

# Estimation on Thermal Conductivities of Filled Polymers

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## Synopsis

A new thermal conduction model is proposed for filled polymer with particles, and predicted values by the new model are compared with experimental data. The model is fundamentally based on a generalization of parallel and series conduction models of composite, and further modified in taking into account that a random dispersion system is isotropic in thermal conduction. The following equation is derived from the new model;  $\log \lambda = V \cdot C_2 \cdot \log \lambda_2 + (1 - V) \cdot \log(C_1 \cdot \lambda_1)$ . Therefore, when thermal conductivities of polymer and particles ( $\lambda_1, \lambda_2$ ) are known, thermal conductivity of the filled polymer ( $\lambda$ ) can be estimated by the equation, with any volume content of particles ( $V$ ). The new model was proved by experimental data for filled polyethylene, polystyrene and polyamide with graphite, copper, or  $\text{Al}_2\text{O}_3$ .

## INTRODUCTION

There have been many reports that thermal conductivity of polymers was improved by filling with various types of particles and a thermal conduction model was proposed for two-phase systems.<sup>1-4</sup> But, in the previous report, it was reported that thermal conductivity predicted by several thermal conduction models has not fully agreed with experimental data at more than 10 vol % of particles for polyethylene and poly(vinyl chloride) filled with carbon black or graphite. Because the quantity of conductive chains to be formed by gathering of particles has been known to increase rapidly at about 10 vol % and cause a difference between predicted values and experimental data, we proposed a model for thermal conduction of two-phase systems, considering the effect of formed conductive chains. Values predicted by the model agreed with experimental data to high volume content, but did not agree at the region from 10 to 20 vol %.

In this study, we will propose a new model for thermal conduction of two-phase systems on the basis of another idea to predict thermal conductivity even at the region from 10 to 20 vol %, and compare measured thermal conductivity data with values predicted by the new model. We will discuss application of the new model in general.

## EXPERIMENTAL

### Preparation

Test specimens were prepared by mixing molten polyethylene, polyamide, or polystyrene with various contents of graphite, copper, or aluminum oxide under reduced pressure. The properties of materials utilized are shown in Table I.

TABLE I  
 Properties of Materials

Material	Density <sup>d</sup> (g/cm <sup>3</sup> )	Thermal conductivity (cal/sec cm °C)	Electric conductivity (Ω <sup>-1</sup> cm <sup>-1</sup> )
Polyethylene <sup>a</sup>	0.938	$6.96 \times 10^{-4}$	$2.5 \times 10^{-16}$
Polyamide <sup>b</sup>	0.975	$4.60 \times 10^{-4}$	$3.7 \times 10^{-16}$
Polystyrene <sup>c</sup>	1.065	$3.33 \times 10^{-4}$	$1.5 \times 10^{-16}$
Graphite	2.307	0.5 <sup>e</sup>	$1.4-2 \times 10^3$
Copper	8.94	0.946 <sup>e</sup>	$5.98 \times 10^2$
Al <sub>2</sub> O <sub>3</sub>	3.751	$7.91 \times 10^{-2e}$	—

<sup>a</sup>MW = 5000.

<sup>b</sup> $\rho = 255$  cP (200°C).

<sup>c</sup> $\rho = 167$  cP (200°C).

<sup>d</sup>Obtained by the air-comparison method.

<sup>e</sup>Cited by "Thermophysical Properties of Matter."

### Measurement

Measurements of thermal conductivities were performed by utilizing the Dynatech thermal conductance tester Model TCHM-DV. The Dynatech thermal conductance tester is based on the comparison method. The standard specimen is made of Pyrex glass. The size of the specimen is 50 mm in diameter and 5 mm in thickness. The measurements were performed at 50°C.

Electric conductivity of the same specimen that was used for the measurements of thermal conductivity was measured. Electric conductivity of high-resistivity material was calculated by measuring the current yielded when voltage of 500 VDC is applied, while for low-resistivity material, voltage of 10 VDC is applied. The temperature for measurement was  $23 \pm 2^\circ\text{C}$  and the relative humidity was  $50 \pm 5\%$ .

## RESULTS AND DISCUSSION

### Thermal Conductivities of Polymers Filled with Graphite

Thermal and electric conductivities of polyethylene, polyamide, and polystyrene filled with various contents of graphite are indicated in Figure 1. The electric conductivities of polyethylene and polystyrene begin to increase rapidly around the point where graphite accounts for, 10% in volume, indicating that many graphite particles touch each other to begin to form graphite conductive chains which may connect one electrode with the other. However, electric conductivity of polyamide seems to begin to form graphite conductive chains around the point of 8% in volume content of graphite. The following explanation for this phenomenon is possible: Molten polyamide can break aggregate of graphite less efficiently than the other polymers. Consequently, some graphite aggregates remained in the polyamide and act as conductive chains.

### Thermal Conductivities of Polyethylene Filled with Particles

Thermal and electric conductivities of polyethylene filled with various volume contents of particles of graphite, copper, or aluminum oxide are

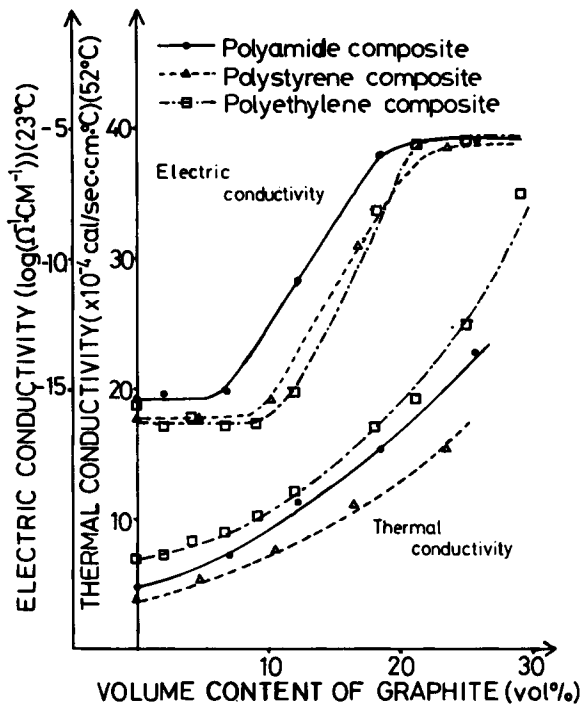


Fig. 1. Thermal and electric conductivities of polyethylene, polyamide and polystyrene filled with graphite.

indicated in Figure 2. Both electric conductivities of polyethylene filled with copper and graphite begin to increase rapidly around the point where particle accounts for 10% in volume, and particle conductive chains in both the systems seem to increase analogously as volume contents of particles. Consequently, it seems that differences between the thermal conductivities of those polyethylenes are caused by differences between thermal conductivities of copper and graphite.

#### Conduction Models

There are many types of composition systems in which a polymer is filled with particles. In those systems, thermal conductivity of composite is the highest, in the event that the formed conductive block which all particles are gathered to form and the block of polymer are arranged in parallel in the direction of thermal flux (parallel conduction), and is the lowest in the case of those blocks which are arranged in series in the direction of thermal flux (series conduction) (Fig. 3). Thermal conductivities of composites in parallel and series conduction can be estimated respectively by the following equations.

*Parallel conduction:*

$$\lambda = V \cdot \lambda_2 + (1 - V) \cdot \lambda_1 \quad (1)$$

*Series conduction:*

$$1/\lambda = V/\lambda_2 + (1 - V)/\lambda_1 \quad (2)$$

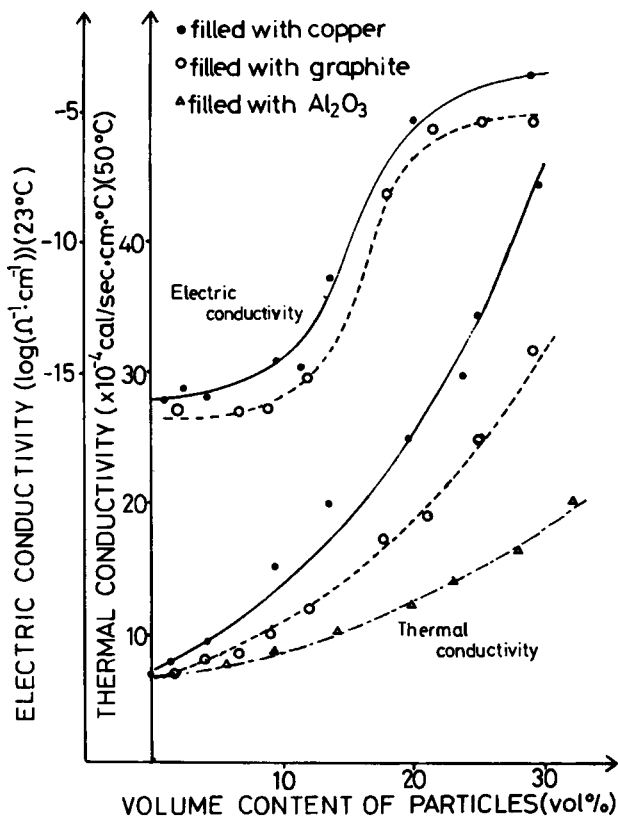


Fig. 2. Thermal and electric conductivities of polyethylene filled with particles.

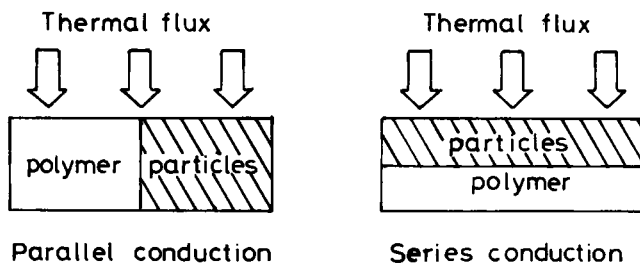


Fig. 3. Conduction models.

where  $\lambda$  = thermal conductivity of composite,  $\lambda_1$  = thermal conductivity of polymer,  $\lambda_2$  = thermal conductivity of particles, and  $V$  = volume content of particles. We assume a generalization of eqs. (1) and (2) to the following eq. (3). Where, if  $n = 1$  or  $-1$ , eq. (3) corresponds to eq. (1) or (2).  $n$  is smaller than 1 and larger than  $-1$ ,

$$\lambda^n = V \cdot (\lambda_2)^n + (1 - V) \cdot (\lambda_1)^n \quad (3)$$

Because eq. (3) is formed on the basis of the assumption that all phases (particles, matrix, and composite) have continuous forms, thermal conductiv-

ity of particles seemed to contribute to change to that of composite as much as that of matrix. However, because few particles contribute to form conductive chains in the dispersion system, the thermal conductivity of particles seemed to contribute to change to that of composite less than that of matrix. Therefore, index ( $n$ ) is replaced by index ( $C_2 \cdot n$ ) and eq. (3) is converted into eq. (4)

$$\lambda^n = V \cdot (\lambda_2)^{C_2 \cdot n} + (1 - V) \cdot (\lambda_1)^n \quad (4)$$

where  $C_2$  is a factor of ease in forming conductive chains of particles and is smaller than 1 and larger than 0. The more easily particles are gathered to form conductive chains, the more thermal conductivity of particles contributes to change to that of composite. Therefore,  $C_2$  becomes closer to 1. It has been reported that, in the preparation of a composite, particles can effect crystallinity and crystal size of polymer, and change the thermal conductivity of polymer.<sup>5,6</sup> This effect is taken into consideration and  $\lambda_1$  is replaced by  $C_1 \cdot \lambda_1$ . Therefore, eq. (4) is converted into

$$\lambda^n = V \cdot (\lambda_2)^{C_2 \cdot n} + (1 - V) \cdot (C_1 \cdot \lambda_1)^n \quad (5)$$

If the dispersion state can be made uniform,  $n$  can be assumed to be in the neighborhood of 0, and  $\lambda^n$  may be approximated by  $1 + n \cdot \log \lambda$ .

Consequently, eq. (5) can be converted into the following equation:

$$\log \lambda = V \cdot C_2 \cdot \log \lambda_2 + (1 - V) \cdot \log(C_1 \cdot \lambda_1) \quad (6)$$

#### *Application of the New Model to Experimental Data*

Figures 4 and 5 show the logarithm of the thermal conductivities of the experimental data plotted against the volume contents of particles. All experi-

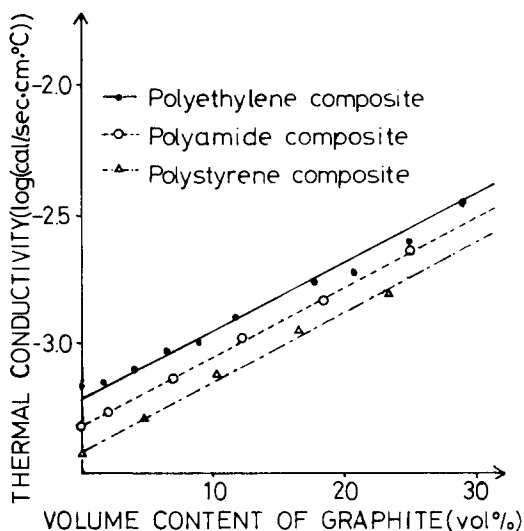


Fig. 4. Thermal conductivity of polyethylene, plyamide and polystyrene filled with graphite.

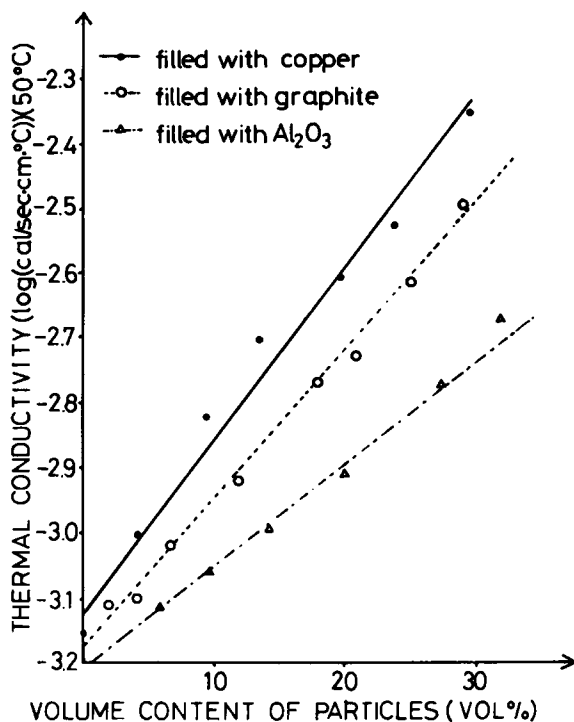


Fig. 5. Thermal conductivity of polyethylene filled with particles.

mental data points are approximately on a straight line. Therefore, the experimental data can be explained by the new model. Values of coefficients  $C_1$  and  $C_2$  are indicated in Table II, calculated by the experimental data. Values of  $C_1$  are almost approximately 1. But,  $C_1$  is less than 1 in the case of polyethylene filled with graphite. It seems reasonable to speculate that the graphite particles may effect the secondary structure of polyethylene and change its thermal conductivity. In the case of a polymer filled with graphite,  $C_2$  becomes smaller in the order of polyamide, polystyrene, polyethylene.  $C_2$  in the case of polyamide is 4.5% larger than that of polyethylene. Electric conductivities of polymer filled with graphite more rapidly increase in the same order. Therefore,  $C_2$  is a larger value in the system where conductive chains begin to increase more rapidly.  $C_2$  of polyethylene filled with various particles was almost the same. Consequently, it is verified that the ease of

TABLE II  
Values of  $C_1$  and  $C_2$

Materials	$C_1$	$C_2$
Polyethylene filled with graphite	0.898	0.882
Polyethylene filled with copper	1.073	0.888
polyethylene filled with Al <sub>2</sub> O <sub>3</sub>	0.859	0.902
Polyamide filled with graphite	1.017	0.922
Polystyrene filled with graphite	1.024	0.892

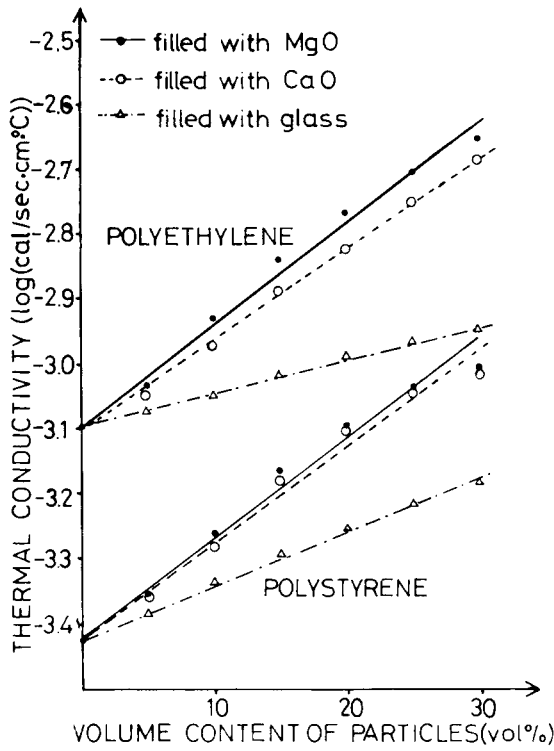


Fig. 6. Thermal conductivity of polyethylene and polystyrene filled with particles.

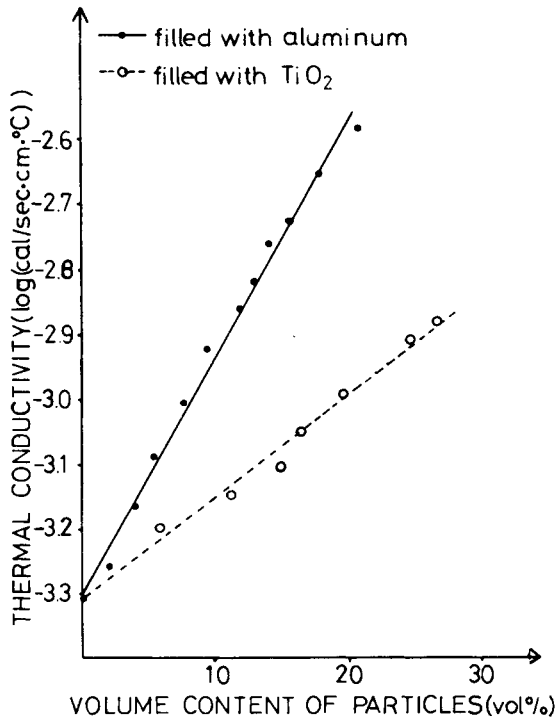


Fig. 7. Thermal conductivity of poly(methyl methacrylate) filled with particles.

particles to form conductive chains increases  $C_2$ , although other factors, which have not been confirmed, may also increase  $C_2$ .

Sundatrom and Lee have reported thermal conductivities of polyethylene and polystyrene filled with glass, MgO, or CaO.<sup>7</sup> Also Yamada and co-workers have reported thermal conductivities of poly(methyl methacrylate) filled with Al or TiO<sub>2</sub>.<sup>8</sup> Those data can also be explained by the new model, as illustrated by Figures 6 and 7.

Consequently, the new thermal conduction model may be applied in general, although more detailed investigation would be necessary in the future, for characterization of those factors  $C_1$  and  $C_2$ .

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