Thermal Conductivities of Blends of Polyethylene/SEBS Block Copolymer and Polystyrene/SEBS Block Copolymer

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SYNOPSIS

Thermal conductivities of two series of blends of polystyrene and styrene–ethylene/butyrene–styrene block copolymer (PS/SEBS), and polyethylene and styrene-ethylene/butylene-styrene block copolymer (PE/SEBS) were measured. Here the PS part and hydrogenated polybutadiene (EB; ethylene-butene-1 copolymer) part of SEBS were confirmed to be miscible in PS and PE homopolymers, respectively, by the differential scanning calorimetry. The thermal conductivity of PS/SEBS increased, while that of PE/SEBS blends decreased monotonically, with increasing SEBS content. No significant changes in the range where microphases usually occur were noted. The thermal conductivities of PS/SEBS and PE/SEBS were explained by modifications of our equation for composites. Thermal conductivity of EB in SEBS was estimated from that of PS/SEBS blend as 4.9 $\times 10^{-4}$ cal/s cm °C. Further, the thermal conductivity of PE/SEBS could be predicted by substituting the obtained value of EB into the modified equation. Therefore, the modified equations were confirmed to be applicable to thermal conductivities of PS/SEBS and PE/SEBS blends. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Among the numerous reports on polymer blends,[1-3] some have established,[4,5] by transmission electron microscopy (TEM), small-angle x-ray spectrometry (SAXS), and x-ray diffraction, that segregated microphases, especially, in a blend of polystyrene (PS) and styrene–butadiene–styrene (SBS) block copolymer or polyethylene (PE) and SBS block copolymer can become spheres, cylinders, or lamellae. Some reports[6-9] discuss various properties of blends of PE and PS with SEBS block copolymer which has two components of PS and hydrogenated polybutadiene (PBd). However, there are few reports on the thermal conductivity of polymer blends, although it is a fundamental property important in processing of polymer blends. In a previous report,[10] we discussed thermal conductivity of a ternary blend of PS/SEBS block copolymer/PE.

In this study, we measured thermal conductivities of blends of PE/SEBS and PS/SEBS. We also discuss the applicability of our prediction model for thermal conductivity of a composite, which already has been proposed.[11,12]

EXPERIMENTAL

Preparation

PE, PS, and SEBS block copolymer were supplied, respectively, by Mitsui Petrochemical Co. Ltd., Sanyo Chemical Industries Co. Ltd., and Shell Kagaku Co. Ltd. They were designated as Highwax 100P, Highmer ST95, and Kraton G1652, respectively. Some properties of the materials utilized are shown in Table I.

Blending was carried out as follows: For the PS/SEBS blend, low-molecular weight PS and SEBS were mixed in toluene at room temperature, and then toluene was removed by evaporation under vacuum to yield solid residue. Test specimens were made of

Table I   Properties of Materials

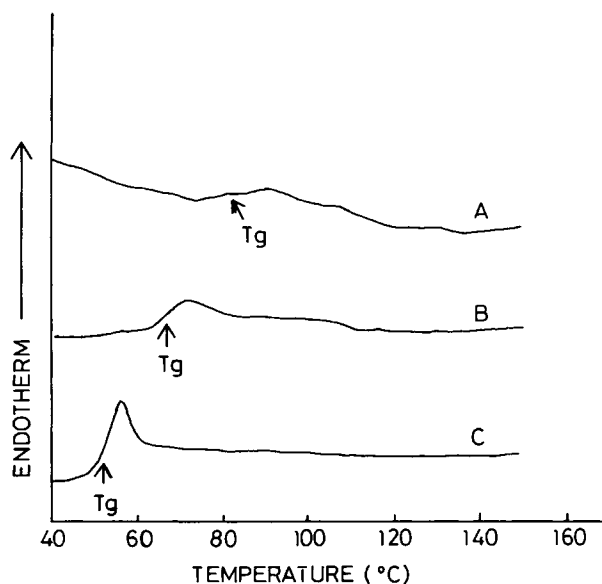| Materials	Density (g/cm^3)	Thermal Conductivity (cal/s cm °C)
Polyethylene[a]	0.928	8.1×10^{-4}
Polystyrene[b]	1.065	3.8×10^{-4}
SEBS block copolymer[c]	0.999	6.6×10^{-4}

[a] $M_w = 800$.
[b] $M_w = 4310, M_n = 1420$.
[c] EB:PS = 71:29.

the residue by compression molding (200°C). For the PE/SEBS blend, after low-molecular weight PE and SEBS were mixed in toluene at 140°C, methanol was added to precipitate the blend from the solution. After removing methanol under vacuum from the blend, test specimens were made by compression molding (200–230°C).
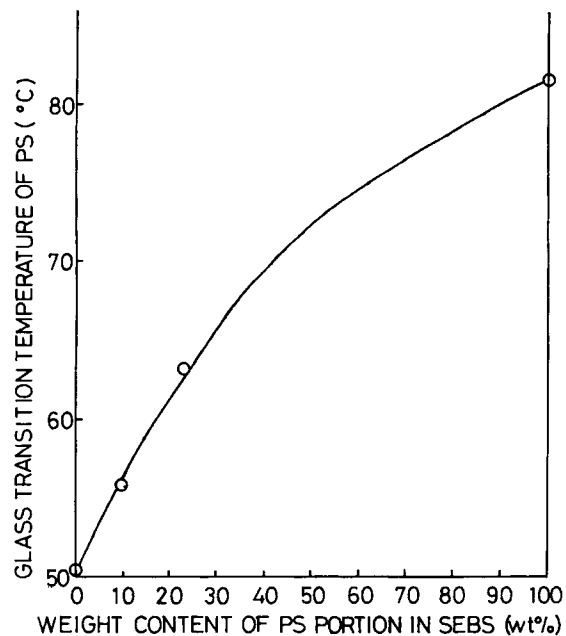
SEBS block copolymer has a PS endblock and hydrogenated PBd midblock. The midblock is equivalent to an ethylene-butene-1 copolymer. PS content of the block copolymer was estimated at 29% by the nuclear magnetic resonance (NMR).

Measurement of Thermal Behavior

Melting temperature, heat of fusion, and glass transition temperature (T_g) of polymers were measured

Figure 2   Glass transition temperature (T_g) of PS phase in several PS/SEBS blends plotted against weight content of PS part of SEBS.

by a differential scanning calorimeter (DSC), Rigaku DSC 8230. All measurements were performed at a constant incremental rate of 10°C/min. The degree of crystallinity of PE was calculated using 8.7 kJ/mol,[13] heat of fusion for PE with 100% crystallinity.

Measurement of 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 specimen is 50 mm diameter × 5 mm thickness. All measurements were performed at 50 ± 3°C.

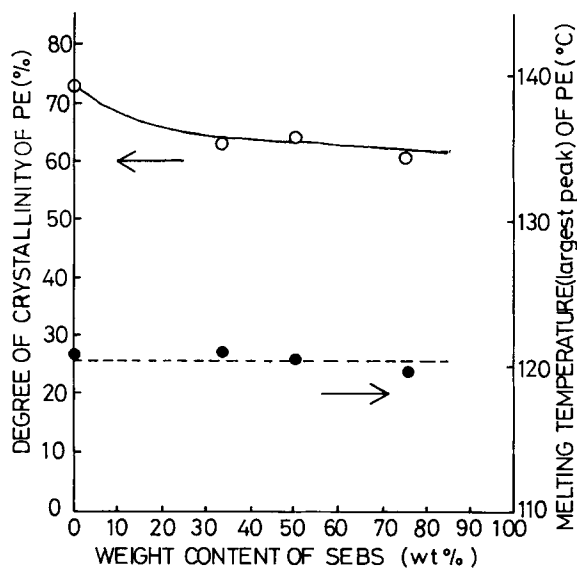## RESULTS AND DISCUSSION

Thermal Behavior

Figure 1 shows DSC traces of SEBS(A), SEBS/PS blend (B; SEBS/PS = 50/50), and PS(C). T_g of PS segments shifted from 81.6°C (A) to 63.2°C (B) to 50.4°C (C). The changes in T_g along with the increasing ratio of the PS in SEBS to total PS content [PS segment in SEBS/(PS segment in SEBS + PS homopolymer)] is shown in Figure 2.

Figure 1   DSC traces of several PS/SEBS blends (content of SEBS; A = 100 wt %, B = 50 wt %, C = 0 wt %).
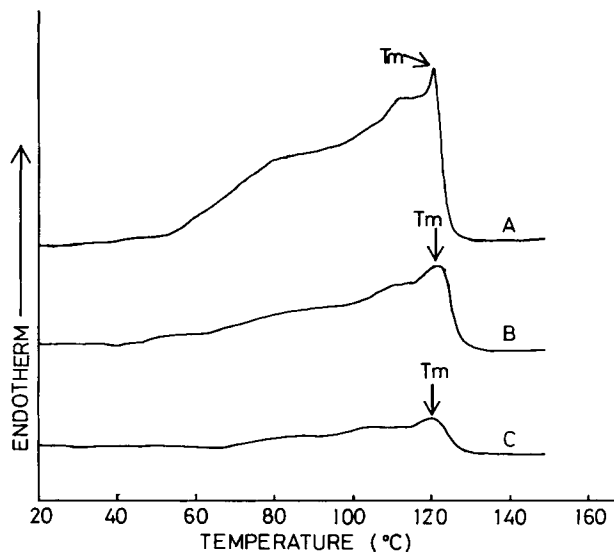
Figure 3 DSC traces of several PE/SEBS blends (content of SEBS; A = 0 wt %, B = 50 wt %, C = 75 wt %).

The PS portion of SEBS was confirmed to be miscible with PS homopolymer. Heat of fusion of SEBS was not detectable in Figure 1. Hydrogenated polybutadiene has an ethylene-butene-1 (EB) copolymer structure which is quite similar to PE. Therefore, the ratio of EB can be considered equivalent to PE with its degree of the crystallinity almost zero (noncrystalline PE).

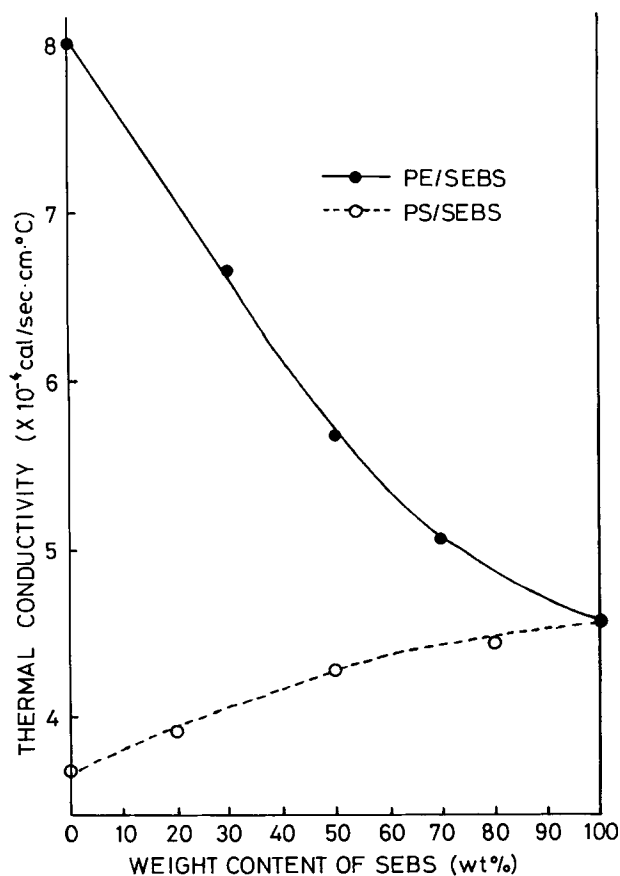Figure 3 shows in DSC traces of PE and several PE/SEBS blends endothermic changes over a wide

temperature range. The melt temperature (T_m) of PE was kept constant, even in the blends with various contents of PE (Fig. 4). Degree of crystallinity of PE homopolymer slightly decreased with the increase in SEBS until 20–30 wt %, and then remained constant (Fig. 4). This phenomenon was attributed to the miscibility of the EB portion of SEBS in the amorphous phase of PE, which presumably disturbed the crystallization of PE.

Thermal Conductivity

Thermal conductivity of the PE/SEBS blend decreased with increasing of SEBS, while that of the PS/SEBS blend increased (Fig. 5).

Studies using TEM, SAXS, and x-ray diffraction[4,5] have established that segregated microphases can be spherical, cylindrical, or lamellar. The following microphases have been observed in PB/SBS block copolymer blend:[5] for PB, spheres (up to 16 vol %), short rods (16–18 vol %), cylinders (18–36 vol %); for PB and SBS, lamellar structure

Figure 4 Degree of crystallinity and melting temperature $(T_m;$ the largest peak) of PE phase in several PE/SEBS blends.

Figure 5 Thermal conductivities of PE and PS blended with various contents of SEBS.

(36–60 vol %); and for SBS, cylinders (60–80 vol %) and spheres (over 80 vol %). Similar change in morphologies were expected for PS/SEBS blends and PE/SEBS blends, however any detectable change in thermal conductivities of those blends was observed over the entire range of SEBS content.

APPLICATION OF CONDUCTION MODEL TO EXPERIMENTAL DATA

Modification of Thermal Conduction Model for Polymer Blends

Models for thermal conduction in polymer blends rarely have been reported. Because the blend of PE/SEBS or PS/SEBS is regarded as a composite, thermal conduction models for composites can be expected to be applied for these blends. As discussed in our previous reports,[11,12] our model proved to be in excellent agreement with experimental data. Equation (1) is derived from our model.

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

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

In this report, we tried to modify the model for the present composite by regarding the block copolymer as "fillers" and the homopolymers as "polymer." However, the volume composition in the blend is not clear, because EB and PS portions in SEBS are miscible, respectively, to PE and PS homopolymers. Further, thermal conductivities of SEBS and PE may be affected by their crystallinity and crystal size. Thus, by replacing volume fraction by weight fraction, eq. (1) was modified to eq. (2).

$$\log \lambda = W C_2 \log(C_{12}\lambda_2) + (1 - W)\log(C_{11}\lambda_1) \quad (2)$$

where, λ = thermal conductivity of a polymer blend, λ_1 = thermal conductivity of a homopolymer, λ_2 = thermal conductivity of a block copolymer, C_2 = a factor relating to the ease in forming conductive particle chains of a block copolymer, C_{11} and C_{12} = factors relating to crystallinity and crystal size of the homopolymer and the block copolymer, respectively, and W = weight content of the block copolymer. Eq. (2) means that $\log \lambda$ takes a linear relation with W.

Further, we showed[12] that eq. (1) could be modified for a three-phase composite system. Similarly, eq. (2) can be modified to eq. (3) for a three-phase blend system.

$$\log \lambda = W_1\log(C_{11}\lambda_1) + W_2 C_{22}\log(C_{12}\lambda_2) \\ + W_3 C_{23}\log(C_{13}\lambda_3) \quad (3)$$

For A polymer/A–B block copolymer,

  Component 1: A homopolymer

  Component 2: B block part of A–B block copolymer

  Component 3: A block part of A–B block copolymer

Considering that components 1 and 3 are the same structure, this three-phase system can be treated as a two-phase system, A (homopolymer + block copolymer)/B (block copolymer). Then, eq. (3) can be rearranged as follows, since $\lambda_1 = \lambda_3$, $C_{11} = C_{13}$, $C_{23} = 1$ and $W_1 + W_2 + W_3 = 1$.

$$\log \lambda = W_2(C_{22}\log(C_{12}\lambda_2) \\ - \log(C_{11}\lambda_1)) + \log(C_{11}\lambda_1) \quad (4)$$

Therefore, thermal conductivity of the PS/SEBS blend was estimated by the following equation.

$$\log \lambda = A W_{\text{BPEB}} + B$$

$$A = C_{22}\log(C_{12}\lambda_{BPEB}) - \log(C_{11}\lambda_{PS})$$

$$B = \log(C_{11}\lambda_{PS}) \quad (5)$$

where, λ_{PS} = thermal conductivity of PS, λ_{BPEB} = thermal conductivity of EB portion of SEBS, W_{BPEB} = weight content of EB portion of SEBS in total blend. C_{11}, C_{12}, and C_{22} are defined as corresponding factors in eq. (4).

Similarly, eq. (4) is modified to eq. (6) for the PE/SEBS blend, where PE homopolymer, PS portion of SEBS and EB portion of SEBS correspond to components 1, 2, and 3, respectively. Here, the structure of component 1 is not the same as that of component 3.

$$\log \lambda = A'(W_{PE} + W_{BPEB}) + B'$$

$$A' = (1 + 1/m)\log(C_{11}\lambda_{PE}) - C_{22}\log(C_{12}\lambda_{BPPS}) \\ - (1/m)C_{23}\log(C_{13}\lambda_{BPEB})$$

$$B' = C_{22}\log(C_{12} \cdot \lambda_{BPPS}) - (1/m) \cdot \log(C_{11} \cdot \lambda_{PE}) \\ + (1/m)C_{23}\log(C_{13}\lambda_{BPEB}) \quad (6)$$
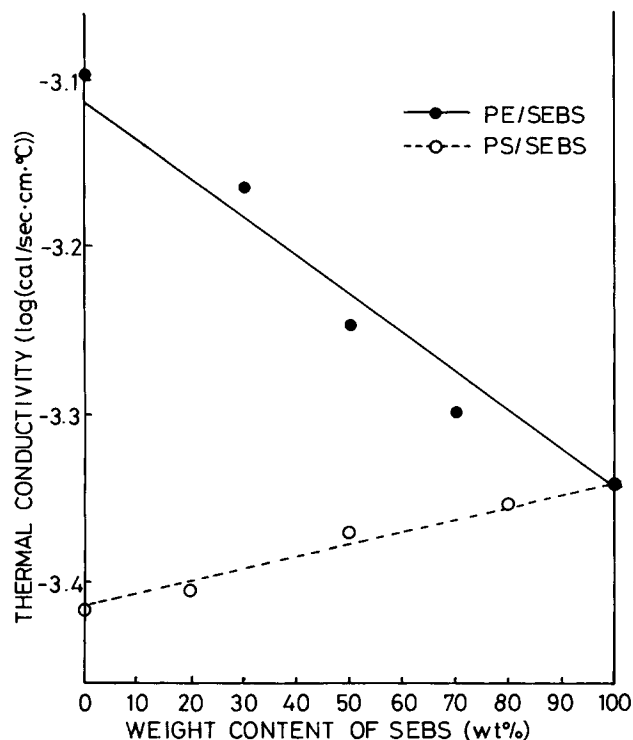
Figure 6 Logarithms of thermal conductivities of PE and PS blended with various contents of SEBS.

where, λ_{PE} = thermal conductivity of PE, λ_{BPEB} = thermal conductivity of EB portion of SEBS, λ_{BPPS} = thermal conductivity of PS portion of SEBS. W_{PE} = weight content of PE, W_{BPEB} = weight content of EB portion of SEBS and C_{11}, C_{12}, C_{13}, C_{22}, and C_{23} are defined as eq. (4). Then, the ratio (m; PS/ EB) of the two components in block copolymer (SEBS) is kept constant (29 : 71).

Here, since components 1 and 3 in eq. (6) are of similar structure, they are considered to form the same phase. The system then could be treated as a two-phase blend system of (PE + EB portions of SEBS)/PS portion of SEBS. Thus, w is defined as the total weight content of PE phase i.e., $w = W_{PE}$

+ W_{BPEB} in eq. (6) while $w = W_{BPEB}$ in eq. (5). Both eqs. (5) and (6) mean that $\log \lambda$ takes a linear relation with w.

Further, since EB is a kind of PE, it can be assumed that $\lambda_{PE} = \lambda_{BPEB}$, $C_{11} = C_{12}$ and $C_2 = 1$, in eq. (6), resulting in $A = A'$ and $B = B'$. Thus, eqs. (5) and (6) can be unified to eq. (7).

$$\log \lambda = Cw + D$$

$$C = A = A' = C_2\log(C_{12}\lambda_{PE}) - \log(C_{11}\lambda_{PS})$$

$$D = B = B' = \log(C_{11}\lambda_{PS}) \tag{7}$$

Equation (7) is equal to eq. (2) for the PE/PS blend, meaning that $\log \lambda$ takes a linear relation with w. If this is correct, the data of thermal conductivities of PS/SEBS and PE/SEBS blends might be plotted against the composition of PE/PS blend, by using eq. (6).

Application of the Thermal Conductivity Equation to Experimental Data

Figure 6 shows the logarithms of thermal conductivities of PE/SEBS and PS/SEBS blends, plotted against the weight content of SEBS [W in eq. (2)]. For each blend, experimental data points are approximate on each line. Therefore, the experimental data can be explained by eq. (2).

Values of C_{11}'s and $C_2 \log(C_{12} \lambda_2)$ are estimated from the intercepts and the slopes, respectively, of the lines, as indicated in Table II. The estimated values of $C_2 \log(C_{12} \lambda_2)$ for both blends were almost equal to the calculated ones by assuming $C_{12} = C_2 = 1$. Thus, it might be considered that C_{12} and C_2 for both blends are 1. The value of C_{11} for PS/SEBS blend is equal to 1, while that for PE/SEBS blend is <1. This is explained by the results of DSC measurement. The degree of crystallinity of PE in PE/ SEBS blends was smaller than that of PE itself.

Table II   Coefficients in Eq. (2)

Blend System	C_{11}	$C_2 \log(C_{12} \lambda_2)$		
		Estimated[a]	Calculated[b]	Error (%)
PS/SEBS	1.002	−3.34	−3.34	0
PE/SEBS	0.988	−3.35	−3.34	−0.3

[a] By the slope of the straight line in the relation of logarithm of thermal conductivity of the blend and the weight content of SEBS.
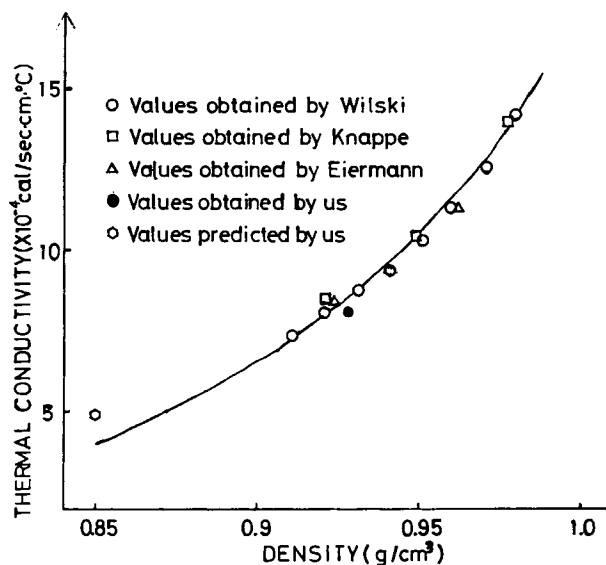[b] By assuming that both of C_2 and C_{12} are equal to 1.
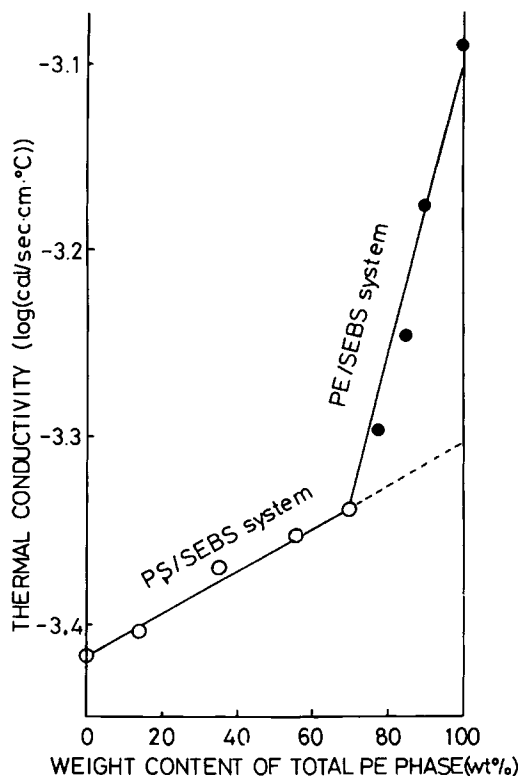
Figure 7 Thermal conductivities of PE/SEBS and PS/SEBS blends plotted against weight content of total PE phase (w).

Figure 8 Thermal conductivity of PE having various densities.

Thus, SEBS was considered to decrease the thermal conductivity of PE in the blend.

Although segregated microphases in homopolymer/block copolymer blends should become spherical, cylindrical, or lamella,[4,5] no distinct change, in logarithms of thermal conductivities of these blends, was detected with the morphological changes.

Figure 7 shows the logarithms of thermal conductivities of PE/SEBS and PS/SEBS blends plotted against w, weight content of total PE phase (PE + EB) in the blend. Experimental data points are plotted on the crosspoint of two lines at $w = 71$ wt % (Table III). Each line proves the applicability of eq. (5) $(w \leq 71$ wt %; PS/SEBS blend system)

and eq. (6) $(w \geq 71$ wt %; PE/SEBS blend system), respectively. However, this result was inexplicable by eq. (7). Therefore, thermal conductivities of PS/SEBS and PE/SEBS blends could not be substituted by that of a PE/PS blend. The crosspoint at 71 wt % must have occurred because of difference in the thermal conductivity of PE and EB [i.e., the assumption of $A = A'$, $B = B'$ does not hold between eqs. (5) and (6)]. Considering that C_{11}, C_{12}, and C_{22} in eq. (5) were all approximately 1, thermal conductivity of 100% EB was estimated from eq. (4) as 4.9×10^{-4} cal/s cm °C. It corresponds to the cross point (Δ) of the break line and the coordinate $(w = 100\%)$ in Figure 7. By comparing with the reported data[14] of thermal conductivity of PE, the thermal conductivity of EB obtained here was found to be almost equal to that of noncrystalline PE (density $= 0.85$), as shown in Figure 8.

By using the above obtained thermal conductivity of EB in a PS/SEBS blend, an intercept (B') and a slope (A') in eq. (6) for a PE/SEBS blend, were estimated and are indicated in Table III. The esti-

Table III Values of Slope (A and A') and Intercept (B and B') in Eqs. (5) and (6)

Weight Content of w (wt %)	Slope	Intercept	Corresponding to Equation	Correlation Coefficient
0–70	0.113	−3.42	eq. (5)	0.991
70–100	0.804	−3.91	eq. (6)	0.989
(70–100; est.)	0.817	−3.91	eq. (6)	—

mated values were approximately equal to experimental data, therefore, it is proved that the thermal conductivity of PE/SEBS blend is predictable by substituting that of EB in PS/SEBS blends into eq. (6). Therefore, eqs. (5) and (6) were confirmed to be applicable to thermal conductivities of PS/SEBS and PE/SEBS blends, respectively.

CONCLUSION

We measured thermal conductivities of PS/SEBS and PE/SEBS blends, where the PS and the EB portions of SEBS were confirmed to be miscible in PS and PE homopolymer, respectively, by DSC. The thermal conductivity of PS/SEBS increased, while that of PE/SEBS decreased monotonously, with increasing SEBS content, showing no detectable change at the range where changes in microphases of blends usually occur.

The thermal conductivities of PS/SEBS and PE/SEBS blends were explained by an equation modified [eq. (2)] from our equation for composites. Equations (5) and (6) also were applicable to experimental data, although a simplification of the two equations into eq. (7) for PE/PS blend system was unsuccessful. Thermal conductivity of the EB portion of SEBS was estimated as 4.9×10^{-4} cal/s cm °C, and was found almost equal to that of noncrystalline PE. It was proved further that thermal conductivity of PE/SEBS blend is predictable using the conductivity of EB. Therefore, it is confirmed that eqs. (5) and (6) were applicable to the thermal conductivity, of PS/SEBS and PE/SEBS blends respectively.

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