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Thermal diffusivity and conductivity of PMMA/PC blends

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A miscible PMMA/PC blend was prepared by a rapid casting method, and its miscibility was confirmed by d.s.c. The specific heat capacity of the two-phase blend (5/5) was larger than that of the one-phase blend. The thermal diffusivity and the conductivity of the blend (5/5) slightly decreased with the increase of temperature up to 450–460 K (LCST), and then decreased abruptly with increasing of temperature. The thermal diffusivity at solid state was always smaller than the one estimated by the linear relation with PC content, while in liquid state it always changed linearly with PC content. On the other hand, the experimental thermal conductivity in the liquid state was always smaller than the value estimated by the linear relationship with PC content, while in the solid state it changed linearly. Finally, we discussed adaptability of prediction equations appearing in literature to the conductivity. The Filippov, NEL and power law equations were found to describe adequately the thermal conductivities of PC/PMMA blends in liquid and solid states. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

There have been many reports concerning miscible polymer blends[1–14]. Most of them dealt with poly(methyl methacrylate) (PMMA)/bisphenol A polycarbonate (PC) blends[4–14]. Gardlund reported[4,5] that the melt blends of PMMA and PC was partially miscible, due to the n–π complex formation between the ester group of PMMA and the phenyl ring of PC. Recently, it was found[6,7] that a single phase, i.e. miscible blend of PMMA and PC, could be obtained by the rapid solvent casting method. Since then, the miscible blend has been investigated by n.m.r., d.s.c. and d.m.a. measurements. The results of these studies showed the following. (a) The miscible blend is a single phase system under the lower critical solution temperature (LCST)[8–12]. (b) The local motions of the PC backbone are inhibited by the presence of PMMA[9]. (c) The PC/*a*-PMMA blend is homogeneous on a scale of 200–300 Å and heterogeneous on a scale of 20–30 Å[13]. (d) The LCST of the PC/*a*-PMMA blend may be close to its glass transition temperature (T_g), while that of the PC/*iso*-PMMA blend is over 40 K higher than that of the former blend. Additionally, both LCST and the upper critical solution temperature (UCST) appeared in the PC/*syn*-PMMA blend[14].

Since any electronic effects are absent in most polymers, heat conduction occurs as a result of lattice vibrations, similarly to crystalline dielectrics[15]. Thus, theoretical consideration of the thermal conductivity (λ) of those polymers leads to the Debye equation[15]:

$$\lambda = (1/3)Cvl \tag{1}$$

where C is the specific heat capacity per unit volume, v is the average phonon velocity, and l is the phonon mean free path. l of an amorphous polymer is an extremely small constant (i.e. a few angstroms)[16], because an amorphous state is considered to have numerous numbers of defects which cause phonon scattering[15]. It is known that the thermal conductivity of an amorphous polymer increases to T_g with increasing temperature, while it decreases above T_g[15]. This occurs because thermal conductivity of an amorphous polymer obeys the temperature dependence of C below T_g, while the distances of polymer chains above T_g are too large for the thermal conductivities to obey the temperature dependence of v. Thus, the effect of v on the thermal conductivity is smaller in the small distance range of polymer chains, while in the large distance range, it overcomes that of C.

Thermal diffusivity (α) is defined as:

$$\alpha = (C_p\rho)/\lambda \tag{2}$$

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

We have been studying[17–21] the thermal conductivity behaviour of polymer blends, which is a fundamental and important factor in processing. In particular, the behaviour is important for the simulation of the melt flow of a polymer in a mould, and it is of interest to determine how miscibility affects the thermal diffusivity and conductivity of polymer blends. Thermal diffusivity was measured by laser flash method, a useful means for a small thin test sample[22–24].

Hitherto, several types of miscible blends have been discussed[19–21]. In the blend of lower molecular weight polystyrene/coumaron resin (PS/Co blend)[20], which showed a miscibility over all blend compositions, the thermal conductivity was approximately linearly related to blend composition. The thermal conductivity *versus* composition curve of a miscible poly(vinyl chloride) (PVC)/PMMA[21] blend showed a minimum of 85 wt% of PMMA, because strong compositional local fluctuations occurred around this composition.

In this report, a miscible PMMA/PC blend was prepared and its miscibility was confirmed by d.s.c. and i.r. spectrometry. Then, thermal diffusivity, specific heat capacity and density of the blend in glass and liquid states were measured by the laser flash method, d.s.c. and the density gradient method (or *PVT* measurement), respectively. The thermal conductivity of the PMMA/PC blend was calculated from these results and the change of thermal diffusivity, specific heat capacity, density and thermal conductivity around LCST discussed. Furthermore, the adaptation of the prediction equations[25–28] for thermal conductivity, to the experimental data was attempted.

EXPERIMENTAL

Materials and preparation

Atactic PMMA and PC were supplied by Mitsubishi Rayon Co. Ltd and Mitsubishi Gas Chemical Co. Ltd, respectively. Their average molecular weight was determined by g.p.c. analysis relative to a polystyrene standard using tetrahydrofuran (THF) as a solvent (*Table 1*).

PMMA (15 g) or PC (15 g) was purified by precipitation from THF poured into n-hexane (1000 ml) or methanol (1000 ml), and then dried under vacuum for 4 h.

For preparing PMMA/PC blend film, a mixture of PMMA and PC was dissolved in THF. The polymer concentration was 2 wt%. The film specimen of PMMA/PC blend were prepared by the following rapid casting method: at first, thin films (10–50 μm) of PMMA/PC blend were prepared by rapid casting on glass petri dishes at room temperature, under vacuum (20–50 mmHg). Then, the thin blend films were dried at 393 K for 15 h. After 10–50 sheets of them were piled up, a film specimen (300 μm) was formed by pressing the pile at 443 K. All the specimens were clear.

Table 1 Molecular weight, determined by g.p.c.

Polymer	M_w	M_n
Poly(methyl methacrylate)	44 000	19 000
Polycarbonate	89 000	50 000

Measurements

Thermal diffusivity. Measurement of thermal diffusivity was performed by utilizing the thermal constant tester (TC7000; Shin-ku Riko Inc.) based on the laser flash method. Thermal diffusivities in glass and liquid states were measured, after holding specimens for 5 min at a target temperature. The measurement of temperature dependency of thermal diffusivity was performed step by step, after holding a target temperature for 30 min. The specimens were 10 mm in diameter and 300 μm in thickness.

Specific heat capacity, density and thermal conductivity. The specific heat capacity of polymer was measured using a differential scanning calorimeter (SSC 5200; Seiko Instrument Ltd). α-Al_2O_3 was used for the standard specimen. The density of the polymer at 296 ± 3 K was measured by the density gradient method (solvent; toluene/tetrachloromethane). The temperature dependency of density was measured by isothermal mode of operation of an apparatus for PVT measurement, which was devised by P. Zoller (Gnomix Co.). The increasing rate of temperature was 0.33 K min^{-1}. Volume values used for estimating density were measured under atmospheric pressure ($P =$ 0 MPa).

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

Thermal behaviour and i.r. spectra. The glass transition temperature (T_g) was measured by d.s.c. (SSC 5200; Seiko Instrument Ltd). All the measurements were made at a heating rate of 10 K min^{-1}. T_g observed on the second scan was adopted for experimental data.

LCST was measured by combining the hot stage (Mettler FP 82) and u.v. spectra photometer (U-3210; Hitachi Co. Ltd). Thus, the change of transparency of light (400 nm) of the film specimen was detected by heating it at an increase rate of 2, 5 or 10 K min^{-1}. Then, LCST was determined as a bending point in the curve of the transparency against temperature, as shown in *Figure 1*.

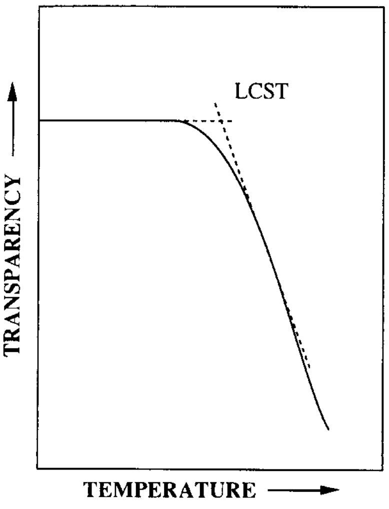

Figure 1 Transparency vs temperature

I.r. spectra of thin blend films (10–50 μm) were measured by *FT*i.r. (PE1600; Perkin-Elmer Co. Inc.).

RESULTS AND DISCUSSION

Thermal behaviour and i.r. spectra

Figure 2 shows the T_g of PMMA/PC blend *versus* weight content of PC. The blend of each composition showed only one T_g, which changed with PC content along a curve predicted by the Couchman equation[29]. Thus, it was confirmed that the blend is miscible over all compositions.

The 'T_g width' is estimated as the temperature range from the initial temperature to the end temperature of the glass transition. It may reflect the magnitude of local compositional fluctuations in polymer blends, giving a qualitative implication as to the relative homogeneity or miscibility of the system[30]. The T_g width of the PMMA/PC blend did not vary greatly (*Figure 3*), suggesting that local compositional fluctuations did not occur much in the blend.

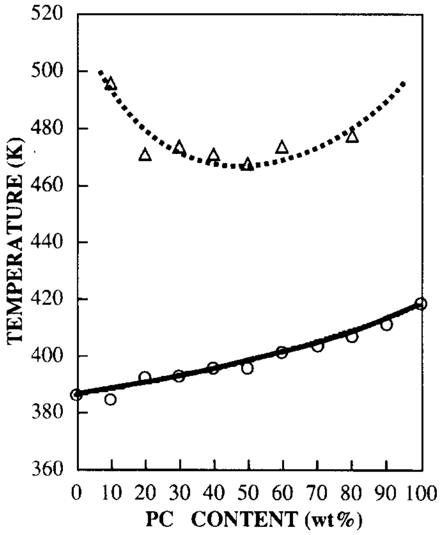

Figure 2 T_g and LCST of PMMA/PC blend: △; LCST, ○; T_g, ——; predicted values by Couchman equation

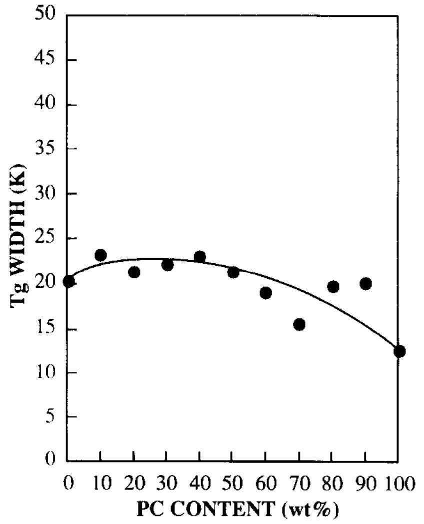

Figure 3 T_g width of PMMA/PC blend

LCST data, measured by the increase rate of 10 K min^{-1}, were plotted against PC content (*Figure 2*). The blend was considered to show one phase under LCST. Here, LCST was found to decrease with lowering of the increase rate of temperature (*Figure 4*), because of the effect of the conversion rate from one phase to two phases.

The i.r. spectrum of the PMMA/PC(3/7) blend was compared with that of PMMA, as shown in *Figure 5*. The peak of the spectrum of the blend was observed at the same wavenumber as that in PMMA. It was reported by Painter and Coleman[31,32] that the formation of a hydrogen bond generated a new peak at lower wavenumber than the original one of the carbonyl group in the i.r. spectrum. Thus, the carbonyl group peaks in the i.r. spectra of the blend and PMMA were arranged to equal height, and then the spectrum of PMMA was

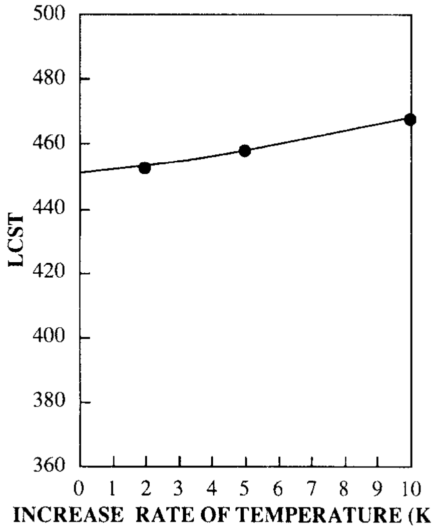

Figure 4 LCST of PMMA/PC (5/5) blend measured at different increase rates of temperature

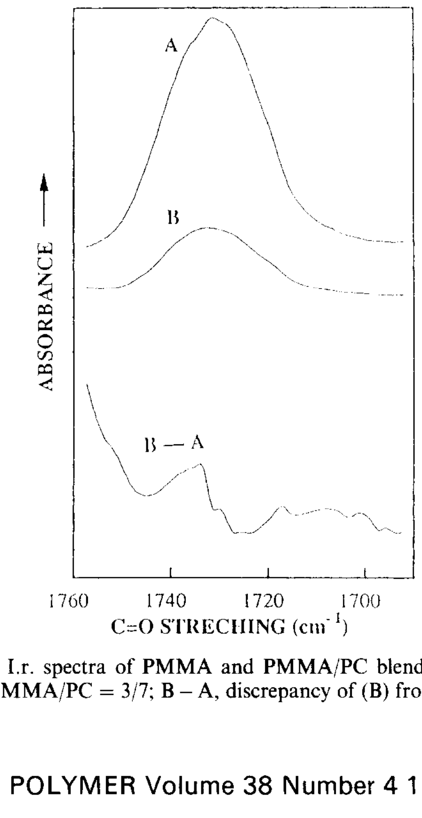

Figure 5 I.r. spectra of PMMA and PMMA/PC blend: A, PMMA only; B, PMMA/PC = 3/7; B – A, discrepancy of (B) from (A)

subtracted from that of the blend. The discrepancy of the i.r. spectra, thus obtained (*Figure 5*), was approximately 0 in the lower wavenumber range. Consequently, the miscibility of the blend could not be confirmed by the i.r. method, although the discrepancy became larger in the higher wavenumber range due to the existence of the carbonate group in PC.

Density and specific heat capacity

Figure 6 shows the temperature dependence of the density of a PMMA, PC and PMMA/PC(5/5) blend, all of which decreased linearly with increasing temperature. In *Figure 7*, the density of a PMMA/PC blend at solid (291 K) and liquid (445 K) states were plotted against PC content. Both curves increased with increasing PC content, always being beneath the estimated linear relations.

Figure 8 shows the specific heat capacity of a PMMA, PC and PMMA/PC(5/5) blend over a wide temperature range, all of them increased with increasing of temperature. Here, two types of curve are shown for the blend: No. 1 type curve was obtained by the ordinary measurement, while No. 2 type curve was obtained by measurement after keeping the blend specimen at the target temperature (460 K) for 30 min. Only one T_g could be distinguished on the No. 1 type curve, while two T_gs appeared on the No. 2 type curve (*Figure 8*). Thus, it was confirmed that No. 1 type and No. 2 type curves represent the specific heat capacity of the one-phase blend and that of two-phase blend of PMMA/PC (5/5), respectively. Therefore, the specific heat capacity of the two-phase blend was found to be larger than that of the one-phase blend.

The specific heat capacity of the PMMA/PC blend at both solid (291 K) and liquid (445 K) states were plotted against PC content, as shown in *Figure 9*. They decreased with increasing PC content, always being larger than the ones estimated from the linear relationship with PC content. This dependency on PC content is in contrast to that of density (*Figure 7*). Thus, this phenomenon was considered to occur, as the result of an increase in intermolecular distance due to a positive volume change by blending.

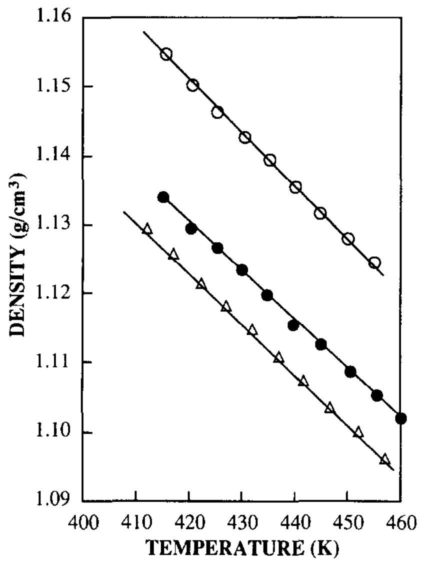

Figure 6 Temperature dependency of PMMA (△), PC (○) and PMMA/PC (5/5) blend (●)

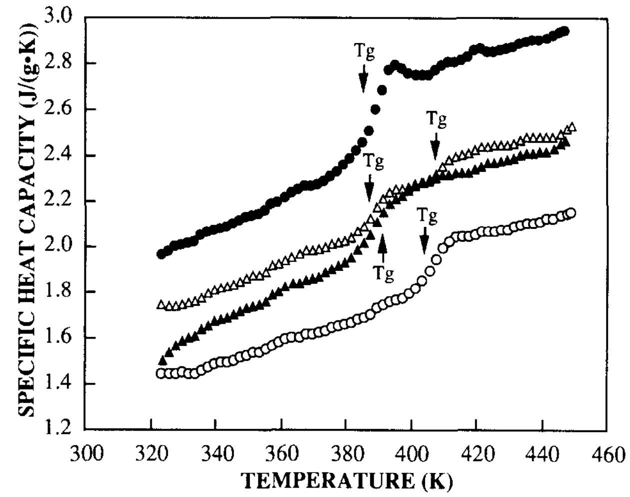

Figure 8 Specific heat capacity of PMMA (●), PC (○) and PMMA/PC (5/5) blend. No. 1 type curve (▲), No. 2 type curve (△)

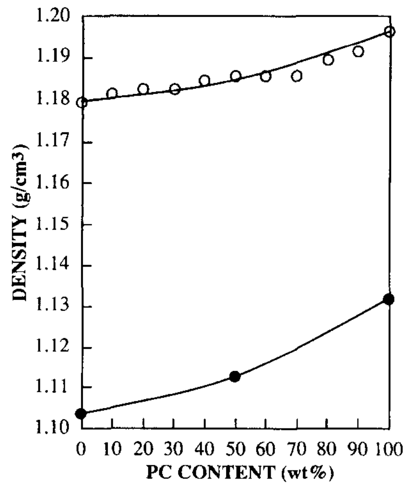

Figure 7 Density of PMMA/PC blend: ○, 291 ± 3 K; ●, 445 ± 5 K

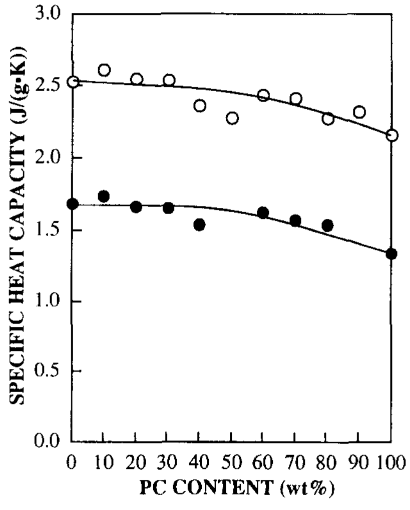

Figure 9 Specific heat capacity of PMMA/PC blend: ●, 293 K; ○, 445 K

Thermal diffusivity

Figure 10 shows thermal diffusivity of the PMMA/PC(5/5) blend measured from 400 to 500 K. After gradual decreasing up to about 440 K, the diffusivity decreased steeply with increasing temperature in the LCST range (450–460 K), then it gradually decreased. Therefore, this phenomenon might mean that LCST can be determined by measurement of thermal diffusivity. The remarkable decrease must have occurred because of the following. From the results of the specific heat capacities, the average distances of polymer chains in the two-phase blend was considered to be larger than that in the one-phase blend. Then, the larger distance was considered to decrease the velocity of phonon (v). In addition, the phase separation above LCST generates numerous numbers of the interfaces in the two-phases blend. These interfaces are known to decrease the phonon mean free path (l)[16]. Thus, it was considered that the thermal diffusivity decreased remarkably around LCST, because thermal diffusivity of an amorphous polymer was affected strongly by the decrease of v and l.

In both solid (291 K) and liquid (445 K) states, the thermal diffusivity of the PMMA/PC blend increased with the increasing PC content, as shown in *Figure 11*. The plots of the diffusivity in solid state *versus* PC content were always beneath the estimated linear relationship, while those in liquid state were on the linear relation.

Thermal conductivity

Figure 12 shows the thermal conductivity change of a PMMA/PC (5/5) blend from 400 to 500 K. After a gradual decrease to 440 K, the conductivity abruptly decreased with increasing temperature in the LCST range (450–460 K), then, it gradually decreased. This temperature dependency was similar to that of thermal diffusivity. The thermal conductivity of a polymer above T_g is strongly affected by v rather than specific heat capacity[16]. In addition, the thermal conductivity is influenced by l[16]. Thus, the abrupt decrease of the thermal conductivity was considered to occur because of the decrease of v and l, similar to the case of the thermal diffusivity. Therefore, it was considerable that the phase separation in the PC/PMMA blend decreased the

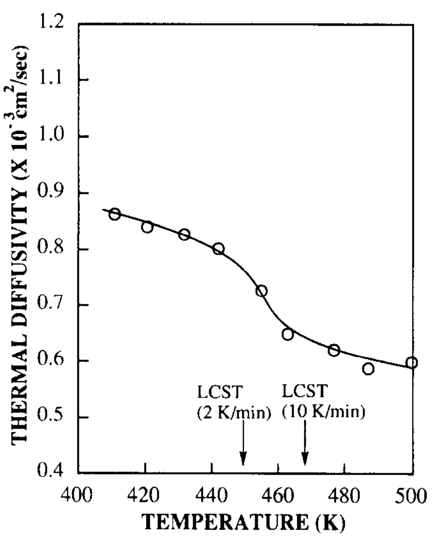

Figure 10 Thermal diffusivity of PMMA/PC (5/5) blend

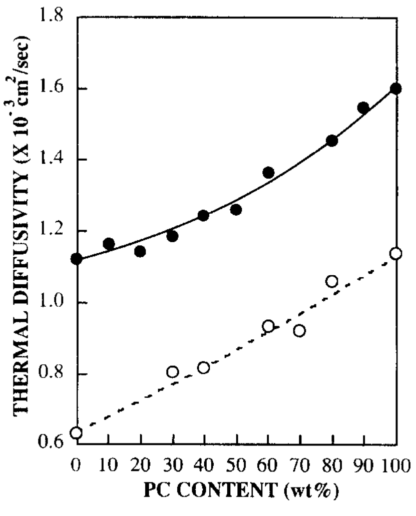

Figure 11 Thermal diffusivity of PMMA/PC blend: ●, 291 ± 3 K; ○, 445 ± 5 K

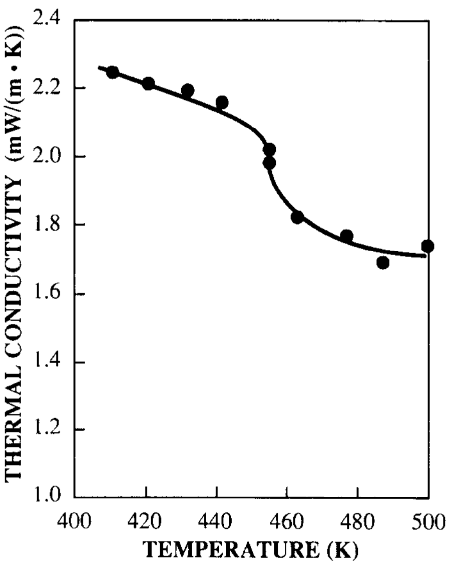

Figure 12 Thermal conductivity of PMMA/PC (5/5) blend

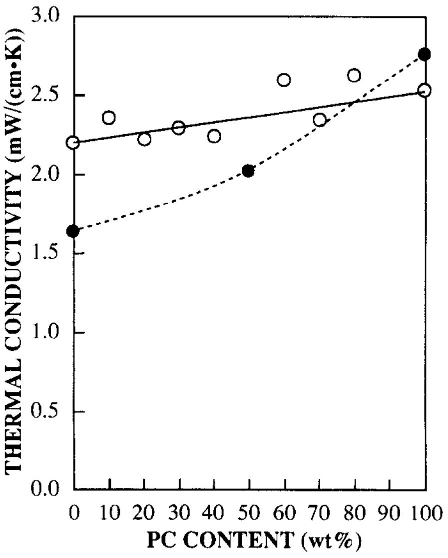

Figure 13 Thermal conductivity of PMMA/PC blend: ○, 291 ± 3 K; ●, 445 ± 5 K

thermal conductivity, because it decreased the phonon velocity and the phonon mean free path.

In both solid (291 K) states, the thermal conductivity of PMMA/PC blend increased with increasing PC content. The conductivity in the liquid state was always smaller than the one estimated by a linear relation with PC content, while it changed linearly in the solid state (*Figure 13*). Here, the conductivity of PC in the liquid state at 445 K was larger than that in the solid state at 291 K. In the temperature range below T_g, the conductivity of amorphous polymers increases slightly with temperature, although in the temperature range above T_g, it decreases slightly with temperature. Then, the thermal conductivity becomes a maximum at T_g. Thus, the thermal conductivity of PC at 445 K was considered to be higher, because 445 K was closer to T_g (420 K) than 291 K.

On prediction equations for thermal conductivity of polymers, Hands *et al.*[25] reported that the thermal conductivity (λ) of polymers in the glass state, except for halogenated polymers, is linearly related to the 3/4th power of their density (ρ):

$$\lambda = A\rho^{4/3} \tag{3}$$

where A = constant. Then, equation (1) can be rearranged to

$$\log\lambda = (4/3)\log\rho + \log A \tag{4}$$

Equation (2) means that $\log\lambda$ is linearly related to $\log\rho$. Thus, the logarithm of the thermal conductivity of the PMMA/PC blend in the glass state (293 K) was plotted against the logarithm of its density (*Figure 14*). The experimental data deviated largely from the predicted line (—) from equation (2), and lay approximately on a line (– – –) whose slope is 11.34. Thus, equation (1) cannot be adapted to fit the experimental data.

We further attempted to adopt several kinds of predictive equations[26–28] which were proposed for thermal conductivities of mixtures of low molecular compounds in the liquid state.

It was reported by Filippov[26] that the thermal conductivity (λ) of a liquid mixture is estimated for a mixture of two non-polar liquids by equation (5), while λ for polar liquids is estimated using equation (6).

$$\lambda = w\lambda_2 + (1-w)\lambda_1 \tag{5}$$

$$\lambda = w\lambda_2 + (1-w)\lambda_1 - 0.72w(1-w)(\lambda_2 - \lambda_1) \tag{6}$$

where λ_1 and λ_2 are the thermal conductivity of liquids 1 and 2, respectively, and w is the weight content of liquid 2.

In addition, NEL[27] and power law[28] equations were proposed for the conductivity of liquid mixtures, as shown in equations (7) and (8), respectively ($\lambda_1 < \lambda_2$).

$$\lambda = w\lambda_2 + (1-w)\lambda_1 - (\lambda_2 - \lambda_1)(w^{3/2} - w) \tag{7}$$

$$\lambda^r = (1-w)\lambda_1^r + w\lambda_2^r \tag{8}$$

where $\lambda_1 < \lambda_2$ and $r = -2$.

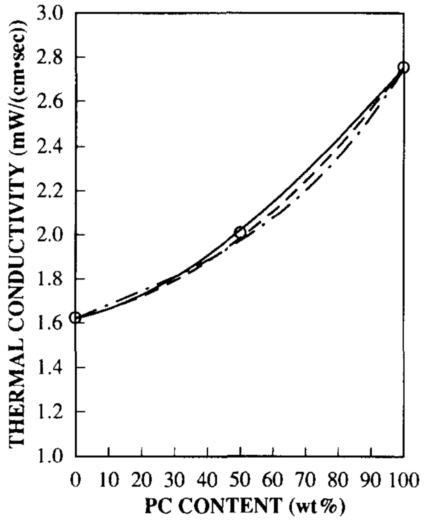

Figure 15 Thermal conductivity of PMMA/PC blend in the liquid state: experimental data (○), equation (4) (– – –), equation (5) (——), equation 6 (–●–)

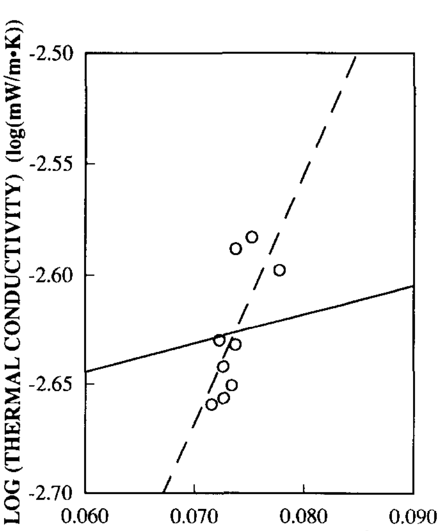

Figure 14 Log(thermal conductivity) vs log(density) in PMMA/PC blend at 291 ± 3 K

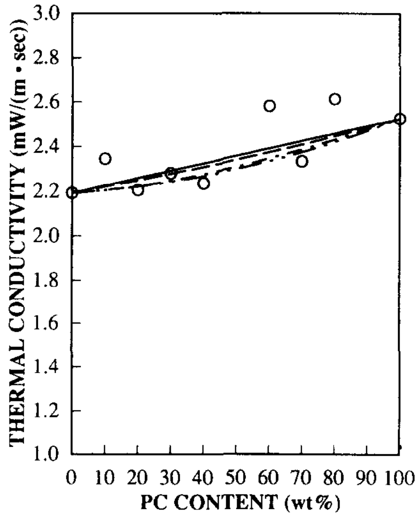

Figure 16 Thermal conductivity of PMMA/PC blend in the solid state: experimental data (○), equation (4) (– – –), equation (5) (——), equation 6 (–●–)

Hitherto, equation (3) could be adapted to the thermal conductivity of the PS/Co blend[20], while equations (3)–(6) could not be adapted to that of the PVC/PMMA blend[21].

The thermal conductivity of PMMA/PC blend was estimated by equations (5)–(8), then, the adaptability of these equations to the experimental data in the liquid and glass states were evaluated, as shown in *Figures 15* and *16*, respectively. Equations (6)–(8) were found to fit adequately the experimental thermal conductivities of PC/PMMA blends in the liquid and solid states. Thus, this result might mean that the effect of the molecular interaction in polymer blends on the thermal conductivity is similar to that in the low molecule mixture.

CONCLUSION

The miscible PMMA/PC blend was prepared, confirming its miscibility by d.s.c. Then, the thermal diffusivity, specific heat capacity, density and thermal conductivity of the blend was measured in the temperature range from glass to liquid states. Furthermore, the adaptation of the prediction equations for thermal conductivity to the experimental data was attempted.

The miscibility of PMMA/PC blend was confirmed by d.s.c., but it could not be done by i.r. spectrometry. The specific heat capacity of the two-phase (5/5) blend was larger than that of the one phase blend. For thermal diffusivity and conductivity of the blend (5/5), they decreased slightly with increasing temperature to 440 K, and then decreased abruptly in the LCST range. The density of the blend in the liquid and glass states increased with increasing PC content, and were smaller than the estimated ones from the linear relationship with PC content, while the specific heat capacity in both the liquid and glass states decreased with increasing PC content, and were larger than the ones estimated from the linear relationship with PC content. The diffusivity in the solid state and the conductivity in the liquid state were smaller than those estimated by the linear relationship with PC content, while the diffusivity in the liquid state and the conductivity in the solid state changed linearly with PC content.

Finally, the Filippov, NEL and power law equations were all found to be sufficiently adaptable to the experimentally determined thermal conductivities of PC/PMMA blends in the liquid and solid states.

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