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DETERMINATION OF THERMAL CONDUCTIVITY BY DIFFERENTIAL SCANNING CALORIMETRY *

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ABSTRACT

A technique has been developed for rapid determination of thermal conductivity of solid materials using a commercial differential scanning calorimeter. An attachment is constructed without modification of the original instrument. Data for a variety of materials are presented and limitations on sample dimensions and other parameters discussed.

INTRODUCTION

Thermal conductivity is one of the fundamental physical properties of both scientific and technological interest. It is particularly important for construction materials used in a thermal environment, where heat transfer, insulation, and storage are of primary concern. Although methods for thermal conductivity measurements are well documented in the literature, including the widely accepted ASTM procedures, and commercial instruments are available, there remains a demand for rapid, versatile techniques for routine scouting research where requirements for sample preparation, temperature equilibration, and instrument operation are less stringent. Attempts have been made previously to utilize dynamic thermal analysis equipment to obtain thermal conductivity data [1—3]. The present work describes a very simple attachment to the DuPont differential scanning calorimeter (DSC) cell for such measurements without modification of the basic instrument. Each determination requires only a few minutes. The technique is highly sensitive and versatile, and suitable for routine determinations.

EXPERIMENTAL

A schematic diagram of the thermal conductivity cell is shown in Fig. 1. A more detailed description of the thermal conductivity attachment is shown in Fig. 2. The thermal conductivity attachment fits firmly onto the DuPont DSC cell. The cylindrical sample is attached to the copper contact rod with the aid of silicone grease. The rod position is adjustable inside the aluminum

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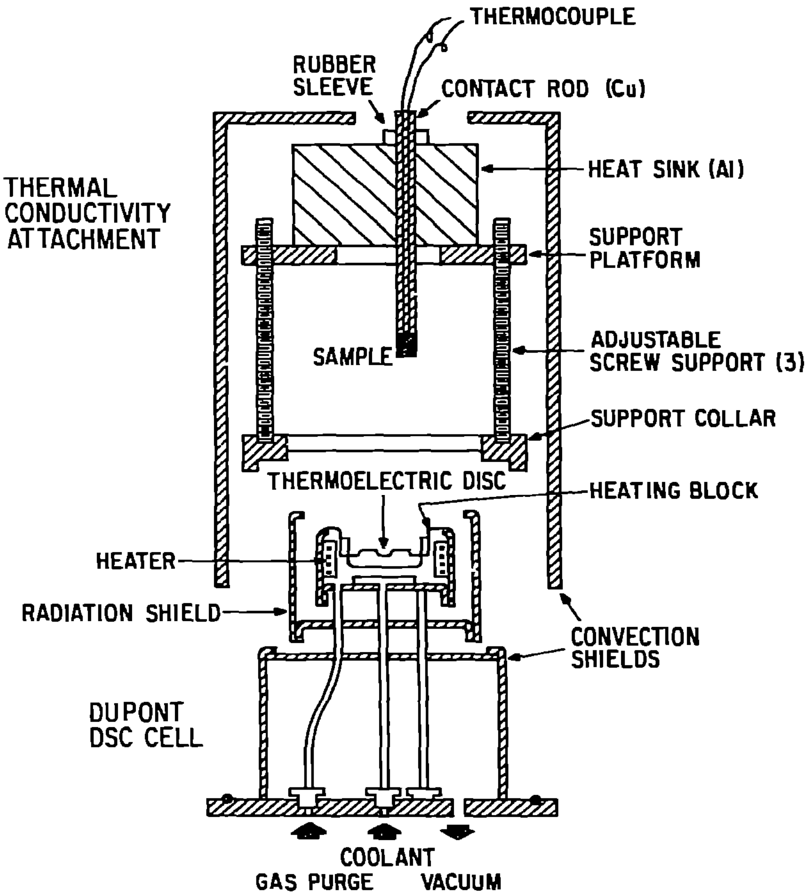

Fig. 1. Schematic diagram of thermal conductivity cell

heat sink and the rubber sleeve so that samples of variable lengths can be lowered onto the thermoelectric disc of the DSC cell. The temperature at the bottom of the sample is read from the recorder of a DuPont 990 thermal analyzer, while the temperature at the top of the sample is measured with a precision potentiometer by a chromel—alumel thermocouple inserted inside the contact rod. The thermal analyzer also provides heat input into the sample.

Even though various approaches can be used for making the measurement such as programmed temperature mode, absolute heat calibration method, etc., we prefer the isothermal mode and calibration with a standard material. In a way, this approach is similar to the popular DSC method for heat capacity measurement employing a sapphire standard. The procedure is best illustrated in Fig. 3 and described as follows.

The recorder zero is first established with the cell base in the normal mode and ΔT zero on the cell base adjusted at maximum sensitivity to coincide with the recorder zero as close as possible. The temperature scale is calibrated according to the standard DSC procedure and checked with melting points of at least two pure metals. A sample in cylindrical form, ca. 15 mm × 6 mm diameter, is coated evenly and lightly with heat-conductive sili-

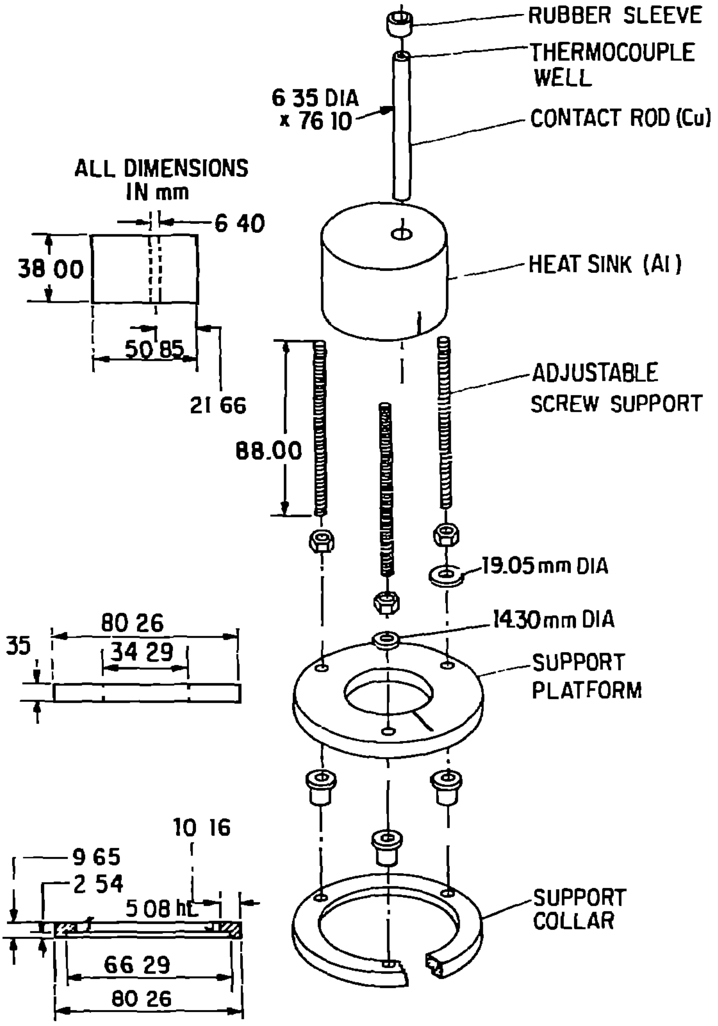

Fig 2 Description of thermal conductivity attachment

cone grease (Dow Corning 340) at both ends, and attached to the end of the contact rod. The sample is then lowered onto the sample platform of the thermoelectric disc. The silicone grease at the end of the sample helps to maintain good contact with the platform. Although the rod position has been prealigned with the sample platform by the guide marks on the heat sink and the support platform, the proper positioning of the sample on the sample platform should be checked with a dental mirror. To provide adequate clearance for the dental mirror, the distance between the support platform and the support collar should be ca. 50 mm or more. The upper convection shield, the size of a 2 lb coffee can, is then placed in position, and the thermocouple inserted inside the contact rod. The DSC cell is quickly brought to the constant measurement temperature. The recorder is switched to time base, and the sensitivity range adjusted to provide suitable reading. Normally a stable signal is reached within 2 min as indicated by the flat curve. The temperatures at the top (T_2) and the bottom (T_1) of the sample are read at this time

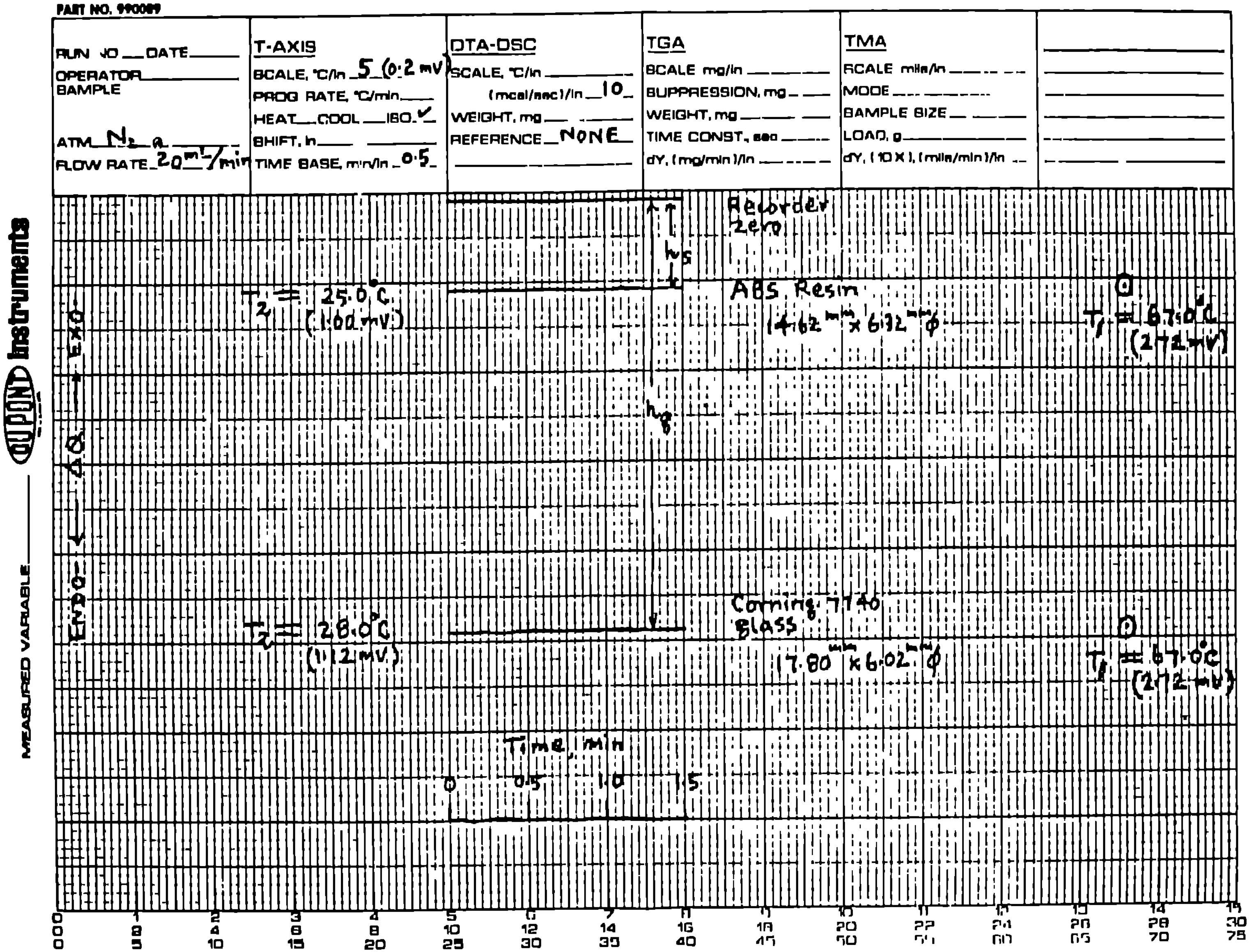

Fig. 3 Illustration of DSC technique for thermal conductivity measurement

from the potentiometer and the 990 recorder, respectively. The heat flux to the sample is represented by the distance, h_s, between the sample curve and the recorder zero curve. The DSC cell is now cooled, and the whole procedure repeated with a calibration standard such as a Corning 7740 glass rod of similar dimensions to obtain its heat flux represented by distance h_g. Values of h_g and h_s are used to calculate the thermal conductivity of the sample at temperature T_1. We have found that an air blank run without the sample is quite close to the recorder zero curve. Although an insulation material placed between the heat sink and the DSC heating block reduces radiation heat from the DSC cell, it causes inconvenience to inspect the sample alignment which is of critical importance. The present cooling procedure has been found to be satisfactory in reducing the accumulation of radiation heat.

RESULTS AND DISCUSSION

Under steady-state conditions, the thermal conductivity of a cylindrical specimen is expressed typically by the Fourier heat flow equation

$$Q = \lambda \times \frac{A}{L} \times \Delta T$$

where Q is the heat flux; λ, thermal conductivity; A, cross-sectional area of specimen; L, length of specimen; and ΔT, temperature difference. After applying the present experimental parameters, the above equation is more conveniently expressed as follows

$$\lambda = \frac{E \times h \times S \times L \times 4.184}{A \times \Delta T}$$

where λ = thermal conductivity (W m^{-1} K^{-1}), E = calibration constant, h = chart deflection (measured distance between recorder zero and signal curve) (in.), S = Y-axis sensitivity (mcal sec^{-1} $in.^{-1}$), L = specimen length (mm), A = specimen cross-sectional area ($mm^2 = 0.785\ D^2$), D = diameter of specimen (mm), ΔT = temperature difference = $T_1 - T_2$ (K), T_1 = temperature at bottom of specimen (hot face) (°C) and T_2 = temperature at top of specimen (cold face) (°C). The E value at a certain temperature is obtained by determining h of a standard with known thermal conductivity and applying the above equation. We found Corning 7740 glass cylinders quite convenient with thermal conductivity values recommended by the National Bureau of Standards [4].

Thermal conductivity measurements can be made with a DSC cell with E value already determined, or with a standard glass run following the sample run. In the latter case, the calculations are simplified by using the following equation

$$\lambda_s = \lambda_g \times \frac{h_s}{h_g} \times \frac{S_s}{S_g} \times \frac{L_s}{L_g} \times \frac{D_g^2}{D_s^2} \times \frac{\Delta T_g}{\Delta T_s}$$

where the subscripts s and g represent the sample and the glass standard, respectively.

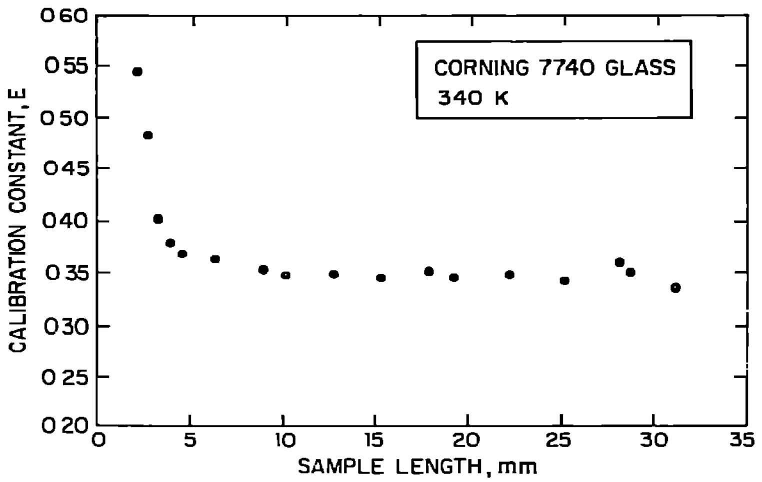

Fig. 4. Sample length effect on calibration constant for thermal conductivity measurement.

The effect of sample length on heat flux has been investigated by determination of E values of a series of standard Corning 7740 glass rods of diameter 6.0 ± 0.2 mm but with lengths varying from less than 2 mm to larger than 30 mm. The results obtained at a temperature of 340 K and using a thermal conductivity value of 1.16 W m^{-1} K^{-1}, are shown in Fig. 4. Reproducibility at each length within a one-month period is ca. 3%. Results obtained from glass rods cut from a Dynatech thermal conductivity standard

TABLE 1

Thermal conductivity data

Material	Thermal conductivity (W/m · K)	
	This work	Literature
Polyethylene, high density	0.503	0 329[5], 0.46 ~ 0.52[7], 0.42 ~ 0.52[8]
Polymethyl methacrylate	0.137	0 208[5], 0.193[6], 0 021[7], 0.19—0.20[8]
Polytetrafluoroethylene	0.326	0 242[5], 0.418[6], 0.251[7,8]
Polypropylene	0.237	0.138[5], 11.7(?)[6], 0.117[7], 0.234[8]
Ionomer resin	0.272	0.243[7]
Polyoxymethylene	0.360	0.225[5], 0.292[6], 0.230[7], 0.406[8]
Polyethylene terephthalate	0 256	0 14 ~ 0.17[7], 0.22 ~ 0.27[8]
Polystyrene, resin	0 140	0 10 ~ 0.16[5], 0 12 ~ 0 13[6], 0 10 ~ 0.14[7], 0 17 ~ 0.20[8]
Polystyrene, foam	0 029	0.033[5], 0.033 ~ 0.040[7]
Polyvinyl chloride	0 149	0 12 ~ 0.17[5], 0 16[6] 0.13 ~ 0.29[7], 0.14 ~ 0.17[8]
Nylon 66	0.320	0 242[5], 0.36 ~ 0.43[6], 0.243[7]
ABS resin	0 157	0.14 ~ 0 21[5], 0.19 ~ 0.34[7]
Poly-4,4′-oxydiphenylene pyromellitimide	0.361	0 370[9]
Quartz	1.27	1 4[4]
Cork	0.005	0.036[10]

(Dynatech Corporation, 99 Erie Street, Cambridge, Mass.) and those purchased from a typical glass supplier such as Wilmad Glass Company (Rt. 40 and Oak Road, Buena, N.J.) are not distinguishable. Apparently, the *E* value increases sharply at sample lengths below ca. 5 mm. There is a wide plateau region after 5 mm up to at least 30 mm. Thus, the choice of sample length is quite flexible, and a length of 10—25 mm is recommended.

Thermal conductivity values of a variety of materials determined at 340 K by this DSC technique are shown in Table 1. Each value is an average of three measurements with a standard deviation of better than ±3%. There is a wide discrepancy in literature values of thermal conductivity of all materials including our standard Corning 7740 [4,8,11]. It is difficult, therefore, to compare our results with those in the literature. Nonetheless, some typical literature values are listed in Table 1 for information.

CONCLUSION

The present work describes a DSC technique for rapid determination of thermal conductivity of solid materials using a commercial dynamic thermal analyzer without modification. A precision of better than 3% is obtainable. With the versatile temperature control of the thermal analyzer, determinations in a wide temperature range are possible. Work is now in progress in our laboratory to devise techniques to handle molten polymers and liquid samples.

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