

Thermal Conductivity of a Polymer Composite Filled with Mixtures of Particles

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Synopsis

A new thermal conduction model is proposed for a polymer system filled with a mixture of several types of particles. Predicted values by the new model are compared with experimental data. The model is derived by extending a model that was previously proposed for a two-phase system. The following equation is derived from the new model: $\log \lambda = V \cdot (X_2 \cdot C_2 \cdot \log \lambda_2 + X_3 \cdot C_3 \cdot \log \lambda_3 + (1 - V) \log (C_1 \cdot \lambda_1))$. When the thermal conductivities of polymer and particles ($\lambda_1, \lambda_2, \lambda_3, \dots$) and a mixing ratio of particles (X_2, X_3, \dots) are known, thermal conductivity of the filled polymer (λ) with several types of particles can be estimated from the equation, with any volume content of particles (V). Furthermore, from each polymer-filler composite (two-phase system) data, the thermal conductivity of a composite filled with different filler particles can be estimated.

INTRODUCTION

Many reports¹⁻⁵ 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 particles of one kind, and only a few discussed the thermal conductivity of a polymer filled with mixed particles of different kinds.

In this study, we measured the thermal conductivity of polyethylene filled with a mixture of several types of particles. A new model of thermal conduction is proposed for the composite, and the predicted values are compared with experimental data. The application of the new model in general is discussed.

EXPERIMENTAL

Preparation of Test Specimens

Test specimens were prepared by mixing molten polyethylene under reduced pressure with various amounts of mixtures of (1) graphite and copper, (2) graphite and Al_2O_3 , (3) copper and Al_2O_3 , or (4) graphite, copper, and Al_2O_3 .

The properties of materials utilized are shown in Table I.

TABLE I
Properties of Materials

Material	Density ^a (g/cm ³)	Thermal conductivity (cal/s cm °C)	Average particle size (μm)
Polyethylene ^b	0.938	6.96×10^{-4}	—
Graphite ^c	2.307	0.5	12.0
Copper ^c	8.94	0.946	3.3
Al ₂ O ₃ ^c	3.751	7.91×10^{-2} ^d	18.5

^aObtained by air-comparison method.

^bMW = 5000.

^c≥ 99% purity.

^dRef. 6.

Measurement of 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 in diameter and 5 mm in thickness. All the measurements were performed at 50°C.

Conduction Models

A new model is proposed for multiphase systems, which is an extension of the two-phase model previously reported.⁷

There are many types of composite systems in which a polymer is filled with a mixture of particles. We can assume two extreme model systems. One is a parallel conduction system where all conduction blocks are aligned parallel to the thermal flux as shown in Figure 1 (left). The other one is a series conduction system where all conduction blocks are aligned in series to a thermal flux (Fig. 1, right). Here, each block is assumed to be composed of an ideally accumulated solid of each type of particle (polymer, filler 1, 2, 3, ..., respectively). The thermal conductivity of the composite is considered to be

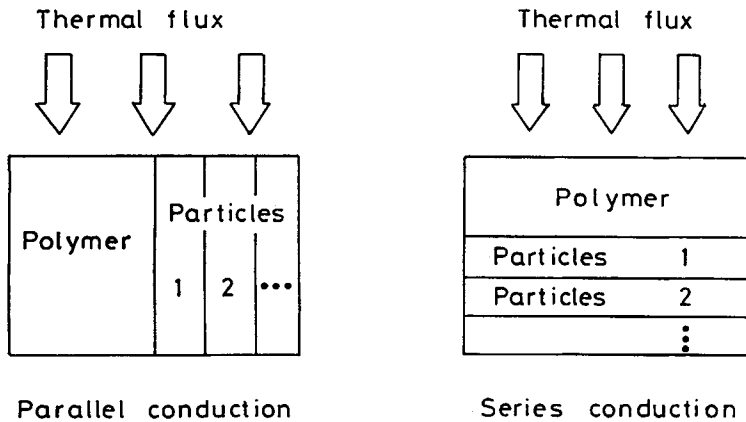


Fig. 1. Thermal conduction model.

the highest in the former model, while the lowest in the latter. The real composite exists in between both models. Thermal conductivities of the composite in parallel and series conduction can be estimated respectively by the following equations:

Parallel conduction:

$$\lambda = V_1 \cdot \lambda_1 + V_2 \cdot \lambda_2 + V_3 \cdot \lambda_3 + \dots \quad (1)$$

Series conduction:

$$1/\lambda = V_1/\lambda_1 + V_2/\lambda_2 + V_3/\lambda_3 + \dots \quad (2)$$

where λ = thermal conductivity of composite, λ_1 = thermal conductivity of polymer, λ_2 = thermal conductivity of particle 1, λ_3 = thermal conductivity of particle 2, V_1 = volume content of polymer, V_2 = volume content of particle 1, and V_3 = volume content of particle 2, with $V_1 + V_2 + V_3 + \dots = 1$. 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 :

$$\lambda^n = V_1 \cdot (\lambda_1)^n + V_2 \cdot (\lambda_2)^n + V_3 \cdot (\lambda_3)^n + \dots \quad (3)$$

Because eq. (3) is formed on the basis of an assumption that all phases (composite, matrix, and particles) have continuous forms, thermal conductivities of both particles and matrix seemed to contribute in an equal manner to that of the composite. However, it is a fact that only a few can participate in forming conductive chains in the dispersion system. Thus, the thermal conductivity of particles should contribute to that of the composite in a lesser degree than that of the matrix. Therefore, index (n) is replaced by index ($C_2 \cdot n$), ($C_3 \cdot n$), \dots and eq. (3) converted into

$$\lambda^n = V_1 \cdot (\lambda_1)^n + V_2 \cdot (\lambda_2)^{C_2 \cdot n} + V_3 \cdot (\lambda_3)^{C_3 \cdot n} + \dots \quad (4)$$

where C_2, C_3, \dots are factors of ease in forming conductive chains of particles, and are 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 the composite, that is, the more closely C_2, C_3, \dots approach 1.

Particle size and interactions of different types of particles may also affect the formation of conductive chains. The smaller the particle size, the larger the particle surface area. Therefore, particles can easily form aggregates and the thermal conductivity of the composite may increase. An interaction of different types of particles can exist and effect the dispersion state in which the thermal conductivity of the composite will change by taking on different values of C_2, C_3, \dots , (e.g., electrostatic repulsion). In the systems in this report, however, no such interaction was observed.

It has been reported that, in the preparation of a composite, particles can effect crystallinity and crystal size of the polymer, and change the thermal conductivity of the polymer.^{7,8} This effect is taken into consideration and λ_1

is replaced by $C_1 \cdot \lambda_1$. Therefore, eq. (4) is converted into

$$\lambda^n = V_1 \cdot (C_1 \cdot \lambda_1)^n + V_2 \cdot (\lambda_2)^{C_2 \cdot n} + V_3 \cdot (\lambda_3)^{C_3 \cdot n} + \dots \quad (5)$$

When the dispersion state is not uniform, the system becomes anisotropic, and its thermal conductivity changes by varying the direction of a thermal flux. If the dispersion state can be made uniform, n can be assumed to be in the median region of 1 and -1 , that is, in the neighborhood of 0, and λ^n may be approximated by $1 + n \cdot \log \lambda$. Therefore, eq. (5) can be converted into

$$\log \lambda = V_1 \cdot \log(C_1 \cdot \lambda_1) + V_2 \cdot C_2 \cdot \log \lambda_2 + V_3 \cdot C_3 \cdot \log \lambda_3 + \dots \quad (6)$$

V_2 and V_3, \dots are replaced respectively by $X_2 \cdot V$ and $X_3 \cdot V$, and eq. (6) becomes

$$\begin{aligned} \log \lambda = V \cdot (X_2 \cdot C_2 \cdot \log \lambda_2 + X_3 \cdot C_3 \cdot \log \lambda_3 + \dots) \\ + (1 - V) \cdot \log(C_1 \cdot \lambda_1) \end{aligned} \quad (7)$$

where $V = V_2 + V_3 + \dots$, $X_2 + X_3 + \dots = 1$, $V_1 = 1 - V$, V is the total content of particles, and X_2, X_3, \dots are mixing ratios of particles. Furthermore, when $X_2 \cdot C_2 \cdot \log \lambda_2 + X_3 \cdot C_3 \cdot \log \lambda_3 + \dots$ is set to P , eq. (7) becomes

$$\log \lambda = V \cdot [P - \log(C_1 \cdot \lambda_1)] - \log(C_1 \cdot \lambda_1) \quad (8)$$

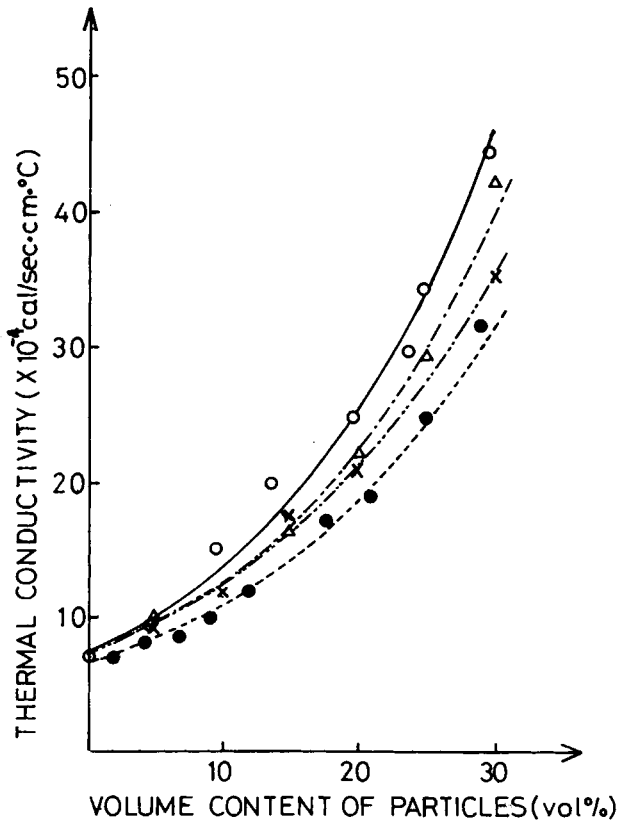


Fig. 2. Thermal conductivity of polyethylene filled with various mixtures of graphite and copper. Cu/C: (○) copper only; (△) 2:1; (×) 1:2; (●) graphite only.

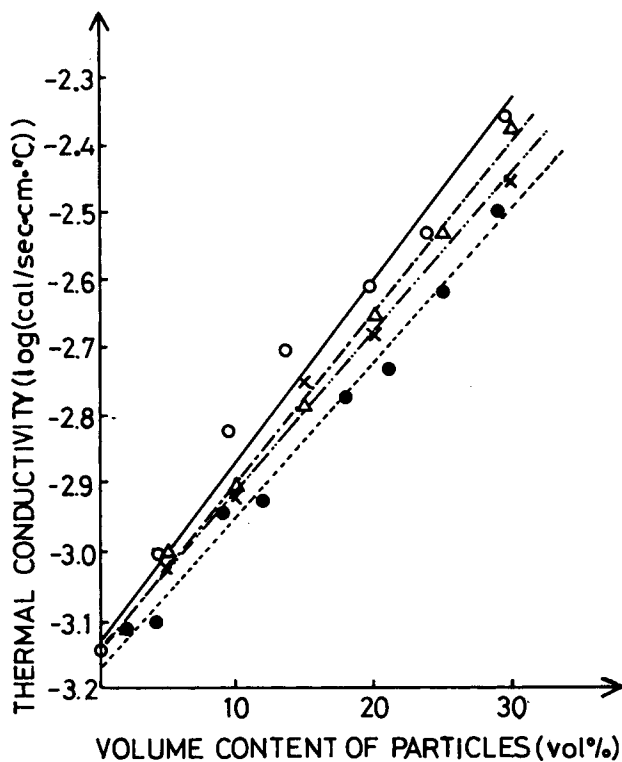


Fig. 3. Logarithms of thermal conductivity of polyethylene filled with various mixtures of graphite and copper. Cu/C: (○) copper only; (Δ) 2 : 1; (×) 1 : 2; (●) graphite only.

RESULTS AND DISCUSSION

Thermal Conductivity of Polyethylene Filled with Graphite-Copper Mixture

Figure 2 shows the thermal conductivities of polyethylene filled with various mixtures of graphite and copper (PE-graphite-Cu) in various proportions. Thermal conductivity of the filled polyethylene increased with increase in the mixing ratio of copper. The logarithms of the thermal conductivities of the experimental data are plotted against volume contents of the mixture of particles in Figure 3. All experimental data points are approximately on a

TABLE II
P Values of Polyethylene Filled with Copper and Graphite

Mixed Ratio Cu : C	P Value		Error (%)
	Predicted	Experimental	
Only	—	3.53	—
2	1	3.39	-1.09
1	2	3.25	-3.28
—	Only	—	3.11

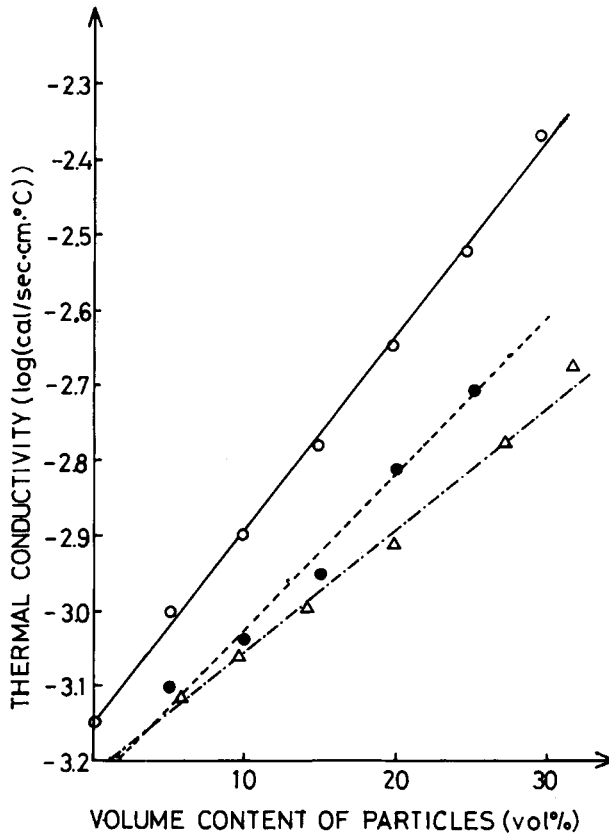


Fig. 4. Logarithm of thermal conductivity of polyethylene filled with a mixture of graphite and Al_2O_3 : (O) copper and graphite (2:1); (●) Al_2O_3 and graphite (2:1); (Δ) Al_2O_3 .

straight line. Therefore, the data can be explained by the new model for a three-phase system.

Because the P value for a three-phase system is expressed as $X_2 \cdot C_2 \cdot \log \lambda_2 + X_3 \cdot C_2 \cdot \log \lambda_3$, it can be estimated from the intercepts and the gradients of two straight lines which are obtained by plotting the logarithms of the thermal conductivities of the respective two-phase systems, that is, the same polymer filled with each one of the same particles as are used in the three-phase system. The estimated P values showed a good coincidence with the experimental data within 3% error in the several ratios of mixtures (C : Cu = 2 : 1 or 1 : 2) (Table II).

Thermal Conductivities of Polyethylenes Filled with Graphite- Al_2O_3 and Copper- Al_2O_3 Mixture

The logarithms of the thermal conductivities of polyethylene filled with various contents of the mixture of graphite and Al_2O_3 (PE-graphite- Al_2O_3) or that of copper and Al_2O_3 (PE-Cu- Al_2O_3) in several proportions, are plotted against volume contents of the mixture of particles in Figures 4 or 5. All data points are approximately on a straight line, proving that thermal conductivity in these three-phase systems can be explained by the new model.

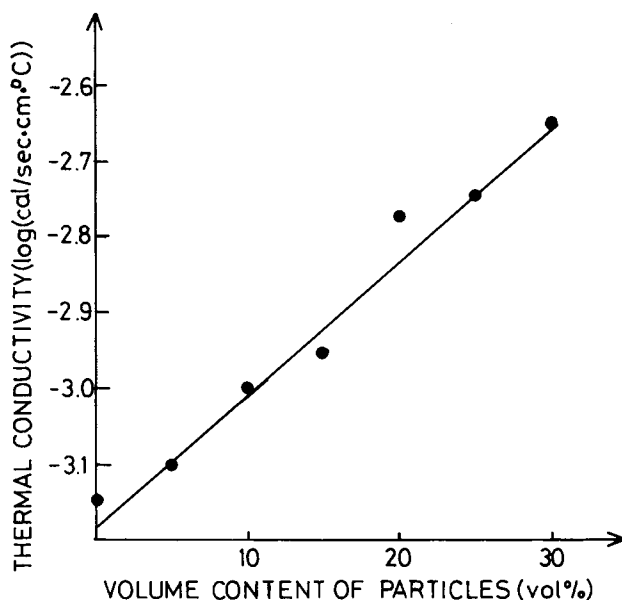


Fig. 5. Logarithm of thermal conductivity of polyethylene filled with a mixture of copper and Al_2O_3 (2:1).

Here, as shown in Figure 4, extrapolation of plots in the PE-Cu-graphite system does agree to the thermal conductivity of polyethylene itself, while the intercept of the PE-graphite- Al_2O_3 system is considerably lower than the original value of polyethylene. The same phenomenon can be observed in the PE- Al_2O_3 system. The above results suggest that C_1 is 1 in eq. (6) for the PE-graphite-Cu system, but it is lower than 1 for PE-graphite- Al_2O_3 or PE- Al_2O_3 . The reason for the latter might be that the presence of Al_2O_3 affects the crystallinity and crystal size of polyethylene resulting in a lower C_1 value.

Estimated P values in these systems were compared with experimental data, and good coincidence was observed between them (Table III). Consequently, thermal conductivity of a polymer filled with particles of two kinds can be predicted by combining thermal conductivities of the same polymer filled with each kind of particles, respectively.

TABLE III
 P Values of polyethylene filled with mixtures of graphite, copper, and Al_2O_3

Particles (Mixed ratio)	P Value		Error (%)
	Predicted	Experimental	
Al_2O_3 and Cu (2:1)	2.81	2.82	0.19
Al_2O_3 and C (2:1)	2.67	2.81	5.26
Al_2O_3 and Cu and C (1:1:1)	3.03	2.76	-8.88
Al_2O_3	—	2.45	—

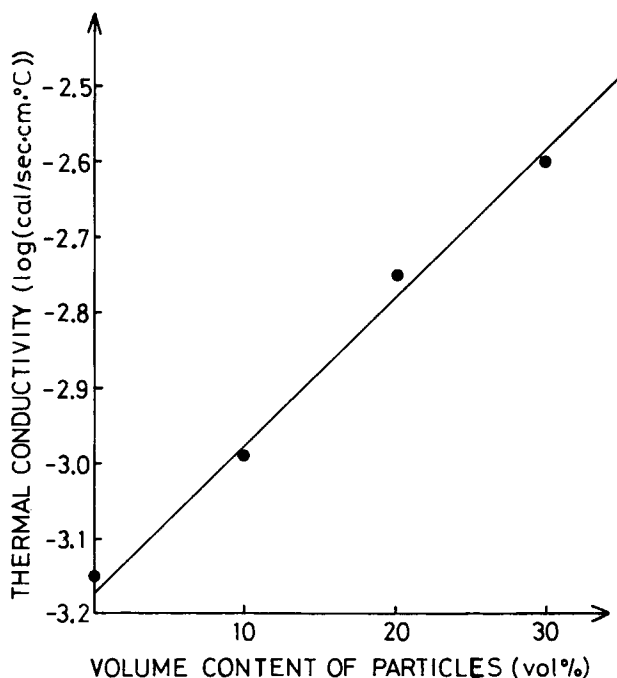


Fig. 6. Logarithm of thermal conductivity of polyethylene filled with a mixture of graphite, copper, and Al_2O_3 .

Thermal Conductivity of Polyethylene Filled with the Mixture of Graphite, Copper, and Al_2O_3

The logarithms of thermal conductivities of polyethylene filled with the mixture of graphite, copper, and Al_2O_3 (PE-graphite-Cu- Al_2O_3) are plotted against volume contents of the mixture of particles as shown in Figure 6. Because all data points are approximately on a straight line, thermal conductivity of the system filled with three types of particles proved to be explainable by the new model. It is considered that C_1 should be relatively small, due to the same effect of Al_2O_3 which decreases the thermal conductivity of polyethylene as observed in the two-phase system.

The estimated P value of the system filled with three kinds of particles was in good agreement with experimental data (Table III).

CONCLUSION

We propose a new model of thermal conduction for a system filled with several types of particles (several phase systems). The predicted values using the new model compare well with experimental data.

The new model may be applied in general to any system filled with several types of particles, although more detailed investigation is necessary on the characterization of factors C_1, C_2, \dots , and the availability of our model to a wide temperature range, and also to a wider filler content range (more than 30%).

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