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

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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.

Introduction

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

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 $\theta_v (= (T - T_i) / (q_v r^2 / \lambda))$ 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.

$$\theta_v = A \ln Fo + B \quad (1)$$

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

$$T_v = a \ln t + b \quad (2)$$

where T_v is the rise in the temperature above the initial

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temperature T_i . Equation (1) is dimensionalized as

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

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

$$\lambda = \frac{VI A}{\pi l a} \quad (4)$$

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

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_{cl} and R_{dl} , 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

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

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

In the present measurements, the magnitudes of the main factors in Eqs. (6) and (7) were estimated as follows. The length and radius of the hot wire were measured with a microcathetometer and microscope, 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 including additional systematic uncertainties were estimated to be 3 and 6 % for the thermal conductivity and thermal diffusivity, respectively.

Experiments

The experimental setup for the present study is almost the same as that described in our previous paper

[8]. A short platinum wire 8.70 mm in length and 51.0 μm in diameter was welded at both ends to platinum lead wires of 1.5 mm in diameter which were supported with a ceramic slat and connected with voltage and current platinum lead wires 0.5 mm in diameter. The ceramic slat was fixed with a stainless-steel rod, which can move up and down. A glass crucible with 50 mm in inner diameter and 100 cm^3 in volume was heated with an electric furnace that was covered with a thermal insulator. The temperatures at the outside of the crucible wall were measured with thermocouples to provide a feedback signal for the temperature controller.

The platinum hot wire was annealed at 800 $^{\circ}\text{C}$ for a few hours, and the temperature coefficient of its electric resistance β was determined through a calibration for the temperature range from 20 to 400 $^{\circ}\text{C}$. The calibrated probe was 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 were dispersed uniformly inside the polymer melt. The air bubbles went up slowly due to the effect of buoyancy. About 3 hours later, the molten polymer became transparent and all of the bubbles disappeared. After the temperature of the polymer melt became uniform and constant, the initial temperature of the polymer melt was measured with the hot wire by

$$T_i = \frac{I}{\beta} \left(\frac{R_i}{R_{t_0}} - 1 \right) \quad (8)$$

where R_{t_0} , R_i are the electrical resistance of the probe at 0 $^{\circ}\text{C}$ 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

$$T_v = \frac{I}{\beta} \left(\frac{R(t) - \varepsilon R_i}{(1 - \varepsilon) R_{t_0}} - 1 \right) - T_i \quad (9)$$

where ε is the electrical resistance ratio of the lead terminals and the entire probe and was 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.

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 $Fo < 200$ [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 $0.01\text{ }^{\circ}\text{C}$, if we allow more than 60 min between successive measurements.

Four kinds of polymers, polycarbonate, polyethylene, polypropylene, and polystyrene supplied by

Sumitomo Chemical Industries Ltd. were measured. These results are the average values of five measurements at the same temperature. In the following Figs. 1 to 8, the filled circles indicate the present results, and the other symbols indicate the various reference values.

Figures 1 and 2 show the measured thermal conductivity and thermal diffusivity of polyethylene, respectively. As shown in Fig. 1, the present values of thermal conductivity in the solid state are between those measured by Eiermann and Hellwege [14] and Kline [15], and decrease monotonically with increasing temperature in the solid state and are almost a constant value in the molten state. The measured thermal diffusivity shown in Fig. 2 also decreases with increasing temperature in the solid state, and is almost a constant value in the molten state.

Figures 3 and 4 show the measured results of polycarbonate. In contrast with polyethylene, the present thermal conductivity in Fig. 3 increases slightly with temperature in the solid state and becomes almost unchanged with temperature in the molten state except for the temperature around $220\text{ }^{\circ}\text{C}$. Further, the present

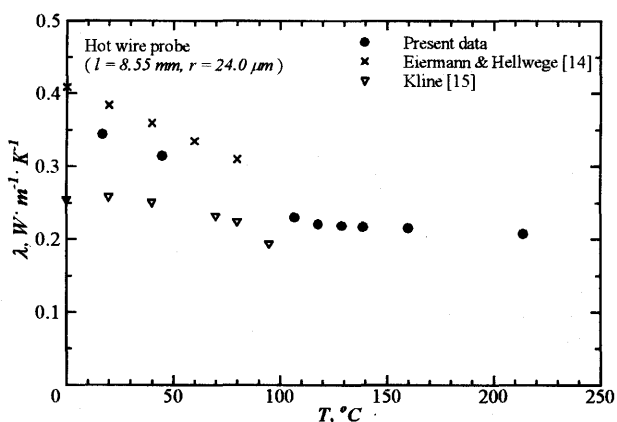


Fig. 1. Measured thermal conductivity of polyethylene.

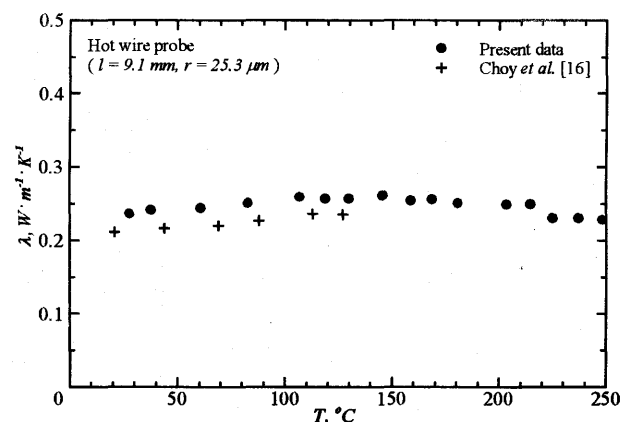


Fig. 3. Measured thermal conductivity of polycarbonate.

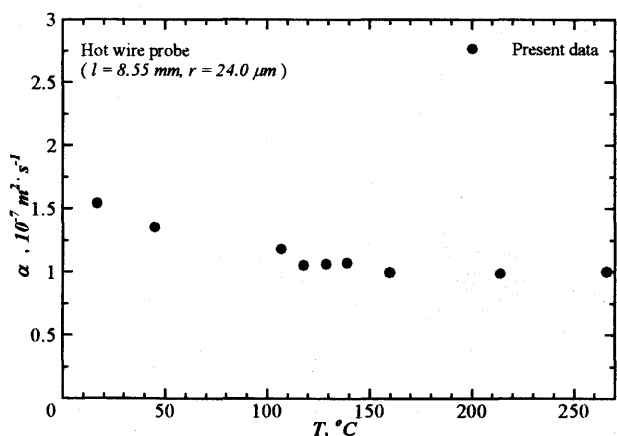


Fig. 2. Measured thermal diffusivity of polyethylene.

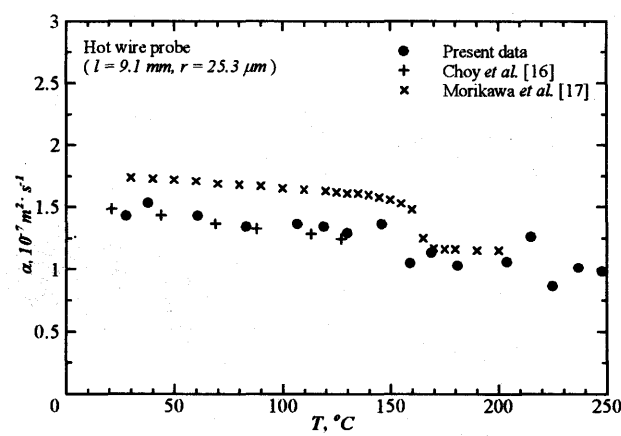


Fig. 4. Measured thermal diffusivity of polycarbonate.

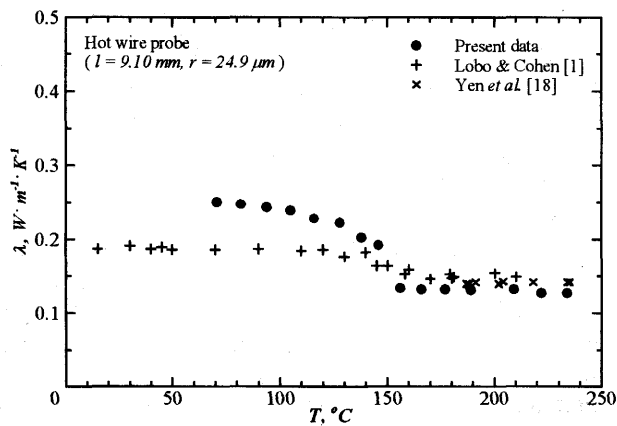


Fig. 5. Measured thermal conductivity of polypropylene.

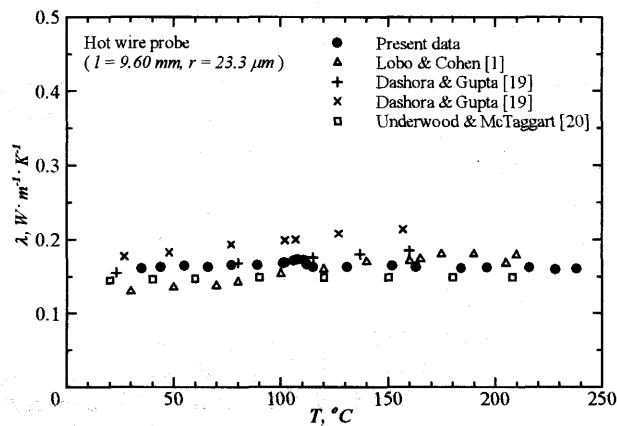


Fig. 7. Measured thermal conductivity of polystyrene.

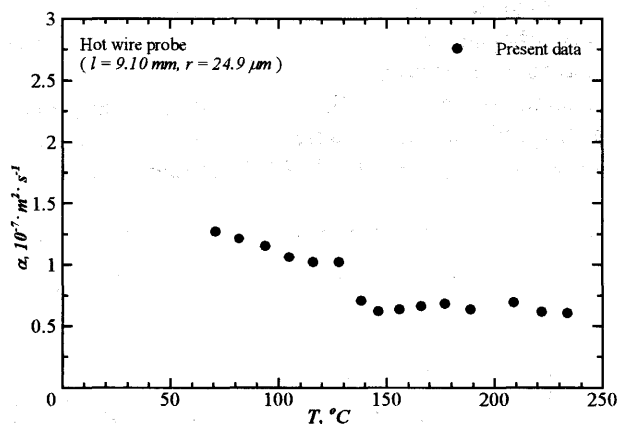


Fig. 6. Measured thermal diffusivity of polypropylene.

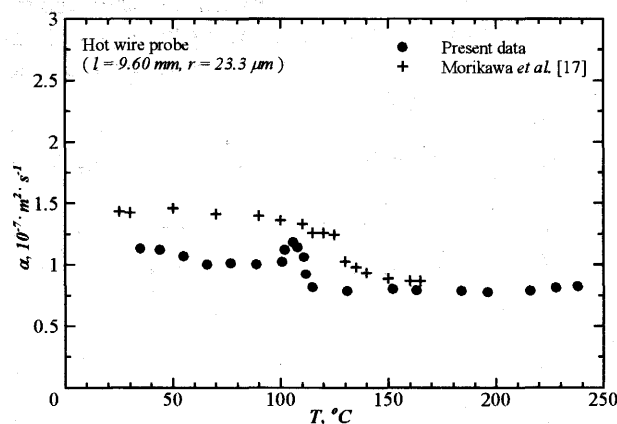


Fig. 8. Measured thermal diffusivity of polystyrene.

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.* in the amorphous state. Similar to the results obtained by Morikawa *et al.*, the present results of the thermal diffusivity also show higher values in the solid state than those in the molten state.

Figures 5 and 6 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 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 6 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 7 and 8 show the measured results of poly-

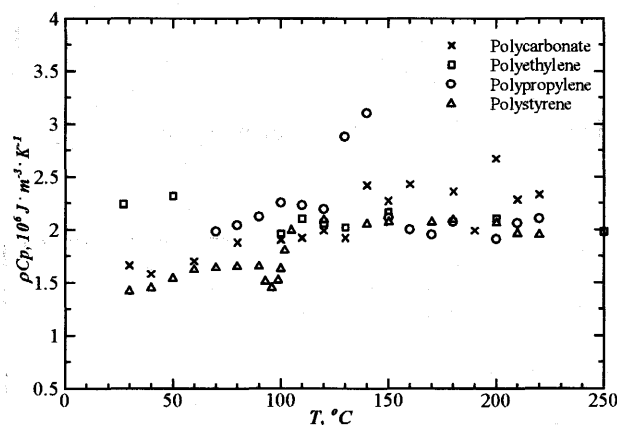


Fig. 9. Products of specific heat and density of four kinds of polymers.

styrene. Figure 7 shows almost no change of the thermal conductivity with temperature. But big changes are observed for the thermal diffusivity (Fig. 8) near the glass transition temperature. The present values shown in Fig. 7 agree 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 x; Lobo and Cohen [1], Δ; and Underwood and McTaggart [20], □. Figure 8 further shows a comparison of the thermal 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 9 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.

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 uncertainties 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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