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APPLICATION OF DSC FOR THE MEASUREMENT OF THE THERMAL CONDUCTIVITY OF ELASTOMERIC MATERIALS *

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ABSTRACT

A rapid method for measuring the thermal conductivity of small samples (cylinders of diameter 5 mm and length 5–8 mm) using an attachment to commercial DSC instrumentation is described. The precision of the technique enables comparison between polymeric materials and assessment of the varying degrees of crystallinity in polyurethane/polyethylene adipate-based elastomers.

INTRODUCTION

In the course of a project on the synthesis of novel polymers it was necessary to evaluate the thermal conductivity, K, of the products. Laboratory scale preparations limited the amount of available material, so it was desirable that the technique should cope with relatively small samples to give a precise and rapid comparison of thermal conductivities on a routine basis. The materials under study were elastomers and could be regarded as thermal insulators having a thermal conductivity typically less than 0.5 W m^{-1} K^{-1}.

Very little reliable data are available for the thermal transport properties of elastomeric materials. Furthermore, there is often a wide spread of thermal conductivity values reported in the literature for a given material. For gum natural rubber, for example, there is a spread of nearly 300% for ambient temperature measurements [1]. Discrepancies of this magnitude

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cannot be due solely to sample variations. This gives some indication of the experimental difficulties associated with thermal conductivity measurement.

Thermal conductivity can be defined as the rate of linear heat flow through a sample and is generally determined by inducing a thermal gradient across a sample and measuring the quantity of energy required at a given time to maintain that gradient. Fourier's law states that the rate of heat transferred per unit area is proportional to the normal temperature gradient. Inserting K, which is constant for a material at a given temperature, gives the equation defining thermal conductivity

$$\frac{Q}{A} \propto \frac{\mathrm{d}T}{\mathrm{d}x}$$

$$K = -\frac{Q}{A}\frac{\mathrm{d}x}{\mathrm{d}T} \tag{1}$$

where K is the thermal conductivity, Q the heat transfer rate, A the cross-sectional area, and $\mathrm{d}T/\mathrm{d}x$ the temperature gradient. (The negative sign is inserted so that the second principle of thermodynamics is satisfied, i.e. heat must flow from high to low temperature.)

In a static system at equilibrium the value of the thermal conductivity of a sample can be calculated from the equation

$$K = \frac{QL}{A\Delta T} \tag{2}$$

which is derived from eqn. (1) assuming normal heat flow through the sample and in which L is the length of the sample over which the thermal gradient exists, and ΔT is the thermal gradient across L.

The majority of methods, including that adopted by the American Society for Testing Materials [2], have been based on the Lees disc technique [3]. However, the large sample size required and the resultant time required for equilibrium of the system inspired this investigation into alternative methods. It was of particular interest to consider the use of conventional thermal analysis instrumentation with the advantages of precise controllable heat sources and direct record of heat flux.

Brennan et al. [4] adopted commercial DSC equipment using the heating head to provide a heat source. The technique cited in ref. 4 was adapted to provide a method of rapidly measuring the thermal conductivity of small samples over a range of temperatures and to provide suitable precision to enable a comparison of test samples to be made.

EXPERIMENTAL

An attachment to the Perkin-Elmer DSC2 was constructed (Fig. 1). This consists of a disc-shaped aluminium heat-sink with a diameter which allows it to be placed over the heating head of the DSC. Below this is a phenolic

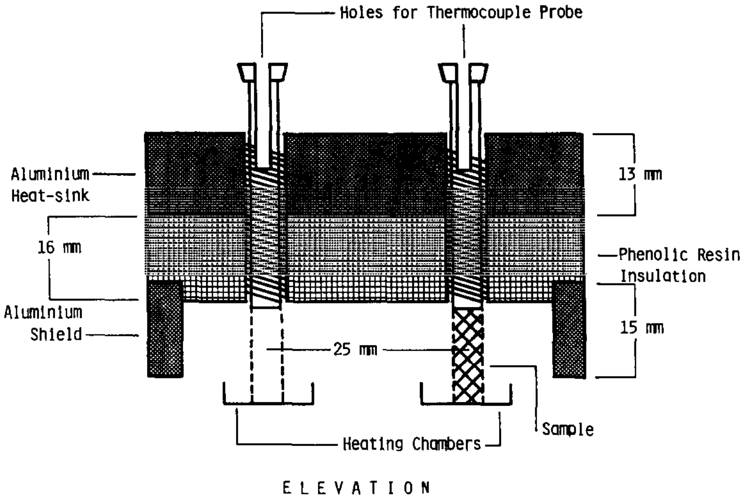

Fig. 1. Attachment to the DSC for measurement of thermal conductivity.

resin insulating disc of the same diameter as the heat-sink. These are both supported on a circular aluminium shield to reduce air movements around the DSC heating chambers. Cylindrical samples (diameter 5 mm, length 5–8 mm) were produced by several methods. A split-steel mould was used for melting thermoplastic polymers or for casting pre-cured samples. Glass tubing of a suitable diameter could also be used for this as it could subsequently be removed from solidified samples by shattering. Sample cylinders could also be punched out of cured bulk products using a suitably sized boring device (diameter 5 mm).

The sample was placed in the heating chamber in contact with the DSC head and the attachment was placed over it. Contact with the heat-sink was guaranteed by careful screwing down of the heat-sink cell screw. Silicone oil was applied to the sample ends to ensure good contact. A thermal gradient was established across the sample which could be calculated from the preset base temperature, T_b (i.e. the temperature of the heating head of the DSC) and the temperature of the heat-sink (i.e. the temperature of the top surface of the sample, T_t). The heat-sink temperature was measured by inserting a thermocouple into the heat-sink cell screw. The energy required to maintain this thermal gradient was calculated from the voltage output of the instrument which was measured externally for greater accuracy.

Figure 2 shows a typical scan of the DSC output during a single thermal conductivity measurement. Equilibrium, and hence a constant thermal gradient, was established for an initial base temperature T_{b1} (indicated by the straight line on the scan). From this initial equilibrium condition the temperature of the DSC heating chamber was increased, typically by 5 K at 5 K min^{-1}, to T_{b2}. This resulted in a surge of energy required to raise the temperature of the sample. Gradually, equilibrium was reached and a new

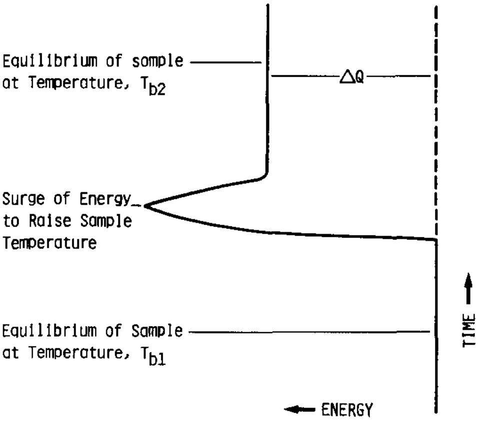

Fig. 2. Typical scan of the DSC output during a single thermal conductivity measurement.

energy input required to maintain the larger temperature gradient. Using this technique, the thermal conductivity at a given temperature range can be calculated in 10 min.

The thermal conductivity, K, can be calculated from the adapted Fourier equation

$$K=\frac{(Q_2-Q_1)L}{A(\Delta T_2-\Delta T_1)} \tag{3}$$

where Q_1 is the heat energy required to maintain the initial thermal gradient (W), Q_2 the heat energy required to maintain the new thermal gradient (W), L the length of the sample (m), A the surface area of the sample in contact with the heating head (m^2), ΔT_1 the difference in temperature across the sample at the initial thermal gradient, i.e. the heating head temperature (T_{b1}) minus the heat-sink temperature (T_{t1}) (K), and ΔT_2 the difference in temperature across the sample at the new thermal gradient ($T_{b2}-T_{t2}$) (K).

The calculation requires the following assumptions.

(a) The heat flow in the cylinder is normal to the plane of the heating head.

(b) All the heat losses from the cylinder, whether due to convection, conduction or radiation (due to the small increase in temperature) are small and can be neglected by virtue of the small temperature difference.

(c) All thermal resistances and conductivities are constant over the temperature range of interest.

(d) There are no thermal gradients in the heat sink.

RESULTS

A series of polymeric materials was examined with the results shown in Table 1. These are comparable with literature values (where published data exist).

TABLE 1

Thermal conductivity of the materials examined

Sample	Thermal conductivity at 300 K ($W m^{-1} K^{-1}$)
Low density polyethylene	0.34
High density polyethylene	0.46
Polypropylene	0.20
Polymethyl methacrylate	0.13
Polystyrene	0.14
Polyethylene terephthalate	0.20
Polyurethane/polyethylene adipate block Copolymer elastomer	0.13
Epoxy cast resins	0.17–0.27
Silicone rubber	0.15
Natural rubber	0.17
PFA cement (55% QM_4)	0.61
PFA cement (40% QM_4)	0.33
Ordinary Portland cement	0.37
Soda glass	0.75

The technique was applied to the investigation of elastomeric block copolymers based on polyurethane and polyethylene adipate (PEA). The polyurethane was synthesised from polybutadiene and hexamethdiisocyanate, which acted as the soft block. Mole percentages of PEA were increased in the elastomers to induce “cold hardening” (crystallisation of the PEA).

The thermal conductivity of these systems was measured and the results are shown in Table 2. This indicates that the technique has sufficient precision to pick up the small differences in conductivity which result from changes in the molar composition. It appears that the conductivity is

TABLE 2

Thermal conductivity of polybutadiene based polyurethane/polyethylene adipate block copolymers with differing mole ratios of polyethylene adipate to polybutadiene

Based on polyethylene adipate of 1260 $gmol^{-1}$ and polybutadiene of 2800 $gmol^{-1}$.

Moles polyethylene adipate Moles of polybutadiene	Thermal conductivity at 300 K ($W m^{-1} K^{-1}$)
0.02	0.11
0.05	0.11
0.08	0.12
0.10	0.13
0.20	0.15
1.00	0.21

TABLE 3

Statistical analysis of thermal conductivity measurements obtained on a silicone rubber sample standard (density 1.242 g dm^{-3})

	Temperature range ($T_{b1}-T_{b2}$) (K)						
	285–290	290–295	295–300	300–305	305–310	310–315	315–320
n	8	8	8	8	8	8	8
$\bar{x}$ (W m^{-1} K^{-1})	0.139	0.144	0.147	0.147	0.147	0.152	0.152
SD	0.006	0.003	0.004	0.005	0.005	0.005	0.002
RSD	4.1	2.0	2.7	3.3	3.4	3.1	1.6

increased as the proportion of polyethylene adipate becomes greater. This is probably due to the increased crystallinity, which has been shown to be present in conventional DSC endotherms. At low PEA concentrations the crystalline content is not sufficient to alter the thermal conductivity.

To assess the precision of this technique a silicone rubber sample was analysed at a range of base temperatures as shown by Table 3. This table indicates that values quoted to two places of decimals are significant.

DISCUSSION

A precise, rapid method for measuring the thermal conductivity of small samples has been established which enables relative comparison of specimens. The method has been successfully used for the measurement of novel elastomeric polymers as well as some commercially available materials. Future applications could include the analysis of insulating materials, dental preparations, and radioactive or unstable materials where small sample size is important.

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