

Measurement Note

Determining thermal conductivity by a differential scanning calorimetry method

Summary

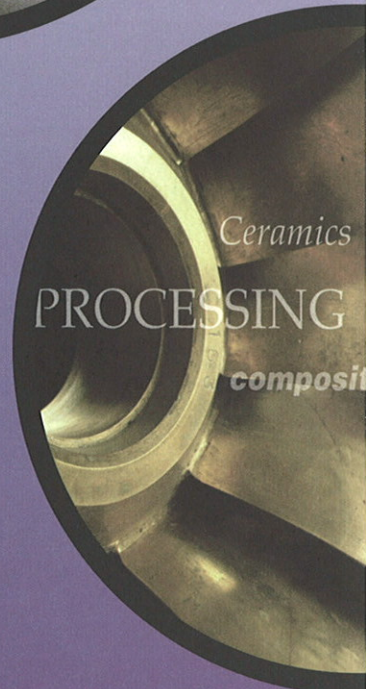
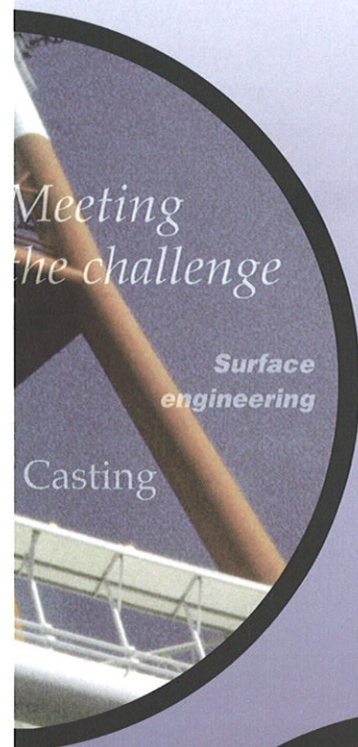
This Measurement Note details a method for determining thermal conductivity values from heat flow curves measured by a differential scanning calorimeter (DSC). The results suggest a degree of promise for the DSC technique. Tests are straightforward to perform using a standard DSC instrument and samples with different thermal resistances can be readily compared. Reasonable values have been obtained for solid bulk samples but the results for coatings were less accurate. Further development of the testing and analysis methods is required to improve accuracy and reliability.

The results obtained were sensitive to the test parameters. If these are tightly controlled then, with the correct selection of a reference material, thermal conductivities for materials can be obtained, which are comparable with literature values. However, the selection of the reference material requires prior knowledge of the sample's thermal conductivity: the thermal conductivity of the reference specimen should be similar to that of the test specimen.

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INTRODUCTION

A technique using a differential scanning calorimeter (DSC) to determine thermal conductivity of materials has been described in the literature by Khanna and co-workers [1]. The heat flow through a specimen is a function of its thermal conductivity and can be determined from the shape of the melting peak of a low melting point solid (e.g. indium) placed on top of the specimen, Figure 1.

This technique is attractive as it uses a standard DSC instrument, without modification, rather than a dedicated purpose built instrument. Furthermore, the measurements are carried out using small samples. However, the accuracy of this method has not been established and the technique has not been standardised. This Measurement Note describes and evaluates the DSC method for assessing thermal conductivity of polymers and also polymer coatings on a steel substrate.

METHOD

Testing was performed using a Perkin Elmer DSC7 power compensated differential scanning calorimeter. The principle of this method is that:

- a small amount of indium (or other material with a melting transition in the temperature range of interest) is placed on top of the specimen to be measured, Figure 1.
- the instrument then heats the specimen at a controlled rate up to and beyond the melting temperature of the indium.

- as the indium begins to melt the rate of melting of the indium will be limited by the flow of heat through the specimen.
- the rate at which heat flows through the specimen is proportional to the thermal conductivity of the specimen.
- by comparing the heat flow rate for the test specimen with that obtained for the reference specimen of known thermal conductivity the thermal conductivity of the test specimen can be determined.

A measure of the heat flow through the specimen can be determined from the gradient of the linear portion of the front of the melting peak, Figure 2. A specimen of low thermal conductivity will result in a shallower slope, whereas a high thermal conductivity will result in a steeper slope.

Khanna et al [1] demonstrated that the gradient of the heat flow curve depends on:

- thermal conductivity,
- heating rate,
- mass of indium used, and
- specimen size.

Based on this, in this work the standard heating rate was 10 °C per minute and the mass of indium was 10 mg $\pm$ 0.5 mg. There is no fundamental reason for these choices of test parameters beyond experimental convenience. However, these parameters need to be consistent and carefully controlled for measurements to be valid. Also, the test specimen should preferably be similar in dimensions to the reference specimen.

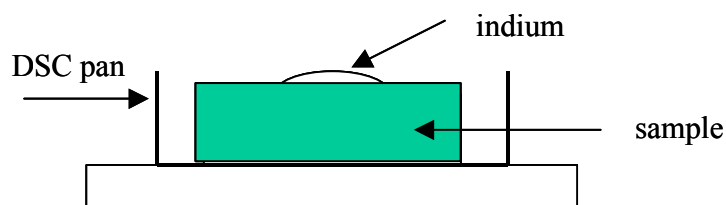


Figure 1: DSC measurement

Specimens were prepared by punching 5 mm diameter disks from flat plates. In order to improve the consistency between measurements it is recommended that the specimen with indium is heated to above the melting point of indium before testing to ensure good thermal contact between the indium and the specimen.

The measurement of thermal conductivity using this technique is nominally at a single fixed temperature. In this series of experiments, this temperature was the melting point of indium (156 °C). Alternative temperatures can be obtained by using materials with other melting temperatures, such as tin (232 °C). However, both the reference and test specimens need to be measured with each different “melting solid” used.

The test data are analysed using the ratio of heat flow through the test specimen to the heat flow through the reference material. It has been shown [1] that where the test and reference specimens are the

same thickness, the thermal conductivity, λ (and elsewhere) can be calculated [1]:

$$\lambda_x = \lambda_s \left(\frac{M_x}{M_s} \right)^2 \quad (1).$$

where M is the gradient of the first half of the melting curve (Figure 2) and the subscripts x and s denote the specimen and reference material respectively. Khanna et al [1] used test and reference specimens of the same thickness, but this is not always possible. Equation 1 can be simply modified to account for different thickness (D):

$$\lambda_x = \lambda_s \left(\frac{M_x}{M_s} \right)^2 \cdot \frac{D_x}{D_s} \quad (2).$$

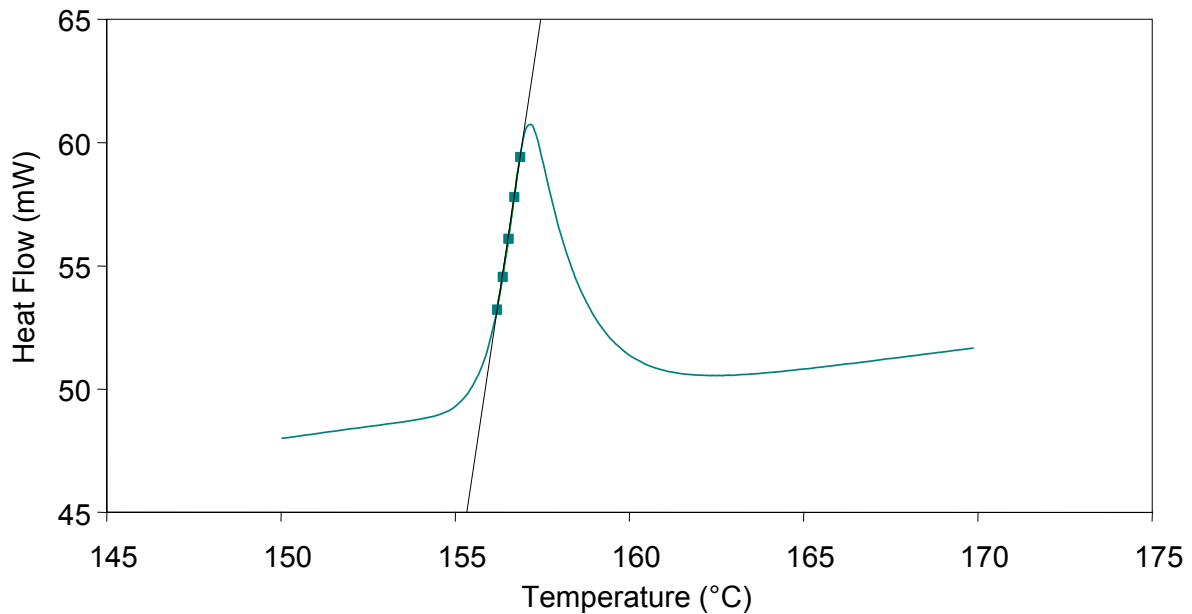


Figure 2. Typical heat flow curve used to define gradients in a thermal conductivity measurement

MEASUREMENTS

The choice of reference sample is important in the analysis of data. It is essential that the reference has a well-defined thermal conductivity. Two reference samples, sapphire and PMMA, were used.

DSC commonly uses sapphire as a reference for heat capacity determination. Pure sapphire has a thermal conductivity of 36 W/(m.K).

The thermal conductivity of a PMMA sample was determined as 0.18 W/(m.K) by the NPL Thermal Team using the standard guarded hot plate method [2].

Various test samples were obtained. Heat flow measurements were made for each of the reference and test materials. The heating curve gradients measured are shown in Table 1, together with typical literature values [3, 4] for thermal conductivities.

Table 1: Sample Materials

Sample	Thickness	Gradient	Literature Thermal Conductivity
	mm	mW/K	W/(m.K)
Reference materials			
Sapphire 1	1.026	10.98	36
Sapphire 2	0.398	19.58	36
PMMA	1.208	1.58	0.18
Sample Materials			
Steel	0.527	19.3	25-60 [3]
PTFE 1	1.03	2.32	0.26 [4]
PTFE 2	1.75	1.73	0.26 [4]

The thermal conductivities of the test materials were calculated using both reference materials using equation 2. These values are presented in Table 2.

The calculated thermal conductivities of the two sapphire specimens, of differing thickness, referenced against each other do not produce the expected value of 36 W/(m.K) but differ from this by up to 23%. This suggests that the assumptions

about the heat flow made in the derivation of equation 2 may not hold.

Table 2: Thermal Conductivities

Reference Sample	Test Sample	Measured Thermal Conductivity
		W/(m.K)
Sapphire 1	Sapphire 1	36
Sapphire 1	Sapphire 2	44.4
Sapphire 1	Steel	57.3
Sapphire 1	PMMA	0.88
Sapphire 1	PTFE 1	1.61
Sapphire 1	PTFE 2	1.52
Sapphire 2	Sapphire 1	29.2
Sapphire 2	Steel	46.5
PMMA	PMMA	0.18
PMMA	PTFE 1	0.33
PMMA	PTFE 2	0.31
PMMA	Steel	11.8
PMMA	Sapphire 1	7.38
PMMA	Sapphire 2	9.11

The thermal conductivity values calculated for steel using the two sapphire reference specimens are both reasonable when compared with the literature values but again differ from each other by ca. 23%. The values obtained for the plastics (PMMA and PTFE) using sapphire 1 as the reference are over four times higher than the literature values.

The values obtained for the plastics with PMMA as the reference are much closer to the literature values. The thermal conductivities of the two different thickness PTFE specimens differ by around 6%. The thermal conductivity values measured for PTFE are approximately 30% higher than the literature value of 0.26 W/(m.K) [3]. However, the thermal conductivity of PTFE is known to depend on the extent of crystallisation and on impurities so the values obtained in this study are not unrealistic.

The thermal conductivities for sapphire and steel determined using PMMA as the reference are approximately one quarter of the expected value.

These data suggest that the choice of reference material is critical for determining reliable values for thermal conductivity. Thus, for best accuracy the reference and test specimens should have similar:

- cross-sections
- thicknesses
- thermal conductivities

MEASUREMENTS ON COATINGS

DSC measurements were made on a range of polymer coated steel sheet specimens to determine the thermal conductivities of the specimens and, by deduction, that of the coatings. Typically the steel was 0.5 mm - 0.7 mm thick and the coating 0.1 mm - 0.2 mm thick.

The thermal conductivity value of the polymer layer was calculated using the fact that the total thermal resistance, R ($\text{m}^2\text{K}/\text{W}$) of a layered system is given by the sum of the thermal resistances of each of the layers. Thus in a two-layer system where the thermal conductivity of one material is known, the conductivity of the unknown layer can be calculated from the system conductivity:

$$\lambda_1 = \frac{D_1}{\left(\frac{D_x}{\lambda_x} - \frac{D_2}{\lambda_2} \right)} \quad (3)$$

where the subscripts 1, 2 and x refer to the unknown layer (polymer), known layer (steel) and bi-layer (polymer and steel) respectively, D is thickness and λ is thermal conductivity.

The values produced for the polymer coatings, with an expected thermal conductivity of approximately 0.17 $\text{W}/(\text{m.K})$, varied between 0.005 $\text{W}/(\text{m.K})$ and 1.2 $\text{W}/(\text{m.K})$ – suggesting significant problems with the measurements. The quality of the coating has a significant effect on the results. Cracks or thin regions will increase the apparent thermal conductivity. Thick regions, voids or porosity will reduce the apparent thermal conductivity. Some specimens, which cracked during tests, produced high system thermal conductivities and nonsense ‘negative’ thermal conductivity values for the coatings.

Table 3: Repeatability Data

Specimen	Specimen gradient	Specimen thickness	Measured thermal conductivity*
	(mW)/K	mm	W/(m.K)
PTFE	2.11	1.026	0.27
PTFE	2.34	1.027	0.33
PTFE	2.48	1.030	0.38
PTFE	2.37	1.030	0.34
avg	2.32	1.03	0.33 ± 0.09
PTFE	1.77	1.693	0.32
PTFE	1.75	1.767	0.32
PTFE	1.61	1.769	0.27
PTFE	1.77	1.780	0.33
avg	1.73	1.75	0.31 ± 0.05
PMMA	1.60	1.208	0.18
PMMA	1.64	1.208	0.19
PMMA	1.51	1.208	0.16
avg	1.58	1.21	0.18 ± 0.01

* ± 95% confidence limits given

MEASUREMENT UNCERTAINTIES

Repeat measurements were made on different specimens of PMMA and PTFE in order to assess measurement uncertainties for polymers. PMMA was used as the reference. The results, summarised in Table 3, show that repeatability in the measured thermal

conductivity value was up to 30% at the 95% confidence level.

An estimate was made of the uncertainty in sample conductivities determined using equation 2. Making the assumptions that (at 1 standard deviation):

- the reference sample conductivity value is accurate to $\pm 5\%$,
- the thickness measurements are accurate to $\pm 1\%$, and
- the repeatability of the gradient measurement for the PMMA standard and PTFE specimens are $\pm 5\%$ and $\pm 7\%$ respectively

then the expected overall relative uncertainty in the measurement at the 95% confidence level is approximately $\pm 20\%$. This suggests that the differences in thermal conductivities found for two thicknesses of sapphire and PTFE may be within experimental uncertainties.

The above analysis does not include systematic uncertainties, such as inconsistent heat flow in the test, and therefore represents the best level of accuracy that would be expected for identically sized reference and test specimens with similar thermal conductivities. The uncertainty in gradient has been estimated from a small number of tests on similar samples – a more detailed study would be needed to provide a better estimate. Also, no account in the analysis has been made for the thermal resistance at interfaces, such as the thermal contact between the specimen and the pan and between the indium and the specimen. The contact between the specimen and the pan is a problem present in all DSC testing.

An analysis of uncertainties in equation 3 was made using $\pm 20\%$ as an estimate of the relative uncertainty of thermal conductivity for the bi-layer and the steel and $\pm 1\%$ uncertainty in the thickness of the bi-layer and the steel layer. It was

shown that, typically, relative uncertainties in the thermal conductivity values for the polymer coating would be $\pm 30\%$. However, the uniformity and stability of the layer thickness was a significant concern in the tests. The condition of the specimens made it difficult to accurately determine the coating thickness. An uncertainty of $\pm 1\%$ in thickness measurements seems unrealistic – increasing this to $\pm 5\%$ leads to uncertainties of up to $\pm 80\%$ in thermal conductivity of the thin film coating, with the relative uncertainty decreasing with increasing coating thickness.

DISCUSSION

Further developments of the techniques are needed in order for the DSC thermal conductivity method to be used with acceptable confidence.

The calculation of thermal conductivity from the heat flow curves assumes a 1-dimensional heat flow from the pan through the specimen to the indium. Contributions from other heat flow paths and additional thermal resistance at the interfaces between components in the system (DSC pan, specimen, indium) are assumed to be the same for the reference specimen and the test specimen. However, the results presented in Table 2 suggest that this assumption may only work where the two specimens have similar thermal properties. Further work to develop a protocol for selecting appropriate reference specimens is required.

Improved methods for analysing specimens with different thicknesses are required. Equation 2 predicts that the ratio of heat flow gradients should be related to the ratio of specimen thicknesses by:

$$\frac{D_s}{D_x} = \left(\frac{M_x}{M_s} \right)^2 \quad (4)$$

Measurements made on two sapphire specimens with different thicknesses gave

$$\frac{D_s}{D_x} = 2.58 \text{ and } \left(\frac{M_x}{M_s} \right)^2 = 3.18$$

suggesting a discrepancy of 23% in thermal conductivity values due to thickness alone. PTFE specimens with different thicknesses gave a smaller discrepancy of 6%.

The variability in results due to variations in specimen thickness appears greater for high conductivity materials such as sapphire ($\lambda = 36 \text{ W/(m.K)}$) than for low conductivity plastics (typically $\lambda < 0.5 \text{ W/(m.K)}$). It may be possible to derive more realistic 2- or 3-dimensional functions to correct for variations of specimen thickness when modelling the heat flow in the specimen. An alternative approach may be to measure different thicknesses of materials of known thermal conductivity in order to produce an empirical relationship between heat flow and specimen thickness.

The effect of the thermal emissivity of the specimens has not been explored but it is possible that significant differences between the emissivity of specimens may alter the heat flow and lead to measurement inaccuracies.

The results obtained for coated bi-layer specimens indicate that considerable development of the method is required in order to obtain reliable results. Accurate values for the thermal conductivity of the bi-layer system and substrate are needed to reduce uncertainties, as are tighter tolerances on the layer thicknesses.

Intercomparisons between different instruments have not been undertaken and, therefore, reproducibility data are not available.

CONCLUSIONS

The results outlined in this Measurement Note suggest a degree of promise for using the DSC technique for measuring thermal conductivity. Tests are straightforward to perform using a standard DSC instrument and samples with different thermal resistances can be readily compared. Reasonable values have been obtained for bulk samples but the results for coatings were disappointing. Further developments of the techniques are needed in order for the DSC thermal conductivity method to be used with acceptable confidence.

The results obtained are sensitive to the test parameters. If these are tightly controlled then, with the correct selection of a reference material, thermal conductivities for materials comparable with literature values can be obtained. However, the selection of the reference material requires that some knowledge of the specimen's thermal conductivity is available: the thermal conductivity of the reference specimen should be similar to that of the test specimen.

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