

Test Method

Thermal conductivity determination of small polymer samples by differential scanning calorimetry

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Abstract

A DSC method that utilizes a very simple accessory designed for measuring thermal conductivity of polymers is described. The method does not require any use of temperature sensors and any modification to the DSC instrument. Measurements by this method are very rapid, each measurement only takes a few minutes. The method is particularly suitable for small samples, such as cylinders of 6 mm in diameter and 2–8 mm in length. In contrast to the existing DSC methods wherein thermal contact resistance usually leads to great deviation in thermal conductivity measurement of samples, the method described in this work minimizes the effect of thermal contact resistance. Thermal conductivities have been obtained from PMMA, PTFE and HDPE samples using this method and the results showed good agreement with the literature values.

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1. Introduction

Thermal conductivity is one of the fundamental physical properties that are commonly used to evaluate construction materials used in a thermal environment. Commercial techniques generally measure thermal diffusivity or effusivity and calculate thermal conductivity using heat capacity values, which are measured separately. Instruments available commercially to thermal conductivity measurement usually require relatively large samples (10 cm × 10 cm × 1 cm). Differential scanning calorimetry (DSC) is a common technique and widely

used in thermal analysis. Jen [1] developed a method to rapidly determine thermal conductivity of solid materials (6 mm in diameter, 2–25 mm in length) by incorporating a temperature sensor into a commercial differential scanning calorimeter. Modulated temperature differential scanning calorimetry (MDSC) has also been widely used in the measurement of thermal conductivity [2,3], and has been recognized as an ASTM standard test method [4], however, MDSC is more expensive compared with DSC.

Several studies have been carried out on the methods for measuring thermal conductivity of solid materials using DSC. Some of them use a technique in which a pure metallic substance is on the top of the sample and is melting to control the temperature [5–7]; others require addition of a

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thermal reservoir with temperature sensors [1,8–10]. The methods in the first category have limitations that thermal conductivity can only be measured at the melting temperature of the pure metallic substance, whereas those in the second category can be used to measure thermal conductivity at a given temperature range but need additional temperature sensors. The methods in the first category advantageously provide simple and rapid measurements, but the thermal contact resistance between the sample and furnace is not taken into account [1,8,9]. In fact, the thermal contact resistance between sample and furnace may not be negligible as compared with the thermal resistance of the sample [11]. Merzlyakov [3] investigated the effects of thermal contact resistance by means of complex mathematics. Camirand [5] also paid attention to the thermal contact resistance and provided a more general theory that gives better results. In this paper, we describe a DSC approach to measuring thermal conductivity of polymers by using a very simple accessory designed as an adaptation of a DSC instrument, without use of temperature sensors and which takes the thermal contact resistance into account. This accessory is mounted on a Perkin-Elmer DSC Pyris1 cell, and no modification of the DSC instrument is required. Measurements with this approach are very rapid, with each measurement only taking a few minutes. This method is particularly suitable for measuring thermal conductivity of small samples, such as cylinders of 6 mm in diameter and 2–8 mm in length.

2. Experiments

2.1. Material

Polymethylmethacrylate (PMMA) JBWY49101 ($\lambda_0 = 0.22 \text{ W m}^{-1} \text{ K}^{-1}$).

Polytetrafluoroethylene (PTFE).

High-density polyethylene (HDPE).

2.2. Sample preparation

Samples were prepared as cylinders of 6 mm in diameter and 2–8 mm in length, with the two end surfaces smooth without any cracks.

2.3. Instrumentation

2.3.1. Perkin-Elmer differential scanning calorimeter Pyris1 (Perkin-Elmer)

2.3.2. DSC accessory

The DSC accessory is shown schematically in Fig. 1. The main components are a copper contact rod, a copper heat-sink, a PTEF insulating sheath and an aluminium flange. The entire device is fixed onto the Perkin-Elmer DSC Pyris1 cell through the aluminium flange. The sample cylinder is mounted between the copper contact rod and the thermoelectric disc of the DSC cell. Heat-conducting silicone grease is applied to the end surfaces to facilitate thermal equilibrium. The position of the copper rod is adjustable vertically to adapt to the variation in sample length. The temperature at the low end of the sample is measured and recorded by the DSC thermal analyzer, whereas the temperature at the upper end of the sample is kept constant by the heat-sink, the temperature of which is controlled by the internal water jacket connected to an isothermal water bath. The thermal analyzer also provides heat input into the sample.

2.3.3. Calibration

Temperature calibration is performed according to the procedures given in the instrument manual (Practice E 967). An indium reference is used and heated at a rate of 1 K/min. The heat flow signal is

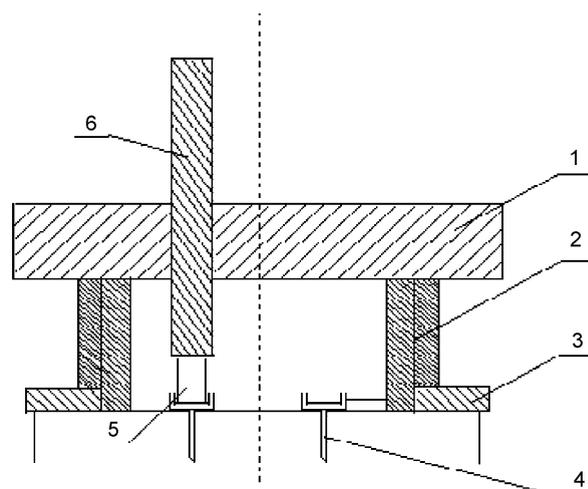


Fig. 1. Schematic diagram of accessory: 1: copper heat-sink; 2: PTEF insulating sheath; 3: aluminium flange; 4: DSC cell; 5: cylindrical sample; and 6: copper contact rod.

calibrated in accordance with the procedures given in the instrument manual (Practice E 968, for indium reference).

2.4. Experiments

A sample cylinder coated with heat-conducting silicone grease on both ends is mounted between the contact rod and the sample platform of the DSC instrument. The silicone grease ensures good contacts with the copper rod and the platform. The temperature at the upper end of the sample is kept at a constant T_1 through the copper rod and the heat-sink. Initially, the temperature of the DSC cell is set to T_1 . Normally a stable signal is obtained within 2 min as indicated by the flat trace. Then, the temperature of the lower end of the sample is increased to T_2 , whereas the temperature of the upper end of the sample is still kept at T_1 . In a short time, a stable thermal flow signal is obtained. This indicates that a thermal gradient across the sample has been established and a steady state is achieved. The thermal flow signals and temperatures at both ends of the sample are recorded using the DSC recorder.

3. Theory

Basic knowledge of DSC and heat transfer related to the topic described in this paper can be found in literature [12,13]. For a sample cylinder (cross section area A , length L) mounted in the sample furnace, the thermal gradient across the sample is given by Fourier's law [14],

$$Q = \lambda \Delta T \frac{A}{L}, \tag{1}$$

where λ is the average thermal conductivity in the temperature range of T_1 – T_2 , Q is the heat transfer rate, A is the cross sectional area of the cylinder and $\Delta T/L$ is the temperature gradient. The amount of heat (Q) required to maintain the temperature gradient is equal to the difference between DSC readings at T_2 and T_1 ,

$$Q = H_2 - H_1. \tag{2}$$

From Eqs. (1) and (2), the thermal conductivity can be calculated as

$$\lambda = \frac{QL}{A\Delta T} \tag{3}$$

and the total thermal resistance R between the copper rod and furnace can be expressed by definition as

$$R = \frac{\Delta T}{Q} \tag{4}$$

as shown in Fig. 2. R is equal to the sum of the thermal contact resistances and sample thermal resistance,

$$R = R_1 + R_2 + R_s, \tag{5}$$

where R_1 is the thermal contact resistance between the sample and the furnace, R_2 the thermal contact resistance between the sample and the copper rod and R_s the thermal resistance of the sample. R_s is defined as

$$R_s = \frac{L_s}{\lambda_s A_s}, \tag{6}$$

where L_s is the height, λ_s is the thermal conductivity and A_s is the cross sectional area, of the sample. By combining Eqs. (4)–(6), the total thermal resistance is as below:

$$R = R_1 + R_2 + R_s = R_1 + R_2 + \frac{L_s}{\lambda_s A_s}. \tag{7}$$

Assuming the thermal contact resistances ($R_1 + R_2$) are the same for all the samples, the total thermal resistance R is proportional to the ratio of L_s and A_s . Therefore, for a set of samples of a given polymer prepared with different lengths, the total

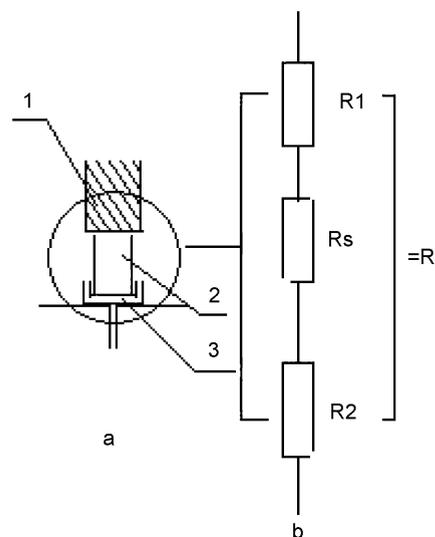


Fig. 2. The schematic view of the furnace (a) and its block diagram (b): (a) 1: copper contact rod; 2: cylindrical sample; 3: DSC cell; (b) R , total thermal resistance; R_1 , R_2 , thermal contact resistance.

thermal resistance plotted against L_s/A_s gives a straight line. The slope of the line equals $1/\lambda_s$, from which the thermal conductivity of the sample can be determined. A standard thermal standard material (such as PMMA) can be used to evaluate any systematic error. If the measured thermal conductivity of the standard is λ'_r and the theoretical thermal conductivity is λ_r , then a calibration constant K can be obtained from the following equation:

$$\lambda_r = K\lambda'_r. \quad (8)$$

This calibration constant K can be used in sample analyses to correct the systematic error (if any) in the thermal conductivity measurement. That is, for an unknown sample, the actual thermal conductivity λ_s can be calculated from the calibration constant K and the experimentally determined thermal conductivity λ'_s based on

$$\lambda_s = K\lambda'_s. \quad (9)$$

4. Results and discussion

Fig. 3 is a typical DSC signal for a single thermal conductivity test. The temperature of the copper rod and furnace was kept at 303 K initially, when a steady signal (H_1) was obtained, as shown by the flat output curve. Then, the temperature of the low end of PMMA was increased to 333 K, whereas the temperature of the copper rod was still kept at 303 K. As shown in Fig. 3, the DSC signal increased rapidly as the sample was heated. Once a stable thermal gradient (303–333 K) was established across the PMMA sample, a steady signal (H_2) was

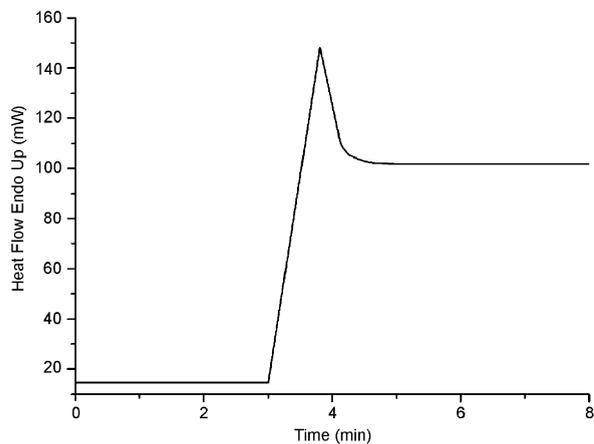


Fig. 3. Typical scan of the DSC output (PMMA, T : 303–333 K).

reached, as shown from the flat output curve. The heat transfer rate Q in the temperature gradient of 303–333 K can be calculated from these DSC signals, that is $Q = H_2 - H_1$. Repeated DSC tests for the same material of different lengths provide a set of Q values (corresponding to the sample lengths) and the total thermal resistance can be calculated according to Eq. (4). Fig. 4 shows the plot of the measured total thermal resistance values of PMMA samples vs. the height/area ratios. As expected, a straight line was obtained, and the PMMA thermal conductivity λ'_s can be calculated from the slope k , that is $\lambda'_s = 1/k$. After the systematic error correction based on Eq. (9), an average is obtained for the thermal conductivity of PMMA (303–333 K), that is $\bar{\lambda}$ (303–333 K) = 0.21 ± 0.01 . Similarly, PTFE and HDPE samples were analyzed using this approach and their thermal conductivity values are listed in Table 1. The measured values are in good agreement with the reference values reported in the literature.

The test method developed in this work, which utilizes DSC equipped with a very simple accessory made in-house, can minimize the effect of the thermal contact resistance on thermal conductivity measurement. However, one of the limitations in the current method is that a one-dimensional model is used to simplify the real three-dimensional problem. In addition, an assumption is made that the thermal contact resistance is the same for all samples. However, thermal contact resistance actually changes slightly for different temperature ranges and also varies from sample to sample. Other issues that need to be addressed include: heat loss by convection and radiation [5]; dilation of the

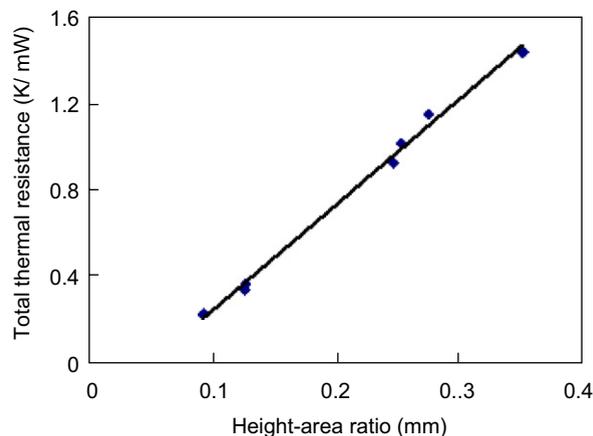


Fig. 4. Total thermal resistance vs. height–area ratio for PMMA.

Table 1
Thermal conductivity data of different materials

Material	Thermal conductivity (W/mK)	
	Measured value	Reference value
PMMA	0.21 ± 0.01	0.20–0.24 [10]
PTFE	0.32 ± 0.01	0.33 [1], 0.20–0.32 [15]
HDPE	0.44 ± 0.02	0.42–0.52 [1], 0.46 [9]

samples; the temperature variations at the contact surfaces [8]; the difference in sample diameters; and the flatness and the smoothness of the surfaces at both sample ends [5,10,16]. Studies on these issues are currently under way.

5. Conclusion

A new DSC method that utilizes a very simple accessory made in-house has been developed for measuring thermal conductivity of polymers. The method does not require any use of temperature sensors and any modification to the DSC instrument. Measurements with this method are very rapid, each measurement only takes a few minutes. It is particularly suitable for thermal conductivity measurement of small samples, such as cylinders of 6 mm in diameter and 2–8 mm in length. PMMA, PTFE and HDPE materials have been analyzed using this method and the resultant values are in good agreement with the reference values reported in literature. The results show that the method developed in this work can minimize the effect of the thermal contact resistance on thermal conductivity measurement. Limitations of the method and topics of future study are also addressed.

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