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THERMAL CONDUCTIVITY OF POLYMER MELTS *

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ABSTRACT

The Du Pont 910 DSC cell and base have been modified for the measurement of steady-state heat flux and temperature gradients through molten polymeric specimens. This is a comparative method for thermal conductivity determination. The calculation for polymer melts is based on the measured thermal quantities and a calibration factor obtained from reference materials. The measurements at several steady-state temperatures can be carried out consecutively. Furthermore, the thermal diffusivity κ can be obtained from the relationship $\kappa = \lambda/\rho C_p$, where λ is the thermal conductivity, ρ is density, and C_p is specific heat. Construction of sample holders and modifications of the DSC cell and base are described.

INTRODUCTION

Thermal conductivity (TC) is an important physical property of materials and describes the ability of that material to conduct heat. The property dictates the design of processing machinery and controls the speed of many mixing, extruding, and molding operations. The principle of measurement is based on the Fourier heat flow relation. The property expresses the quantity of heat transmitted, owing to unit temperature gradient per unit length under steady-state conditions in a direction normal to a surface of unit area.

Basic methods used for measuring thermal conductivity of liquids, either horizontal plane layer, concentric cylinder, hot wire, or thermal-comparator, have been described in books [1–3], papers [4–11] and ASTM [12], and will not be repeated here. Almost all reported data were measured in steady-state methods which are widely regarded as the most accurate. As important as the property is, very few publications or instrument companies have addressed the subject and the needs. Approaches [13–15] based on heat flux and temperature data of differential scanning calorimetry (DSC), Fig. 1B, have shown merits in measurements in the range 40–60 °C and are useful in

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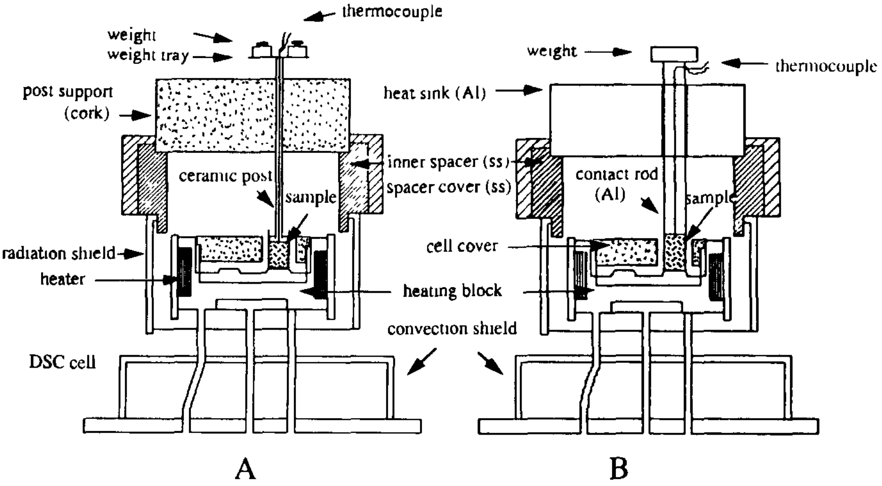

Fig. 1. Thermal conductivity cells for (A) polymer melts and (B) polymer solids.

routine scouting research where requirements of thermal conductivity measurements are less stringent.

This paper demonstrates that a modified DSC can be extended for thermal conductivity measurements of polymer melts. Furthermore, thermal diffusivity of polymer melts can be calculated with specific heat and melt density data.

EXPERIMENTAL

TC cell for polymer melts (Fig. 1A)

The thermal conductivity cell is essentially the Du Pont 910 DSC cell with the following modifications. The stainless steel spacer and cover that fit over the DSC cell are replicas of those of Sircar and Wells [15]. However, as shown in Fig. 1B, the large aluminum heat sink concept for measuring TC of polymer solids did not apply to the polymer melts. Instead, a non-conductive material of cork, diameter 2 in, from standard stock room supply was placed atop the spacer. A small hole was drilled vertically in the cork so as to align with the sample platform of the DSC (about 0.15 in off the center of the cork) and to fit a $\frac{1}{16}$ in × $3\frac{1}{2}$ in ceramic tube through smoothly. A K-type thermocouple, threaded from top to bottom of the ceramic tube, was used for measuring the temperature (T_2) of the upper end of a molten polymeric sample. An aluminum "shoe", diameter 4.75 mm, was fitted over the bottom of the ceramic tube and was adjacent to the thermocouple in order to contact the upper end of the sample. A weight tray (a part from Du Pont 943 TMA) placed at the top of ceramic tube held 20–30 g weight during the measurements to facilitate the heat conduction through better contacts.

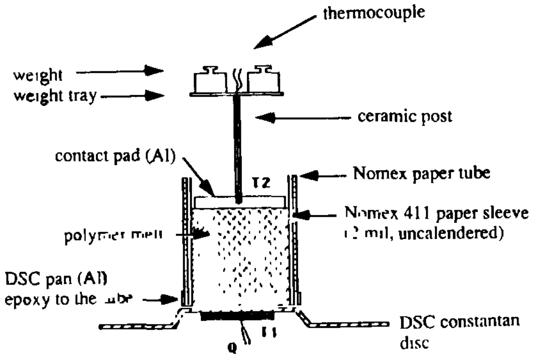

Fig. 2. Sample holder for thermal conductivity measurements.

A cork cover with a hole lined up with the sample platform was placed in the cell heater area to minimize heat losses, see Fig. 1. A commercial DSC open-top glass tower and a plain glass sheet were placed over the cell as another convection shield.

Sample holder

Low thermally conductive Nomex paper tubes ($\frac{1}{4}$ in (outer diameter) × 0.031 in (wall) × 0.4 in (length)) with DSC aluminum pans epoxied at one end were selected as the sample holders. The Nomex paper tubes were again lined with Nomex 411 paper sleeves (low thermal conductivity, $\lambda = 0.04$ W m^{-1} K^{-1}) for further insulation. The sample holder is shown in Fig. 2.

Sample preparation

Polymeric slabs are preferred, since 4.75 mm diameter cylinders can be punched out and placed inside the holders. The thinner cylinders can be stacked to make up 5–6 mm of height. To prevent air bubbles from forming at the interfaces of the stacked sample cylinders during the heating, all samples were melted in DSC and pressed down firmly with a Teflon plunger to ensure a flat surface.

External reference junction

An external reference junction P/C board from Du Pont 943 TMA (part No. 942106-902), powered from a 8.2 V d.c. power supply with isolated ground, was tied in to the B-channel (derivative channel) in the DSC cell base. A K-type thermocouple and output cable were attached to the reference junction P/C board (Fig. 3). The output cable was then plugged into the back of the DSC cell base. Because of this connection, the new B-signal

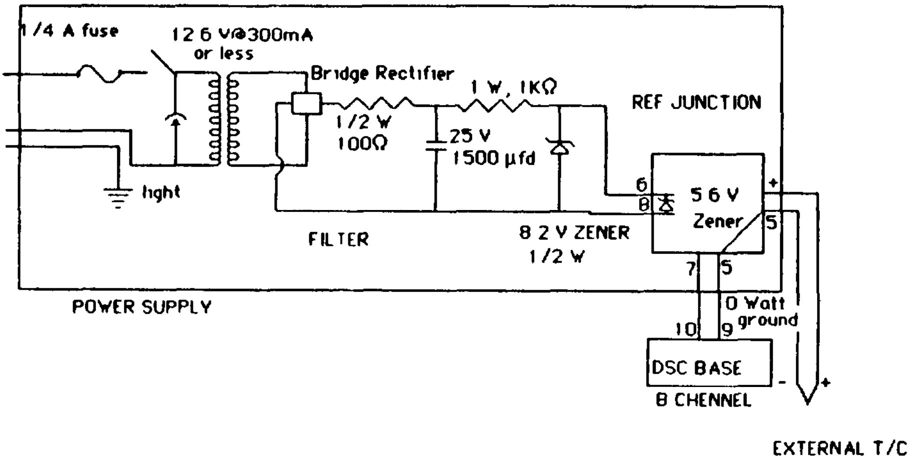

Fig. 3. External reference junction tie in to the B channel of the DSC.

(the external auxilary signal instead of derivative signal) which is the T_2 thermocouple reading in digitized form, becomes a part of the data files.

Measurements

The sample (4.75 mm × 6 mm) inside the holder was placed on the DSC sample platform. The external thermocouple/"shoe" was lowered until it touched the top of the sample. A Dow Corning 340 silicone heat sink compound was applied sparingly on the solid–solid interfaces—from the DSC platform to the bottom of sample holder and from the top of the sample to the "shoe". The alignment can be adjusted by viewing through the windows in the spacer/cover. Multiple isothermal steps can be achieved by stringing the methods from the computer, a Du Pont 9900 TA system. A true zero of the heat flow and accurate reading of T_1 and T_2 are essential for the precision of the data. There should be no heat flow in DSC at the start of the isothermal measurements. This can be achieved by waiting sufficiently long after the set-up (20 min) for a temperature equilibration and then setting the residual heat signal to zero via a voltage offset. T_1 is standardized using the DSC temperature calibration prodecure; T_2 is room temperature.

RESULTS AND DISCUSSION

In all the traditional thermoconductivity experiments (the horizontal plane, the concentric cylinder, and the hot wire methods) the errors in heat losses by radiation and convection were either taken into account in the calculation or eliminated from apparatus as much as possible through better design of the cell. In DSC method, one obtains λ by comparing the heat

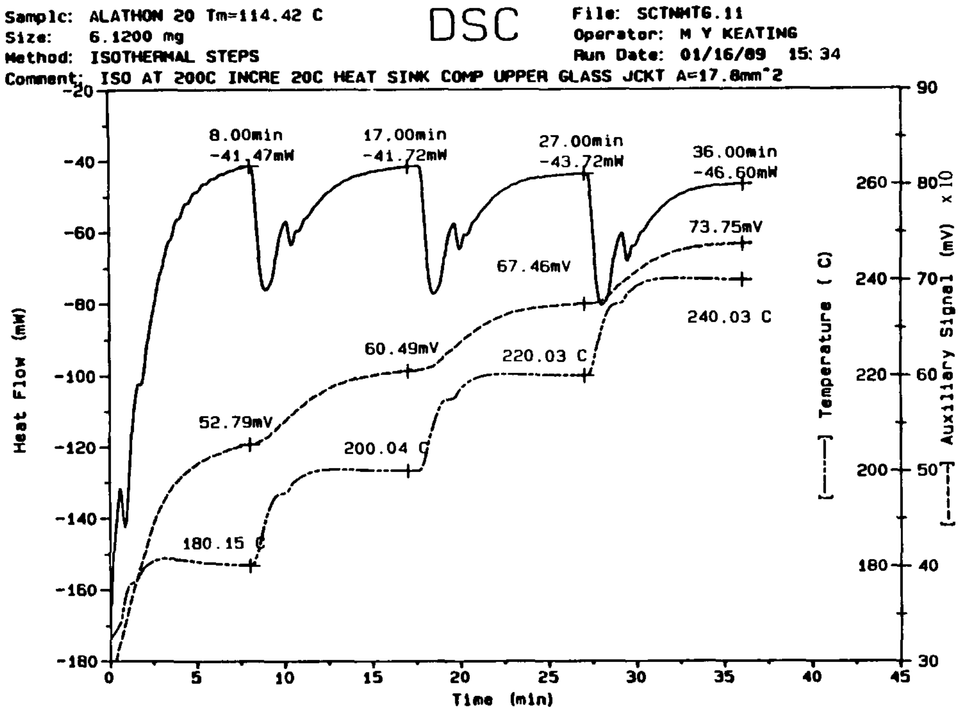

Fig. 4. Heat flux (mW), auxiliary signal (mV), and temperature (°C) versus isothermal time in a conductivity measurement.

data with that of a reference material; these errors are canceled in the calculation. The shortcoming of the comparative method is that it depends on reliable reference material.

As demonstrated in Fig. 4, three signals of an actual thermal conductivity data file were plotted against time—the heat flux signal (mW), the auxiliary signal T_2 (mV), and temperature T_1 (°C). It took about 6–8 min for an isothermal step to reach a steady state, at which the quantities of these signals were read and used to compute the thermal conductivity data. The inner diameter of the Nomex holder is the diameter of all samples.

Fuller and Fricke [4] and Lohe et al. [8,9] agreed on the thermal conductivity of high density polyethylene (Marlex) at 180–240 °C and several other polymers at the same temperature range using different methods. Their thermal conductivity values ($\lambda_{200^\circ\mathrm{C}} = 0.266$ W m^{-1} K^{-1}, 0.263 W m^{-1} K^{-1}) on HDPE (Marlex) were used in this technique as the reference. A cured natural rubber compound [15,16] of reproducible conductivity ($\lambda_{25^\circ\mathrm{C}}$ = 0.151 W m^{-1} K^{-1}) was also used for the elastomeric reference material. A cell constant K was then obtained for the cell and was used for the calculation of λ values of other polymer specimens.

$$\lambda = K(Q/\Delta T)(L/A) \tag{1}$$

TABLE 1

Thermal conductivity of polymer melts

Materials	$\lambda_{200\,°C}$ (W m^{-1} K^{-1})		$\lambda_{220\,°C}$ (W m^{-1} K^{-1})		$\lambda_{240\,°C}$ (W m^{-1} K^{-1})	
	This work	Lit.	This work	Lit.	This work	Lit.
HDPE (Marlex)	0.26	0.26, 0.27	0.28	0.29	0.30	0.31
LDPE (Alathon)	0.23	0.22, 0.24	0.24	0.24	0.26	0.26
PP (Shell)	0.20	0.21	0.21	0.21	0.22	0.21
PS (Styron)	0.21	0.17	0.23	0.17	0.24	0.17
Nylon 6	–	–	0.24	0.13, 0.21, 0.31	0.28	0.13, 0.21, 0.31
POM (Delrin)	0.27	–	0.28	–	–	–
Surlyn HP	0.24	–	0.25	–	0.24	–
TPE	0.20	–	0.22	–	–	–
EVA	0.22	–	0.24	–	–	–

The thermal conductivities of eight polymers other than the reference are shown in Table 1. Five of them are comparable with the results of Fuller and Fricke [4], Lohe et al. [8,9], and Khanna et al. [11]. The samples are identified generically, although it is known that small amounts of additives and process aids are present. The precision of the measurement is good to the second decimal place in W m^{-1} K^{-1}. It should be noted that cell constant K increases with temperature and varies with the material of the

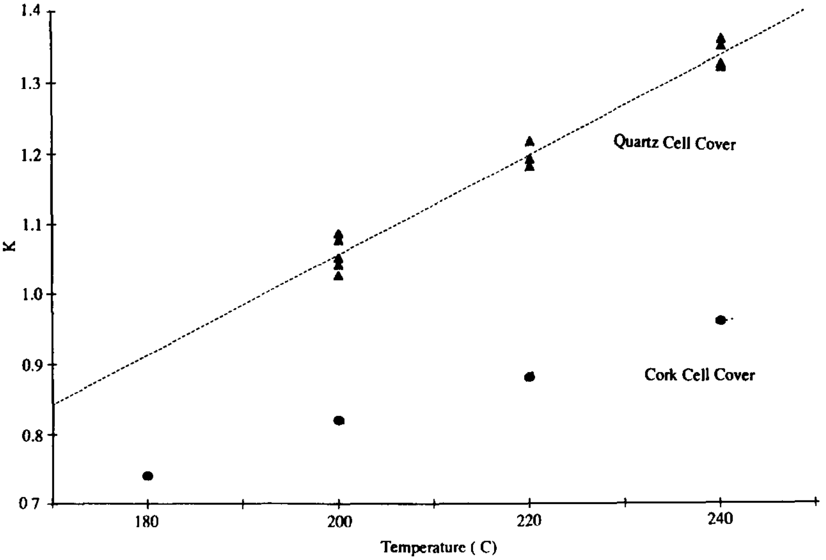

Fig. 5. Cell constants versus measuring temperatures and cell cover type.

TABLE 2

Thermal diffusivity κ of polymer melts at 200 °C

Material	λ ($W\ m^{-1}\ K^{-1}$)	C_p ($J\ g^{-1}\ K^{-1}$)	ρ ($g\ cm^{-3}$)	κ ($cm^2\ s^{-1}$) This work	κ ($cm^2\ s^{-1}$) Lit.
HDPE (Marlex)	0.26	2.738	0.893	10.6×10^{-4}	10.3×10^{-4}
LDPE (Alathon)	0.23	2.601	0.863	10.0×10^{-4}	–
PP (Shell)	0.20	2.725	0.774	9.5×10^{-4}	6.6×10^{-4}
PS (Styron)	0.21	2.118	1.014	9.8×10^{-4}	7.5×10^{-4} 8.2×10^{-4} 12.8×10^{-4}
Nylon 6	0.23	3.096	1.058	7.0×10^{-4}	–
POM (Delrin)	0.27	2.380	1.268	9.0×10^{-4}	8.0×10^{-4}
Surlyn HP	0.24	2.361	0.925	10.9×10^{-4}	–
TPE	0.20	2.378	0.897 [a]	9.4×10^{-4}	–

[a] Density at 177 °C.

cell cover. Figure 5 shows that the cell constant for the cell covered by quartz is larger than the one covered by cork. The cork cell cover was used for all the data reported in this paper.

The thermal conductivities λ of these polymers are converted to thermal diffusivities κ using their heat capacities C_p and melt densities ρ at 200 °C.

$$\kappa = \lambda/(\rho C_p) \qquad (2)$$

This is in good agreement with the thermal diffusivities reported by Ballman and Shusman [17], Shoulberg [18], and Karl et al. [19] from direct measurements, as shown in Table 2.

CONCLUSION

The conductivities of polymer melts vary minutely with temperature, as opposed to polymer solids. Of the polymers measured the thermal conductivities fall in the range 0.2–0.3 $W\ m^{-1}\ K^{-1}$. The calculated diffusivities again agree with the values reported from direct measurements. The range of thermal diffusivities is from 7×10^{-4} to 11×10^{-4} $cm^2\ s^{-1}$.

The precision is good to the second decimal place.

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