Thermal Conductivity of a Polyethylene Filled with Disoriented Short-Cut Carbon Fibers

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SYNOPSIS

Thermal conductivity of polyethylene composites, filled with randomly dispersed and disoriented (oriented at random) carbon fibers with various aspect ratios, were investigated. Orientation of fibers was quantitatively evaluated by Hermans' parameter. In specimens of isotropic composites, i.e., filled with randomly dispersed and disoriented fibers, thermal conductivity increased with an increase in the fiber length. The result is discussed in comparison with electric conductivity of the composites and explained by the contact probability of filled fibers. Further, it was confirmed that our model previously proposed could be adopted to predict thermal conductivity of the isotropic composite filled with carbon fibers. Also, the effect of fiber length of the C_2 parameter included in the model is discussed and C_2 was found to have a linear relation with the aspect ratio of fibers at a sufficiently large value. In this study, a shape factor of a filler (aspect ratio) could be directly introduced into the equation, which was shown in our previous paper.

INTRODUCTION

Many reports have been published on the improvement of thermal conductivity of polymer composites filled with carbon fibers.[1-3] Only a few reports among them discussed the effects of fiber length on the thermal conductivity of composites,[4,5] where the aspect ratio of fibers was rather limited at 12 and degree of orientation of fibers was evaluated qualitatively by X-ray and optical microscopy methods. There have been some reports on anisotropic parameters of composites filled with fibers, where fiber orientation was expected to affect the properties of the composites.[6-8] Maccullough et al. applied Hermans' parameter to the study of the modulus of the sheet-molding compound.[6,7] Here, Hermans' parameter was shown to be useful to distinguish the small difference in orientation.

In this study, we prepared polyethylene composites filled with carbon fibers with various aspect ratios (L/D) (L_w/D = 1–45.3) and determined their fiber orientation by using Hermans' parameter. Then, we estimated the contact probability of fibers by measuring electric conductivity of the composite and discussed the effect of fiber length on the thermal conductivity of "isotropic" composites. Finally, we discussed the applicability of the prediction model for thermal conductivity, which had been proposed in the previous reports,[9-12] to the composites and estimated the effects of fiber length on parameters included in the model.

EXPERIMENTAL

Materials

Low molecular weight polyethylene was used as a matrix. Four types of carbon fibers: powdery, A, B, and C with various lengths, supplied by Toray Co., were used as fillers. The properties of the materials utilized are shown in Tables I and II.

Preparation of Test Specimens

Test specimens were prepared by mixing molten polyethylene with various contents of carbon fiber under reduced pressure, followed by casting.

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Table I Properties of Materials

Material	Density[a] (g/cm^3)	Thermal Conductivity (cal/s cm °C)	Electric Conductivity (Ω^{-1} cm^{-1})
Polyethylene[b]	0.938	6.8×10^{-4}	2.5×10^{-14}
Carbon fiber[c]	1.988	$1.2\text{–}4.8 \times 10^{-2}$ [d]	$3.3\text{–}6.3 \times 10^{2}$ [d]

[a] Measured by air-comparison method.
[b] MW = 5000.
[c] TORAYCA MLD (PAN-based carbon fiber) supplied by Toray Co.
[d] Ref. 13.

Measurement

Fiber Length

An optomicroscopic photograph of a bulk of raw carbon fibers was taken, and fiber-length measurements were made on about 250 pieces of fibers in the photograph. Weight and number average lengths were estimated from the data. The length's distribution of C-type fibers in the specimens was similar to that in raw materials (Fig. 1). It was thus considered that the carbon fibers were scarcely cut down during the preparation of the specimens.

Anisotropic Parameter (Hermans' Parameter)

The anisotropy of the composite was estimated by using Hermans' parameters (H_y, H_z, and H_{yz}).[6,7] H_y represents anisotropy along the direction (Y) in a plane vertical to thermal flux. H_z and H_{yz} represent anisotropies along the direction (Z) of thermal flux, in plane and in space, respectively.

The square plates (25 × 25 mm) were obtained by cutting the specimens that were used for the thermal conductivity measurement (Fig. 2). Thin layers parallel to XY and YZ surfaces of these plates were sliced from the plates for optomicroscopic observation.

Orientation angles of the fillers were measured based on the Y- or Z-direction for about 300 pieces of carbon fibers observed in the microscopic photography for each of the layers.

By substituting the observed orientation angle data to θ_{yi} (or θ_{zi}) in eq. (1), H_y (or H_z) was calculated:

$$H_y \text{ (or } H_z) = \{(2/n) \sum [\cos^2\theta_{yi} \text{ (or } \theta_{zi})]\} - 1 \quad (1)$$

where $-1 \leqq H_y$ (or H_z) $\leqq 1$, and n is the number of fibers measured. If H_y (or H_z) is equal to 0, carbon fibers can be estimated to orient at random, i.e., the composite is considered as "isotropic," in the XY (or YZ) plane.

H_y (or H_z) in the plane, however, does not directly represent anisotropy in space. To explain anisotropy of thermal conductivity in space, we propose a new anisotropic parameter (H_{yz}) in space. Figure 3 shows a fiber in space, where $\tan A_i = m/l$, $\tan C_i = m/n$, and $\cos B_i = n/l$. These relations are combined in eq. (2):

$$\cot^2(\pi/2 - A_i) = \cot^2(\pi/2 - C_i)\cos^2 B_i \quad (2)$$

Hermans' parameter (H_{yz}) in space is obtained by eq. (3):

$$H_{yz} = [(3/n) \sum \cos^2\theta_{yzi} - 1]/2 \quad (3)$$

Table II Diameter and Length of Carbon Fibers

Type of Carbon Fiber	Diameter [D (μm)]	Number-Average Length [L_n (μm)]	L_n/D	Weight-Average Length [L_w (μm)]	L_w/D
Powdery	1.0	—	1.0	—	1.0
A	7.5	36.5	4.9	44.9	6.0
B	7.5	100.7	13.4	162.2	21.6
C	7.5	163.3	21.8	340.0	45.3

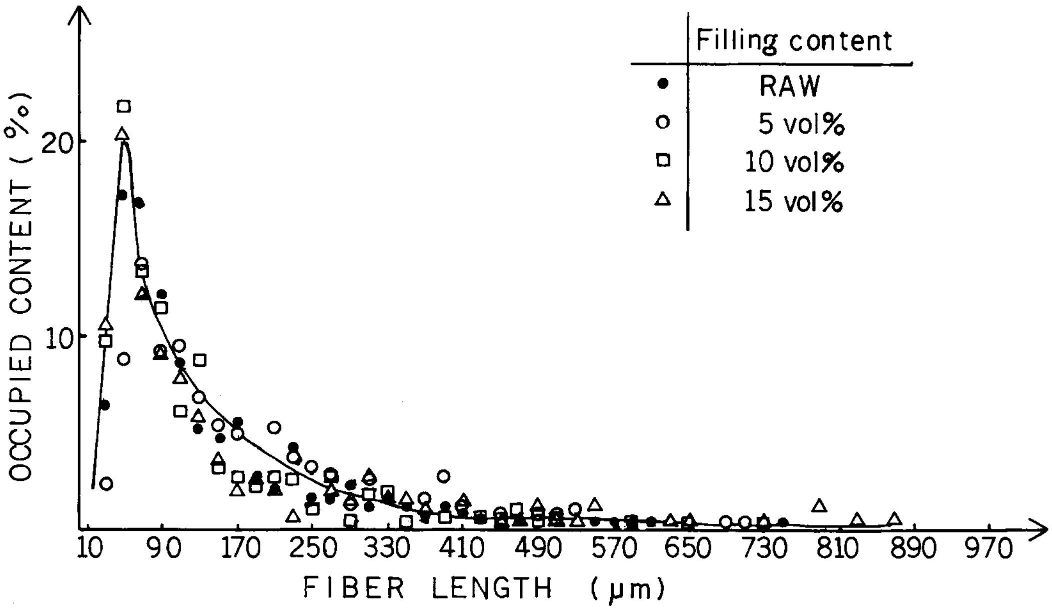

Figure 1 Length distribution of C-type carbon fibers, before and after the preparation of specimens.

Since θ_{yzi} equals $\pi/2 - A_i$, $\cos^2\theta_{yzi}$ can be expressed as follows:

$$\cos^2\theta_{yzi} = \cot^2(\pi/2 - A_i)/[1 + \cot(\pi/2 - A_i)] \quad (4)$$

Further, $Bi = \theta_{yi}$ and $Ci = \theta_{zi}$. Eq. (3), thus, becomes eq. (5) by substituting eqs. (2) and (4):

$$H_{yz} = (\tfrac{1}{2})\{(3/n)\sum[X_i^2/(1 + X_i^2)] - 1\}$$
$$X_i^2 = \cot(\pi/2 - \theta_{zi})\cos^2\theta_{yi} \quad (5)$$

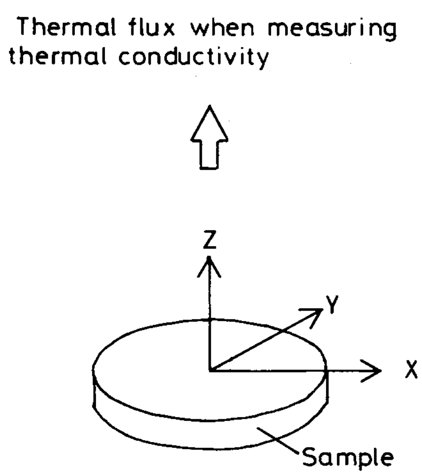

Figure 2 Shapes of specimens for measuring thermal conductivity.

where $-\frac{1}{2} \leqq H_{yz} \leqq 1$. If $H_{yz} = 0$, carbon fibers are oriented at random and the composite is considered as "isotropic" in space. Theoretically, θ_{yi} and θ_{zi} should represent for the same piece of fiber. However, observation of both θ_{yi} and θ_{zi} for the same fiber specimen was experimentally difficult. The

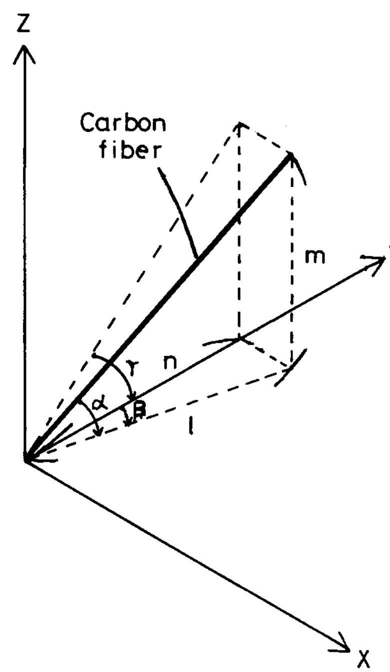

Figure 3 Orientation angles of a carbon fiber to the Z-direction in space.

measured θ_{yi} and θ_{zi}, thus obtained, were of different specimens. The data were combined randomly for substituting to eq. (5) to obtain H_{yz}.

Electric Conductivity

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

Thermal Conductivity

The 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 ± 3°C.

RESULTS AND DISCUSSION

Electric Conductivity

Figure 4 shows electric conductivities of the composites filled with various types of carbon fibers, for the Z-direction, which is the direction of thermal flux when measuring thermal conductivity. All specimens show virtually the same level of conductivity as that of the matrix polymer until the filler fraction reaches a percoration threshold (PT) where a rapid increase in conductivity starts. After passing over the critical volume fraction (CVF) of each system, each curve gradually approaches a certain value. Here, CVF was determined as the fraction at the midst of electric conductivity of the base value below PT and that after saturation. With increasing the fiber length, CVF shifted to a smaller value (Table III). It was considered that the probabilities of fibers touching increased with the increase of fiber length.

Table III Critical Volume Fraction (CVF) in Polyethylene Composite

Type of Carbon Fiber	CVF
Powdery	0.301
A	0.152
B	0.046
C	0.016

Further, thermal conductivities (ρx and ρy) of the composite for the X- and Y-direction were measured, and so electric anisotropies (EAx/y and EAz/y) were estimated by eqs. (6) and (7), respectively:

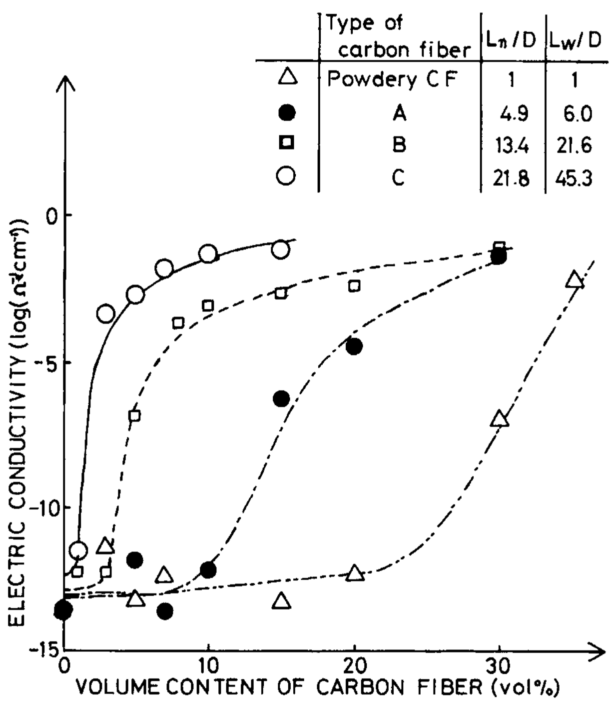

Figure 4 Electric conductivity of polyethylene composite for the Z-direction.

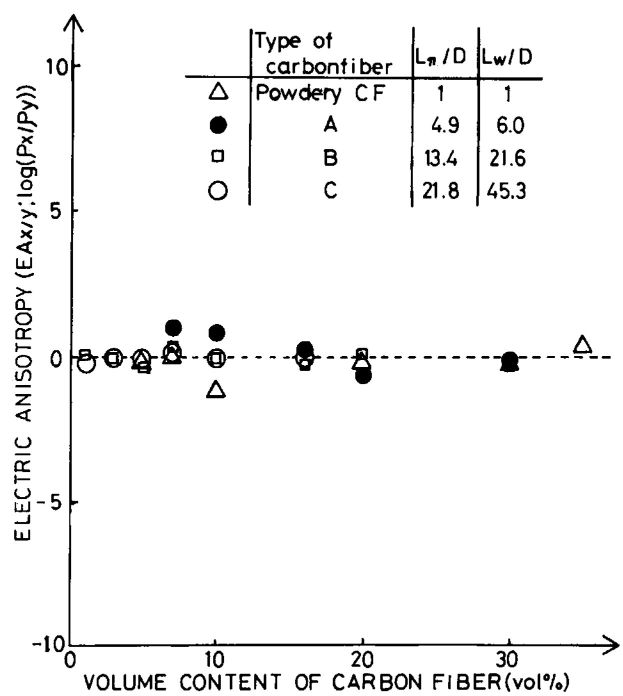

Figure 5 Electric anisotropy (EAx/y) of polyethylene composite.

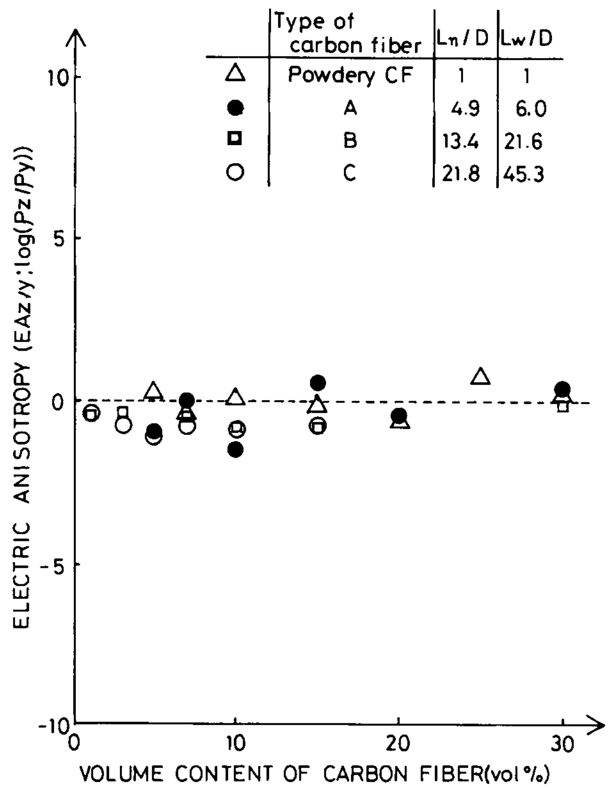

Figure 6 Electric anisotropy (EAz/y) of polyethylene composite.

$$EAx/y = \log(\rho x/\rho y) \quad (6)$$

$$EAz/y = \log(\rho z/\rho y) \quad (7)$$

EAx/y and EAy/z in the composites were indicated in Figures 5 and 6, respectively. In the type of powdery carbon fibers, both EAx/y and EAy/z were almost equal to 0 over all regions. Thus, it was confirmed that powdery carbon fibers were randomly dispersed in the composites. Also, in the other types of carbon fibers, EAx/y and EAy/z were almost equal to 0 over all regions. Therefore, carbon fibers were confirmed to be randomly dispersed and oriented at random, in all types of the composites.

Anisotropy in the Composites

Figures 7–9 show H_y, H_z, and H_{yz}, respectively, of composites filled with several types of carbon fiber. For composites filled with A and B types of fibers, H_y, H_z, and H_{yz} are all about 0, implying random orientation of fibers. Thus, the composites could be regarded as isotropic. The composite filled with C-type fibers is also considered practically disoriented, although a little deviation from the 0 line was observed in H_z (Fig. 8).

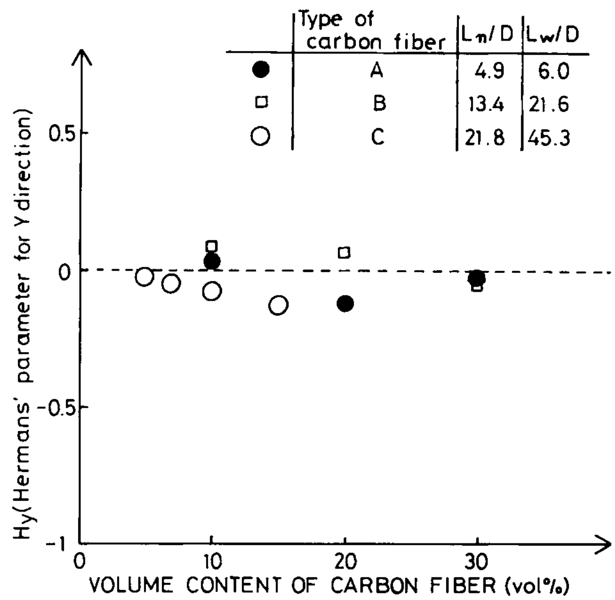

Figure 7 H_y (Hermans' parameter for the Y-direction in the XY face) in polyethylene composite filled with several types of carbon fibers.

Thermal Conductivity

Figure 10 shows thermal conductivity of the composites versus carbon fiber content. In the isotropic composite, the longer the fiber length, the larger was the thermal conductivity that could be observed. For example, in the case of B-type carbon fibers, thermal conductivity was 1.8 times higher than that of pow-

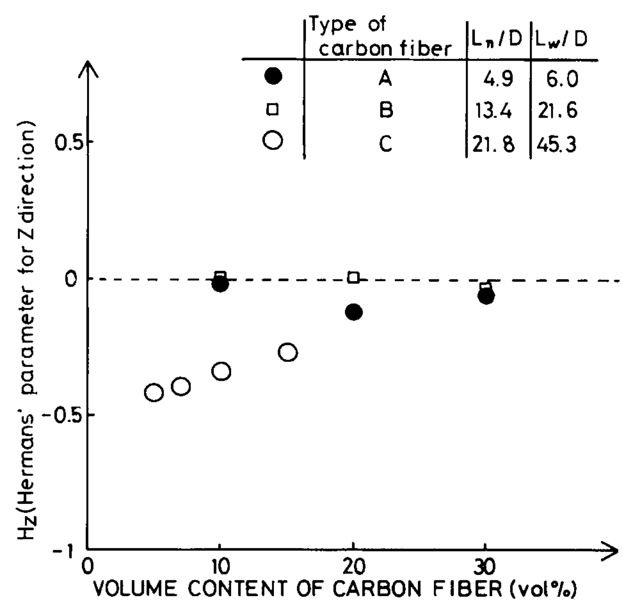

Figure 8 H_z (Hermans' parameter for the Z-direction in the YZ face) in polyethylene composite filled with several types of carbon fibers.

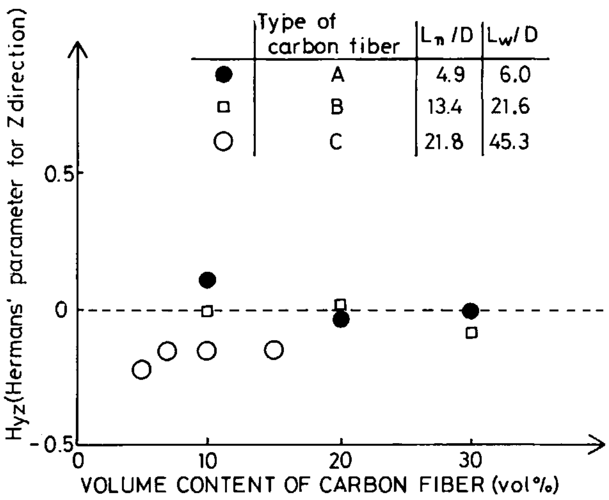

Figure 9 H_{yz} (Hermans' parameter for the Z-direction in space) in polyethylene composite filled with several types of carbon fibers.

dery fiber-filled one at 30 vol %. The increase in thermal conductivity with the increase in fiber length might be due to the increase in the numbers of touching fiber chains, as was proved by the electric conductivity data mentioned above.

APPLICATION OF CONDUCTIVE MODEL TO EXPERIMENTAL DATA

Numerous theoretical and empirical models have been proposed to predict thermal conductivity of two-phase systems. Our previous reports also discussed several models.[9-11] Few reports, however, discussed the models for polymer composites filled with short-cut types of carbon fibers.

In this report, we tried to apply our model[9] to the experimental data:

$$\log \lambda = VC_2 \log \lambda_2 + (1 - V)\log(C_1\lambda_1) \quad (8)$$

where λ = thermal conductivity of a composite, λ_1 = thermal conductivity of a polymer, λ_2 = thermal conductivity of a filler, V = volume content of a filler, C_1 = factor of the effect on crystallinity and crystal size of a polymer, and C_2 = factor of ease in forming conductive chains of a filler.

Few fillers contribute to form conductive chains in the dispersion system, while matrix polymer is almost continuous. Thus, the contribution of fillers to the thermal conductivity of a composite seems to be less than that of the matrix.

In general, most of conduction models have been organized by assuming the shape of the filler. For example, the Maxwell–Eucken model assumes that a spherical block, where all the fillers gather, exists at the center of a cubic block of the composite. Thus, the shape factor was directly introduced to the prediction equations derived from those models, whereas our equation did not define any shape factor of filler directly. Conversely, it was not assumed in the conduction model. It was found, however, by the measurement of the electric conductivity of the composite in this study that the increase in fiber length promoted the formation of conductive chains. The situation, thus, should result in the increase in thermal conductivity of the composite via any change of C_2 value in the equation. The way of change in C_2 might be reversed to fiber length, i.e., the longer is the fiber length, the smaller becomes C_2, in order to increase $C_2 \log \lambda_2$ (where λ_2 is lower than 1 cal/s cm °C in practically all filler except diamond).

In Figure 11, logarithms of thermal conductivity of the composites is plotted against the volume content of carbon fibers. Experimental data of each filler series are approximately on each straight line. Therefore, the experimental data of thermal con-

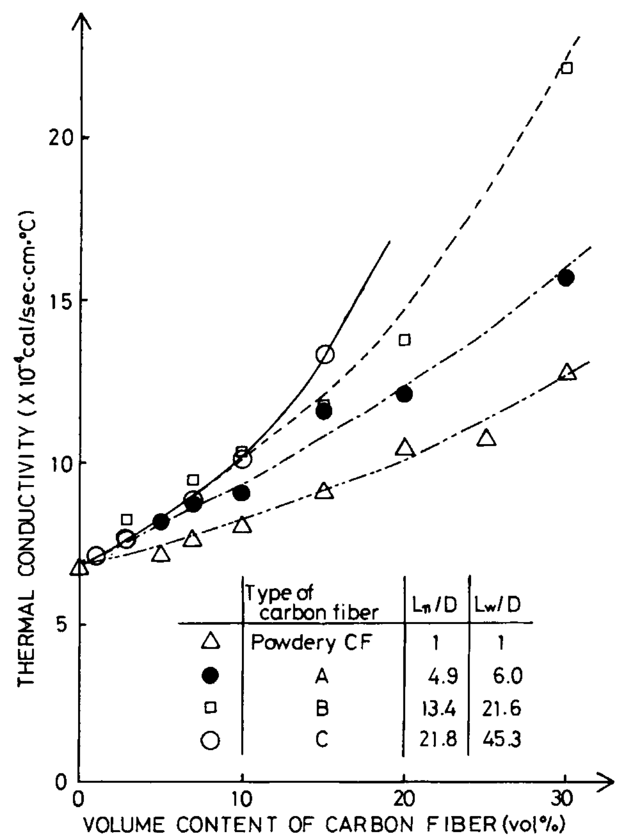

Figure 10 Thermal conductivity of polyethylene composite.

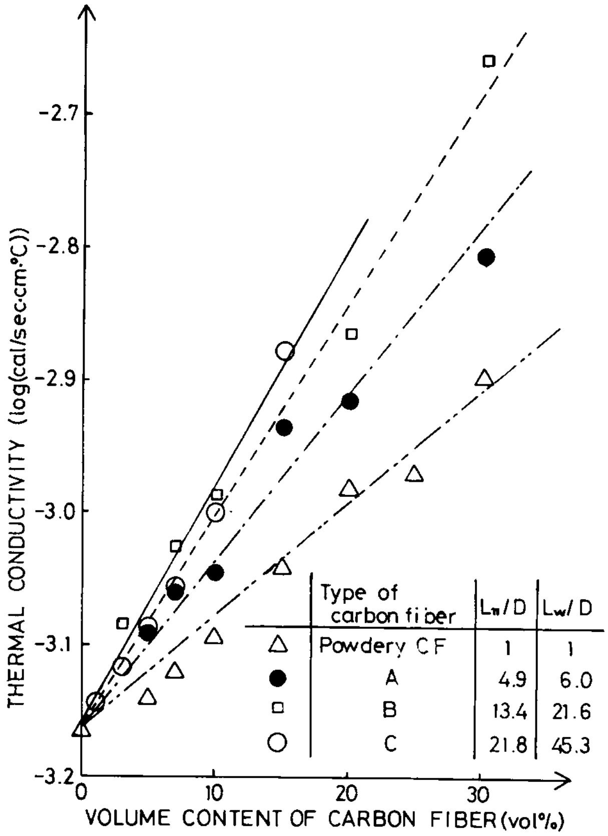

Figure 11 Thermal conductivity of polyethylene composite.

ductivity of isotropic composite filled with various types of carbon fibers can be explained by eq. (8).

Values of coefficients C_1 and C_2 were calculated from the experimental data of thermal conductivity of the composites (Figs. 12 and 13). The values of C_1 were approximately 1. This means that the secondary structure of polyethylene seems to be unaffected by carbon fibers, whereas C_2 became smaller with the increase of aspect ratio (L/D) of carbon fibers. This means that, in the isotropic composite, the increase in fiber length promoted the formation of conductive chains, decreasing the C_2 value.

The CVF value in electric conductivity of a composite is a useful indicator of the degree of ease in forming conductive chains. Thus, C_2 was plotted against the logarithm of CVF in Figure 14. All C_2 were approximately on a straight line. Thus, the relation of C_2 and CVF can be represented by eq. (9):

$$C_2 = A \log(\mathrm{CVF}) + B$$

$$A = 0.386$$

$$B = 1.35 \qquad (9)$$

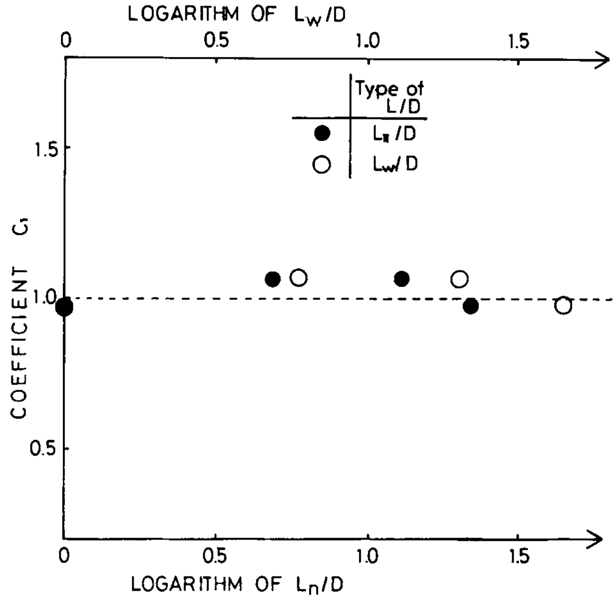

Figure 12 Coefficient C_1 in eq. (6) ($\lambda_{CF} = 1.2 \times 10^{-2}$ cal/s cm °C).

A similar relation was already found by us for composites in several types of dispersion systems.[12] Therefore, this relation is confirmed to be empirically valid.

Carmona et al. proposed a geometric scaling law to explain a dispersion system of carbon fibers in epoxy resin matrix[14] and concluded that eq. (10) was adoptable for estimating the critical volume fraction in the cases of sufficiently large aspect ratios (L/D):

$$\mathrm{CVF} = n[1/(L/D)]^2 \qquad (10)$$

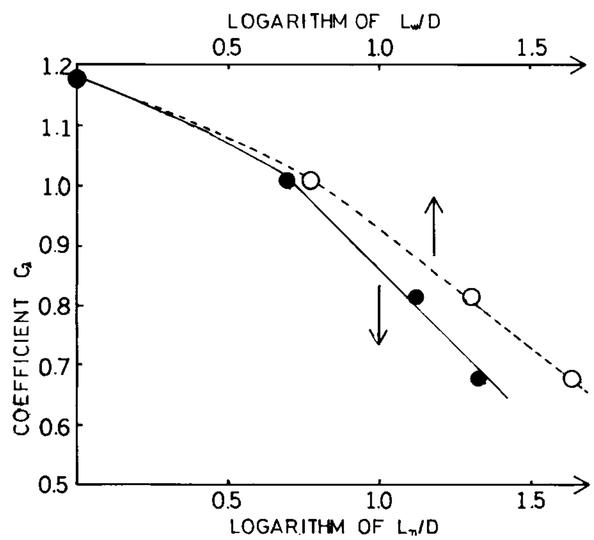

Figure 13 Coefficient C_2 in eq. (6) ($\lambda_{CF} = 1.2 \times 10^{-2}$ cal/s cm °C).

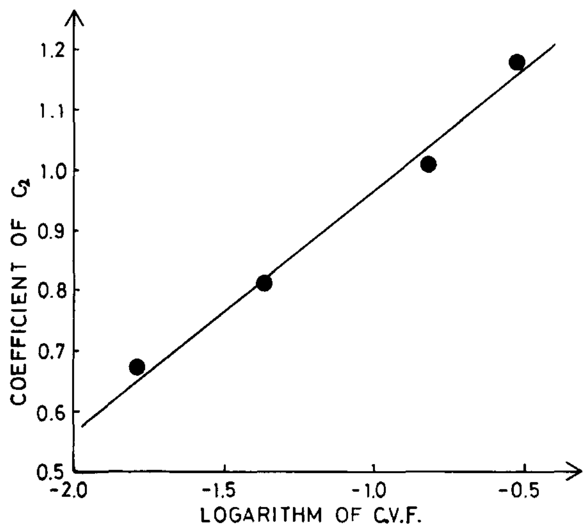

Figure 14 Relation between critical volume fractions and coefficient C_2.

where n is the constant coefficient. Therefore, eq. (9) becomes eq. (11) by substituting eq. (10) into eq. (9):

$$C_2 = C \log(L/D) + E$$
$$C = -2A$$
$$E = B - 2A \log n \tag{11}$$

In Figure 13, C_2 shows a linear relation with $\log(L/D)$ at $L/D > 0.6$ for both axes of L_n/D and L_w/D. In this case, parameter C_2 can be expressed by eq. (11). Therefore, eq. (8) becomes eq. (12) by substituting eq. (11) into eq. (8):

$$\log \lambda = V[C \log(L/D) + E] \log \lambda_2 + (1 - V) \log(C_1\lambda_1) \tag{12}$$

Equation (12) indicates that a shape factor of a filler is directly introduced into our model, which explains the thermal conductivity of polymer composites filled with carbon filler with various aspect ratios.

CONCLUSIONS

1. We measured thermal conductivity of a polyethylene/carbon fiber composite that was quantitatively evaluated to be isotropic, by Hermans' parameter and electric anisotropy methods.
2. It was proved by comparing thermal conductivity with electric conductivity of the composite that conductive-chain-formation became easier with an increase of the fiber length, which increased the thermal conductivity of the composite.
3. It was confirmed that our model previously proposed could be adopted to predict thermal conductivity of the isotropic composite filled with carbon fibers. Also, it was found that the C_2 value in our model showed a linear relation with logarithms of the critical volume fraction observed in electric conductivity and with logarithms of the aspect ratio of carbon fiber at a sufficiently large aspect ratio. Therefore, it was considered that a shape factor of filler could be directly introduced into our model, although the aspect ratio was limited to a sufficiently large value.

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