Thermal Conductivity of a Polymer Filled with Particles in the Wide Range from Low to Super-High Volume Content

Y. AGARI, A. UEDA, M. TANAKA, and S. NAGAI, *Osaka Municipal Technical Research Institute, 6-50, 1-Chome, Morinomiya, Joto-ku, Osaka, 536, Japan*

Synopsis

Polyethylene and polystyrene composites filled with high-volume content of filler particles (quartz or Al_2O_3) were prepared by ordinary melt-casting method to effectively increase the thermal conductivity. The result, however, suggested that fractional void volume essentially occupied by filler particles is left unfilled when high or super-high content of filler is used. After investigating the relation between the mixing ratio of different sized filler particles and the fractional voidage under various compression intensities, a mixture of filler was found to give minimum fractional voidage. Polymers filled with such an optimum mixture of fillers for minimum fractional voidage were then prepared under compression. Thus, expected monotonous increases in thermal conductivity in the wide range from low to super-high filler content were obtained. Further, it was confirmed that a predictive model proposed by us agreed quite satisfactorily with the experimental data in comparison with many other models.

INTRODUCTION

Many reports[1-12] have been published on the improvement of thermal conductivity of a polymer by filling with various types of particles, and several thermal conduction models have been proposed for two-phase systems. Most of them, however, discussed the thermal conductivity of a polymer filled with less than 30% volume content of particles, but few[13] discussed the case of high or super-high volume content (larger than 30 vol %). Thermal conduction systems containing such a high or super-high volume of particles are "attached" systems in which particles interact with each other and affect the position of particles in a composite. Therefore, it is considered that the powdery properties of particles (the ease of forming an aggregate of particles, limit of packing, etc.) greatly affect the thermal conductivity of the composite.

In this study, we measured the apparent density of particles in the powder under different pressures, and calculated the fractional voidage (FV), which is related to "critical particle volume content (CPVC), the highest volume content of particles necessary to fill a polymer matrix. By taking account of the effect of the fractional voidage on thermal conductivity of a composite, we obtained a composite with super-high volume content of particles. In previous reports,[11,12] thermal conduction models proposed by Maxwell and Eucken, Bruggeman, Nielsen, Cheng and Hochen, and ourselves, were discussed, focusing on of 0–10 vol % (low) or 10–30 vol % (medium) content of filler particles.

Journal of Applied Polymer Science, Vol. 40, 929–941 (1990)
 CCC 0021-8995/90/5-60929-13$04.00

TABLE I
Properties of Materials

	Particle size[c] (μm)	Thermal conductivity (cal/s cm °C)
Polyethylene[a]	10	6.8×10^{-4}
Polystyrene[b]	36	3.9×10^{-4}
Quartz	16	Parallel to c-axis 2.3×10^{-2} d
	156	Vertical to c-axis 1.4×10^{-2} d
Al_2O_3	9	8.0×10^{-2} d
	65	

[a] MW = 5000.
[b] ρ = 167 cP (200 °C).
[c] Average value.
[d] Reference values to TPRC data.[14]

Therefore, this report, discusses application of these models to experimental data up to the region of 30–60 vol % (high) or larger than 60 vol % (super-high).

EXPERIMENTAL

Materials

As materials for polymer matrix, low-molecular-weight polyethylene and polystyrene were used. As filler particles, quartz and Al_2O_3, with different par-

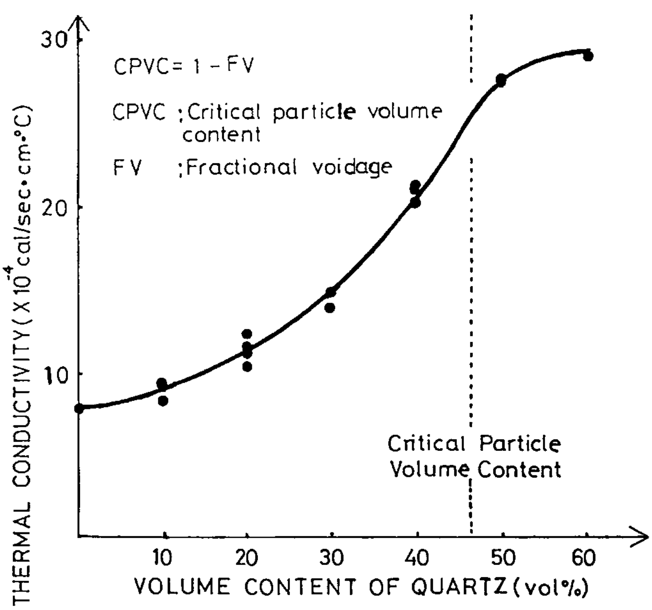

Fig. 1. Thermal conductivity of polyethylene filled with quartz (156 μm).

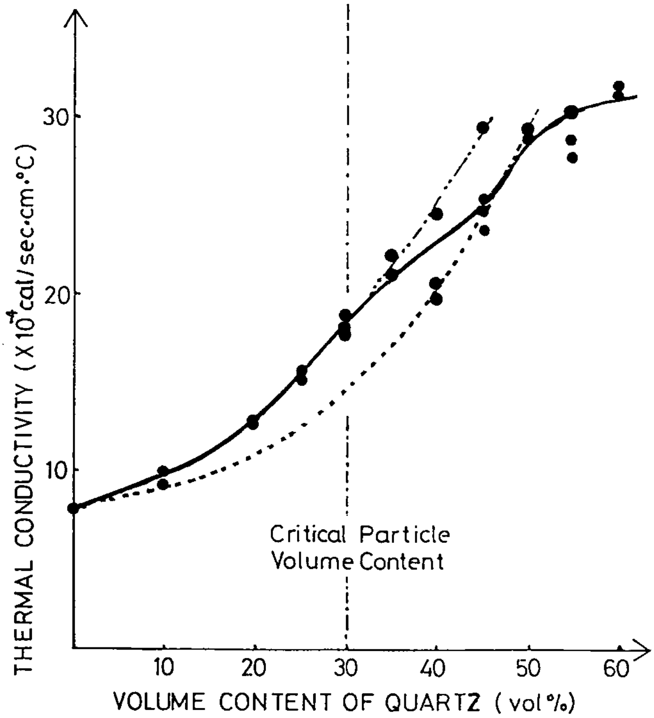

Fig. 2. Thermal conductivity of polyethylene filled with quartz (16 μm).

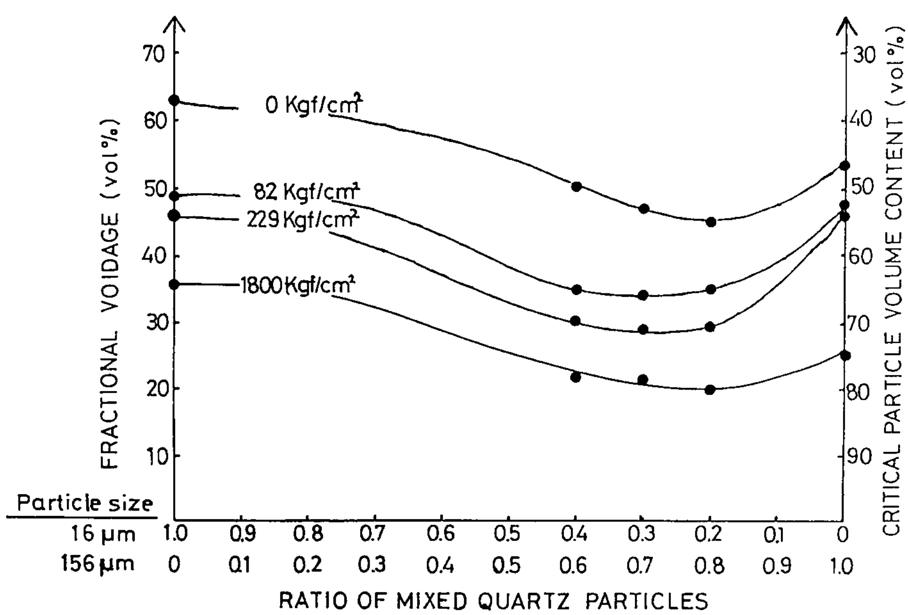

Fig. 3. Fractional voidage of mixtures of quartz under compression.

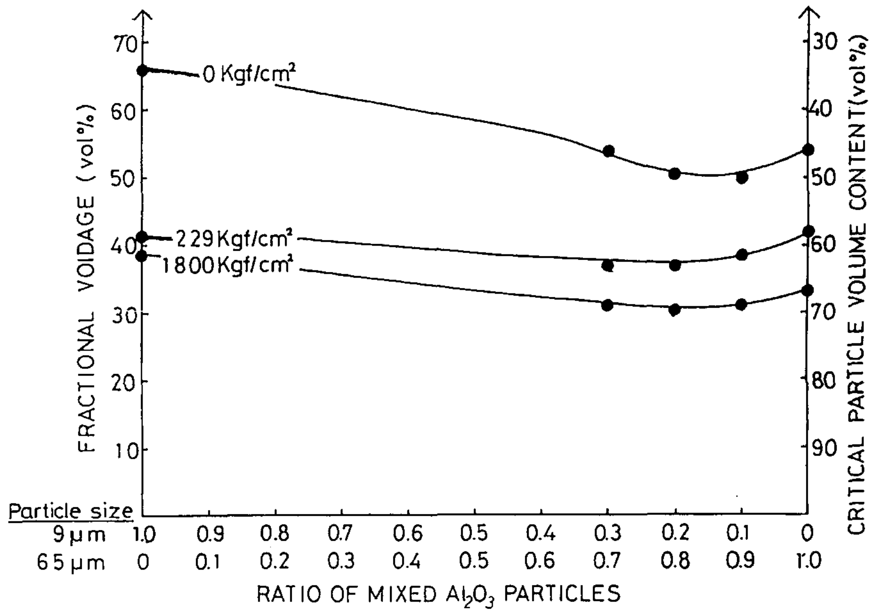

Fig. 4. Fractional voidage of mixtures of Al_2O_3 under compression.

ticle sizes, were selected. The properties of the materials utilized are shown in Table I.

Preparation of Test Specimens

Test specimens were prepared by two methods: melt-casting; compression molding of a mixture of polymer matrix (powdery state) and filler particles. The filler content was varied from 10 to 80 vol %.

Measurement

Thermal conductivity. Measurement of thermal conductivity was performed by utilizing the Dynatech thermal conductance tester Model TCHM-DV, which is based on the comparison method. The standard specimen is made of Pyrex glass. The size of the specimen is 50 mm diameter and 5 mm thickness. All measurements were performed at 50 ± 3°C.

Fractional voidage of particles. A constant weight of filler particles was charged into a steel cylinder (50 mmϕ, 50 mm depth), equipped with a piston, and was compressed under various pressures. Apparent volume occupied by particles under each pressure was determined by measuring the displacement of the piston, and the fractional voidage (FV) at each pressure was calculated.

RESULTS AND DISCUSSION

1. Thermal conductivities of melt-cast polyethylene filled with quartz. Thermal conductivities of melt-cast polyethylene filled with various volume contents of quartz (av particle size 156 μm and 16 μm) are indicated,

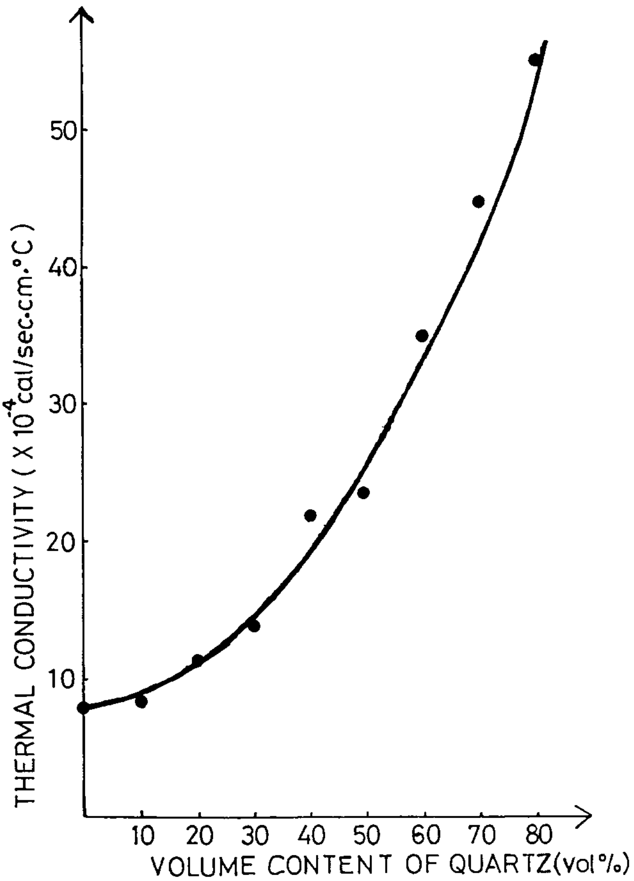

Fig. 5. Thermal conductivity of polyethylene filled with the mixture of quartz (156 : 16 μm = 8 : 2).

respectively, in Figures 1 and 2. In the larger particle system (Fig. 1), thermal conductivity increased monotonously in the range of filler content up to 50 vol %, but, it did not change further. Here, FV is considered to affect the packing limit of filler particles. Experimentally determined FV under atmospheric pressure was 52 vol %. This means that the critical particle volume content (CPVC) is 48 vol %.

$$CPVC = 1 - FV \qquad (1)$$

Thus, any melt-cast composite filled with this quartz will remain void if the matrix does not equal or exceed FV. Therefore, the saturation observed in the curve above 48 vol % of filler content in Figure 1 suggests the inclusion of voids, i.e., polymer matrix needs to be larger than 52 vol %.

In the smaller quartz particle system (Fig. 2), thermal conductivity increased monotonously, and after reaching an inflection point around 35 vol %, varied widely and reached a saturated value at 50 vol % of filler. Since this system is composed of filler particles of quartz as fine as 16 μm, the particles seem to

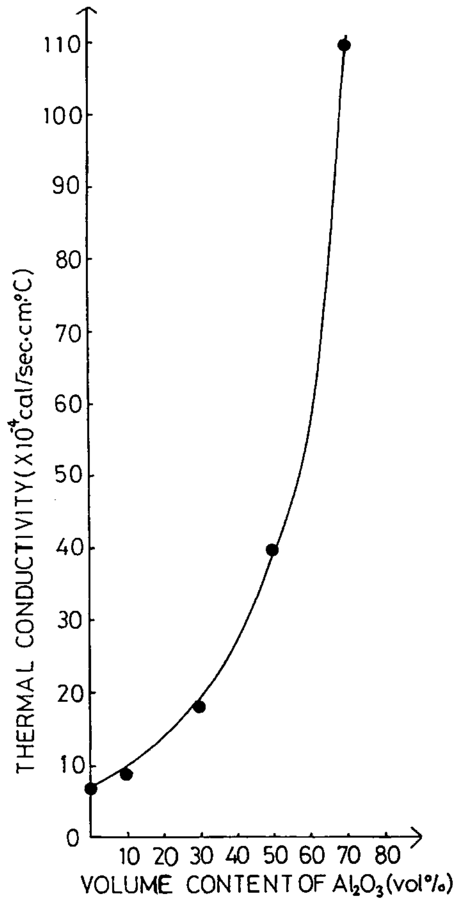

Fig. 6. Thermal conductivity of polyethylene filled with the mixture of Al_2O_3.

form many aggregates in the composite. The fact that the position of the curve of this fine filler system (——) is higher than the larger particle system (---) suggests that network structures made of the aggregates effectively increase the thermal conductivity until the filler content reaches its CPVC, which was determined as 37 vol %. However, when the filler content exceeds CPVC, the aggregate may easily be broken by a rather small force such as pressure or shear applied during the preparation of specimens. Finally, such a break down process would not occur so easily when the filler content reaches the limit of packing (48 vol %), where the curve shows a plateau.

2. Fractional voidages of the mixed fillers of different sizes. Since the results mentioned above suggest that FV of filler particles plays an important role in the composite with super-high filler content, we tried to prepare filler particles with smaller FV, by mixing two kinds of fillers of different particle sizes. Thus, mixtures of various ratios of quartz with average particle sizes of 156 μm and 16 μm were prepared. The FV was measured on each mixture under compression. As shown in Figure 3, FV became minimum (20 vol %) at a filler ratio (156 : 16 μm = 8 : 2) under 1800 kg/cm^2.

TABLE II
Difference in Percent Between Calculated and Measured Thermal Conductivity of Polyethylene Filled with Quartz

	Volume content of particles	Maxwell–Eucken model	Bruggeman model	Cheng–Vochen model	Nielsen model	Model proposed by us
Using 2.3×10^{-2}	10	11.7	12.8	32.3	12.0	11.0
cal/s cm °C	20	−0.6	6.7	26.5	−0.9	1.4
for quartz	30	1.2	23.4	37.7	8.1	7.8
	40	−11.0	18.9	33.2	2.7	−3.9
	50	−1.6	52.2	79.1	52.2	7.8
	60	−8.2	57.2	45.0	107.1	−1.0
	70	−2.6	81.2	> 200.0	> 200.0	−1.3
(Fig. 7)	80	−14.9	117.6	> 200.0	> 200.0	1.7
Using 1.4×10^{-2}	10	1.7	10.2	26.5	2.6	11.0
cal/s cm °C	20	−4.7	3.7	19.7	−3.5	1.4
for quartz	30	−0.6	14.6	31.1	4.3	7.8
	40	−1.6	8.1	20.4	0.9	−3.9
	50	−9.1	25.2	47.4	28.9	7.8
	60	−16.0	22.8	90.4	93.7	−1.0
	70	−10.2	33.8	> 200.0	> 200.0	−1.3
(Fig. 8)	80	2.3	44.7	> 200.0	> 200.0	1.7

Similarly, FVs of the mixtures of Al_2O_3 (65 μm and 9 μm) were measured, and a minimum (30 vol %) at a ratio (65 : 9 μm = 8 : 2) was found (Fig. 4). Therefore, it is expected that a void-free polymer composite filled with the mixture of quartz (156 : 16 μm = 8 : 2) up to 80 vol % and that of Al_2O_3 (65 : 9 μm = 8 : 2) up to 70 vol % can be prepared by compression molding.

3. Thermal conductivity of polyethylene filled with quartz or Al_2O_3 by the compression molding method. Figures 5 and 6 show the thermal

TABLE III
Difference in Percent Between Calculated and Measured Thermal Conductivity

	Volume content of particles	Maxwell–Eucken model	Bruggeman model	Cheng–Vochen model	Nielsen model	Model proposed by us
PS–SiO_2 (using 2.3	30	−30.1	−12.5	−8.6	−29.5	1.3
$\times 10^{-2}$ cal/s cm	50	−45.7	−7.0	−3.0	−14.6	−8.8
°C for quartz)	70	−39.3	46.8	> 200.0	> 200.0	14.5
(Fig. 9)						
PS–SiO_2 (using 1.4	30	−30.1	−15.4	−8.9	−29.5	1.3
$\times 10^{-2}$ cal/s cm	50	−48.0	−21.5	−12.1	−24.1	−8.8
°C for quartz)	70	−42.7	9.9	> 200.0	> 200.0	14.5
(Fig. 10)						
PE–Al_2O_3	10	−2.6	0.7	16.0	5.0	1.0
	30	−18.5	1.6	6.7	15.8	0.7
	50	−28.9	23.1	23.1	9.2	4.5
(Fig. 11)	70	−22.6	99.1	> 200.0	> 200.0	6.0

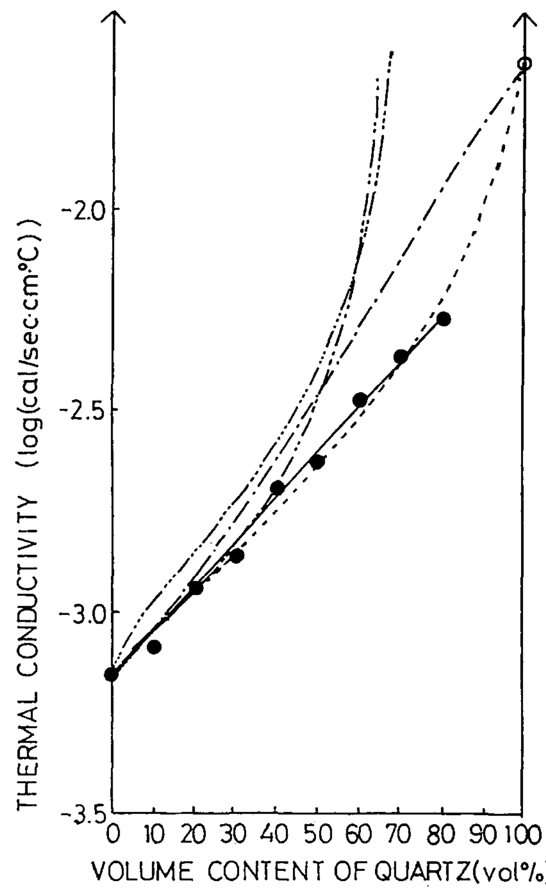

Fig. 7. Thermal conductivity of polyethylene filled with quartz (using 2.3×10^{-2} cal/s cm °C; 156 : 16 μm = 8 : 2); (●) experimental data; (——) predicted curve in our study; (-------) Maxwell–Eucken curve; (-·-·-·-) Bruggeman curve; (-·····-) Nielsen curve; (-·······-) Cheng–Vochen curve.

conductivities of polyethylene filled, respectively, with mixtures of quartz (156 : 16 μm = 8 : 2) and Al_2O_3 (65 : 9 μm = 8 : 2). As was expected above, thermal conductivity increased monotonously until the filler content reached 80 vol % (Fig. 5) and 70 vol % (Fig. 6), respectively. This means that the thermal conductivity of a void-free composite has been primarily measured up to super-high volume content of filler particles.

APPLICATION OF VARIOUS MODELS TO EXPERIMENTAL DATA

Numerous theoretical and empirical models[2,7–12] have been proposed to predict the effective thermal conductivity in a two-phase system. Recently, in the regions of low (0–10 vol %) and medium (10–30 vol %) volume content, some reports studied Nielsen[4,5] and Cheng–Vochen[1] models. Our previous reports[11,12] also discussed equations (3)–(7), proposed, respectively, by Maxwell and

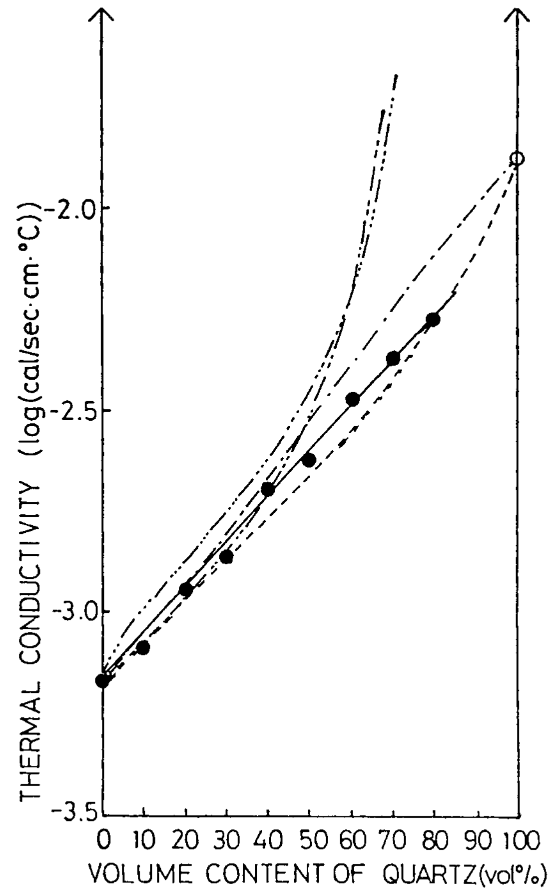

Fig. 8. Thermal conductivity of polyethylene filled with quartz (using 1.4×10^{-2} cal/s cm °C; 156 : 16 μm = 8 : 2); (●) experimental data; (——) predicted curve in our study; (---------) Maxwell-Eucken curve; (– • – • –) Bruggeman curve; (– • • – • • –) Nielsen curve; (– • • • – • • • –) Cheng–Vochen curve.

Eucken, Bruggeman, Nielsen, Cheng and Vochen, and ourselves, where our new semitheoretical model, Eq. (7), showed best agreement with experimental data in the same regions as above. However, there have been only a few reports which discussed the thermal conductivity of polymer composites filled with up to high (30–60 vol %) or super-high (g < 60 vol %) content of filler particles.

In this report, we tried to apply these models, (2)–(6) to the experimental data.

The Maxwell-Eucken equation:

$$\lambda = \frac{2\lambda_1 + \lambda_2 + 2V(\lambda_2 - \lambda_1)}{2\lambda_1 + \lambda_2 - V(\lambda_2 - \lambda_1)}\lambda_1 \tag{2}$$

Bruggeman's equation:

$$1 - V = \frac{\lambda_1 - \lambda}{\lambda_2 - \lambda_1}\left(\frac{\lambda_1}{\lambda}\right)^{1/3} \tag{3}$$

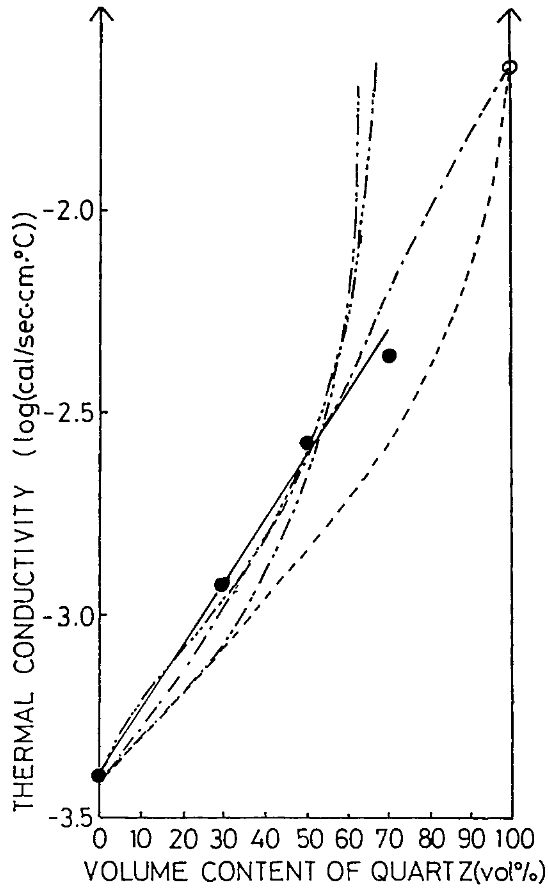

Fig. 9. Thermal conductivity of polystyrene filled with quartz (using 2.3×10^{-2} cal/s cm °C; 156 : 16 μm = 8 : 2); (●) experimental data; (——) predicted curve in our study; (------) Maxwell–Eucken curve; (–·–·–·–) Bruggeman curve; (–··–··–) Nielsen curve; (–···–···–) Cheng–Vochen curve.

The Cheng–Vochen equation:

$$\frac{1}{\lambda} = \frac{1-B}{\lambda_1} + \frac{1}{\{C(\lambda_2-\lambda_1)[\lambda_1 + B(\lambda_2-\lambda_1)]\}^{1/2}} \times \ln\frac{[\lambda_1 + B(\lambda_2-\lambda_1)]^{1/2} + B/2[C(\lambda_2-\lambda_1)]^{1/2}}{[\lambda_1 + B(\lambda_2-\lambda_1)]^{1/2} - B/2[C(\lambda_2-\lambda_1)]^{1/2}} \quad (4)$$

$$B = \left(\frac{3V}{2}\right)^{1/2}, \qquad C = \left(\frac{2}{3V}\right)^{1/2}$$

Nielsen's equation:

$$\lambda = \frac{1+ABV}{1-B\psi V}, \qquad B = \frac{\lambda_2/\lambda_1 - 1}{\lambda_2/\lambda_1 + A}, \qquad \psi = 1 + \frac{V(1-\phi m)}{\phi m} \quad (5)$$

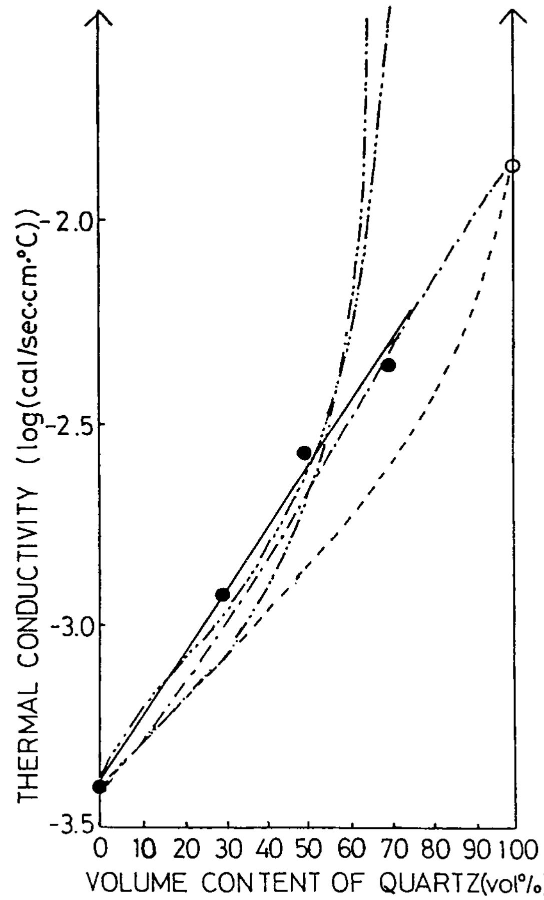

Fig. 10. Thermal conductivity of polystyrene filled with quartz (using 1.4×10^{-2} cal/s cm °C; 156 : 16 μm = 8 : 2); (●) experimental data; (——) predicted curve in our study; (-------) Maxwell-Eucken curve; (–·–·–·–) Bruggeman curve; (–···–··–) Nielsen curve; (–·······–) Cheng-Vochen curve.

A, ϕm = coefficients of particle size and shape.

Equation proposed by us:

$$\log \lambda = VC_2 \log \lambda_2 + (1 - V)\log(C_1\lambda_1) \quad (6)$$

where C_1 = factor of the effect on crystallinity and crystal size of polymer and C_2 = factor of ease in forming conductive chains of particles.

Throughout eqs. (3)–(6), λ = thermal conductivity of a composite, λ_1 = thermal conductivity of a polymer, λ_2 = thermal conductivity of particles, and V = volume content of particles.

In Figures 7–11, logarithms of experimental data of the thermal conductivities and those of the values predicted by those models, are plotted against a wide range of filler content. Comparisons of experimental data with the predicted values by these models were investigated from low (0–10), through medium (10–30), and high (30–60), to super-high (> 60) volume content in Tables II

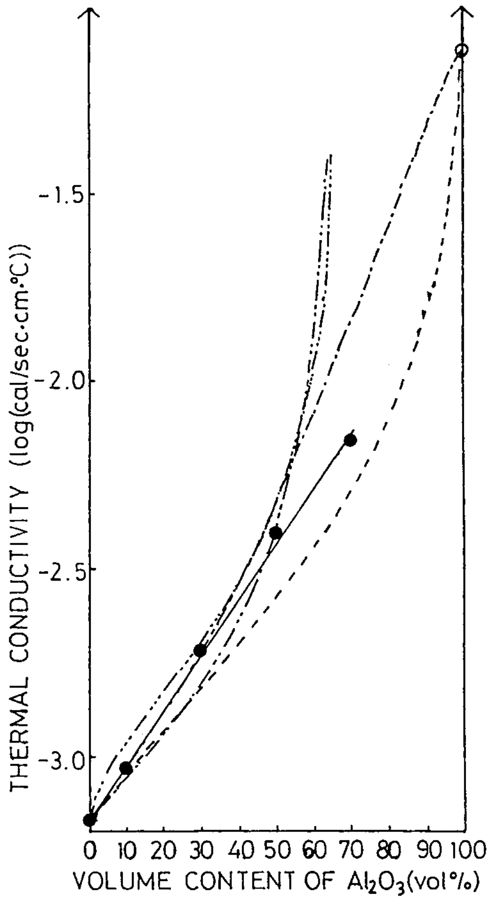

Fig. 11. Thermal conductivity of polyethylene filled with Al_2O_3 (65 : 9 μm = 8 : 2); (●) experimental data; (——) predicted curve in our study; (---------) Maxwell–Eucken curve; (-·-·-·-) Bruggeman curve; (-··-··-) Nielsen curve; (-···-···-) Cheng–Vochen curve.

and III. Equation (2) predicts well only the polyethylene–quartz system (Figs. 7 and 8), while Eq. (3) shows good agreement with experimental data only in the polystyrene–quartz system (Figs. 9 and 10). Neither Eq. (4) nor (5) can fit the experimental data in any system. It is clearly demonstrated that the

TABLE IV
Factors of C_1 and C_2

	Used values for quartz (cal/s cm °C)	C_1	C_2
PE–SiO_2	2.3×10^{-2}	1.00	1.26
PE–SiO_2	1.4×10^{-2}	1.00	1.11
PS–SiO_2	2.3×10^{-2}	1.06	1.12
PS–SiO_2	1.4×10^{-2}	1.06	1.01
PE–Al_2O_3	—	1.03	1.53

predicted values of Eq. (6) perfectly agree with the experimental data for a wide range from low to super-high volume content (Fig. 11).

Values of coefficients C_1 and C_2 in Eq. (6), indicated in Table IV, were calculated by the experimental data and all values of C_1 are approximately 1. Hence, the secondary structure of these polymers seems to be unaffected by these particles. Each system showed a different value of C_2. The value of C_2 may be affected not only by the ease in forming conductive chains of particles, but also by thermal contact resistance between polymer and particles. However, these effects on C_2 values could not be estimated.

CONCLUSION

A polymer–filler system with up to super-high volume content of filler particles without voids has been prepared. The model proposed by us for a two-phase system was found to agree with the experimental data and can be applied quite satisfactorily for low to super-high filler content.

References

1. D. W. Sundsrom and Y. D. Lee, *J. Appl. Polym. Sci.,* **16,** 3159 (1972).
2. L. E. Nielsen, *J. Appl. Polym. Sci.,* **17,** 3819 (1973).
3. R. P. Kusy and R. D. Corneliussen, *Polym. Eng. Sci.,* **15,** 107 (1975).
4. D. M. Bigg, *Polym. Eng. Sci.,* **19,** 1188 (1973).
5. D. M. Bigg, *Polym. Composites,* **7,** 125 (1986).
6. E. Yamada, K. Takahashi, and T. Ota, First Jpn. Symp. Thermophysical Properties, 1980, p. 129.
7. A. Eucken, Fortchg. Gebiete Ingenieurw., B3, *Forschungsheft,* **353,** 16 (1932).
8. D. A. Bruggeman, *Ann. Phys.,* **24,** 636 (1935).
9. S. C. Cheng and R. I. Vachon, *Int. J. Heat Mass Transfer,* **12,** 249 (1969).
10. R. M. Scarisbrick, *J. Phys.,* **D6,** 2098 (1973).
11. Y. Agari and T. Uno, *J. Appl. Polym. Sci.,* **30,** 2225 (1985).
12. Y. Agari, M. Tanaka, S. Nagai, and T. Uno, *J. Appl. Polym. Sci.,* **32,** 5705 (1986).
13. K. Hani, T. Takei, and M. Kodama, *Polym. Preprint Japan,* **33**(4), 798 (1984).
14. Y. S. Touloukian, Ed., *Thermophysical Properties of Matter.* IFI/Plenum, New York, 1970, Vol. 1.

Received October 22, 1988
Accepted June 8, 1989