

# Thermal Conductivities of Composites in Several Types of Dispersion Systems

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## SYNOPSIS

We measured thermal conductivities as well as electric conductivities of some composites in several types of dispersion systems. The dispersion state, that is, the ease in forming conductive chains in these composites, was estimated by the characteristic electric conductivities and compared with the thermal conductivities. Thus, it became clear that thermal conductivity of a composite was significantly affected by the dispersion state in the composite. Further, it was confirmed that the predictive model proposed in the previous report was adaptable to the thermal conductivity of the composites in several types of dispersion systems. It was made clear that the dispersion state of a composite affected the values  $C_1$  and  $C_2$  in the previous model.

## INTRODUCTION

Many reports have been published on the improvement of thermal conductivity of polymer composites.<sup>1-8</sup> Only a few reports, however, discussed the effect of type of dispersion system on thermal conductivity of the composite.

In this study, we measured thermal conductivity as well as electric conductivity of polyethylene filled with graphite by four methods: (a) powder mix, (b) solution mix, (c) roll-milled mix, and (d) melt mix. We estimate the ease in forming conductive chains of graphite particles from electric conductivity and discuss the effect of type of dispersion system in a composite on the thermal conductivity of the composite. Further, we discuss the applicability of our predictive model for thermal conductivity, which was proposed in the previous reports,<sup>8</sup> to experimental data and estimate the effect of ease in forming conductive chains, that is, dispersion state in a composite, on parameters included in the model.

## EXPERIMENTAL

### Materials

Low molecular weight polyethylene was used as a material for the matrix. Graphite was used as filler.

Some properties of the materials utilized are shown in Table I.

### Preparation of Test Specimens

Test specimens were prepared by four methods as follows:

#### (a) Powder mix

The specimens were cast by melting a mixture of powdery polyethylene and graphite.

#### (b) Solution mix

The specimens were made by dispersing graphite in polyethylene dissolved in toluene and melting the mixture after removal of the toluene.

#### (c) Roll-milled mix

The specimens were made by melting polyethylene kneaded with graphite on a roll mill.

#### (d) Melt mix

Specimens were made by dispersing graphite in molten polyethylene.

## Measurement

### Electric Conductivity

Measurement of electric conductivity on high-resistivity materials was aided by applying up to 500 VDC, and that on low-resistivity materials, by 10 VDC.

### Thermal Conductivity

The measurement of thermal conductivity was performed by utilizing the Dynatech thermal conduc-

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**Table I** Properties of Materials

	Density <sup>a</sup> (g/cm <sup>3</sup> )	Thermal Conductivity (cal/s cm °C)	Electric Conductivity (Ω <sup>-1</sup> cm <sup>-1</sup> )
Polyethylene <sup>b</sup>	0.938	$6.96 \times 10^{-4}$	$2.5 \times 10^{-16}$
Graphite <sup>c</sup>	2.307	$5.0 \times 10^{-1}$	$1.4-2 \times 10^8$

<sup>a</sup> By air-comparison method.

<sup>b</sup> Supplied by Allied Chemical:  $M_w = 5000$ .

<sup>c</sup> Supplied by Showa Denko.

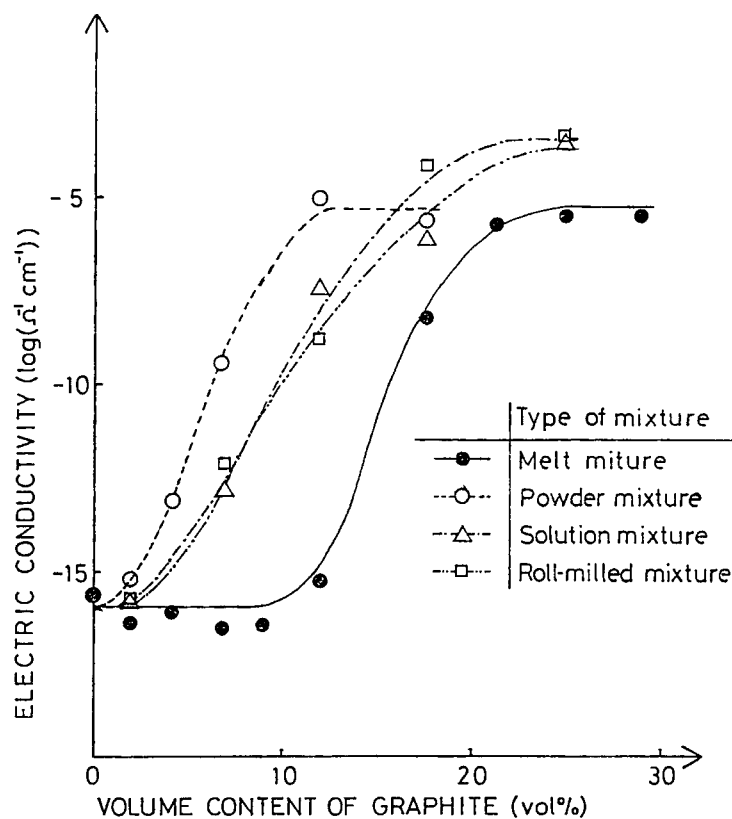
tance tester model TCHM-DV, which is based on the comparison method. The standard specimen is made of Pyrex glass. Specimen size was 50 mm in diameter and 5 mm in thickness. All measurements were performed at  $50 \pm 3^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Electric Conductivity

Figure 1 shows electric conductivities of the composites prepared by the four methods. All of them are virtually the same as that of the matrix polymer

below a certain filler fraction (percolation threshold; PT) and then increase rapidly beyond it. After passing over the critical volume fraction (CVF) of each system, they gradually approach a certain value. Here, CVF was determined as the fraction corresponding to the midst of electric conductivity between the base value below the PT and the saturated. PT was determined as a fraction corresponding to the inflection point of the curve where a rapid increase occurs. Both the percolation thresholds (PT) and the critical volume fractions (CVF) appeared in the following order, as indicated in Table II: powder mixture < solution mixture = roll-milled mixture < melt mixture. It was con-



**Figure 1** Electric conductivities of the composites in several types of dispersion systems.

**Table II Electric Characteristics of Composites**

	Melt Mixture	Roll-Milled Mixture	Solution Mixture	Powder Mixture
Percolation threshold	0.12	0.03	0.04	0.01
Critical volume fraction	0.15	0.10	0.10	0.06

sidered that the number of particles, touching each other, decrease in this order.

The reason why PTs and CVFs of the roll-milled mixture as well as solution mixture were smaller than those of melt mixture is explained as follows: In the roll-milled mixture, aggregates of graphite particles could not be sufficiently broken by milling because the viscosity of molten polyethylene was very low. In the solution mixture, graphite particles were able to surround the crystals of polyethylene that were separate in the toluene solution. Thus, the formations of conductive chains in the roll-milled mixture and in the solution mixture are considered to be easier than that in the melt mixture.

In the powdery mixture, since graphite particles were arranged to surround powdery polyethylene (honeycomb) structure, the formation of conductive chains can be considered the easiest and, therefore, PT and CVF are the smallest for this method.

### Thermal Conductivity

Figure 2 shows thermal conductivities of the composite prepared by the four methods. They became higher in the following order: melt mixture < roll-milled mixture = solution mixture < powdery mixture. By summarizing this result together with the result of the electric conductivity, it becomes clear that the easier the formation of conductive chains in the composite the higher is the thermal conductivity of the composite in total. A gap between experimental data and the curve predicted by the Maxwell-Eucken equation<sup>9</sup> became large when the graphite content was increased over that volume content that approximately corresponds to the percolation point for electric conductivity of the composite (Fig. 2). This result indicates more clearly that the ease in forming conductive chains greatly affects the thermal conductivity of a composite.

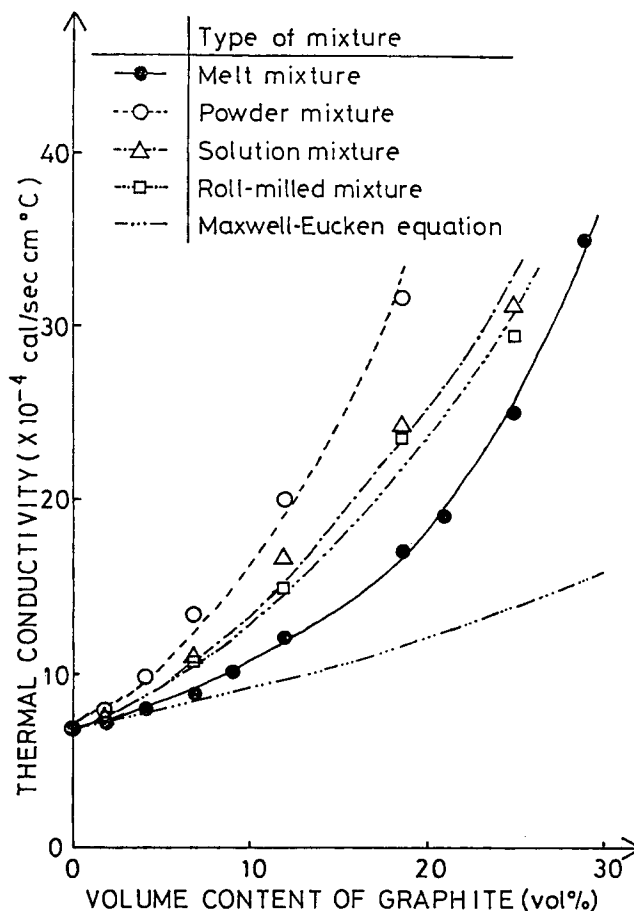
### APPLICATION OF CONDUCTIVE MODEL TO EXPERIMENTAL DATA

Several theoretical and empirical models have been proposed to predict thermal conductivity of two-

phase systems.<sup>3,4,7,8</sup> Our previous reports discussed our model, from which Eq. (1) was derived, which proved to give excellent agreement with experimental data.<sup>8</sup> However, there have been few reports that discussed the dispersion state, i.e., ease in forming conductive chains and its effect on thermal conductivity in a composite.

In this report, we modify our model to include a parameter for the dispersion state, i.e., ease in forming conductive chains, and compare it with the experimental data:

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



**Figure 2** Thermal conductivities of the composites in several types of dispersion systems.

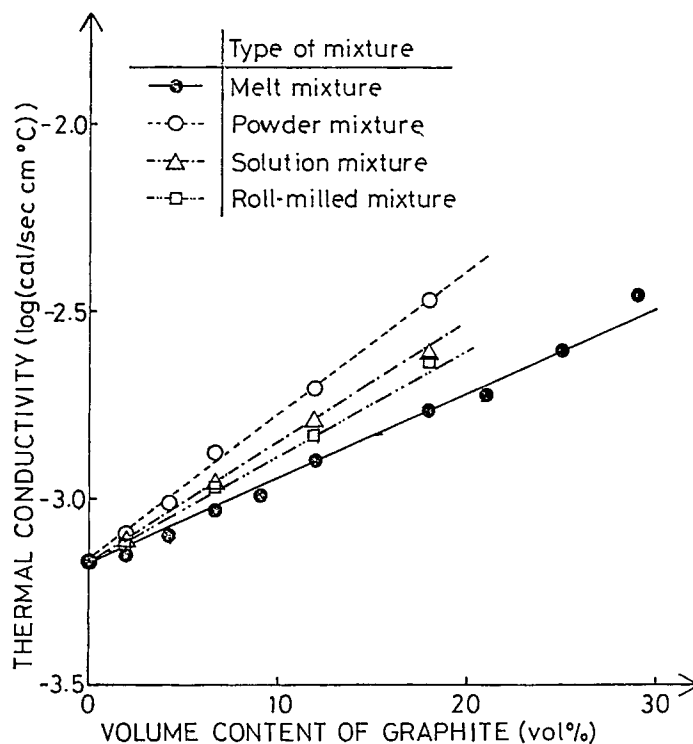


Figure 3 Thermal conductivities of the composites in several types of dispersion systems.

where  $\lambda$  = thermal conductivity of the composite,  $\lambda_1$  = thermal conductivity of the polymer,  $\lambda_2$  = thermal conductivity of filler,  $V$  = volume content of filler,  $C_1$  = factor relating to the effect on crystallinity and crystal size of a polymer, and  $C_2$  = factor relating to the ease in forming conductive chains of filler.  $C_2$  is expected to vary with variation of dispersion state.

Figure 3 shows logarithms of thermal conductivities of the composites prepared in this study, plotted against the volume content of graphite. All experimental data approximate a straight line. Therefore, thermal conductivities of composites with various dispersion states can be expressed by Eq. (1).

Values of  $C_1$  and  $C_2$ , calculated from the experimental data, are indicated in Table III.  $C_1$  reduces in the following order: powder mixture > solution

Table III Coefficients of  $C_1$  and  $C_2$

	Melt Mixture	Roll-Milled Mixture	Solution Mixture	Powder Mixture
$C_1$	0.888	0.980	0.967	1.007
$C_2$	2.322	0.718	0.073	-1.880

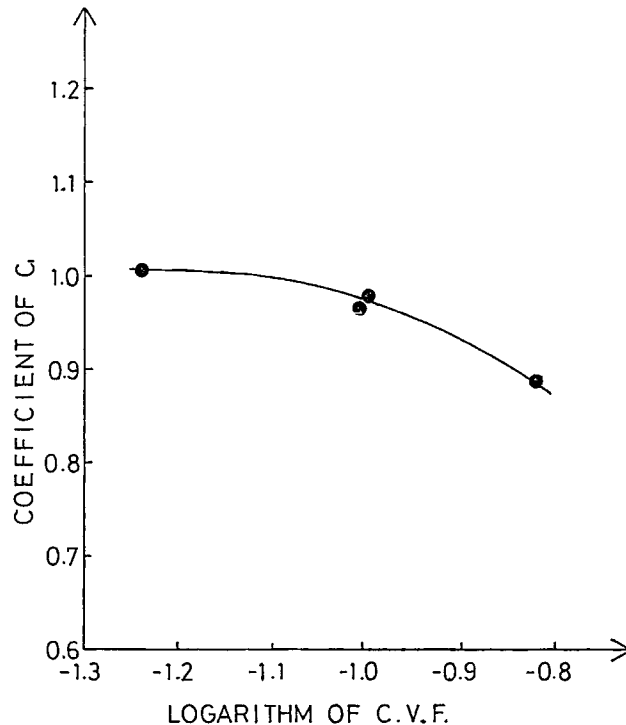


Figure 4 Relation between critical volume fractions and values of  $C_1$ .

mixture = roll-milled mixture > melt mixture.  $C_2$  increases in contrast to the above: powder mixture < solution mixture = roll-milled mixture < melt mixture. It can be considered that the cause in the variation of  $C_1$  and  $C_2$  is in the ease in forming conductive chains that differ by the types of dispersion state.

CVF value in electric conductivity of a composite is a useful indicator of the degree of ease in forming conductive chains. Thus,  $C_1$  and  $C_2$  were plotted against CVF in Figures 4 and 5, respectively.  $C_1$  decreased with increasing CVF. It is believed that the stronger the interaction at the interface of polyethylene and graphite, the higher becomes CVF, where graphite acts to obstruct crystallization of polyethylene.  $C_2$  drastically increased with CVF. It is thought that the stronger the interaction of graphite and polyethylene, the more difficult becomes the formation of conductive chains. Another expression of the change of  $C_2$  (from -2 to 2) is that the thermal conductivity of the powder-mixed composite is as high as that of the melt-mixed composite containing

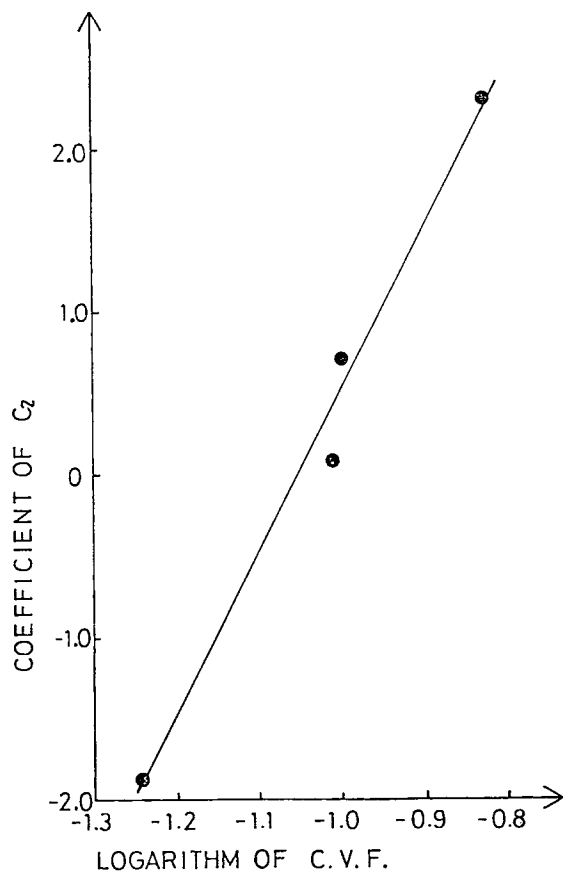


Figure 5 Relation between critical volume fractions and values of  $C_2$ .

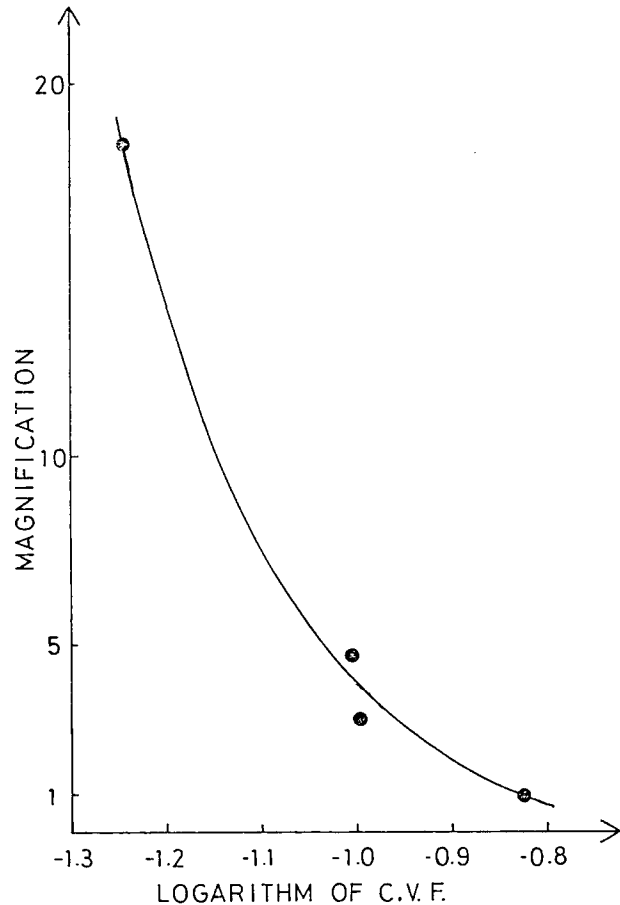


Figure 6 Magnification of thermal conductivity of particles in the assumption.

particles whose thermal conductivity is itself 18 times higher than that of graphite (Fig. 6).

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Received May 7, 1990  
 Accepted June 19, 1990