Electrical and Thermal Conductivities of Polyethylene Composites Filled with Biaxial Oriented Short-Cut Carbon Fibers

Y. AGARI,[1,*] A. UEDA,[1] and S. NAGAI[2]

[1]Department of Plastics, Osaka Municipal Technical Research Institute, 6-50, 1-Chome, Morinomiya, Joto-ku, Osaka, 536 Japan; and [2]Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, 10-1, 6-Chome, Hakozaki, Higashi-ku, Fukuoka 812, Japan

SYNOPSIS

Polyethylene composites filled with various types of carbon fiber were prepared for electrical and thermal conductivity measurements. By estimation of the anisotropic parameter (Hermans' parameter), the fibers were confirmed to be significantly biaxially oriented in the composites. The critical volume fractions in the electrical conductivity of these composites for the two oriented directions (X and Y) were equal to each other and smaller than that for a direction (Z) vertical to the above. The electrical anisotropy, i.e., ratio of electrical conductivity of the composite for the Z direction to the X and Y directions varied drastically with increase in filler content. The longer the length of carbon fiber was, the higher became the electrical conductivity of the biaxially oriented carbon fiber composites for all directions. But, the thermal conductivity of the composite was almost unchanged for the Z direction, even if fiber length was sufficiently long. Our equation, previously proposed, proved adaptable to these thermal conductivities. The factors of C_p and C_f in the equation are kept unchanged, in spite of increasing fiber length. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Many reports[1-9] have been published on the improvement of the electrical or thermal conductivities of polymers by filling with electrically or thermally conductive fillers, respectively. The electrical conductivity of a composite is known to vary with the change of volume fraction of fillers in a characteristic way (Fig. 1). Below a certain filler fraction (percolation threshold), the electrical conductivity of the composite is virtually the same as that of the matrix polymer. As the filler fraction increases beyond the threshold, the conductivity rapidly increases and then gradually approaches a certain value. The thermal conductivity of the composite, on the other hand, is known to increase exponentially with increasing filler content.

There are also several reports[10-12] on the electrical and thermal conductivities of polymers filled with fibers. However, few reports discuss the effects of fiber orientation on the conductivities of the composites. In our previous reports[15,16] on the electrical and thermal conductivities of disoriented short-cut carbon fiber composites, it was confirmed that fibers were oriented at random, using an anisotropic parameter of Hermans' parameter.[13,14] On the other hand, biaxial fiber orientation was found to appear in the composites prepared by several types of molding methods.

In this study, several polyethylene composites filled with various types of biaxially oriented carbon fiber were prepared. Also, after estimation of the degree of fiber orientation by Hermans' parameter, we discuss the effect of biaxial orientation of fiber on thermal and electrical conductivities.

* To whom correspondence should be addressed.

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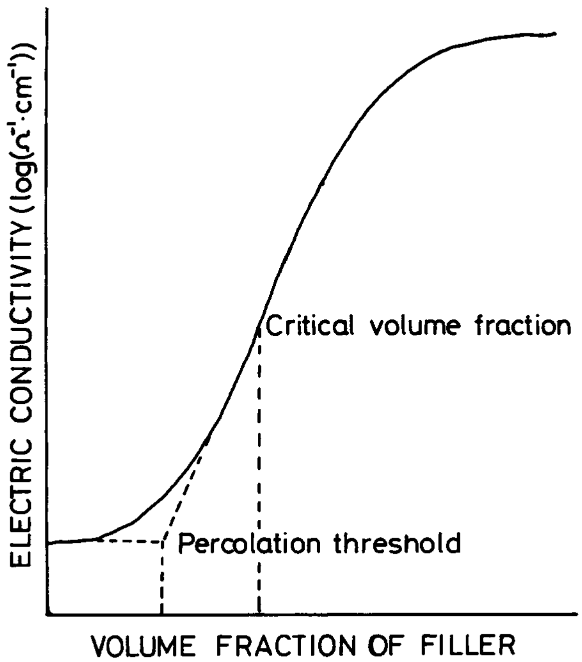

Figure 1 A typical electrical conductivity curve of a composite filled with conductive fillers.

EXPERIMENTAL

Materials

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

Preparation of Test Specimens

Test specimens for measuring thermal conductivity were prepared by mixing molten polyethylene with various contents of carbon fiber under reduced pressure followed by casting through an open face (XY face) of a disc mold for the specimen indicated in Figure 2. Test specimens for measuring electrical conductivity were made by cutting square plates (25 × 25 mm) from the above cast specimens.

Measurement

Fiber Length

An optomicroscopic photograph of bulk raw carbon fibers was taken and fiber length measurements were made on about 250 pieces of fibers in the photograph. Weight-average and number-average lengths were estimated from the data.

The mixing method and the type of fibers and polyethylene used in this study were those described in the previous report,[15] where, by comparing the length distribution of carbon fibers in the specimens with that in raw materials, the carbon fibers were confirmed to be scarcely cut down during the preparation of the specimens.

Anisotropic Parameter

The anisotropy of the composite was estimated by using Hermans' parameter (H_y, H_z, and H_{yz}). H_y represents anisotropy along a direction (Y) in a plate vertical to thermal flux. H_z and H_{yz} represent anisotropy along the direction (Z) of thermal flux and electric current, in plane and in space, respectively.

After measuring thermal conductivity, we cut a square plate (25 × 25 mm) from the specimens (Fig. 2) and then cut thin layers from the XY and YZ faces of these plates for optomicroscopic observation.

Orientation angles based on the Y or Z direction for about 300 pieces of carbon fibers dispersed in each layer were measured on photomicrographs. By substituting the orientation angles to θ_{yi} (or θ_{zi}) in eq. (1), H_y (or H_z) was estimated:

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

Table I Properties of Materials

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

[a] Measured by the air-comparison method.
[b] MW = 5000.
[c] TORAYCA MLD supplied by Toray Ltd.
[d] Ref. 17.

Table II Diameter and Length of Carbon Fibers

Type of Carbon Fiber (CF)	Diameter D (μm)	Number–average Length Ln (μm)	Ln/D	Weight–average Length Lw (μm)	Lw/D
Powdery CF	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

where $-1 \leq H_y \leq 1$, and n is the number of fibers measured. If H_y (or H_z) is equal to 0, carbon fibers are oriented 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 the anisotropy of thermal conductivity in space, we proposed the parameter (H_{yz}) in space in the previous report. By substituting the orientation angles to θ_{yi} and θ_{zi} in eq. (2), H_{yz} is estimated:

$$H_{yz} = (1/2)[(3/n)\Sigma\{X_i^2/(1 + X_i^2)\} - 1] \quad (2)$$

$$X_i^2 = \cot(\pi/2 - \theta_{zi})\cos^2\theta_{yi}$$

where $-\frac{1}{2} \leq H_{yz} \leq 1$. If $H_{yz} = 0$, carbon fibers are oriented at random and the composite is considered as isotropic. Theoretically, θ_{yi} and θ_{zi} should represent data on the same fiber. Experimentally, however, observation of both θ_{yi} and θ_{zi} on the same fiber specimen was difficult to realize. The measured θ_{yi} and θ_{zi}, thus obtained, are on separate specimens. The data were combined randomly for substituting in eq. (2) to obtain H_{yz}.

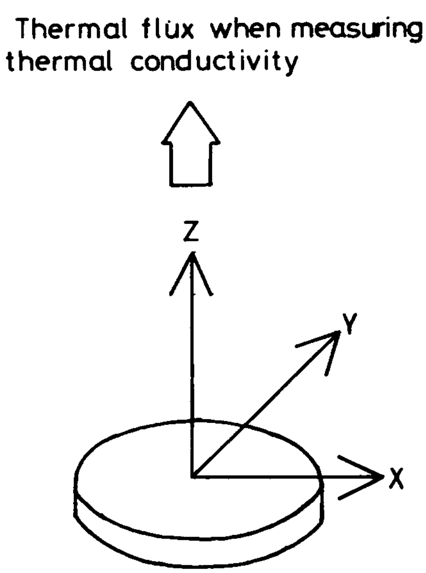

Figure 2 The shape of specimens for measuring thermal conductivity.

Electrical Conductivity

Electrical conductivity was measured for three directions: X, Y, and Z. The X and Y directions, perpendicular to each other, are vertical to the Z direction, the direction of thickness of the specimen.

Measurement procedures are as follows: Electrical conductivity of high-resistivity material was calculated by measuring current yielded when a voltage of 500 VDC was applied, whereas for low-resistivity material, it was calculated by measuring the voltage yielded when a constant current of 1 mA to 100 nA was applied. The temperature for measurement was 23 ± 2°C and the relative humidity was 50 ± 5%.

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, as shown in Figure 2. All the measurements were performed at 50 ± 3°C.

RESULTS AND DISCUSSION

Anisotropy in the Composites

Figures 3 and 4 show H_y and H_z for fiber-filled polyethylene, especially for the Y direction in the XY face and the Z direction in the YZ face, respectively. All H_y's were estimated as about 0, and, hence, all types of fibers were considered to be at random from low- to high-volume contents. On the other hand, H_z's were found within −0.5 and −1.0, implying that

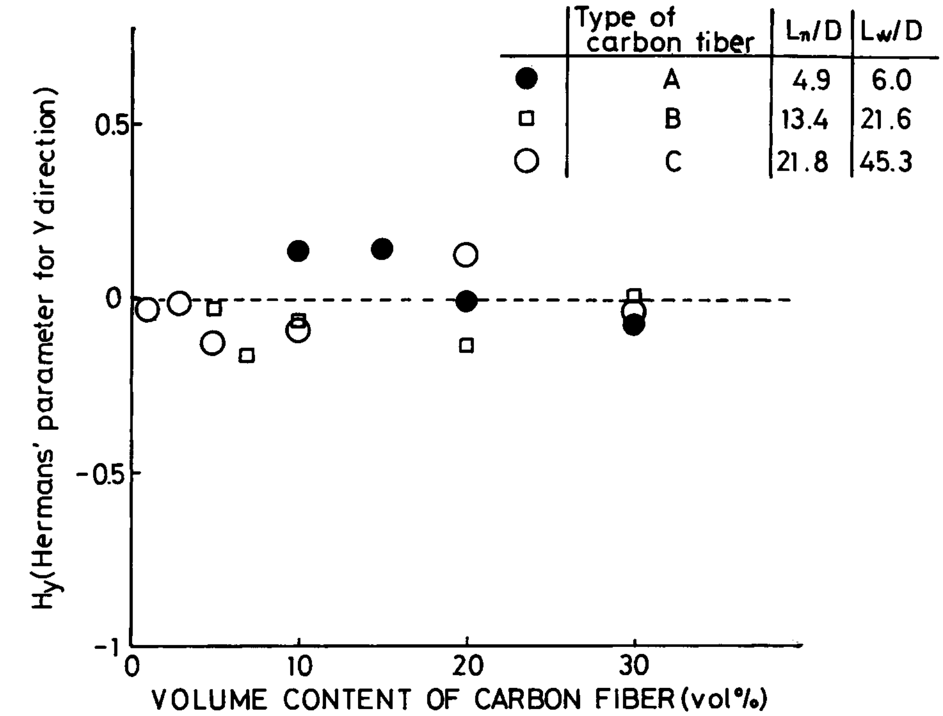

Figure 3 H_y (Hermans' parameter for the Y direction in the XY face) in the composites.

fibers are highly oriented vertical to the thermal flux. Further, all H_{yz}'s were within −0.3 and −0.5, as shown in Figure 5, implying a considerable degree of fiber orientation. Therefore, carbon fibers in the composite were presumed to be highly oriented vertical to the thermal flux and electric current. In

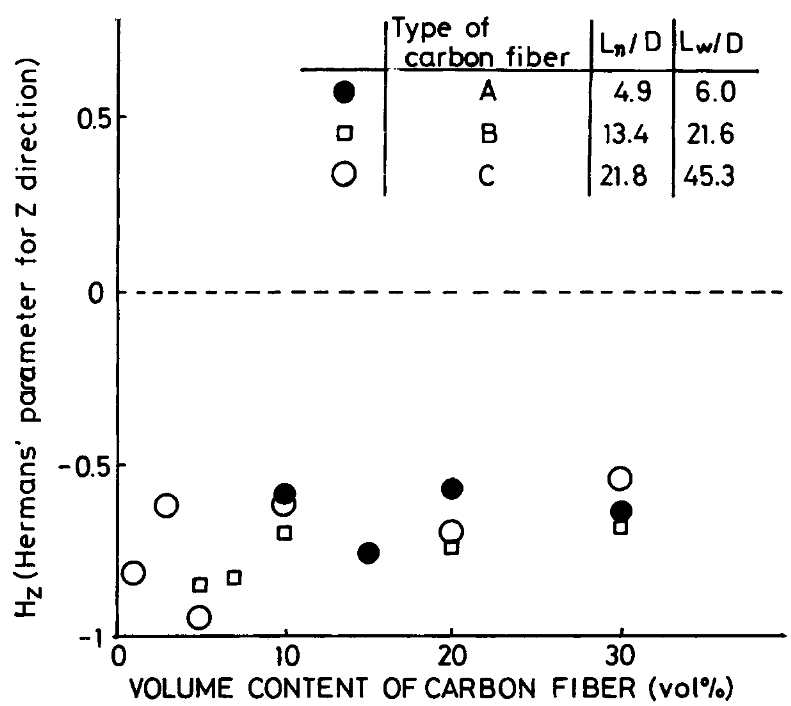

Figure 4 H_z (Hermans' parameter for the Z direction in the YZ face) in the composites.

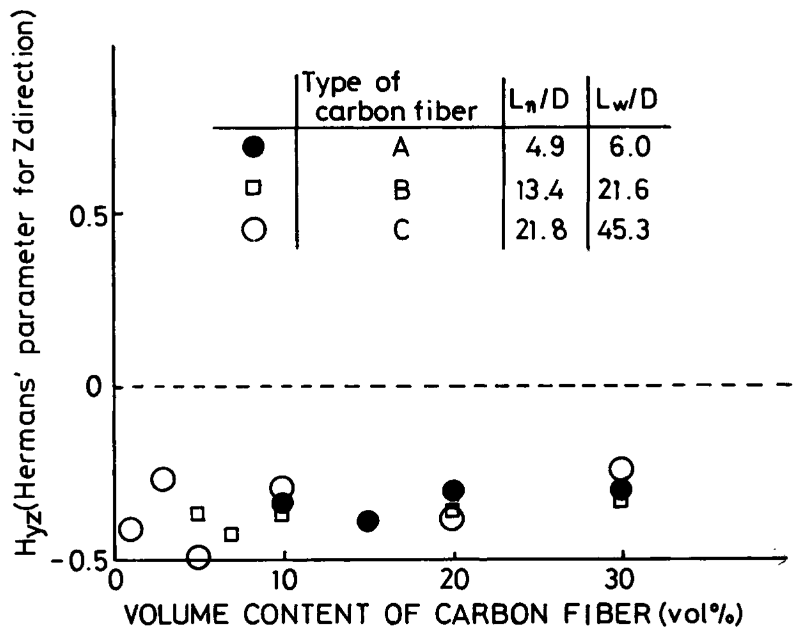

Figure 5 H_{yz} (Hermans' parameter for the Z direction in space) in the composites.

summary, it was found that carbon fibers oriented at random for the X and Y directions, but oriented vertical to the Z direction (the direction of thermal flux). Thus, carbon fibers were considerably oriented biaxially along the X and Y directions in the composites.

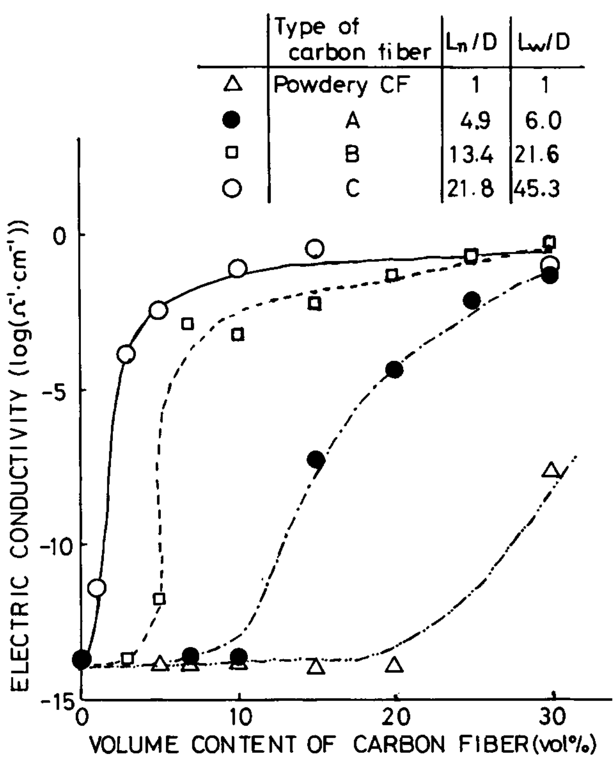

Figure 6 Electrical conductivity of the composites for the X direction.

Electrical Conductivity of the Composites

Electrical conductivities of the composites filled with several types of carbon fibers are indicated in Figures 6–8 (for the X, Y, and Z directions, respectively). All the electrical conductivities increased as depicted in Figure 1 and gradually approached $10^{-1}\ \Omega^{-1}\ \text{cm}^{-1}$.

The critical volume fractions were determined and are shown in Table III. The critical volume fractions for the X, Y, and Z directions were named C_x, C_y, and C_z, respectively. In the case of the composite filled with powdery carbon fibers (aspect ratio = 1), C_x, C_y, and C_z were equal to each other. Thus, the powdery carbon fibers were confirmed to be dispersed at random in the composite system. For the other types of carbon fibers, C_x and C_y were almost the same, whereas C_z was larger than were C_x and C_y. These results agree with the ones of Hermans' parameter on the composites. Thus, it can be confirmed for the composites that carbon fibers were dispersed without any orientation in the XY plane, whereas they were significantly oriented to the Z direction in the YZ and XZ planes. It was considered to occur because the probability of fiber contact for the X and Y directions were considered to be almost the same, but much larger than that for Z directions. This means that carbon fibers are oriented biaxially along the X and Y directions, similar

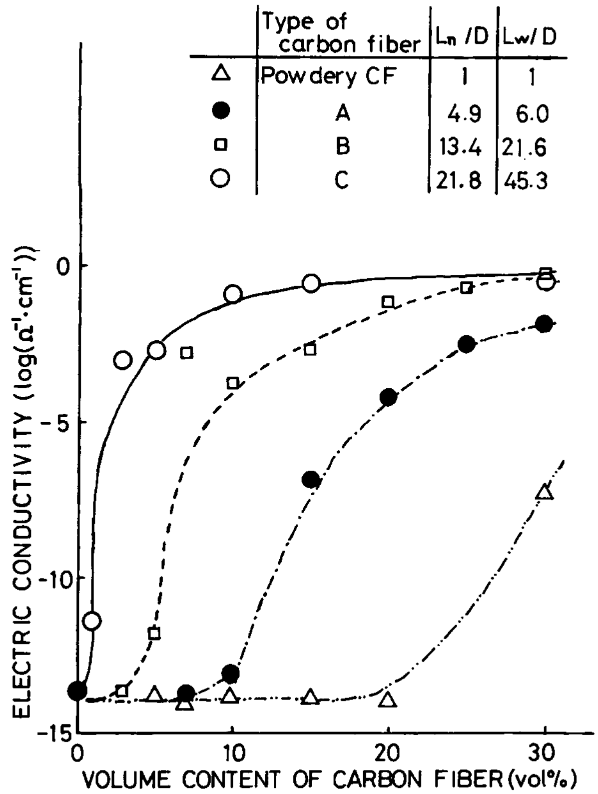

Figure 7 Electrical conductivity of the composites for the Y direction.

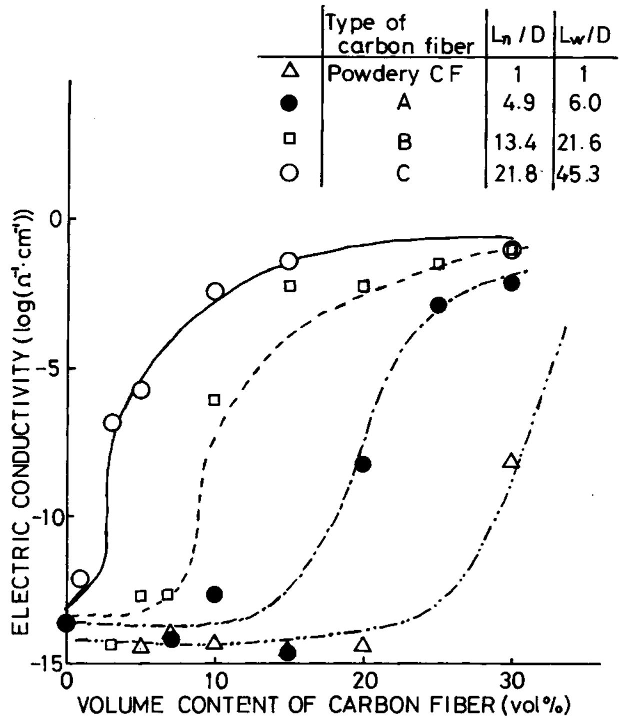

Figure 8 Electrical conductivity of the composites for the Z direction.

to the results of the anisotropy parameter (Hermans' parameter).

Electrical Anisotropy

Electrical anisotropies ($EA_{x/y}$ and $EA_{z/y}$) were estimated by eqs. (3) and (4), respectively:

$$EA_{x/y} = \log(\sigma_x / \sigma_y) \quad (3)$$

$$EA_{z/y} = \log(\sigma_z / \sigma_y) \quad (4)$$

where, σ_x, σ_y, and σ_z are electrical conductivity of a composite for the X, Y, and Z directions, respectively.

Both $EA_{x/y}$ and $EA_{z/y}$ in the composites filled with powdery carbon fibers were almost equal to 0, as shown in Figures 9 and 10, and it was considered that the composites were electrically isotropic. However, $EA_{z/y}$'s of composites filled with the other types of carbon fibers varied drastically with an increase in filler content, whereas $EA_{x/y}$'s of these composites stayed at almost 0. Especially when filled with type B carbon fiber, the peak of variation of $EA_{x/y}$ reached −10 at 7 vol % of fillers. Thus, the composite was electrically conductive at this composition for the X and Y directions, while acting as an insulator in the Z direction. This phenomenon can be explained by a gap between $C_y(C_x)$ and C_z, because all peaks of the anisotropy did appear in the filler content region between C_y and C_z. On the other hand, since $EA_{z/y}$'s of other compositions than the above were almost 0, the composite must be almost isotropic from the electrical viewpoint, when filler contents were less than C_y or more than C_z.

The electrical conductivity of a composite is affected mainly by the probability of filler touching. The probability is near 0 when the volume fraction

Table III Critical Volume Fraction in Electrical Conductivity

Type of Carbon Fiber (CF)	Critical Volume Fraction		
	C_x	C_y	C_z
Powdery CF	0.316	0.302	0.313
A	0.157	0.154	0.203
B	0.049	0.065	0.103
C	0.018	0.012	0.033

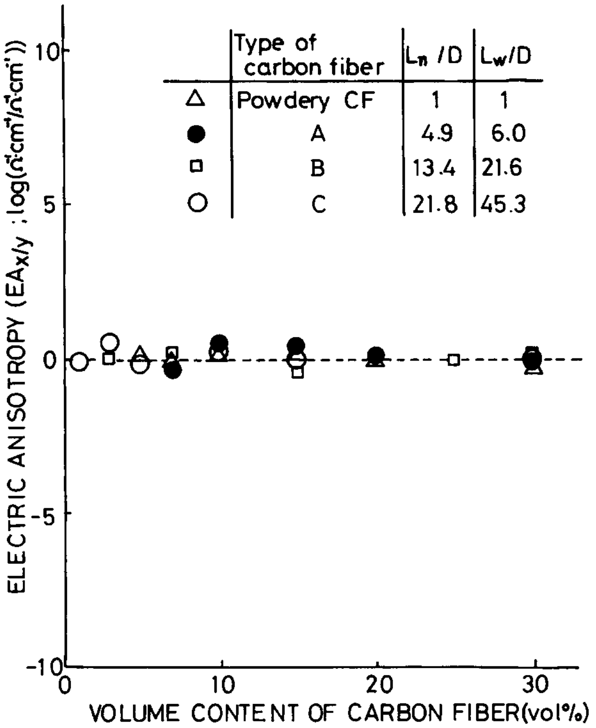

Figure 9 Electrical anisotropy ($EA_{x/y}$) in the composites.

of the filler is lower than a percolation threshold, whereas it is almost saturated to 1 in a sufficiently high fraction region where the touching probability must almost be unaffected by fiber orientation.

Thermal Conductivity of the Composites

Figure 11 shows that the thermal conductivities of the composites fit one curve irrespective of the types of fillers from a powdery one to longer fibers in a wide range of filler content. Thus, the increase in fiber length did not affect the thermal conductivity of the composite where carbon fibers were highly oriented vertical to the thermal flux.

Many theoretical and empirical models[7,15] have been proposed to predict the thermal conductivity of two-phase systems. Our previous reports[15,16] also discussed several models, of which our model was proved to be in excellent in agreement with experimental data. Further, eq. (5) proved to be adaptable to the thermal conductivity of polyethylene filled with disoriented short-cut carbon fibers:

$$\log \lambda = V C_f \log(\lambda_2 / C_p \lambda) + \log(C_p \lambda_1) \quad (5)$$

where λ is the thermal conductivity of a composite, λ_1; the thermal conductivity of a polymer, λ_2; the thermal conductivity of the filler, V; the volume content of the filler, C_p; a factor relating to the effect on crystallinity and crystal size of the polymer, and C_f; a factor related to ease in forming conductive chains of filler.

Here, we have tried to apply eq. (5) to the experimental data of this study. Figure 12 shows logarithms of thermal conductivity of the composites against the volume content of carbon fibers. All experimental data points are approximately on one straight line. Therefore, the experimental data can be explained by eq. (5).

Values of C_p and C_f kept approximately constant ($C_p = 1.00$ and $C_f = 0.535$) in spite of increasing fiber length. Thus, in the composite filled with biaxially oriented fibers ($H_{yz} \leq -0.3$), the effect of increasing fiber length on thermal conductivity was considered to be canceled by the fiber orientation in the vertical direction to the thermal flux.

CONCLUSION

We prepared polyethylene composites filled with various types of biaxially oriented carbon fiber and

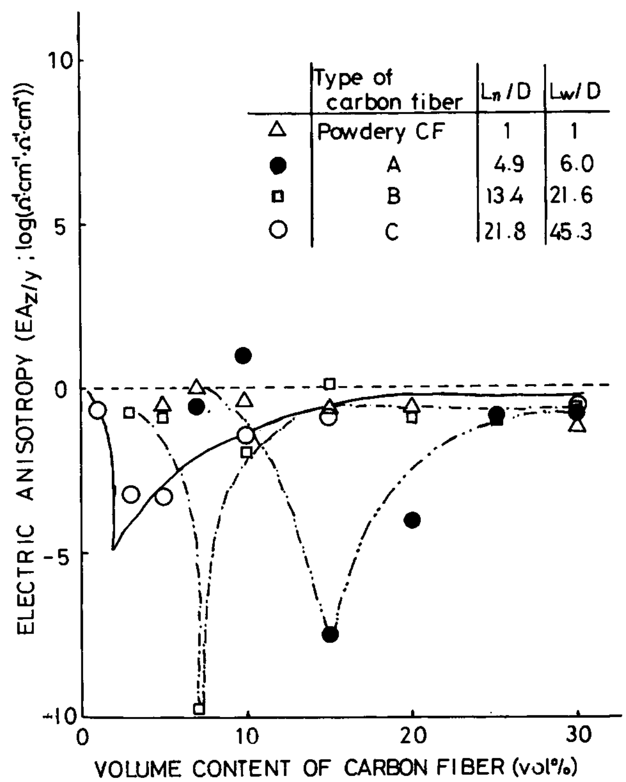

Figure 10 Electrical anisotropy ($EA_{y/z}$) in the composites.

then discussed the effect of biaxial orientation of fibers on electrical and thermal conductivities of the composites. Thus, the following conclusions were made.

1. The prepared composites were estimated by the anisotropic parameter (Hermans' parameter). It was found by the results of H_y, H_z, and H_{yz} that carbon fiber was significantly oriented vertical to thermal flux, i.e., biaxially oriented in the composites.
2. The critical volume fraction (C_x) was equal to C_y but smaller than C_z in the biaxially oriented carbon fiber composite. Therefore, it was considered that carbon fibers touched each other more readily in the biaxially oriented directions than in the vertical one.
3. The electrical anisotropy ($EA_{z/y}$) of the composites varied drastically with increase in filler content. Especially when filled with B type of carbon fiber, a peak of variation reached −10 at 7 vol % of filler. On the other hand, the $E_{x/y}$ of the composite was almost 0.

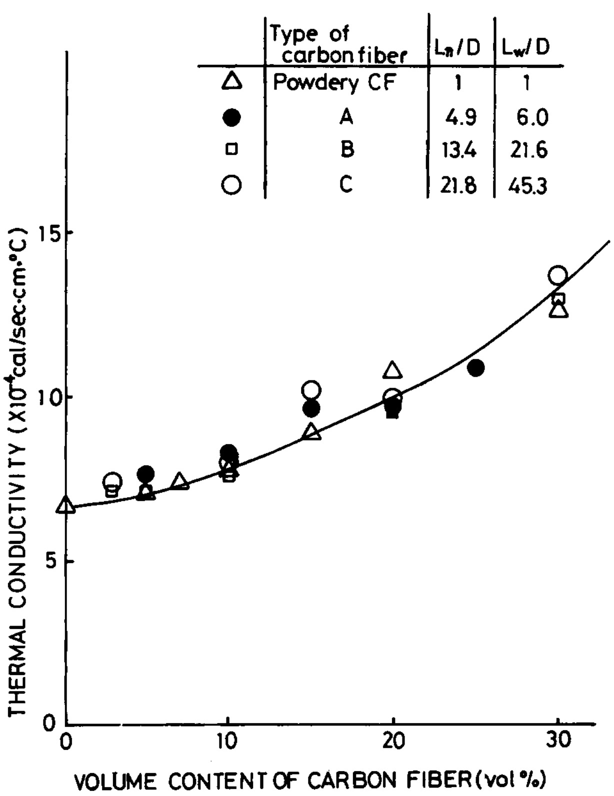

Figure 11 Thermal conductivity of the composites.

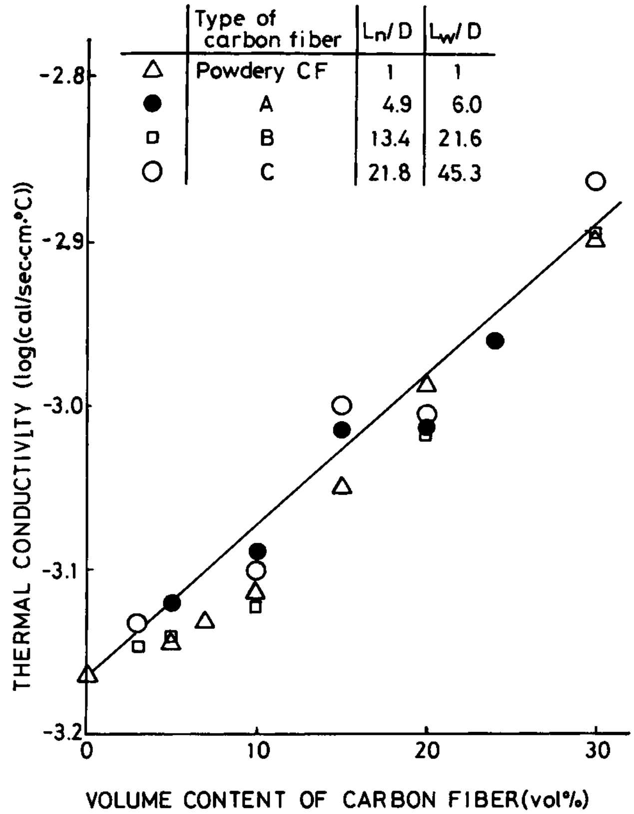

Figure 12 Logarithm of thermal conductivity of the composites against volume content of carbon fibers.

4. The longer the length of the carbon fiber was, the higher became the electrical conductivity of the biaxially oriented carbon-fiber composites for all directions. But, the thermal conductivity of the composite was almost unchanged in the vertical direction to the biaxial-orientation plane, even if fiber length was long.
5. Our equation previously proposed proved adaptable also to the thermal conductivities of these composites. C_p and C_f were unchanged, in spite of increasing fiber length.

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