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Thermal conductivity of polymers, glasses and ceramics by modulated DSC ☆

S.M. Marcus, R.L. Blaine *

TA Instruments, Inc., 109 Leukens Drive, New Castle, DE 19720, USA

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Abstract

This study describes a new method for the measurement of the thermal conductivity of insulating materials in the range from 0.1 to 1.5 W °C^{-1} m^{-1} which generally covers polymers, ceramics and glasses. The method is based on modulated DSC and includes no modification or additions to the apparatus itself. One additional calibration step is required to compensate for heat loss through the inert purge gas surrounding the test specimen. Best case precision is in the order of 2%, with mean values compared to literature values within 1%. While work to date includes only temperatures near ambient, measurements above and below ambient seem possible. Further work is also currently in progress to evaluate the applicability of this method to a broader range of materials.

Keywords: Ceramics; Conductivity, MDSC; Novel; Polymer; Precision

1. Introduction

Thermal conductivity is a measure of the ease with which temperature is transmitted through a material and is a basic material property. Materials with high thermal conductivity are called "conductors" and those with low conductivity are called "insulators". Solid conductors (such as metals) typically have thermal conductivities in the range 10–400 W °C^{-1} m^{-1}, while insulators (such as

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* Corresponding author.

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polymers, glasses and ceramics) have values in the range 0.1–2 W $^\circ C^{-1}$ m^{-1}. Furthermore, thermal conductivity changes as a weak function of temperature and rarely changes by a factor of ten within a general class of materials.

Determination of a material's thermal conductivity is important in evaluating its utility for specific applications. In many of these applications, a textbook value or a single measurement near the temperature of use is sufficient to make a decision. In a few cases, however, the material's composition varies widely enough that regular measurement of thermal conductivity is required. For example

(1) The manufacturers of active electronic components need to know the thermal conductivity of their encapsulating materials to be able to determine the heat dissipation of their devices. Incomplete heat dissipation may result in the premature failure of the active element.

(2) The solar energy enthusiast needs to know the thermal conductivity of the solid materials used to store the sun's heat energy to be able to calculate heating and cooling capacity [1].

(3) Mine engineers are interested in the thermal conductivity of the rock though which they work [2]. Knowledge of the rock's conductivity enables calculation of the ventilation capacity required to dissipate heat being delivered to the mine shaft from the warm surroundings.

(4) Radioactive waste management engineers need to know the thermal conductivity of the cement and grouts used to immobilize radioactive waste because the decay steadily generates heat which must be safely dissipated [3].

(5) Process and manufacturing engineers involved with the manufacture, storage, and shipping of bulk chemicals need to know the thermal conductivity (along with several other reaction parameters) in order to predict and eliminate potential thermal hazards.

In all of these cases (one-time measurement or on-going multiple measurements), the ability to measure thermal conductivity easily and with modest amounts of material is useful.

2. Theory

Thermal conductivity can be measured using several different instrumental techniques. One of these is based on differential scanning calorimetry (DSC). DSC is a thermal analysis technique which measures heat flow into or out of a material as a function of temperature or time. DSC is primarily used to measure transition temperatures and associated heats of reaction in materials, particularly polymers. Measurement of glass transition temperature, melting point, percentage crystallinity, degree of cure, decomposition temperature, and oxidative stability are specific examples of some of the more common DSC measurements.

The most widely used approach for making DSC measurements in the "heat flux" DSC, in which the sample and reference materials (usually contained in metal pans) are placed on a thermoelectric disk inside a temperature-programmed environment (Fig. 1). Heat flow in this approach is measured using the thermal

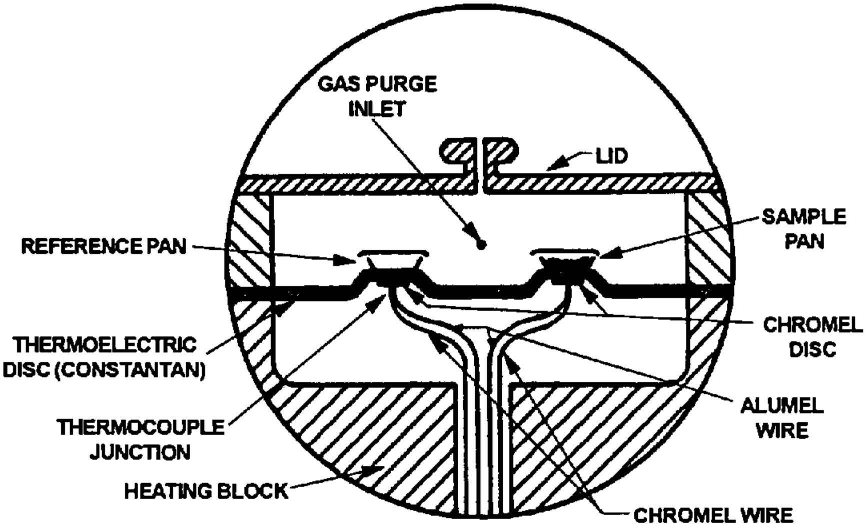

Fig. 1. Schematic of the heat flux DSC.

equivalent of Ohm's law where $dQ/dt = d\theta/R$ (Q is heat, t is time, θ is temperature, R is thermal resistance of the thermoelectric disk) [4,5]. Several researchers including Chiu and Fair [6], Sircat and Wells [7], Keating and McLaren [8] and Duswalt [9] have modified heat flux DSCs to measure the thermal conductivity of insulating materials such as thermoplastic solids, elastomers, thermoplastic melts and pyrotechnics, respectively. In their work, a test specimen is placed in the DSC cell in contact with the sample platform. The DSC sensor measures both the temperature of one side of the specimen and the heat flow into it. A heat sink of known temperature is constructed to contact the opposite side of the test specimen. From the recorded heat flow and the temperature difference between the DSC cell and the heat sink (along with the test specimen dimensions), thermal conductivity can be calculated using the equation

$$dQ/dt = -KA\ d\theta/dx \tag{1}$$

where Q is heat in J, t is time in s, K is thermal conductivity in W °C^{-1} m^{-1}, θ is temperature in °C, x is height of test specimen in m, and A is cross sectional area of the test specimen in m^2.

This DSC measurement of thermal conductivity works well but requires modification of the commercially available DSC cell, as well as very careful attention to experimental detail. A recent extension of traditional DSC, called modulated DSC, however, minimizes these limitations.

Modulated DSC (MDSC) is a patented technique from TA Instruments in which the test specimen is exposed to a linear heating method which has a superimposed sinusoidal oscillation (temperature modulation), resulting in a cyclic heating profile similar to that shown in Fig. 2 (solid line). Deconvolution (separation) of the

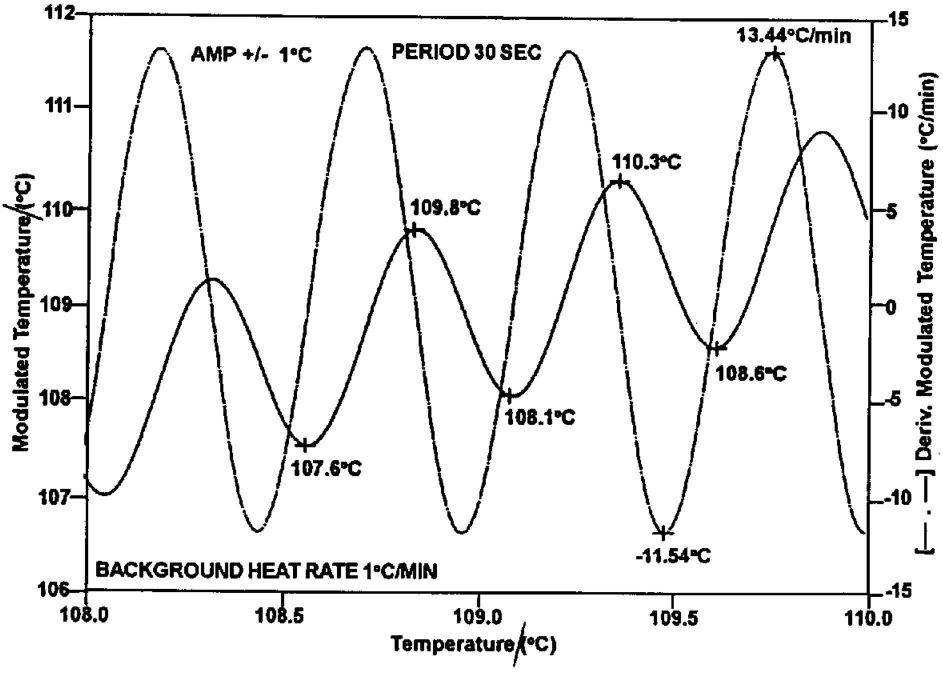

Fig. 2. MDSC heating profile.

resultant experimental heat flow during this cyclic treatment provides not only the "total" heat flow available from conventional DSC, but also separates that total flow into its reversing (heat capacity related) and non-reversing (kinetic) components, thereby providing unique insights into materials, including

(1) Separation of the reversing and non-reversing characteristics of thermal events [10];

(2) Improved resolution of closely occurring or overlapping transitions [11,12];

(3) Increased sensitivity for subtle transitions [13];

(4) Direct measurement of heat capacity.

It is the latter capability (direct measurement of heat capacity) which is of primary interest in this discussion because heat capacity and thermal conductivity are related properties.

MDSC users have observed that the best heat capacity results are obtained when experimental conditions are selected to obtain maximum temperature uniformity across the test specimen. Small, thin specimens, long oscillation periods and complete encapsulation of the test specimen in sample pans of high conductivity (aluminum has a conductivity of about 235 W $^{\circ}C^{-1}$ m^{-1}) [14] produce the best results. When test conditions lie outside these guidelines, the value of the measured heat capacity declines. This is thought to be due to the thermal conductivity of the material preventing uniform temperature conditions across the test specimen.

Table 1
Apparent specific heat capacity in J °C^{-1} g^{-1} ($\theta = 25$°C, amplitude = 1.0°C, period = 80 s)

Material	Encapsulated	Open	Ratio
Polystyrene	1.38	0.621	0.45
Polytetrafluoroethylene	2.13	0.920	0.43
Soda lime glass	0.657	0.525	0.80
Pyrex® 7740 glass	0.668	0.532	0.80

Alternatively, the effect of the specimen's thermal conductivity may be maximized through the use of thick test specimens and the use of open sample pans which results in the application of the temperature oscillation to only one side of the test specimen.

Table 1 lists the apparent specific heat of a series of materials comparing a thin specimen encapsulated in aluminum sample pans/lids and a thick specimen in an open pan only. The apparent specific heat values can be quite different under these two conditions. The difference in apparent specific heat values measured under these conditions, as seen in their ratio, is greater for low thermal conductivity materials, like polystyrene and polytetrafluoroethylene, than for the higher conductivity materials such as ceramic and glasses. The ratio for the low conductivity polymers is about 0.44 while that for somewhat more conductive glasses and ceramics is 0.80. High conducting aluminum samples yielded a ratio of 1.00. This ratio is an indication of the ease with which temperature uniformity may be achieved across the test specimen and may be used to measure thermal conductivity.

In contrast to the steady state heat flow approach of Chiu and others mentioned previously, the modulated heat flow of MDSC establishes a dynamic equilibrium in the test specimen permitting the measurement of thermal conductivity by applying a cyclic temperature program to only one side of the test specimen.

The one-dimensional heat flow model described in Eq. (1) can be expanded using the modulated heat flow generated by the MDSC, to yield

$$(\mathrm{d}Q/\mathrm{d}t)^2 = 2(Z\theta_0 KA)^2 \frac{[1 - 2\mathrm{e}^{2ZL}\cos 2ZL + \mathrm{e}^{4ZL}]}{[1 + \mathrm{e}^{2ZL}\cos 2ZL + \mathrm{e}^{4ZL}]} \tag{2}$$

where K is thermal conductivity in W °C^{-1} m^{-1}, $\mathrm{d}Q/\mathrm{d}t$ is heat flow amplitude in J s^{-1}, ω is angular frequency in 2π s^{-1}, ρ is sample density in g cm^{-3}, C_p is sample specific heat in J °C^{-1} g^{-1}, $Z^2 = \omega\rho C_p/(2K)$, θ_0 is temperature modulation amplitude in °C, L is sample length in cm, A is sample cross sectional area in cm^2, M is sample mass in g, and C is apparent heat capacity in J °C^{-1}.

Additional assumptions are

(1) The specimen is a right circular cylinder with cross sectional area A and length L with parallel end faces. The specimen has density ρ and specific heat C_p.

(2) The face of the specimen at the heat source follows the applied temperature modulation.

(3) The heat flow through the opposing face is zero.

(4) There is no heat flow through the side of the specimen.

For materials with low thermal conductivity, the e^{4ZL} term is large and dominates the terms in brackets on the right of the equation, driving it to unity. Rearranging Eq. (2), noting that $C = (dQ/dt)/(\omega T_0)$ and $\omega = 2\pi/P$ (period), and solving for K yields

$$K = (2\pi C^2)/(C_p \rho A^2 P) \tag{3}$$

For a right circular cylinder, $\rho = M/AL$ and $A = \pi d^2/4$. Eq. (3) becomes

$$K = (8LC^2)/(C_p M d^2 P) \tag{4}$$

Sample length L, diameter d and mass M are easily measured physical parameters. The specimen's specific heat C_p may be measured using the MDSC under the optimum conditions described previously. The period P is an experimental parameter. And the apparent heat capacity C is the measured parameter from the thermal conductivity optimized experimental conditions.

Thus, MDSC provides all the experimental information needed to calculate thermal conductivity.

3. Experimental

The general experimental procedure for determining thermal conductivity values at a specific temperature is now described. A key ingredient in any high precision measurement is securing a test specimen of uniform and known geometry. This is also the case here. The preparation of the test specimen in the shape of a right, circular cylinder of 6.35 mm diameter, by cutting specimens from quarter-inch extruded or molded rods, seemed to be a practical approach. Other shapes may be used but the cylinder is convenient to machine or extrude and simplifies the measurements.

Normal calibration of MDSC was performed using indium metal and sapphire standard reference materials. Thermal conductivity calibration was performed using a reference material of low, known conductivity. We used polystyrene specimens 0.4 and 3–4 mm in thickness and the same diameter as the unknowns.

The specific heat capacity C_p of the unknown material was obtained using standard MDSC procedures and a thin (<0.5 mm) specimen. The apparent heat capacity C of the unknown material was determined using a thick (>3.0 mm) test specimen. The specimen mass, length and diameter were also measured. The heat capacity measurements were improved by putting a thin aluminum foil disk (wetted on both sides with silicone oil) between the test specimen and the DSC measurement platform. This disk acts to provide a more uniform heat transfer path. An equivalent foil disk with silicone oil is used on the reference position of the cell to balance the thermal effects of the aluminum.

Using the specific heat C_p and apparent heat capacity thus determined, the observed thermal conductivity K_o was calculated using Eq. (4). Substituting this value, along with the thermal conductivity calibration constant D into Eq. (6) yields the thermal conductivity K of the unknown.

In this study, four insulators were evaluated at 25°C using an MDSC oscillation amplitude of 1°C and an oscillation period of 80 s.

4. Results

Table 2 compares the values obtained by MDSC with literature values. These results show that the accuracy of the measurement declines with decreasing thermal conductivity. This is due to a bias of about 0.03–0.04 W $^\circ\mathrm{C}^{-1}$ m^{-1} between the observed values and the literature values. This bias, while not large for the higher conductivity glasses, affects the lower conductivity material by producing the appreciable deviation from literature values.

The loss of thermal energy through the sides of the test specimen is thought to be the source of the discrepancy (bias) in Table 2 between the thermal conductivities measured and the literature values. For very low thermal conductivity samples, such as polystyrene ($K = 0.14$ W $^\circ\mathrm{C}^{-1}$ m^{-1}), the thermal conductivity of the nitrogen purge gas surrounding the test specimen (0.026 W $^\circ\mathrm{C}^{-1}$ m^{-1}) is an appreciable fraction (about one quarter) of the specimen conductivity. Hence, under flowing purge gas conditions, the assumption of no heat flow through the sides of the sample is not strictly true.

In principle, the effect of purge gas may be reduced by the use of vaccum or low conductivity gases such as argon, krypton and xenon (0.018, 0.010, and 0.0058 W $^\circ\mathrm{C}^{-1}$ m^{-1}, respectively [17]). The use of a vacuum was explored, but was unsuccessful because it increased the noise of the measurement and therefore increased inprecision. Its use was abandoned. The use of low conductivity purge gases was not pursued in this study because a calibration approach described in the following paragraphs was developed and was found to be accurate and precise.

Modeling the premise of heat loss through the sides of the test specimen creates a thermal conductivity calibration constant D which may be used to correct for this effect. The value for D is obtained using a calibration material of low thermal conductivity, e.g. polystyrene, and Eq. (5)

$$D = (K_\mathrm{o} K_\mathrm{r})^{0.5} - K_\mathrm{r} \tag{5}$$

where D is the thermal conductivity calibration constant, K_o the observed reference material thermal conductivity in W $^\circ\mathrm{C}^{-1}$ m^{-1}, and K_r the true reference material thermal conductivity in W $^\circ\mathrm{C}^{-1}$ m^{-1}.

Table 2

Comparative thermal conductivities (in W $^\circ\mathrm{C}^{-1}$ m^{-1}) without correction for loss through purge gas

Material	Experimental	Literature	Variation
Polystyrene [6,9]	0.17	0.14	21%
Polytetrafluoroethylene [6,9]	0.37	0.33	12%
Soda lime glass	0.76	0.71	7%
Pyrex® 7740 [15,16]	1.12	1.10	2%

Table 3
Comparative thermal conductivities (in W °C^{-1} m^{-1}) with correction for loss through purge gas

Material	Experimental	Literature	Variation
Polystyrene	0.14	0.14	0%
Polytetrafluoroethylene	0.34	0.33	3%
Soda lime glass	0.73	0.71	3%
Pyrex® 7740	1.09	1.10	1%

For 6.35-mm-diameter test specimens, the value D is typically 0.014 W °C^{-1} m^{-1}. This value may then be substituted into Eq. (6) to obtain the thermal conductivity of unknown specimens

$$K = [K_o - 2D + (K_o^2 - 4DK_o)^{0.5}]/2 \tag{6}$$

where K_o is now the observed conductivity of the unknown specimen.

Using the determined value of the thermal conductivity calibration constant and Eq. (6), the values in Table 2 are upgraded to the values presented in Table 3.

The accuracy of any method for the measurement of thermal conductivity is dependent upon the availability of reference materials with which a comparison may be made. Pyrex® 7740 is one of the few materials which may serve as a standard reference material as it has been well tested by the National Institute for Standards and Technology (NIST) [16]. As Table 3 indicates, the accuracy of this approach for Pyrex® 7740 is about 1% using the mean value of triplicate determinations. The literature values in Table 3 for the other materials evaluated represent those generally reported [6,9]. In all cases, the MDSC determined values agreed within about 3%.

The precision of MDSC thermal conductivity measurements can be estimated by treating Eq. (3) using the principle of propagation of uncertainties to obtain

$$\mathrm{d}K/K = 3\,\mathrm{d}C_p/C_p + \mathrm{d}M/M + \mathrm{d}A/A + \mathrm{d}L/L + \mathrm{d}P/P \tag{7}$$

where the differential values represent the percent uncertainty in the individual measurement. Because mass M, length L, period P, diameter A can all be determined with a precision of <0.1%, the precision of the thermal conductivity measurement is dominated by the precision of the apparent heat capacity and specific heat determinations; $\mathrm{d}C_p/C_p$ is estimated to be approx. 1% so the thermal conductivity precision should be 3–4%. This estimation is confirmed by experimental results presented in Table 4. The pooled coefficient of variation of the four measurement is 4.7%.

Chiu and his co-workers estimated the precision of their DSC approach to be about 3%, and others have estimated its accuracy at about 5%. Duswalt has made considerable improvement in this approach using a ratio method comparing experimental results with those for a reference material of known value [9]. The ASTM test method E1225 estimates precision at 7%, and D4351 shows repeatability (precision) values in the order of 5.6%. Reproducibility values of 11% are obtained when applied to polymers [18].

Table 4
Precision

Material	Mean/W °C^{-1} m^{-1}	Coeff. var/%
Polystyrene	0.14	2.2
Polytetrafluoroethylene	0.34	2.3
Soda lime glass	0.73	7.5
Pyrex® 7740	1.09	4.7

The ratio method of Duswalt was used as a reference with which the results of the MDSC approach were compared. Duswalt's value for these same test specimens are those presented as literature values in Table 3 for polystyrene and polytetrafluoroethylene.

Thus the approach described here appears to provide accuracy and precision at least equivalent to other methods in common use for insulators without the necessity for a specialized apparatus.

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