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Measurements of the Thermal Conductivity and Thermal Diffusivity of Polymer Melts with the Short-Hot-Wire Method[1]

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In this paper, the thermal conductivity and thermal diffusivity of four kinds of polymer melts were measured by using the transient short-hot-wire method. This method was developed from the hot-wire technique and is based on two-dimensional numerical solutions of unsteady heat conduction from a wire with the same length-to-diameter ratio and boundary conditions as those in the actual experiments. The present method is particularly suitable for measurements of molten polymers where natural convection effects can be ignored due to their high viscosities. The results have shown that the present method can be used to measure the thermal conductivity and thermal diffusivity of molten polymers within uncertainties of 3 and 6%, respectively. Further, the thermal conductivity and thermal diffusivity of solidified samples were also measured and discussed.

KEY WORDS: molten polymers; solidified polymers; thermal conductivity; thermal diffusivity; transient short-hot-wire method.

1. INTRODUCTION

The measurements of thermal conductivity and thermal diffusivity of polymer materials in a molten state have always presented difficult

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problems. These are mainly because of factors like thermal contact resistance, inhomogenities in the sample, different measurement methods [1], etc. Due to the lack of experimental data and difficulties involved in accurate measurements, approximations were often used in the past. However, even though a number of correlations associating such structural variables as molecular weight of the polymer, crystallinity, orientation, etc. with the thermal conductivity were proposed [2–3], accurate measurements of thermal properties are still essential. Since Ross et al. [4] (1984) reviewed the transient and/or steady state methods used to measure the thermal properties of polymers, some researchers [5–6] have continuously made great efforts to improve their measurement accuracy and/or to develop new reliable measurement methods. The present authors [7] (1993) proposed a method the so-called "Transient Short-Hot-Wire Method" which can be used to measure the thermal conductivity and thermal diffusivity of liquids simultaneously. By using this method, the thermal conductivity and thermal diffusivity of water and organic liquids [8], alternative refrigerants in the liquid phase [9], and molten carbonates [10] have been measured successfully. In this paper, the thermal conductivity and thermal diffusivity of four kinds of commercial polymers are measured in the temperature range from 20 to 250°C at atmospheric pressure. Because the present method uses a short hot wire (about 10 mm long) as the probe, only a small amount of test sample is needed. This makes it easy to solve the problem of inhomogenities in the sample. Uncertainty analysis shows that the present method can be used to measure the thermal conductivity and thermal diffusivity of polymers within uncertainties of 3 and 6%, respectively.

2. PRINCIPLE OF MEASUREMENT

As described in our previous papers [7–10], the present method was developed from the conventional hot-wire technique and is based on two-dimensional numerical solutions of unsteady heat conduction from a short wire with the same length-to-diameter ratio and boundary conditions as those used in the actual experiments. The following procedure was proposed to determine simultaneously the thermal conductivity and thermal diffusivity of a liquid. The numerical results for the dimensionless temperature θ_v $(=(T-T_i)/(q_v r^2/\lambda))$ are approximated by a linear equation in the logarithm of the Fourier number Fo $(=(\alpha t)/r^2)$, where the coefficients A and B are determined by the least-squares method.

$$\theta_v = A \ln \mathrm{Fo} + B \tag{1}$$

The measured temperature rise of a wire can also be approximated by a linear equation with coefficients a and b in the above time range as

$$T_v = a \ln t + b \tag{2}$$

where T_v is the rise in the temperature above the initial temperature T_i. Equation (1) is dimensionalized as

$$T_v = \frac{q_v r^2}{\lambda} A \ln t + \frac{q_v r^2}{\lambda} \left(A \ln \frac{\alpha}{r^2} + B \right) \tag{3}$$

Comparing the corresponding coefficients of Eqs. (2) and (3), the thermal conductivity and thermal diffusivity of a liquid are expressed by

$$\lambda = \frac{VI}{\pi l} \frac{A}{a} \tag{4}$$

$$\alpha = r^2 \exp\left(\frac{b}{a} - \frac{B}{A} \right) \tag{5}$$

where r and l are the radius and length of the hot wire, and V and I are the voltage and current supplied to the wire, respectively. Equations (4) and (5) are similar to those obtained for the conventional transient hot-wire method [11], except that the A and B depend on the aspect ratio L, parameters R_{c1} and R_{d1}, etc. so that an iterative process is required to evaluate thermal properties accurately.

From Eqs. (4) and (5) the relative uncertainties of the thermal conductivity and thermal diffusivity are estimated as

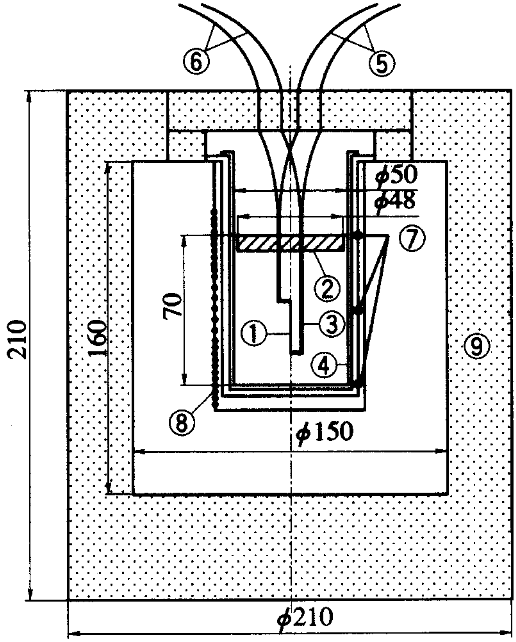
$$\frac{\delta\lambda}{\lambda} = \left\{ \left(\frac{\delta V}{V} \right)^2 + \left(\frac{\delta I}{I} \right)^2 + \left(\frac{\delta l}{l} \right)^2 + \left(\frac{\delta A}{A} \right)^2 + \left(\frac{\delta a}{a} \right)^2 \right\}^{\frac{1}{2}} \tag{6}$$

$$\frac{\delta\alpha}{\alpha} = \left\{ \left(\frac{2\delta r}{r} \right)^2 + \left[\delta \left(\frac{B}{A} \right) \right]^2 + \left[\delta \left(\frac{b}{a} \right) \right]^2 \right\}^{\frac{1}{2}} \tag{7}$$

In the present measurements, the magnitudes of the main factors in Eqs. (6) and (7) were estimated as follows. The effective length and radius of the hot wire were estimated by measuring the thermal conductivity and thermal diffusivity of pure water and toluene, and both $\delta l/l$ and $\delta r/r$ are accurate to 1%. The possible uncertainty in the slope of the temperature against ln t includes the uncertainties induced by electrical noise and the timing of the voltage measurements. The maximum deviation of the temperature measurement from Eq. (2) is less than 0.2%. The values of $\delta a/a$ and $\delta(b/a)$ are around 0.01 and 0.04, respectively. From numerical solutions, $\delta A/A$ is found to be 0.002 and $\delta(B/A)$ is 0.003. The voltage and current through the wire were measured with digital multimeters and the values of $\delta V/V$ and $\delta I/I$ in the measurement are less than 10^{-4}. Therefore, the total uncertainties of this method were estimated to be 3 and 6% for the thermal conductivity and thermal diffusivity, respectively.

3. EXPERIMENTS

Figure 1 shows the transient short-hot-wire cell used in the present study. A short platinum wire 8.70 mm in length and 51.0 μm in diameter



(1) Pt hot wire (d = 51.0 μm, l = 8.70 mm) (2) Ceramic slat

(3) Pt lead terminal (d = 1.5 mm) (4) Glass crucible (ϕ = 50 mm)

(5) Voltage lead wire (6) Current lead wire

(7) Thermocouples (8) Electric furnace

(9) Insulating material

Fig. 1. Schematic of experimental setup.

(1) is welded at both ends to platinum lead wires of 1.5 mm in diameter (3) which are supported with a ceramic slat (2) and connected with voltage (5) and current (6) platinum lead wires 0.5 mm in diameter. The ceramic slat is fixed with a stainless-steel rod which can move up and down. A glass crucible (4) 50 mm in inner diameter and 100 cm^3 in volume is heated with an electric furnace (8) which is covered with a thermal insulator (9). The temperatures at the outside of the crucible wall are measured with thermocouples (7) to provide a feedback signal for the temperature controller.

The platinum hot wire is annealed at 800°C for a few hours, and the temperature coefficient of its electric resistance β is determined through a calibration for the temperature range from 20 to 400°C. The calibrated probe was carefully cleaned with an ultrasonic cleaner, then slowly inserted into the glass crucible, and then the solid pellet samples were carefully filled in the crucible before heating. At the beginning of the molten state, many air bubbles are dispersed uniformly inside the polymer melt. The air bubbles go up slowly due to the effect of buoyancy. About 3 hours later, the molten polymer becomes transparent and all of the bubbles disappear. After the temperature of the polymer melt becomes uniform and constant, the initial temperature of the polymer melt was measured with the hot wire by

$$T_{\mathrm{i}} = \frac{1}{\beta}\left(\frac{Ri}{Rt_0} - 1\right) \tag{8}$$

where Rt_0, Ri are the electrical resistance of the probe at 0°C and the initial temperature, respectively. On the other hand, when the probe was heated, the wire temperature rised but the lead terminal temperature remained at the initial temperature because of its large heat capacity. Therefore, the hot-wire temperature rise was estimated as

$$T_{\mathrm{v}} = \frac{1}{\beta}\left(\frac{Rt(t) - \varepsilon Ri}{(1-\varepsilon)\, Rt_0} - 1\right) - T_{\mathrm{i}} \tag{9}$$

where ε is the electrical resistance ratio of the lead terminals and the entire probe and is about 0.03 for the present probes.

The measurement system is similar to that described in Ref. 10. It consists of a dc power supply and voltage and current measuring and control systems, that is, two digital multimeters, a personal computer, and a PI/O controller. The power supply (Advantest R6245) can generate a maximum constant current of 600 mA with 0.01-mA resolution. Two DMs (Keithley 2002) are the same type and have a 8.5-digit accuracy at a sampling rate of 18 per s. The PC controls both switching and logging of data.

4. RESULTS AND DISCUSSION

At first, the characteristics of the short-hot-wire probe are examined by using pure water and toluene as standard liquids of known thermal conductivity and thermal diffusivity. The temperature evolutions for these liquids are compared with corresponding numerical results, and the evaluated thermal conductivity and thermal diffusivity are compared with reference values [12]. Then, the effective hot-wire length and diameter and the electrical resistance ratio are determined. The length differs by, at most, 3% from that measured with a microcathetometer. The reason for the difference is attributed mainly to an uncertainty of accurate welding positions on the lead terminals. The thermal conductivity and thermal diffusivity of these standard liquids have been measured under normal gravity conditions, because the effect of natural convection will not appear, at least in the range $\mathrm{Fo} < 200$ [13]. The reproducibility of the hot-wire temperature rise is examined for water, and it is confirmed that the differences among the repeated data are within 0.01°C, if we allow more than 60 min between successive measurements.

Four kinds of polymers, polycarbonate, polyethylene, polypropylene, and polystyrene were measured. These samples were supplied by Sumitomo Chemical Industries Ltd. The measured values of the thermal conductivity, thermal diffusivity, and the product of specific heat and density with their dispersions are shown in Table I. These data are the average values of five measurements at the same temperature. In the following Figs. 2 to 9, the filled circles indicate the present results, and the other symbols indicate the various reference values.

Figures 2 and 3 show the measured thermal conductivity and thermal diffusivity of polyethylene, respectively. As shown in Fig. 2, the present values of the thermal conductivity are between those measured by Eiermann and Hellwege [14] and Kline [15], and decrease monotonially with increasing temperature in the solid state and are almost a constant value in the molten state. Since the polyethylene is a semi-crystalline polymer, the value of the thermal conductivity in the solid state depends mainly on its degree of crystallinity. This is considered to be the main reason why the present results differ from the values obtained by Eiermann and Hellwege [14] and Kline [15] in the solid state. The measured thermal diffusivity shown in Fig. 3 also decreases with increasing temperature in the solid state, and is almost a constant value in the molten state.

Figures 4 and 5 show the measured results of polycarbonate. In contrast with polyethylene, the present thermal conductivity in Fig. 4 increases slightly with temperature in the solid state and becomes almost unchanged with temperature in the molten state except for the temperature around

Table I. Measured Thermal Conductivity, Thermal Diffusivity, and Product of Specific Heat and Density

Substance	Temperature (°C)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	α ($10^{-7} m^2 \cdot s^{-1}$)	ρCp ($10^6 J \cdot m^{-3} \cdot K^{-1}$)	Dispersions of λ, α, and ρCp ($\pm$%)
Polyethylene (Code:L405) (MFR:4.0)	17	0.344	1.54	2.24	0.22, 3.22, 3.01
	45	0.314	1.35	2.32	1.04, 2.67, 1.61
	107	0.230	1.18	1.96	0.26, 0.69, 0.88
	118	0.220	1.05	2.10	0.41, 2.22, 2.27
	129	0.218	1.06	2.06	0.33, 3.14, 2.91
	139	0.217	1.07	2.02	0.52, 0.18, 0.34
	160	0.215	0.99	2.16	0.26, 3.08, 3.14
	214	0.207	0.99	2.10	0.65, 2.99, 2.43
Polycarbonate (Code: 301-6) (MFR: 6.0)	28	0.236	1.43	1.66	0.27, 1.36, 1.14
	38	0.241	1.53	1.58	0.26, 3.87, 3.69
	61	0.244	1.43	1.70	0.25, 0.78, 0.53
	83	0.251	1.34	1.87	0.66, 4.76, 4.31
	107	0.259	1.36	1.90	0.48, 2.12, 1.76
	119	0.257	1.34	1.92	0.30, 1.34, 1.44
	130	0.257	1.29	1.99	0.17, 2.22, 2.09
	146	0.261	1.36	1.92	0.70, 2.11, 1.90
	159	0.254	1.05	2.42	0.05, 2.92, 2.91
	169	0.256	1.13	2.27	0.42, 2.83, 2.44
	181	0.251	1.03	2.43	0.25, 0.96, 0.78
	204	0.249	1.06	2.43	0.23, 0.62, 0.39
	215	0.249	1.26	1.99	0.12, 1.38, 1.37
	225	0.230	0.86	2.67	0.54, 2.91, 2.44
	237	0.230	1.01	2.28	0.39, 1.08, 1.38
	248	0.228	0.98	2.33	0.02, 6.84, 6.61
Polypropylene (Code: H501) (MFR: 3.5)	71	0.250	1.27	1.98	0.41, 1.87, 1.57
	82	0.247	1.21	2.04	0.38, 2.34, 2.05
	94	0.243	1.15	2.12	0.70, 2.67, 2.34
	105	0.239	1.06	2.25	0.17, 1.52, 0.81
	116	0.228	1.02	2.23	0.18, 1.44, 1.36
	128	0.222	1.02	2.19	0.86, 2.80, 2.21
	138	0.202	0.71	2.88	1.80, 7.58, 9.66
	146	0.192	0.62	3.10	0.73, 3.37, 2.61
	156	0.134	0.64	2.11	0.17, 0.41, 0.58
	166	0.132	0.66	2.00	0.05, 3.01, 2.92
	177	0.132	0.68	1.95	0.74, 4.46, 3.83
	189	0.131	0.63	2.07	0.59, 4.17, 3.50
	209	0.132	0.69	1.91	0.25, 2.00, 1.86
	222	0.127	0.61	2.06	0.44, 1.55, 1.11
	234	0.127	0.60	2.10	0.51, 6.00, 5.34

Table I. *(Continued)*

Substance	Temperature (°C)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	α ($10^{-7}\,\mathrm{m^2 \cdot s^{-1}}$)	ρCp ($10^6\,\mathrm{J \cdot m^{-3} \cdot K^{-1}}$)	Dispersions of λ, α, and ρCp ($\pm$%)
Polystyrene (Code: E183) (MFR: 4.0)	35	0.161	1.13	1.42	0.77, 6.25, 5.61
	44	0.163	1.12	1.45	0.92, 5.77, 5.00
	55	0.164	1.07	1.54	0.37, 1.50, 1.39
	66	0.163	1.00	1.62	0.39, 1.71, 1.33
	77	0.165	1.01	1.64	0.25, 5.74, 5.35
	89	0.165	1.00	1.65	0.25, 1.75, 1.98
	101	0.168	1.02	1.65	0.51, 1.12, 0.99
	102	0.169	1.12	1.51	0.76, 3.89, 3.87
	106	0.171	1.18	1.45	0.67, 4.69, 4.09
	108	0.173	1.14	1.52	0.52, 2.43, 1.95
	111	0.172	1.06	1.63	0.87, 4.91, 4.12
	112	0.166	0.92	1.80	0.14, 0.67, 0.65
	115	0.163	0.82	1.99	0.07, 0.27, 0.24
	131	0.163	0.78	2.09	0.85, 2.10, 2.97
	152	0.164	0.80	2.05	0.54, 2.79, 2.22
	163	0.163	0.79	2.07	0.28, 1.28, 1.55
	184	0.161	0.78	2.07	0.59, 3.75, 3.44
	196	0.162	0.78	2.09	0.33, 0.85, 0.53
	216	0.162	0.79	2.06	0.27, 2.07, 1.83
	228	0.159	0.81	1.96	0.44, 0.82, 0.86
	238	0.160	0.82	1.95	0.61, 5.88, 5.41

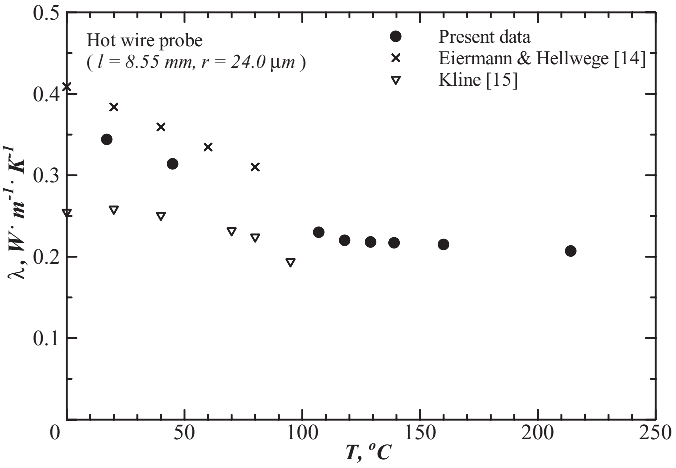


Fig. 2. Measured thermal conductivity of polyethylene.

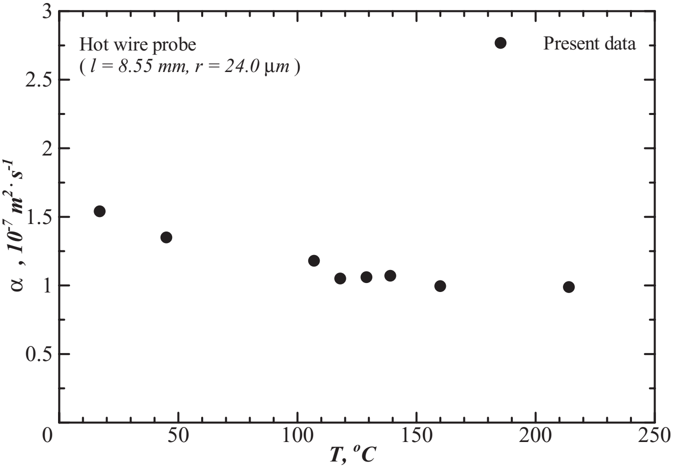


Fig. 3. Measured thermal diffusivity of polyethylene.

220°C. Further, the present data are about 10% higher than those obtained by Choy et al. [16] with the flash radiometry method. As for the thermal diffusivity, the present results are almost same as the values obtained by Choy et al. [16] in the amorphous state and the values obtained by Morikawa et al. [17] in the molten state, but about 15% lower than those obtained by Morikawa et al. [17] in the amorphous state.

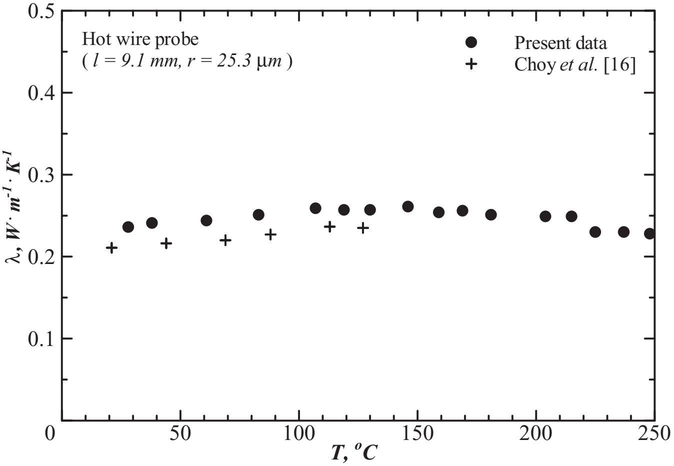


Fig. 4. Measured thermal conductivity of polycarbonate.

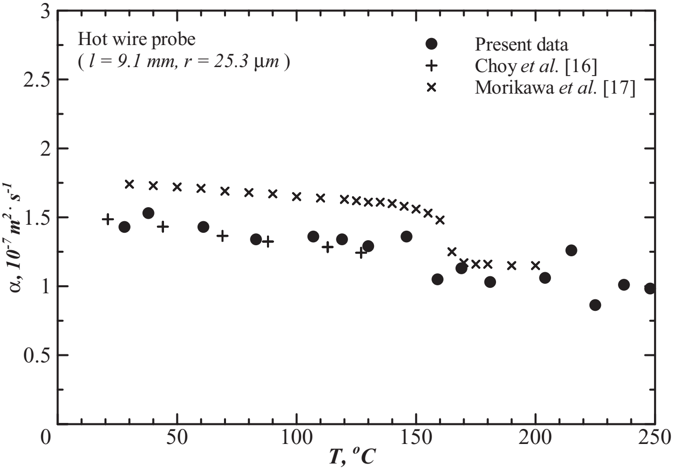


Fig. 5. Measured thermal diffusivity of polycarbonate.

Similar to the results obtained by Morikawa et al. [17], the present results of the thermal diffusivity also show higher values in the solid state than those in the molten state. However, the present results fluctuate sharply with temperature in the molten state.

Figures 6 and 7 show the measured results of polypropylene. Because the polypropylene is a semi-crystalline polymer, both the thermal conductivity and thermal diffusivity are much higher in the solid state as

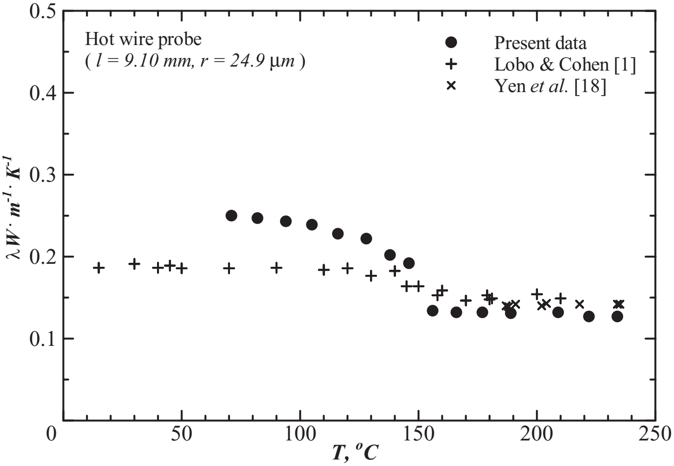


Fig. 6. Measured thermal conductivity of polypropylene.

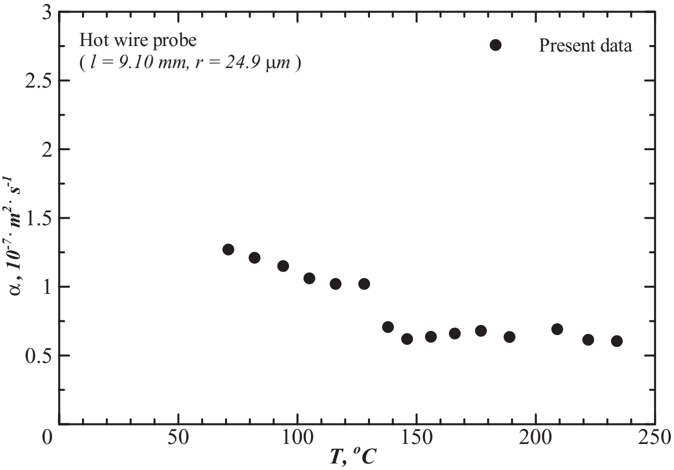


Fig. 7. Measured thermal diffusivity of polypropylene.

compared to its molten state. The present values of the thermal conductivity agree with those of Refs. 1 and 18 in the molten state, but show a big difference in the solid state. Figure 7 also shows the values of the thermal diffusivity decrease with increasing temperature in the solid state, and go down greatly around the melt transition temperature, then become almost a constant value in the molten state.

Figures 8 and 9 show the measured results of polystyrene. Figure 8 shows almost no change of thermal conductivity with temperature. But

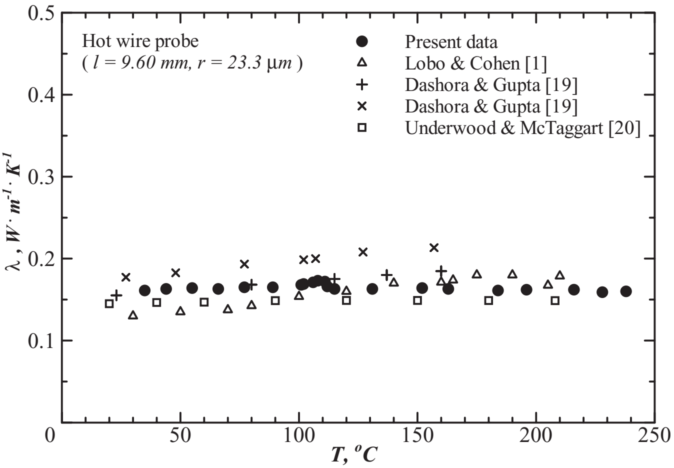


Fig. 8. Measured thermal conductivity of polystyrene.

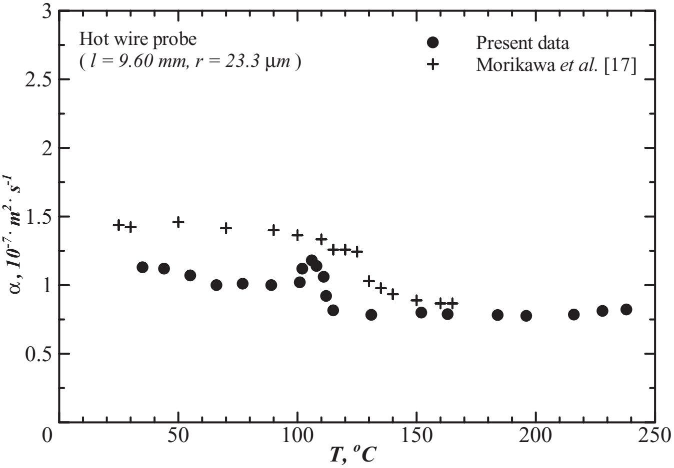


Fig. 9. Measured thermal diffusivity of polystyrene.

large changes are observed for the thermal diffusivity (Fig. 9) near the glass transition temperature. The present values shown in Fig. 8 agree well with those obtained by Dashora and Gupta [19] for the polystyrene Monsanto HT 99-L2020, the symbol +, but differ from those obtained by Dashora and Gupta [19] for the rubber-modified polystyrene Monsanto HT 88-1000, the symbol ×; Lobo and Cohen [1], △; and Underwood and McTaggart [20], □. Figure 9 further shows a comparison of the thermal

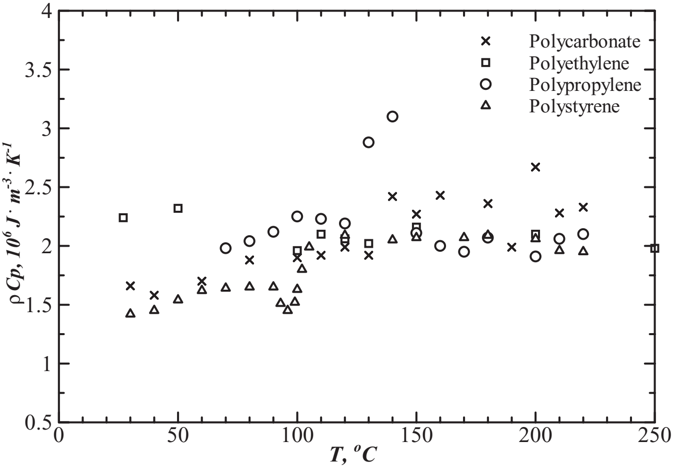


Fig. 10. Products of specific heat and density of four kinds of polymers.

diffusivity between the present results and the reference values obtained by Morikawa et al. [17]. It is noted that there is a big difference between them in the amorphous state and also near the melt transition temperature, but they close each other in the molten state.

Figure 10 shows the products of specific heat and density for the above four kinds of polymers. It is noted that the product values of polyethylene and polystyrene are almost unchanged with temperature in the molten state although they fluctuate near the melt transition temperatures. The value of polypropylene shows a maximum value at the melt transition temperature, and that of polycarbonate fluctuates sharply with temperature in the molten state.

5. CONCLUSIONS

The thermal conductivity and thermal diffusivity of four kinds of commercial polymers have been measured. The main conclusions are as follows.

1. The transient short-hot-wire method can be effectively used to measure simultaneously the thermal conductivity and thermal diffusivity of polymers in molten and solidified states, because of the need for only a small amount of test sample and the negligible effect of natural convection.
2. The estimated uncertanties of measurements for the thermal conductivity and thermal diffusivity are 3 and 6%, respectively.
3. Because the thermal conductivity in the solidified state depends on the degree of crystallinity, systematic measurements should be done in the near future.

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