

Thermal Conductivity of Polyethylene/Polystyrene Blends Containing SEBS Block Copolymer

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SYNOPSIS

We measured the thermal conductivity of a polyethylene/polystyrene blend containing SEBS block copolymer, which has two components of polystyrene block and hydrogenated polybutadiene block, and discussed the effect of phase inversion on the thermal conductivity by observing the morphology of the blend. Further, we examined the applicability of the thermal conduction model for composites, which was proposed in our previous reports, to this blend system. By plotting the logarithm of the thermal conductivities of the blends vs. the weight content of polyethylene, it was found that the experimental data lie approximately on a straight line with an increase in polyethylene until the range of dual-phase continuity (phase inversion), and then the data move on another straight line beyond the range of dual-phase continuity. Thus, our model to explain the thermal conductivity of the polymer blend was proved. Further, both coefficients *A* and *B* in our model took linear relations with the weight content of the block copolymer, and the model was, thus, more strongly confirmed to be applicable to thermal conductivity of polymer blends.

INTRODUCTION

There have been numerous reports on immiscible polymer blends.¹⁻³ Some reports discussed various properties of polyethylene (PE)/polystyrene (PS) blends containing SEBS block copolymer, which has two components of polystyrene block and hydrogenated polybutadiene block, as a compatibilizer.⁴⁻⁹ Few reports, however, have focussed upon the thermal conductivity of polymer blends, although conductivity is a fundamental property that is important in processing of polymer blends. Further, the phase morphology of a polymer blend changes with its composition, going from a dispersion of one component in the other, through phase inversion, to the reverse structure.¹⁰ Phase inversion affects the thermal conductivity of the blend.

In this study, thermal conductivity of PE/PS blends, containing a SEBS block copolymer, was measured, and the phase morphology of the blend

was examined by polarized optic microscopy. The effect of phase inversion on the thermal conductivity of the blend is discussed. Further, the applicability of a prediction model for the thermal conductivity of two phase systems, which has been proposed in previous reports,^{11,12} is examined. Here, a polymer blend is regarded as a composite.

EXPERIMENTAL

Preparation

Specimens were made by mixing molten low molecular weight PE, containing SEBS block copolymer, with a molten low molecular weight PS. PE (Highwax 100P), PS (Highmer ST95), and SEBS block copolymer (Kraton G1652) were supplied by Mitsui Petrochemical Co. Ltd., Sanyo Chemical Industries Co. Ltd., and Shell Kagaku Co. Ltd., respectively. Some properties (density, thermal conductivity, and molecular weight) of the materials utilized are shown in Table I.

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The SEBS block copolymer has polystyrene end-blocks and a hydrogenated polybutadiene midblock, which is equivalent to an ethylene-butene-1 copolymer and is expected to be compatible with PE. Any heat of fusion for the PE part of the block copolymer could not be detected by a Rigaku DSC 8230 differential scanning calorimeter. Thus, the degree of crystallinity of the PE part was considered to be almost 0.

Measurement

Morphology

Phase morphologies of polymer blends were examined by polarized optical microscopic observation, using an Olympus 13H2. A sample for observation was made by inserting the molten blend (180°C) between a slide and a cover glass, followed by cooling to room temperature.

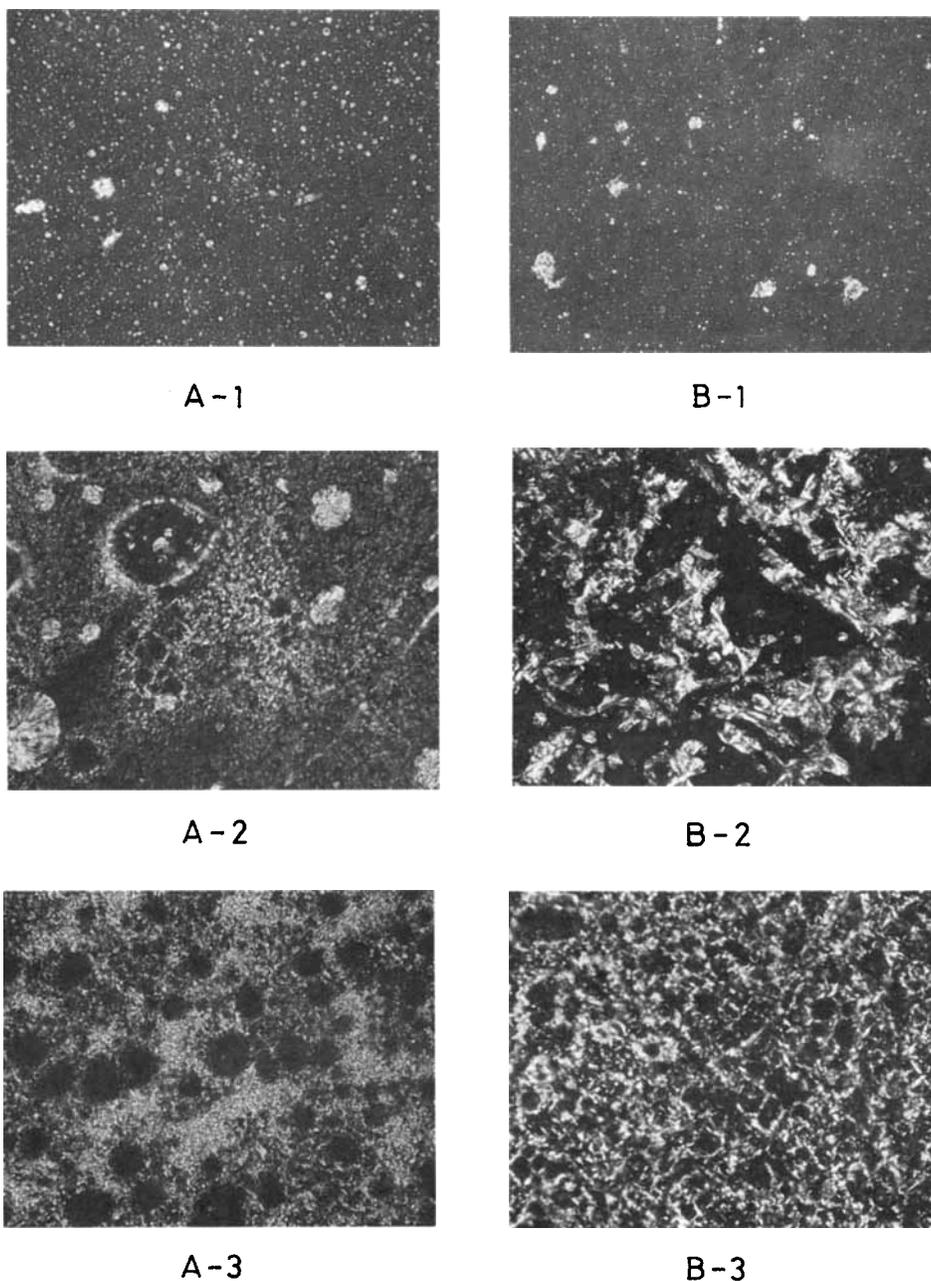


Figure 1 Polarized optical micrographs of PE/PS blend containing SEBS block copolymer. (A-1) PE = 10 wt %, SEBS = 2.0 wt %; (A-2) PE = 20 wt %, SEBS = 2.0 wt %; (A-3) PE = 40 wt %, SEBS = 2.0 wt %; (B-1) PE = 10 wt %, SEBS = 4.8 wt %; (B-2) PE = 20 wt %, SEBS = 4.8 wt %; (B-3) PE = 30 wt %, SEBS = 4.8 wt %.

Table I Properties of Materials

Material	Density (g/cm ³)	Thermal Conductivity (cal/sec × cm × °C)
Polyethylene ^a	0.928	8.09×10^{-4}
Polystyrene ^b	1.065	3.83×10^{-4}
Block Copolymer ^c	0.999	4.57×10^{-4}

^a Highwax 100P, $M_w = 900$, measuring by viscometer method.

^b Highmer ST95, $M_w = 4310$, $M_n = 1420$, measuring by GPC method.

^c Kraton G 1652, PE : PS = 71 : 29.

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 $50 \pm 3^\circ\text{C}$.

RESULTS AND DISCUSSION

Morphology

Phase morphology of an immiscible blend changes with the composition of the blend, from a dispersion system to an inversed dispersion system through phase inversion (dual-phase continuity).¹⁰

In this study, morphology of PE/PS blends containing SEBS block copolymer, with various compositions, was observed by a polarized optic microscope.

In a series of run A, where the block copolymers were added 2.0 wt %, the phase morphology of the blend changed with increasing of PE, from a phase system of "PE dispersed in PS" at 10 wt % of PE (refer to A-1 in Fig. 1), to the phase system of "PS dispersed in PE" at 40 wt % of PE (A-3), through dual-phase continuity at around 20 wt % of PE (A-2), as indicated in Figure 1. Here, the black area corresponds to PS, while the white area corresponds to PE. In a series of run B (including 4.8 wt % of block copolymer), the phase morphologies of blends (B-1, B-2, and B-3) were similar to that of the run A series, except that the dual-phase continuity appearing more clearly at 20 wt % of PE (B-2). The phase morphologies of the other blends were also observed and classified into three types of phase morphologies: "PE dispersed in PS," dual-phase continuity, and "PS dispersed in PE" (Fig. 2). In all the blends added with lower than 23.1 wt % of

the block copolymer, the systems of dual-phase continuities appeared at the region of 20–30 wt % of PE.

The diameter of dispersed particles became smaller with an increase in the content of the block copolymer from 20–50 μm (C-1) to 4–9 μm (C-4), as indicated in Figure 3. This occurred because the block copolymer reduced the interface energy between PE and PS, in order to diminish the size of the dispersed particles.

Thermal Conductivity

Measurement of the thermal conductivity of the PE/PS blend, without the addition of the block copolymer, was impossible, since the two phases separated during sample casting. High interfacial energy between the two phases is considered to cause the phase separation.

Thermal conductivities of PE/PS blends, containing various contents of SEBS block copolymer (compatibilizer), were measurable, and were indicated in Figure 4, where the content of block copolymer for (A) = 2.0 wt %, (B) = 4.8 wt %, (C) = 9.1 wt %, (D) = 16.7 wt %, and (E) = 23.1 wt %. The thermal conductivity seems to increase monotonically with the increase in PE, without any sign of change in the range (20–30 wt % of PE) of dual-phase continuity of the blends.

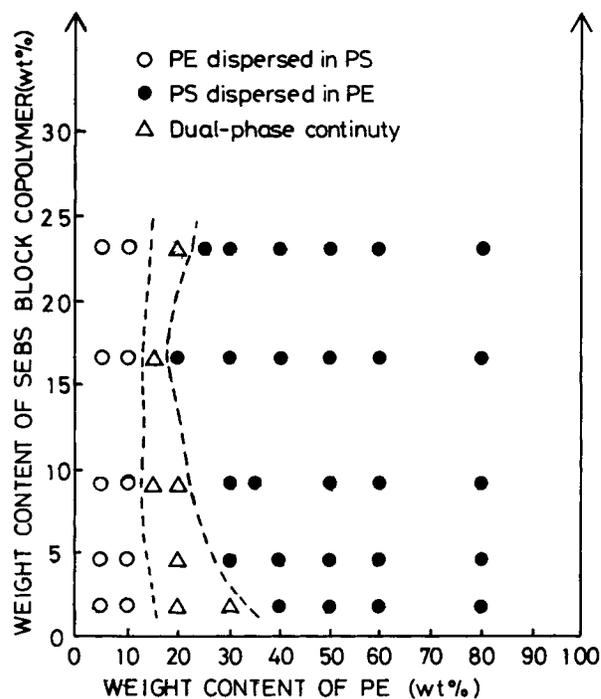


Figure 2 Phase morphologies of various PE/PS blends containing SEBS block copolymer.

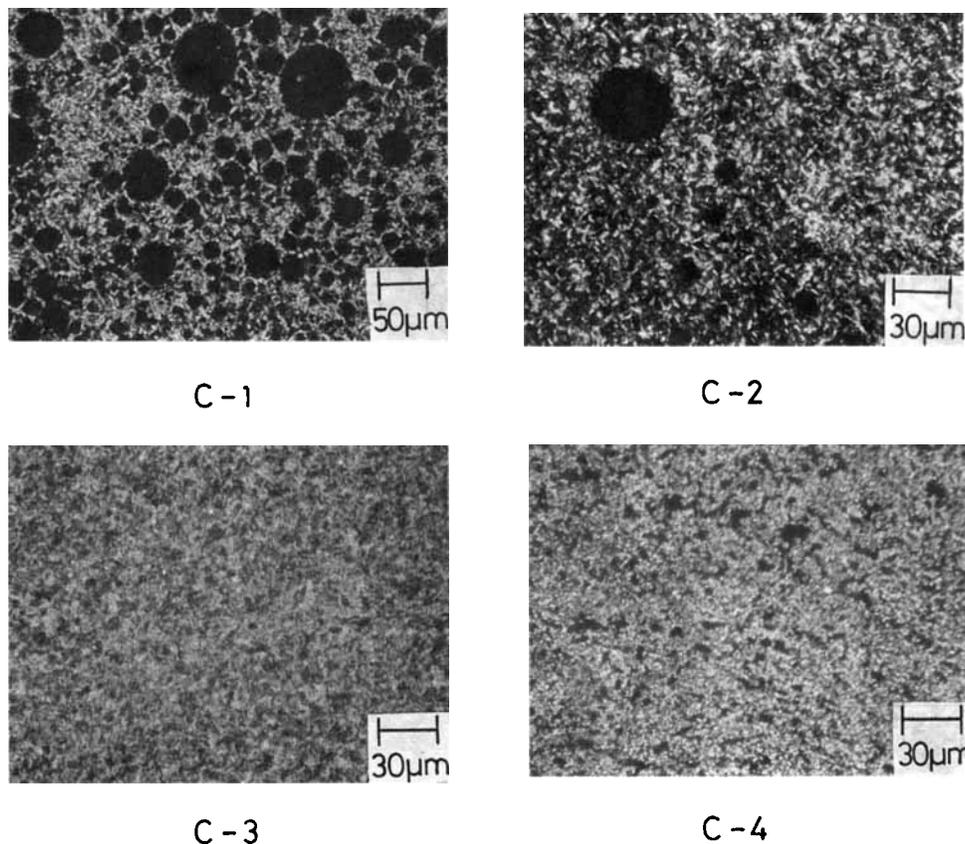


Figure 3 Polarized optical micrographs of PE/PS blend containing SEBS block copolymer. (C-1) PE = 50 wt %, SEBS = 2.0 wt %; (C-2) PE = 50 wt %, SEBS = 4.8 wt %; (C-3) PE = 50 wt %, SEBS = 9.1 wt %; (C-4) PE = 40 wt %, SEBS = 23.1 wt %.

Figure 5 shows the effect of the SEBS block copolymer content on the thermal conductivity of the blends. The thermal conductivities of the blends, rich in PE (100 and 80 wt % of PE), showed a steep decrease with the increasing in the block copolymer, while that of other blends, with lower content of PE (50 and 20 wt %), remained approximately constant. Further, the thermal conductivity of PS increased slightly. This reason for this is that the thermal conductivity of the SEBS block copolymer is smaller than that of PE and slightly larger than that of PS (Table I).

APPLICATION OF CONDUCTIVE MODEL TO EXPERIMENTAL DATA

Modification on an Equation Predicting Thermal Conductivity of a Composite for a Polymer Blend

Few reports have been published on the thermal conductivity of polymer blends. Since blends of mu-

tually immiscible polymers can be regarded as a kind of composite, thermal conductive models for composites are expected to be applicable for polymer blend systems, too.

In our previous reports,¹¹ comparisons were made on several models, and our model gave most satisfactory agreement with the experimental data for polymer/filler composites. Equation (1) is derived from the model.

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

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

It was also found that a modified model is applicable for a composite filled with a mixture of par-

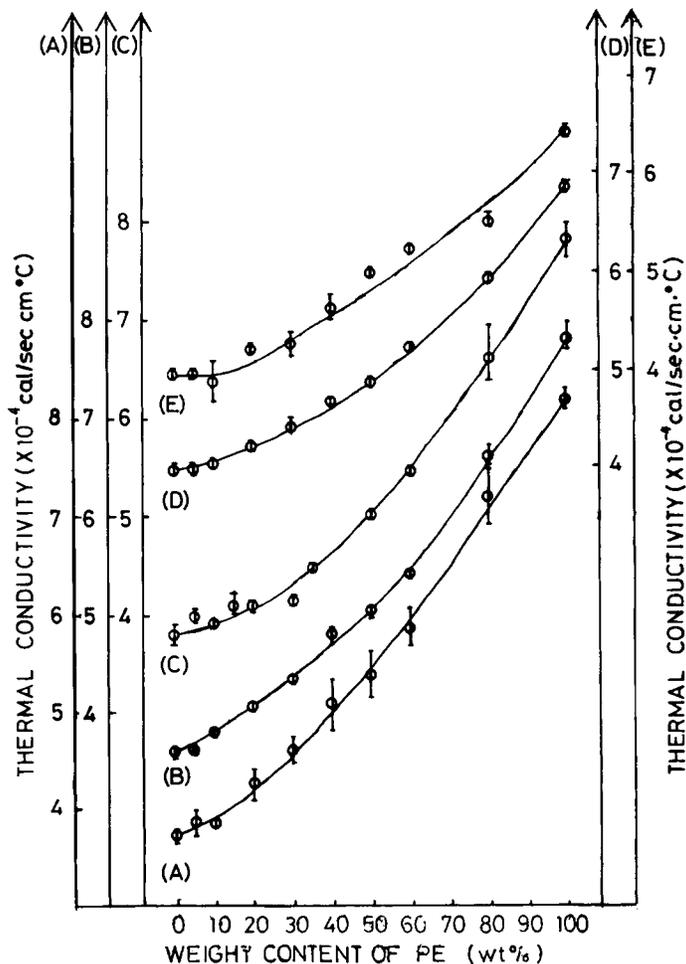


Figure 4 Thermal conductivity of PE/PS blend containing various weight contents of SEBS block copolymer. (A) 2.0 wt %, (B) 4.8 wt %, (C) 9.1 wt %, (D) 16.7 wt%, and (E) 23.1 wt %.

ticles.⁸ Equation 2 is derived from the modified model.

$$\log \lambda = V_1 \times \log(C_1 \times \lambda_1) + V_{21} \times C_{21} \times \log \lambda_{21} + V_{22} \times C_{22} \times \log \lambda_{22} \quad (2)$$

$$V_1 + V_{21} + V_{22} + \dots = 1$$

where λ_{21} = thermal conductivity of filler 1, λ_{22} = thermal conductivity of filler 2, V_{21} = volume content of filler 1, V_{22} = volume content of filler 2, C_{21} = factor relating to the ease in forming conductive chains of filler 1, and C_{22} = factor relating to the ease in forming conductive chains of filler 2.

In this report, we tried to apply the model to the experimental data for the polymer blends, regarding the dispersion phase as filler 1, the block copolymer as filler 2, and the continuous phase as "polymer."

However, the volume composition of the polymer blend is not clear, since the PE and PS chain parts of the block copolymer may exist homogenized in the corresponding homopolymers. Further, thermal conductivities of dispersion phase and block copolymer may be affected by crystallinity and crystal size of PE. Thus, by replacing volume fraction by weight fraction, eq. (2) was modified to eq. (3).

$$\log \lambda = W_1 \times \log(C_{11} \times \lambda_1) + W_2 \times C_2 \times \log(C_{12} \times \lambda_2) + W_3 \times C_3 \times \log(C_{13} \times \lambda_3) \quad (3)$$

λ : Thermal conductivity of polymer blend.

λ_1 : Thermal conductivity of polymer in the continuous phase.

W_1 : Weight content of polymer in the continuous phase.

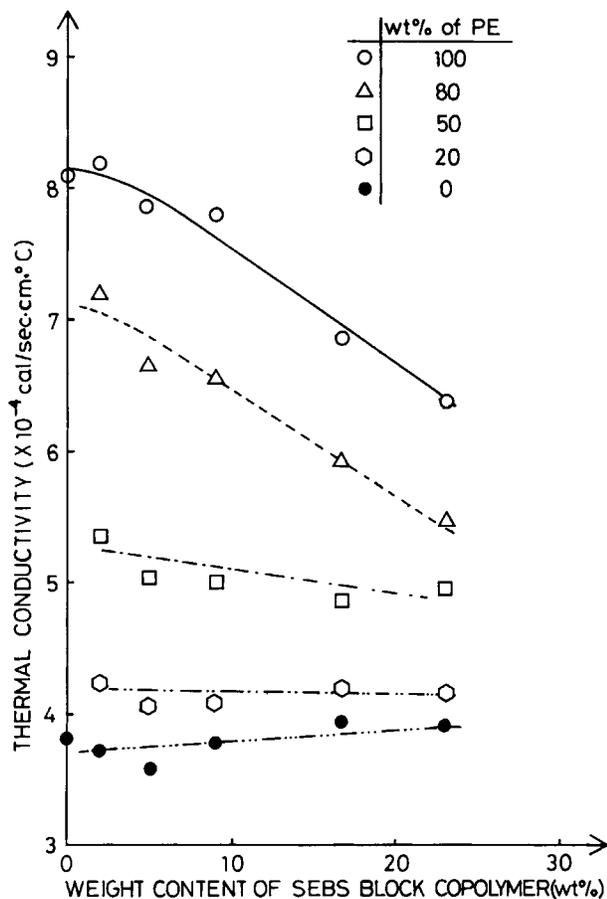


Figure 5 Thermal conductivity of PE/PS blend with various weight contents of SEBS block copolymer, by fixing the PE content (100 wt %, 80 wt %, 50 wt %, 20 wt %, and 0 wt %).

λ_2 : Thermal conductivity of polymer in the dispersed phase.

W_2 : Weight content of polymer in the dispersed phase.

λ_3 : Thermal conductivity of the compatibilizer (block copolymer).

W_3 : Weight content of the compatibilizer (block copolymer).

C_{11}, C_{12}, C_{13} : Factors relating to the crystallinity and crystal size of

1. Polymer in the continuous phase (C_{11}),
2. Polymer in the dispersed phase (C_{12}),
3. Compatibilizer (block copolymer) (C_{13}).

C_2, C_3 : Factors relating to the ease in formation of conductive particle chains of

1. Polymer in dispersed phase (C_2),
2. Compatibilizer (block copolymer) (C_3).

If $W = W_2/(W_1 + W_2)$, eq. (3) is rearranged to eq. (4).

$$\log \lambda = A \times W + B \quad (4)$$

$$A = (1 - W_3)$$

$$\times (C_2 \times \log(C_{12} \times \lambda_2) - \log(C_{11} \times \lambda_1)) \quad (5)$$

$$B = (1 - W_3) \times \log(C_{11} \times \lambda_1)$$

$$+ W_3 \times C_3 \times \log(C_{13} \times \lambda_3) \quad (6)$$

If W_3 is kept constant, eq. (4) means that $\log \lambda$ takes linear relation with W .

Application of the Modified Equation to Experimental Data

Figure 6 shows the logarithm of the thermal conductivities of PE/PS blends added with various contents of block copolymers, plotted against the weight content of PE (W). In all blends, logarithms of thermal conductivity of the blends lie approximately on a straight line up to 20–30 wt % of PE. The phase morphologies of all the blends up to 20–30 wt % of PE were observed to be “PE dispersed in PS,” by the observation of morphology. Thus, the conductivity of such systems up to that content can be explained by eq. (4), assuming that PE was dispersed phase and PS was continuous phase. Above that content of PE, logarithms of the thermal conductivity of the blends approximately lie on another straight line, while the phase morphology was observed to be “PS dispersed in PE.” Thus, the conductivities of the blends above this content can be explained by eq. (4), assuming that PS was dispersed phase and PE was continuous phase.

Here, the slope of the line (A in eq. 4) differs between “PE dispersed in PS” and “PS dispersed in PE;” those lines cross. The cross points of the lines in the blends with various contents of SEBS block copolymer are indicated in Table II. The cross point, in turn, can be utilized for finding the dual-phase continuity range, where the dispersed component, PE, is inverse to the continuous component, because it exists in the range of dual-continuity.

The coefficients A and B in eq. (4) are evaluated and summarized in Table III (for PE dispersed in PS) and Table IV (for PS dispersed in PE). Here, the cross point was assumed as 20 wt % of PE dispersed in 80 wt % of PS for simplicity of calculation. All the correlation coefficients were approximately 1, and so the experimental data of thermal conductivities of the blends were confirmed by eq. (4).

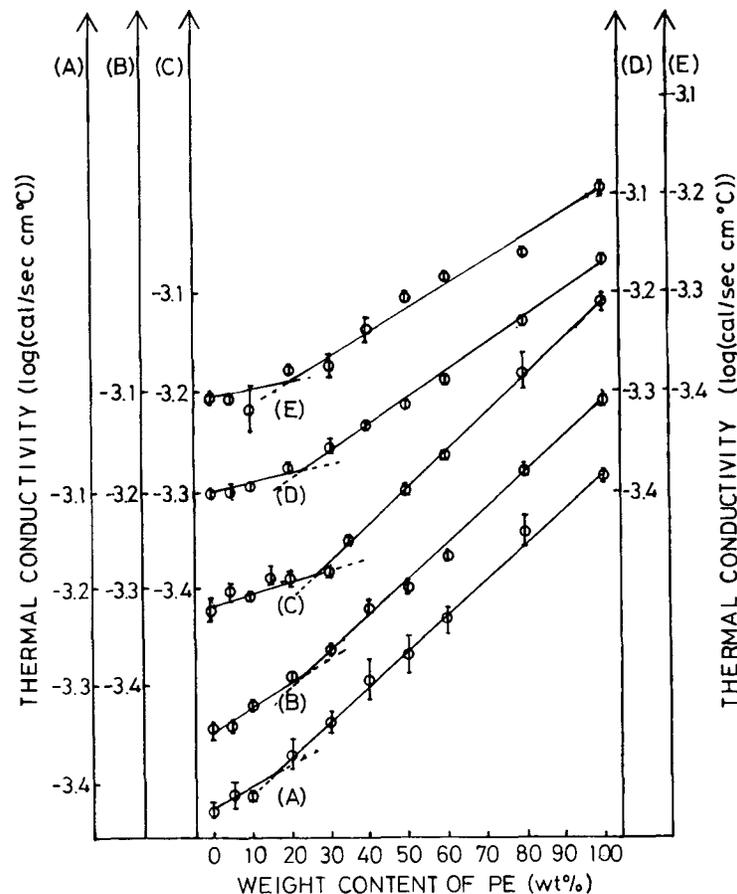


Figure 6 Logarithm of thermal conductivity of PE/PS blend containing various weight contents of SEBS block copolymer. (A) 2.0 wt %, (B) 4.8 wt %, (C) 9.1 wt %, (D) 16.7 wt %, and (E) 23.1 wt %.

Coefficients A and B are plotted against the weight content of the block copolymer and are indicated in Figures 7 and 8, respectively. Both A and B form approximately linear relations with the weight content of block copolymer, although deviation of data from linearity is rather significant for

A . These linear relations of coefficients A and B , against the content of block copolymer, agree with the linear expressions of eqs. (5) and (6). Thus, it was considered that the linear relations of B and A , with the content of the block copolymer, were ex-

Table II Cross Points

Run	Weight Content of Block Copolymer (wt %)	Cross Point (wt % of PE)
A	2.0	0.17
B	4.8	0.27
C	9.1	0.30
D	16.7	0.22
E	23.1	0.27

Table III Values of A and B in Eq. (4) for the System "PE Dispersed in PS"

Run	Weight Content of Block Copolymer (wt %)	A	B	Correlation Coefficient
A	2.0	0.278	-3.43	0.952
B	4.8	0.291	-3.45	0.980
C	9.1	0.162	-3.42	0.927
D	16.7	0.147	-3.41	0.959
E	23.1	0.134	-3.41	0.961

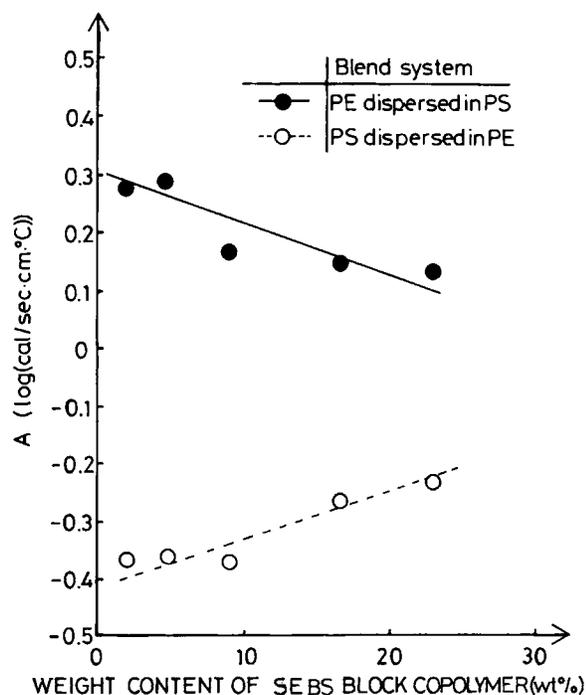
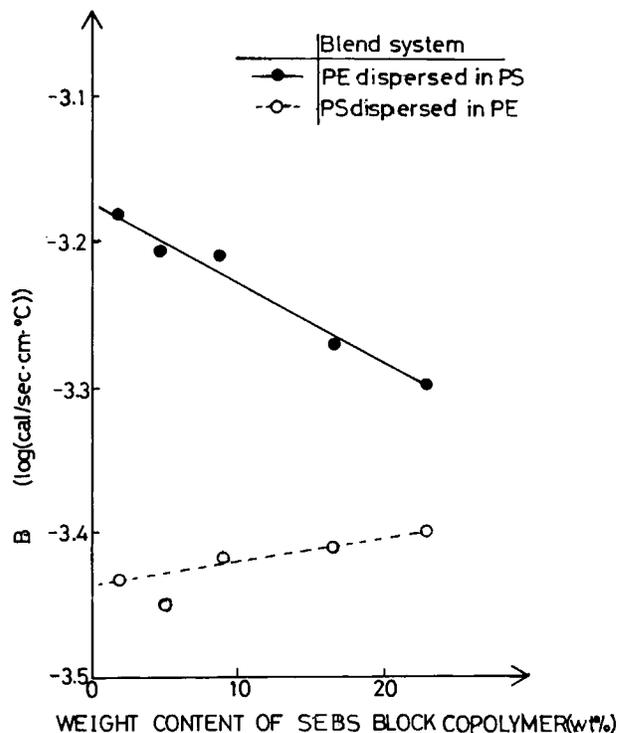
Table IV Values of *A* and *B* in Eq. (4) for the System "PS Dispersed in PE"

Run	Weight Content of Block Copolymer (wt %)	<i>A</i>	<i>B</i>	Correlation Coefficient
A	2.0	-0.365	-3.08	0.998
B	4.8	-0.361	-3.11	0.997
C	9.1	-0.370	-3.11	0.996
D	16.7	-0.265	-3.17	0.996
E	23.1	-0.233	-3.20	0.988

plained by eqs. (5) and (6), respectively. Therefore, it was more clearly proved that eq. (4) can explain the thermal conductivity of polymer blends.

SUMMARY

We measured the thermal conductivities of PE/PS blends containing the SEBS block copolymer as a compatibilizer, after determining the phase inversion range, by polarized optical microscopic observation. We then discussed the effect of phase inversion on the thermal conductivity of the blend.

**Figure 7** Coefficient *A* in eq. (4) vs. weight contents of SEBS block copolymer.**Figure 8** Coefficient *B* in eq. (4) vs. weight contents of SEBS block copolymer.

Further, we examined the applicability of a thermal conduction model for composites, which was proposed our previous reports, to this blend system.

Phase morphology of all the blends changed from a system of "PE dispersed in PS," through the range of dual-phase continuity (20–30 wt %), to a system of "PS dispersed in PE."

The thermal conductivity increased monotonically without showing any change at around the range of dual-phase continuity (20–30 wt % of PE). The thermal conductivity of the blend rich in PE decreased and that of the blend rich in PS kept constant or slightly increased, by increasing of the block copolymer.

Plotting the logarithm of the thermal conductivity of the blends vs. the weight content of PE shows a linear relation, but the slope of the line changes at the range of dual-phase continuity (20–30 wt % of PE). The line for the blend containing less than 20–30 wt % of PE can be explained by eq. (4), where "PE is dispersed in PS," and another line for the blend containing more PE can be explained by eq. (4), where "PS is dispersed in PE."

Further, both coefficients *A* and *B* in our model took linear relations with the weight content of the

block copolymer, and the model was, thus, more strongly confirmed to be applicable to the thermal conductivity of polymer blends.

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