizes, AlN (Shenzhen Industrial Co., Ltd., Shenzhen, China), and wollastonite, graphite, and mica power (Tianyuan Mining Co., Ltd., Shijiazhuang, China) were used as conductive fillers. The curing agent and cocuring agent, 2,5-bis(*tert*-butyl peroxy)-2,5-dimethylhexane and triallyl isocyanurate (TAIC), were obtained from Beijing Chemistry Agency Co. (Beijing, China). Magnesium oxide (MgO), supplied by Shandong Haihua Stock Co., Ltd. (Weifang, China), was used as the cure catalyst. All these materials were used as received, and the physical properties of the matrix and fillers are listed in Table I.

### Sample preparation

The basic formulation contained 5 phr MgO, 2 phr 2,5-bis(*tert*-butyl peroxy)-2,5-dimethylhexane, and 3 phr TAIC. The raw gum was first plasticated for about 5 min on a laboratory two-roll mill with a gear ratio of 1 : 1.22 and a slow-roll speed of 22 rpm. Then, MgO, fillers, TAIC, and peroxide were added, and mixing was continued for about 5 min. Thermal specimens with dimensions of 120 mm × 60 mm × 6 mm and vulcanized rubber sheets used for testing the mechanical properties with dimensions of 120 mm × 60 mm × 2 mm were molded at 170°C with a pressure of 10 MPa for 15 min with a hydraulic molding machine, and then they were oven-cured at 230°C for 24 h.

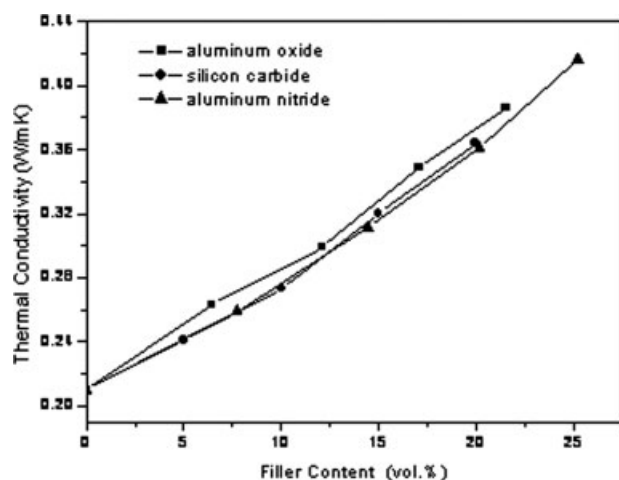
### Characterization

#### Thermal conductivity measurement

The thermal conductivity of the samples was measured on a GRD-3 thermal conductivity meter (Kang Long Technology and Trade, Ltd., Beijing, China) by a modified transient hot-wire method. In this method, a thin, straight wire was placed between the sample and a rectangular insulating material with thermal conductivity less than 0.0030 W/mK and kept there for 4 min to make the sample and wire have the same temperature of about 23°C before testing. Then, the wire was heated by a constant electric current, and the heat of the wire was conducted to the sample; this made the temperature of the sample rise. The differences in the temperature rise between the wire and the sample ( $\Delta T$ ) at the time interval ( $\Delta t$ ) were recorded, and then the conductivity of the sample could be calculated as follows:

$$k = \frac{Q \ln \Delta t}{4\pi \Delta t} \quad (3)$$

where  $Q$  is the heat flow per unit of time per unit of length of the heating wire. Error could be introduced by the heat flow dissipation through the insulating



**Figure 1** Comparison of the thermal conductivity of PMVEs filled with three different fillers as a function of the filler content.

material on the opposite side of the sample as it was not absolutely insulated and the variation in the resistance of the heating wire with the temperature caused a nonconstant power input.<sup>16</sup> In addition, the heat duration time had a crucial influence on the thermal conductivity of the specimen.<sup>6</sup> If the duration time were too long or too short, the exact value of the thermal conductivity would be very difficult to measure. In this case, eq. (3) could be modified as follows:

$$k = F \frac{Q \ln \Delta t}{4\pi \Delta T} - H \quad (4)$$

where  $F$  and  $H$  are the calibrated constants determined by materials of known thermal conductivity.

With this method, there would be no need to consider other material properties, such as the heat capacity and density, which would introduce additional sources of error. In this study, the heat duration time was 60 s, and the time interval recording the temperature rise was 1 s. For each specimen, the thermal conductivity was measured three times, and the average value was used for analysis.

#### Scanning electron microscopy analysis

A Philips FEI Quanta 600 scanning electron microscope (Praha, Czech Republic) was used to investigate the shape of the fillers, which was known to affect the thermal conductivity of the samples. As it was a low-pressure-mode environmental scanning electron microscope, fillers were put into the sample chamber directly without any further treatment, and the vacuum of the sample chamber was 60 Pa.

#### Mechanical property measurement

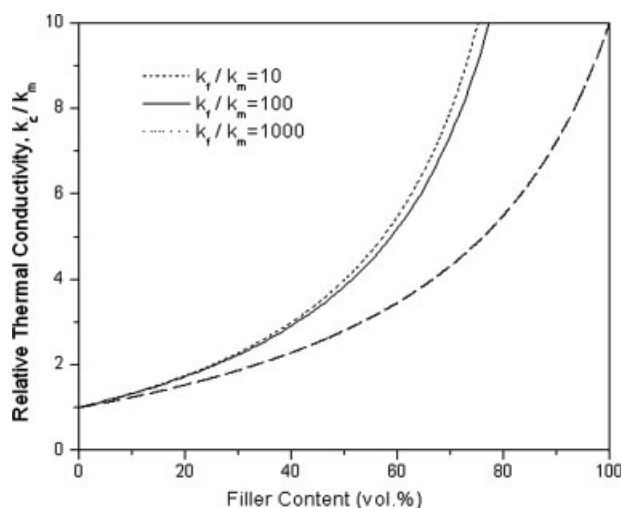
Dumbbell-like specimens with dimensions of 4 mm  $\times$  20 mm in the test part were punched out from the molded sheets. The tensile strength and elongation at break of the samples were measured with a T2000E electric tensile instrument (Youshen Electronic Instrument Co., Ltd., Beijing, China) at a crosshead speed of 500 mm/min.

## RESULTS AND DISCUSSION

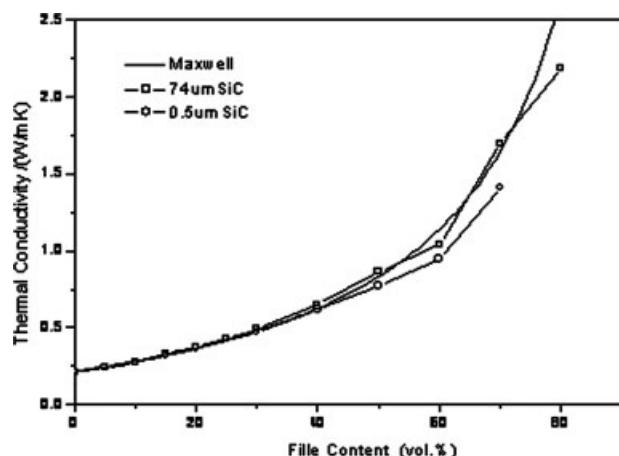
#### Effects of the filler's intrinsic thermal conductivity

Adding fillers with high intrinsic thermal conductivity is one of the common methods for obtaining organic matrix composites with high thermal conductivity. However, this method is limited in some cases. Figure 1 shows a comparison of the thermal conductivity of samples with three different fillers, that is,  $\text{Al}_2\text{O}_3$ , SiC, and AlN, as a function of the filler content. These fillers were all irregular particles and had the same size of 0.5  $\mu\text{m}$ . The ratios of the intrinsic thermal conductivity of  $\text{Al}_2\text{O}_3$ , SiC, and AlN to the thermal conductivity of the matrix were 143, 405, and 762, respectively. However, the effects of these three kinds of fillers on improving the thermal conductivity of the rubber matrix were almost the same.

The results agreed with those of many reports.<sup>6,11,17</sup> This phenomenon is also illustrated schematically with Maxwell's equation in Figure 2. The prediction values of the thermal conductivity increased obviously when the relative thermal conductivities changed from 10 to 100, but the values rarely increased when the relative thermal conductivities increased from 100 to 1000, especially at low filler contents. It was suggested that once the ther-



**Figure 2** Theoretical prediction with Maxwell's equation of the relative thermal conductivity as a function of the filler content.



**Figure 3** Thermal conductivity of SiC-filled PMVE rubber as a function of the filler content.

mal conductivity of the filler became much higher than that of the matrix (>100 times), fillers with higher intrinsic thermal conductivity would have little effect on the whole system at a moderate filler concentration.

#### Effects of the filler volume fraction and diameter

Figure 3 shows the thermal conductivity of the SiC-filled PMVE compound as a function of the filler content. There was a transition loading at about 60 vol %. Below this point, the thermal conductivity of the rubber steadily increased with the increase in the filler loadings. Above this point, the rubber exhibited a rapid increase with the increase in the filler amount and experienced a high thermal conductivity of 2.188 W/mK, 10 times that of the matrix itself, when the volume fraction of 74- $\mu\text{m}$  SiC reached 80 vol %.

The experimental values were in agreement with those predicted by Maxwell's equation when the filler content was below 30 vol %, and this showed that Maxwell's equation predicted fairly well at low filler concentrations. Maxwell's prediction values were much closer to the values of composites filled with larger size SiC for high volume contents (30–70 vol %). At a superhigh volume content (>70 vol %), the prediction values were much higher than the experimental data. This was because when the thermal conductivity of the fillers was far more than that of the polymer,  $k_m$  in the fraction part of Maxwell's equation could be neglected, and eq. (1) could be written as follows:

$$k_c = k_m \frac{1 + 2v}{1 - v} \quad (5)$$

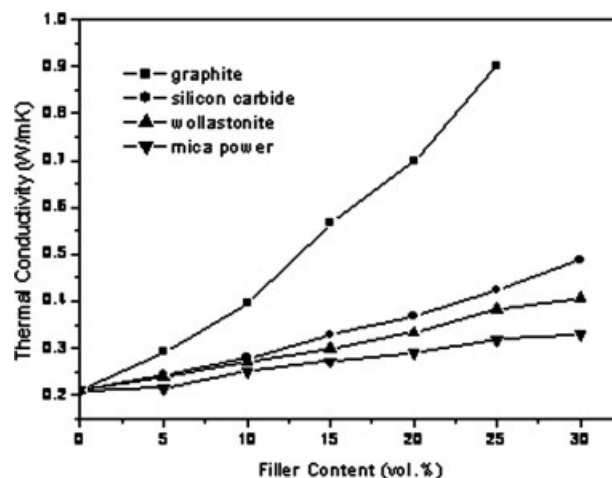
As the volume content of the fillers approached 100%, the prediction values of eq. (5) tended to be

infinitely high. Although the real thermal conductivity of the composite was limited for various reasons such as interfacial thermal resistance, Maxwell's equation was not suitable anymore.

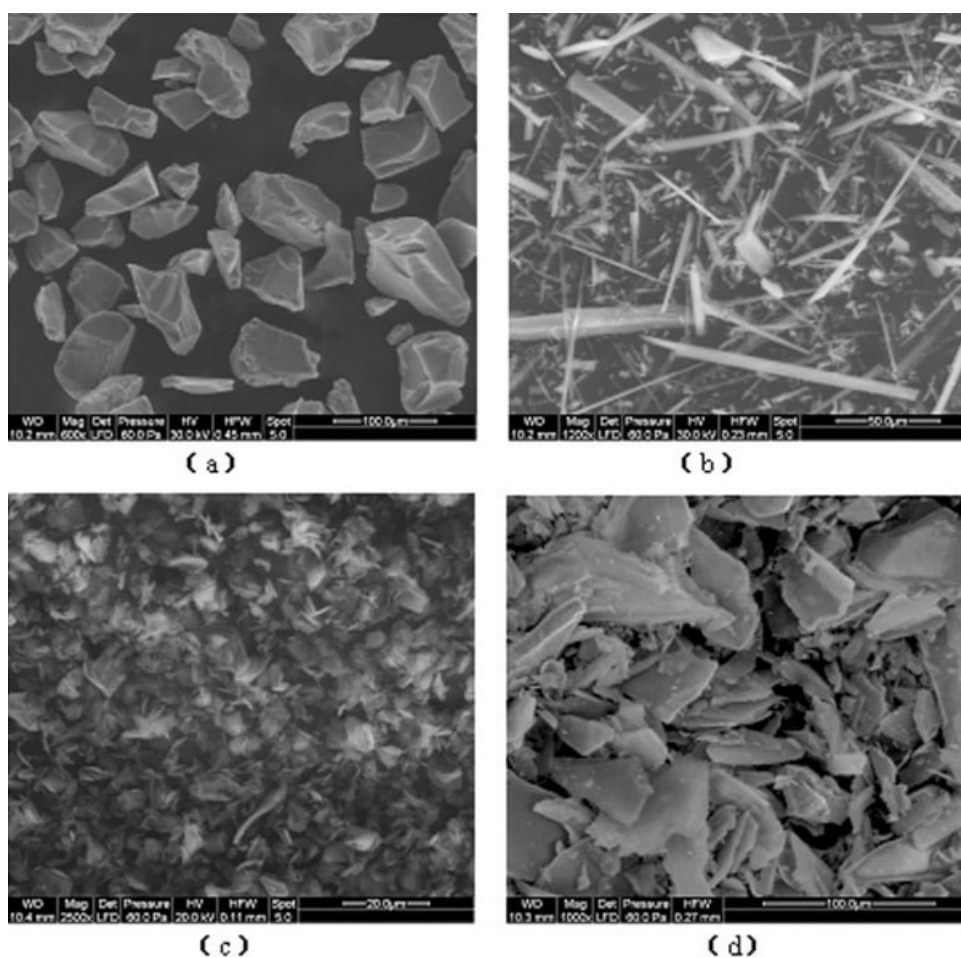
Two important parameters, that is, the number of conducting paths and the real particle density along the heat flow paths, regulate the conductivity in a composite, and the percolation theory can be effective in explaining the formation of filler networks as proposed by Bujard.<sup>18</sup> The currently accepted percolation threshold for a three-dimensional network is about 19.8%.<sup>19</sup> However, Figure 3 does not show a sharp discontinuity until the volume fraction reached 60%. This could not be the percolation threshold as it was defined as a point at which the first conductive path was formed.

Ishida and Rimdusit<sup>20</sup> proposed that the percolation theory could be employed to explain the insulator-conductor transition in path-dependent properties of materials such as electrically conductive composites, and the thermal conductivity seemed to be an intermediate property between a path-dependent property and a bulk property. Thus, the thermal conductivity of the composite depended on both the formation of the filler network (especially in fiber-filled systems) and the filler content. The critical point at 60 vol % in Figure 3 suggested that there must be enough conducting paths and real particle density along the heat flow paths to effectively improve the thermal conductivity of the composite. The two parameters suggested by Bujard<sup>18</sup> were greatly influenced by the filler content for particle-filled polymer systems.

From Figure 3, it can also be seen that the thermal conductivity of the PMVE rubber filled with larger particles was higher than that of the PMVE with smaller particles at the same content. This phenomenon was more pronounced at high filler contents.



**Figure 4** Effects of the filler shape on the thermal conductivity of PMVE rubber.



**Figure 5** Scanning electron microscopy micrographs of different fillers: (a) SiC, (b) wollastonite, (c) graphite, and (d) mica power.

The result was consistent with many reports.<sup>6,13,20</sup> It may be suggested that the use of big particles would lead to the formation of fewer thermally resistant junctions, and this would reduce the interfacial phonon scattering between the matrix and fillers. In addition, the theory of particle packing showed that the maximum packing of smaller particles was less than that of larger particles,<sup>21</sup> so the real particle density along the heat flow paths in larger filler filled composites was greater than that in smaller filler filled composites.

#### Effects of the filler shape on the thermal conductivity

It is well known that the thermal conductivity of polymer–matrix composites is affected by the filler shape. Generally, most thermal conductivity models have assumed an exact shape for the fillers or include a shape factor.

The thermal conductivity of PMVE rubber filled with four differently shaped fillers as a function of content is shown in Figure 4. The morphologies of

the different fillers are shown in Figure 5 and Table I. The intrinsic thermal conductivities of graphite and SiC were both more than 100 times that of the matrix, but the thermal conductivity of PMVE rubber filled with graphite was almost 2 times that of PMVE composites filled with SiC at any given volume content. Finally, PMVE composites with the thermal conductivity of 0.903 W/mK, about 4 times the intrinsic conductivity of PMVE rubber, were made at the graphite content of 25 vol %. The higher conductivity of the graphite-filled sample was possibly due to the following reasons:

1. The flocculent appearance of graphite particles made it easier to distribute in the rubber molecular network and form thermal conductivity paths. This could be further confirmed in the following part.
2. The morphology of graphite was of great advantage for forming good interfacial bonding between these two materials, which could be reflected by the mechanical properties. Figure 6 shows that PMVE rubber filled with graphite

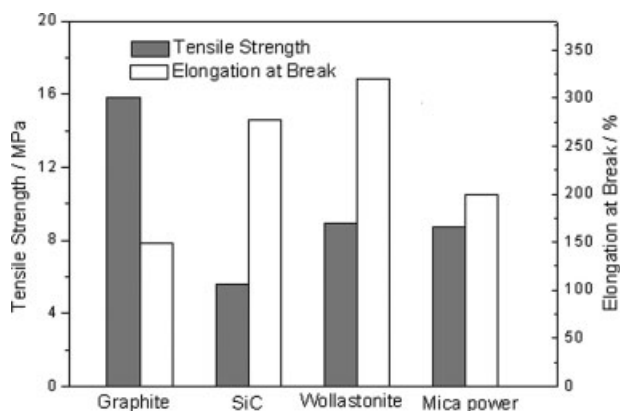


Figure 6 Mechanical properties of PMVE rubber with a filler content of 20 vol %.

had the highest tensile strength and the lowest elongation at break. The good affinity also helped to form less interfacial deflection and decrease the thermal contact resistance.

Although the thermal conductivity of wollastonite was much lower than that of SiC, the thermal conductivity of composites with wollastonite was almost the same as that with SiC when the filler content was lower than 10 vol %. This was because fiberlike fillers were more likely to form conductive chains than irregular fillers at low filler contents. With higher loadings, the thermal conductivity of SiC-filled composites was greater than that of composites with wollastonite, and this suggested that the intrinsic property would play more important roles than the filler shape in controlling the system's conductivity at higher filler contents.

The mica-power-filled composites showed the lowest conductivity for any given filler loadings, although its intrinsic thermal conductivity was greater than that of wollastonite. This suggested that the flakelike filler could not easily form conductive chains.

Modified form of Agari's equation

Agari's equation fits well the experimental data for many different systems over a wide range of filler loadings. However, one of its main disadvantages is that the parameter C<sub>2</sub> is dependent on the unit used, as reported by Lin et al.<sup>11</sup>

In this study, coefficients C<sub>1</sub> and C<sub>2</sub> in Agari's equation were obtained by the fitting of the equation to the experimental data, and they are shown in Table II. The values of C<sub>2</sub> varied greatly for different fillers, suggesting that the ease in forming conductive chains for differently shaped fillers was different, and it was ranked as follows: graphite > wollastonite > SiC > mica power. This agreed with the results discussed earlier. However, for all the fillers

TABLE II Values of C<sub>1</sub> and C<sub>2</sub> Obtained from Agari's Equation Through Data Fitting

	Filler			
	SiC	Wollastonite	Graphite	Mica powder
C <sub>1</sub>	1.01	1.02	1.04	0.992
C <sub>2</sub>	0.280	0.769	0.820	0.030

studied, the values of C<sub>1</sub> were almost the same (ca. 1.0). Because C<sub>1</sub> was the coefficient of the effect of the filler on the crystallinity and crystal size of the polymer, the secondary structure of PMVE seemed to be unaffected. This agreed with PMVE's noncrystal structure.

In Agari et al.'s report,<sup>7</sup> they generalized the parallel conduction and series conduction and considered factor C<sub>f</sub>, which is related to the ease in forming conductive chains of fillers, and they proposed eq. (6):

$$\left(\frac{k_c}{k_m}\right)^n = v \cdot \left(\frac{k_f}{k_m}\right)^{C_f \cdot n} + (1 - v) \tag{6}$$

where n takes a value between 1 and -1 for different composites. On the assumption that the dispersion state can be made uniform, n can be assumed to be in the neighborhood of 0, and then (k<sub>c</sub>/k<sub>m</sub>) will be approximated by 1 + n log (k<sub>c</sub>/k<sub>m</sub>); Agari's equation can be obtained from eq. (6) when k<sub>m</sub> is replaced by C<sub>1</sub>k<sub>m</sub> on the basis of the effect of the filler on the crystallinity and crystal size of the polymer. For noncrystal rubber, such as PMVE, the effect of the filler on the crystallinity and crystal size of the polymer can be negligible. Then, the modified form of Agari's equation deduced from eq. (6) is shown as follows:

$$\log k_c = v \cdot C_f \cdot \log k_f + (1 - v \cdot C_f) \cdot \log k_m \tag{7}$$

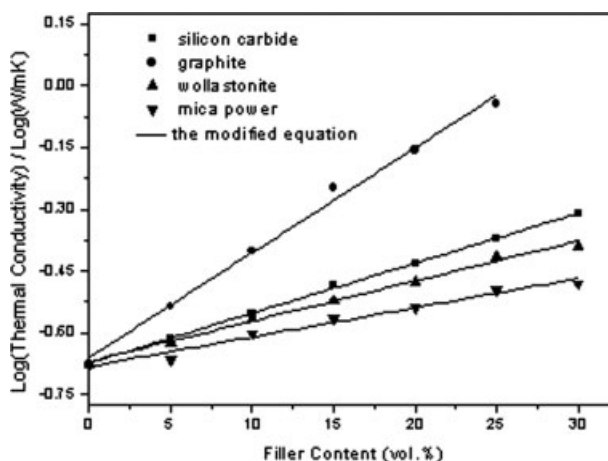


Figure 7 Comparison of the experimental data and the modified form of Agari's equation.

**TABLE III**  
**Comparison of  $C_2$  and  $C_f$  Obtained with Different Units**

Units	SiC		Wollastonite		Graphite		Mica powder	
	$C_2$	$C_f$	$C_2$	$C_f$	$C_2$	$C_f$	$C_2$	$C_f$
$W m^{-1} K^{-1}$	0.280		0.769		0.820		0.030	
$W cm^{-1} K^{-1}$	0.647	0.471	0.847	0.646	0.904	0.884	0.677	0.414
$cal s^{-1} cm^{-1} K^{-1}$	0.695		0.878		0.916		0.732	

where  $C_f$  can be an effective coefficient and then  $vC_f$  is the effective volume fraction of the filler. Here  $C_f$  not only is a measurement of the ease with which particles form conductive chains but also is related to the particle size, the contact resistance between the particle and matrix, the distribution of particles in the matrix, and so forth.

Fitting the modified form of Agari's equation to the experimental data in Figure 4 (see Fig. 7), we found that eq. (7) fitted the experimental data very well, and the coefficients of correlation for the linear regression were 0.999, 0.992, 0.977, and 0.978 for composites filled with SiC, graphite, wollastonite, and mica power separately. Furthermore, the parameter  $C_f$  was independent of the unit used, as can be seen in Table III.

### CONCLUSIONS

The experimental data and Maxwell's equation showed that the thermal conductivity of the composites would not increase remarkably with higher thermal conductivity of the fillers when the thermal conductivity of the fillers was greater than 100 times that of the polymer. Thus, for the composites with large  $k_f/k_m$ , it was efficient to enhance the thermal conductivity with large-aspect-ratio fillers, especially at low volume contents. The thermal conductivity of PMVE filled with 74- $\mu m$  SiC was higher than that of PMVE filled with 0.5- $\mu m$  SiC because of the fewer thermal junctions, which reduced the interfacial phonon scattering, and the higher real particle density along the heat flow paths. A PMVE composite with thermal conductivity of 0.903 W/mK was fabricated with 25 vol % flocculent graphite filler.

A modified form of Agari's equation has been proposed in which the effects of fillers on the crystallinity and the crystal size of the polymer are neglected, and it is expected to be adoptable to noncrystal poly-

mer-matrix composites. It fitted the experimental data in this study well. Most importantly, the parameter  $C_f$  in the modified form of Agari's equation is independent of the unit used, and this overcomes the disadvantage of Agari's equation and makes it possible to compare the effectiveness of different fillers in different matrices.

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