

Thermal diffusivity and conductivity of PS/PPO blends

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A miscible PS/PPO blend was prepared and its miscibility was confirmed by d.s.c. It was found that the miscibility of polymer blends could be evaluated by the measurement of their thermal diffusivity. The conductivity in the liquid state was smaller than that estimated from a linear-relation with the PPO content, but in the solid state, the conductivity was larger than the estimated value. This phenomenon was considered to occur because the strong interactions of polymer chains in the solid state increased the density (negative excess volume), resulting in the increase of the thermal conductivity of the blend. Further, all of Filippov, NEL and power law equations were found to be sufficiently adaptable to the experimentally determined thermal conductivities of PS/PPO blend in the liquid state, but none of them could be adapted to that in the glass state. © 1997 Elsevier Science Ltd.

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INTRODUCTION

There have been many reports concerning miscible polymer blends^{1–3}. A number of miscible pairs are known and, of these, a polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blend has been subjected to special close scrutiny^{4–10}. The PS/PPO blend exhibits a single compositionally dependent glass transition when examined by a variety of techniques, including d.s.c., dynamic mechanical relaxation, and the measurement of dielectric properties. In such studies, PS and PPO are found to be miscible in all proportions, and all evidence indicates that the pair is compatible at the segmental level. It was reported⁹ by measurement of FTi.r., that PS/PPO blend began to demix partially above 373 K. The pressure–volume properties of these blends were reported¹⁰ by Zoller *et al.* Further, considerable data have been acquired on various properties of these blends, mostly in the solid state, but also in the melt.

However, only a few reports have focused on the thermal conductivity of polymer blends^{11–16}, although it is a fundamental and important factor in the processing of polymer blends. Furthermore, it is of interest to determine how miscibility affects the thermal diffusivity and conductivity of polymer blends. Thermal diffusivity has been measured by a laser flash method, a useful means for a small thin test sample^{17–19}.

Because electronic effects are absent in most polymers, heat conduction occurs as a result of lattice vibrations, similarly to that in crystalline dielectrics²⁰. Thus, theoretical consideration of the thermal conductivity (λ) of those polymers leads to the Debye equation

$$\lambda = (1/3)Cv l \quad (1)$$

where C is the specific heat capacity per unit volume, v is the average phonon velocity, and l is the phonon mean free path.

The l value of an amorphous polymer is an extremely small constant (i.e. a few angstroms), because an amorphous state is considered to have numerous numbers of defects. Also, it is known that the thermal conductivity of an amorphous polymer increases up to the T_g with increasing temperature, although it decreases above the T_g ²⁰.

Thermal diffusivity (α) is defined as

$$\alpha = \lambda / (C_p \rho) \quad (2)$$

where C_p is the specific heat capacity at constant pressure, and ρ is the density. Here, because $C_p \rho$ is considerably strongly related to C in equation (1), α is expected to be influenced by v and l .

In our previous reports^{14–16}, several types of miscible blends were discussed. In the blends of lower molecular weight polystyrene/coumaron resin (PS/Co blend)¹⁴, which showed a miscible phase over all blend compositions, the thermal conductivity was approximately linearly related to the blend contents. The thermal conductivity of a miscible poly(vinyl chloride)/poly(methyl methacrylate) (PMMA) blend¹⁵ was found to show a large minimum at 85 wt% PMMA, because strong local compositional fluctuation occurred around that weight content. Further, the thermal conductivity of a miscible PMMA/bis-phenol A polycarbonate (PC) blend agreed¹⁶ with the conductivities which were estimated by several equations (Filippov, NEL and the power law).

In this report, miscible PS/PPO blends were prepared and their miscibilities were confirmed by d.s.c. The thermal diffusivity, specific heat capacity and density of the blends in the glass and liquid states were then measured by a laser flash method, d.s.c. and density

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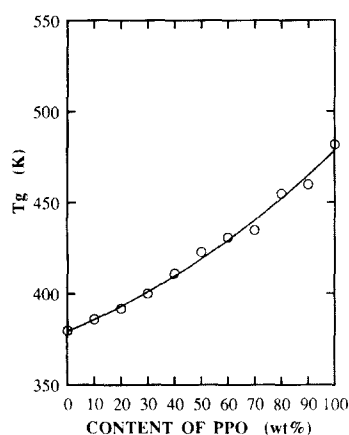
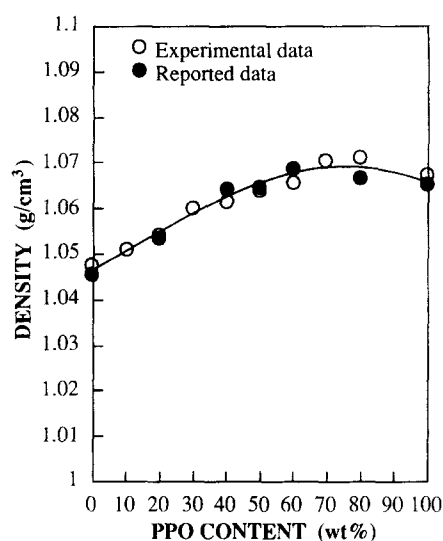

 Figure 1 T_g of PS/PPO blends (d.s.c. method)


Figure 2 Density of experimental data and reported data by Zoller

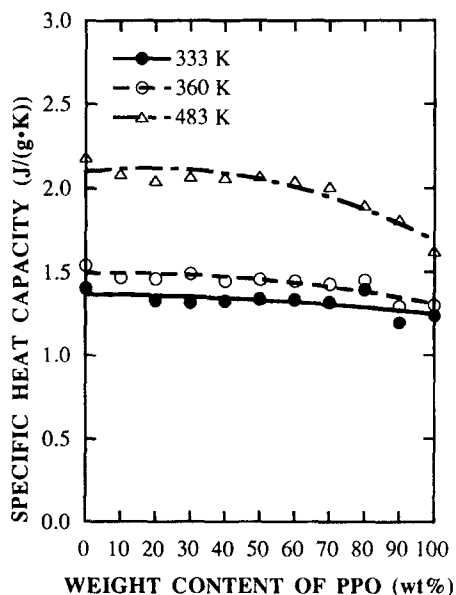


Figure 3 Specific heat capacity of PS/PPO blends

Table 1 Molecule weight of polymers

Polymer	M_n	M_w	M_w/M_n
Polystyrene (PS)	137 500	313 300	2.28
Polyphenylene oxide ^a (PPO)	24 100	63 600	2.64

^a Poly(2,6-dimethyl-1,4-phenylene oxide)

gradient methods, respectively. The thermal conductivity of the PS/PPO blend was calculated from these results and the density in the literature¹⁰. The change in thermal diffusivity and thermal conductivity relative to the blend composition and temperature were also examined. Further, the adaptation of prediction equations²¹⁻²⁴ for thermal conductivity to the experimental data was attempted.

EXPERIMENTAL

Sample preparation

Atactic PS and PPO were supplied by Shin-nittetsu Chemical Co., Ltd, Japan (G20) and Japan GE Plastics Co., Ltd, Japan, respectively. Their average molecular weights were determined by g.p.c. analysis relative to a polystyrene standard using tetrahydrofuran (THF) as a solvent. The results are shown in Table 1.

PS (15 g) or PPO (15 g) was purified by precipitation from chloroform into methanol (100 ml), and then dried under vacuum for 5 h.

To prepare the PS/PPO blend film, a mixture of PS and PPO was dissolved and mixed in chloroform. The polymer concentration was 2 wt%. Consequently, the sample films of PS/PPO blend were prepared by casting on a glass Petri dish at 333 K. The thin blend films were then dried at maintaining temperature, in stepwise manner, from r.t. to 473 K, in the following order: r.t. for 8 h, 383 K for 8 h, 423 K for 8 h, 453 K for 8 h and 473 K for 3 h. All the sample films were clear.

Thermal behaviour measurements

The glass transition temperature (T_g) was measured by d.s.c. (SSC 5200; Seiko Instrument, Ltd, Japan). All measurements were made at a heating rate of 10 K min⁻¹. The T_g on second scan was adopted for the experimental data. The T_g is then determined as T_{mg} (the mid-point temperature of the glass transition: the temperature at the intersection of the straight line equidistant in the vertical axial direction from the straight lines formed by extending the respective base lines and the curve showing a stepped change in glass transition).

Density and specific heat capacity measurements

The specific heat capacity of the polymer was measured using a differential scanning calorimeter (SSC 5200; Seiko Instrument, Ltd, Japan). α -Al₂O₃ was used for the standard specimen. The density of the polymer at 296 + 3 K was measured by the density gradient method (solvent; water/KI solution of water).

Thermal diffusivity measurements

Measurement of thermal diffusivity was performed by utilizing a thermal constant tester (TC7000; Shin-ku Riko, Inc.) based on a laser flash method. Thermal diffusivities from the glass to the liquid states were measured, after holding specimens for 5 min at a target

temperature. The specimens were 10 mm in diameter and about 300 μm in thickness.

Thermal conductivity estimations

The thermal conductivity of the polymer was obtained as the product of thermal diffusivity, specific heat capacity and density.

RESULTS AND DISCUSSION

Thermal behaviour

Figure 1 shows the T_{gs} of PS/PPO blends vs weight content of PC. The blend showed only one T_g . Thus, it was confirmed that the blend was miscible over all compositions.

Density and specific heat capacity

Figure 2 shows the densities of PS/PPO blends against weight content of PPO at 296 K for comparison with the data¹⁰ reported by Zoller *et al.* Our data really agreed with Zoller's data. Thus, Zoller's data on densities are considered to be useful for estimating the thermal conductivity of the blends in the higher temperature range.

In Figure 3, the specific heat capacities of the PS/PPO blends at several temperatures are shown against the weight content of PPO. The specific heat capacity under the T_g range (from the T_g of PS to that of PPO) decreased linearly with increasing PPO content, although above the T_g range it became somewhat larger than the values predicted by the linear relationship to the PPO content.

Thermal diffusivity

Figure 4 shows the thermal diffusivity of various types of PS/PPO blends at several temperatures. After all the diffusivity decreased slightly up to the T_g , it immediately decreased with increasing temperature. Then it decreased slightly. Thus, because the glass transition was considered to cause the immediate decrease in the diffusivity, T_g is estimated by the behaviour of the thermal diffusivity in order to compare with the T_g estimated by the d.s.c. measurement (Figure 5). Both of the T_g s were nearly equal. A similar agreement in the T_g of homopolymers was reported by Hashimoto²⁵. Therefore, it was found that the miscibility of polymer blends could be evaluated by the measurement of thermal diffusivity.

In both the states of solid (300 K, 333 K and 360 K) and liquid (483 K and 507 K), the thermal diffusivity of the PS/PPO blend increased with increasing PPO content. The diffusivity in the solid state was equal to that estimated from the linear relationship to PPO content (Figure 6), while the diffusivity in the liquid state was smaller than the estimated value (Figure 7). It was reported⁹ by measurement of FTi.r., that the PS/PPO blend began to demix partially above 373 K. Thus, it was considered that the partial demixing above the T_g range increased the distances between polymer chains, resulting in decreasing diffusivity of the PS/PPO blend.

Thermal conductivity

The thermal conductivities of PS/PPO blends were calculated by multiplying the experimental thermal diffusivity, the experimental specific heat capacity and Zoller's density data¹⁰, using equation (2). In both states of solid (333 K and 360 K) and liquid (483 K), the

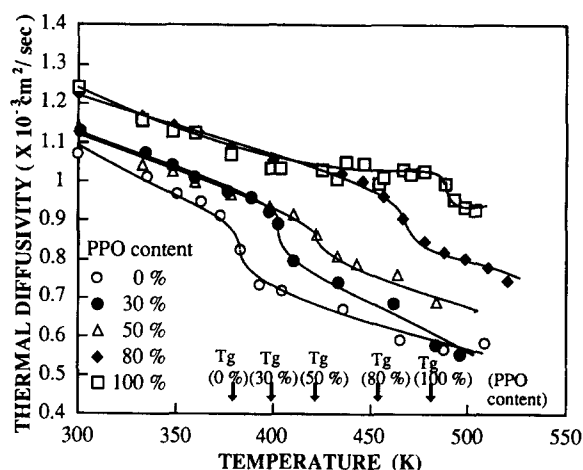


Figure 4 Thermal diffusivity of PS/PPO blends

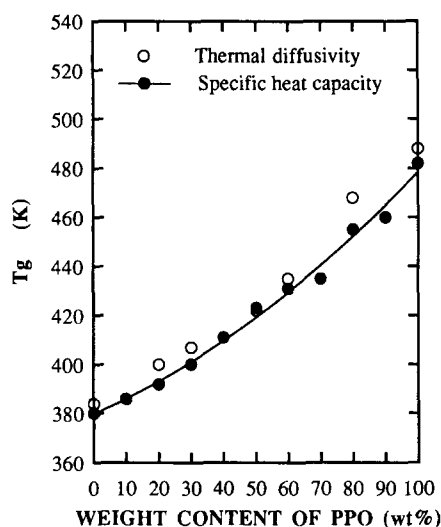


Figure 5 T_g s of PS/PPO blends, obtained by the measurement of thermal diffusivity and specific heat capacity

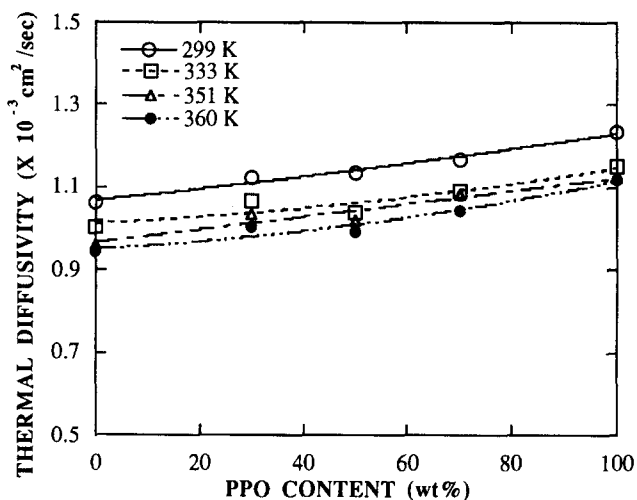


Figure 6 Thermal diffusivities of PS/PPO blends at various temperature below the range of T_g

thermal conductivity of the PS/PPO blends increased with increasing PPO content. The conductivity in the liquid state was smaller than that estimated by the linear relationship to the PPO content, while in the solid state,

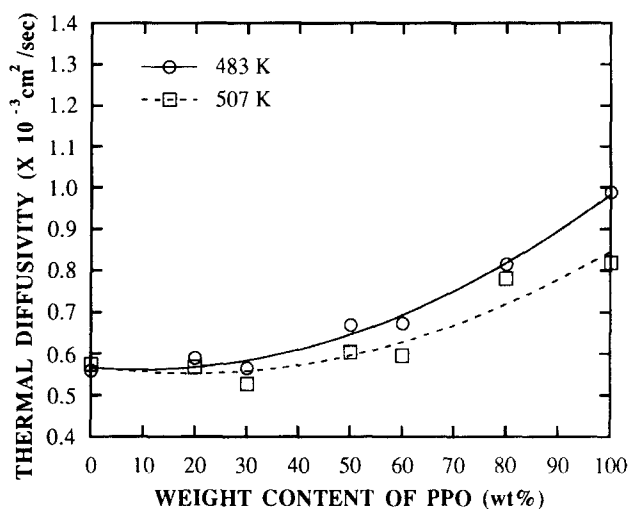


Figure 7 Thermal diffusivity of PS/PPO blends in the range above T_g

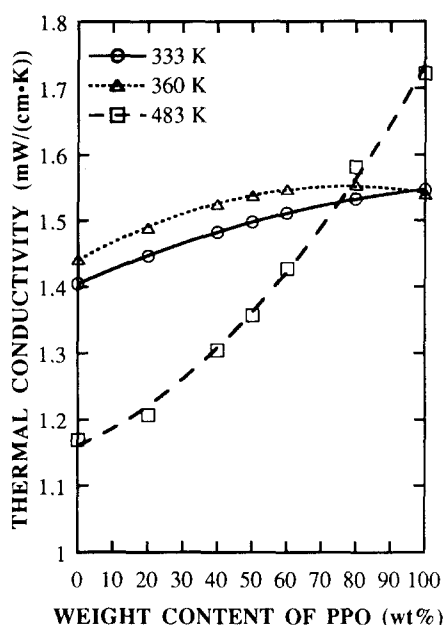


Figure 8 Thermal conductivities of PS/PPO blends at various temperatures

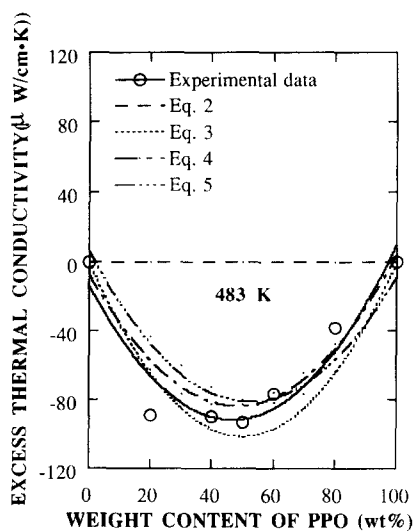


Figure 9 Comparison of experimental data with predicted data of excess thermal conductivity of PS/PPO blend

the conductivity was larger than the estimated value (Figure 8). A phenomenon similar to this change in the conductivity in the solid state has not been found in thermal conductivity of other polymer blends. Further, it has not been found in that of low molecular weight mixtures. Thus, this phenomenon in the solid state can be considered unique in the thermal conductivity of mixtures and blends.

There have been few reports concerning prediction equations for the thermal conductivity of polymers. Thus, because several types of prediction equations²¹⁻²³ were proposed for the thermal conductivities of mixtures of low molecular weight compounds, we attempted to adapt the equations to the experimental data.

Excess thermal conductivity (λ_E) of a blend is estimated by

$$\lambda_E = \lambda - (w\lambda_2 + (1 - w)\lambda_1) \quad (3)$$

where λ , λ_1 and λ_2 are the thermal conductivity of a blend, polymers 1 and 2, respectively, and w is the weight content of λ_2 .

It was reported by Filippov²¹ that the λ_E of a liquid mixture is estimated for a mixture of two non-polar liquids according to equation (4), while the λ_E for that of polar liquids is estimated using equation (5).

$$\lambda_E = 0 \quad (4)$$

$$\lambda_E = -0.72w(1 - w)(\lambda_2 - \lambda_1) \quad (5)$$

Also, NEL²² and the power law²³ equations were proposed for the λ_E of liquid mixtures as shown in equations (6) and (7), respectively ($\lambda_1 < \lambda_2$).

$$\lambda_E = -(\lambda_2 - \lambda_1)(w^{3/2} - w) \quad (6)$$

$$\lambda_E = [(1 - w)\lambda_1^r + w\lambda_2^r]^{1/r} - [w\lambda_2 + (1 - w)\lambda_1] \quad (7)$$

$$r = -2$$

The λ_E of the PS/PPO blend was estimated by equations (4)–(7). The adaptabilities of those equations to the conductivities at 483 K in the liquid state were then evaluated by comparison with the experimental data, as shown in Figure 9. Equations (5)–(7) were found to fit adequately the experimental thermal conductivities of PS/PPO blends in the liquid states (483 K), similar to those of PC/PMMA blends. It meant that the prediction equations for low molecular liquids were adaptable to thermal conductivities of PS/PPO blends in the liquid states.

On prediction equations for thermal conductivity of polymers, Hands *et al.*²⁴ reported that thermal conductivity (λ) of polymers in glass state, except for halogenated polymers, is linear-related with 3/4th power of their density (ρ), as

$$\lambda = A\rho^{4/3} \quad (8)$$

where, A = constant. Then, equation (8) can be rearranged as

$$\log \lambda = (4/3) \log \rho + \log A \quad (9)$$

Equation (9) means that $\log \lambda$ is linear-related with $\log \rho$. Thus, logarithm of thermal conductivity of PS/PPO blends in glass state (333 K and 360 K) was plotted against logarithm of its density in Figures 10 and 11, respectively. At both of these temperatures, the experimental data deviated largely from the predicted line (—) from equation (9), but lie approximately on a line (---) whose

slopes are 3.53 and 2.75, in the cases of 333 K and 360 K, respectively. Thus, equation (9) cannot be adapted to fit the experimental data of the thermal conductivities of PS/PPO blends, in the solid state. On the other hand, equations (4)–(7) could not be adapted to the λ_E of PS/PPO blends, in the glass state (333 K and 360 K), while equation (5) might be comparatively adaptable to the conductivity of PMMA/PC blends in the glass state. Thus, the experimental λ_E in the glass state has one large maximum of 50 wt%, while each of the estimated λ_E values has one large minimum or remains constant. Here, using Zoller's data, the excess density (d_E) is estimated by

$$d_E = d - [wd_2 + (1 - w)d_1] \quad (10)$$

where d , d_1 and d_2 are the densities of a blend, polymers 1 and 2, respectively. The d_E in the glass state had one large maximum at 50 wt%, although it remained constant in the liquid state (Figure 14). Then, the excess specific heat capacity (C_{pE}) is estimated by

$$C_{pE} = C_p - (wC_{p2} + (1 - w)C_{p1}) \quad (11)$$

where C_p , C_{p1} and C_{p2} are the specific heat capacities of a blend, polymers 1 and 2, respectively. The C_{pE} in the liquid state had one large maximum at 60 wt%, although it remained constant in the glass state (Figure 15). Further, the excess thermal diffusivity (α_E) is estimated by

$$\alpha_E = \alpha - (w\alpha_2 + (1 - w)\alpha_1) \quad (12)$$

where α , α_1 and α_2 are the thermal diffusivities of a blend, polymers 1 and 2, respectively. The α_E in the liquid state had one large maximum at 60 wt%, although it remained constant in the glass state (Figure 14).

Thus, in the liquid state, the minimum of α_E overcomes the maximum of C_{pE} , resulting in the minimum of λ_E . However, the large maximum of λ_E in the solid state was found to occur because of the large increase of d_E . Then, the effect of the negative excess volume in the solid state was considered to cause the maximum of λ_E .

It is known that phonon free path of amorphous polymers is quite small²⁰. Thus, the increase of the distance of polymer chains by increasing the temperature up to T_g , increases specific heat capacity at constant volume (C_v) of the polymer²⁰. And so, the increase of C_v increases the thermal conductivity of the polymer. On the other hand, the increase of the distance of polymer chains by increasing of temperature over T_g , decreases phonon velocity (v) of the polymer²⁰, resulting in decreasing of thermal conductivity of the polymer. Thus, it is considered that the increase of the distance of polymer chains by blending, influences C_v of the blend up to T_g , but influences v , over T_g . Further, C_v is strongly effected by the term of $C_p \times d$, while thermal conductivity is obtained by multiplying specific heat capacity at constant volume, phonon free path and phonon velocity [equation (1)].

Therefore, the maximum of λ_E in the glass state and the minimum one in the liquid state were considered to be due to the following.

In the glass state (333 K and 360 K), the strong interactions of polymer chains decreased the distances between the chains⁹. And so, the interaction increased d_E (Figure 14), while it did not almost change C_{pE} (Figure 15). Then, C_{vE} was considered to become larger, since C_{vE} is considered strongly effected by the term $C_{pE} \times d_E$. Further, α_E was kept constant (Figure 16). Thus, λ_E 's in

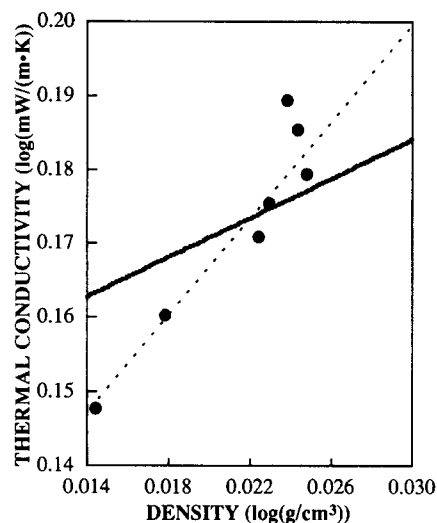


Figure 10 Thermal conductivity vs density (333 K)

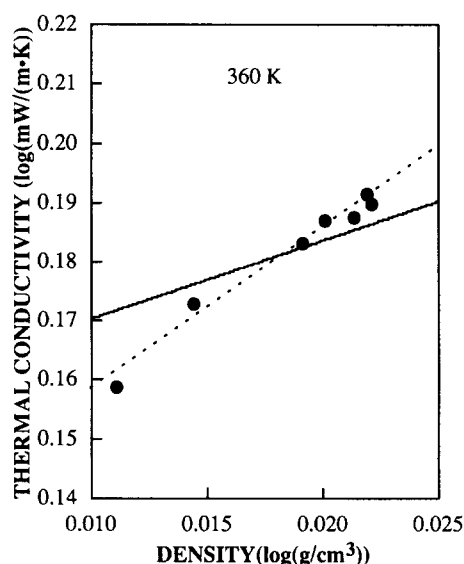


Figure 11 Thermal conductivity vs density (360 K)

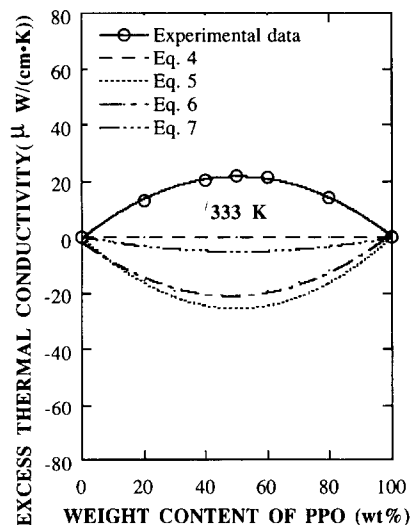


Figure 12 Comparison of experimental data with predicted data of excess thermal conductivities of PS/PPO blend

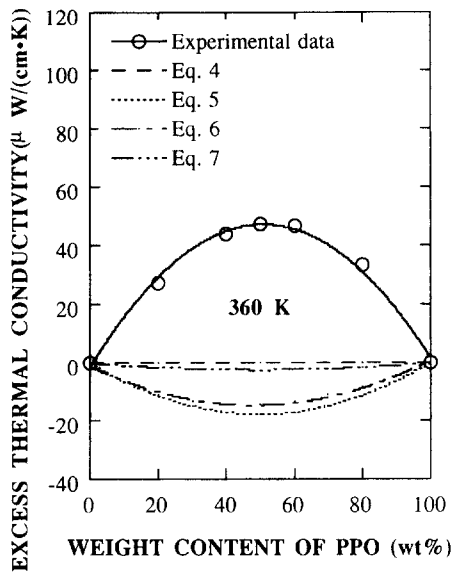


Figure 13 Comparison of experimental data with predicted data of excess thermal conductivities of PS/PPO blend

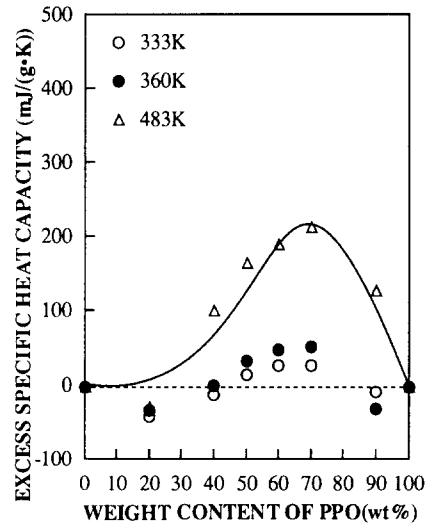


Figure 15 Excess specific heat capacity of PS/PPO blends

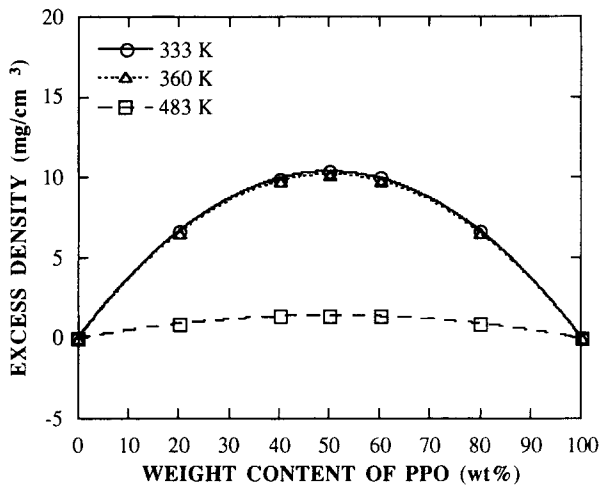


Figure 14 Excess densities of PS/PPO blends

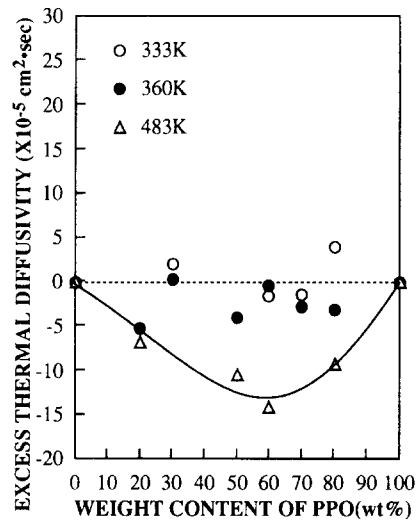


Figure 16 Excess thermal diffusivity of PS/PPO blends

the glass state were considered to have a maximum (Figures 12 and 13), because of the relation of equation (1).

In the liquid state (483 K), the small decrease of the distances between the chains decreased v , resulting in showing the minimum α_E (Figure 16), which is related with the term of $l \times v$. And the small decrease of the distances increased C_{pE} (Figure 15), while it did not change d_E (Figure 14). Thus $\alpha_E (= l \times v)$ decreased, although c_{vE} increased. However, λ_E was considered to show a minimum in the liquid state (Figure 9), because the decrease of α_E overcame the increase of C_{vE} .

In summary, equations (5)–(7) could be comparatively adapted to the thermal conductivity of the PS/PPO blend in the liquid state, while equations (5)–(8) could not be adapted to that in the glass state. This phenomenon was considered to occur because the strong interaction between polymer chains greatly increased the thermal conductivity.

CONCLUSIONS

We prepared miscible PS/PPO blends and confirmed their miscibility by d.s.c. The thermal diffusivity, specific

heat capacity, density and thermal conductivity of the blends were measured in the temperature range from the glass to the liquid states. Further, the adaptation of the prediction equations for thermal conductivity to the experimental data was attempted.

The miscibility of the PS/PPO blend was confirmed by d.s.c. It was found that the miscibility of polymer blends could be evaluated by the measurement of thermal diffusivity. The conductivity in the liquid state was smaller than that estimated by the linear relationship to PPO content, while in the solid state, the conductivity was larger than the estimated value. This phenomenon means that the excess thermal conductivity of the blends had a large maximum at 50 wt%, in the solid state. Then, this maximum of λ_E was found to be caused by the effect of the negative excess volume in the solid state. Further, this was considered to occur because the strong interactions between polymer chains in the solid state increased the thermal conductivity of the blend.

Further, all of Filippov, NEL and the power law equations were found to be sufficiently adaptable to the experimentally determined thermal conductivities of PS/PPO blend in the liquid state, but none of them could be adapted to that in the glass state.

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