

Simple determination of the thermal conductivity of polymers by DSC

Simple DSC measurements can be used to rapidly determine the thermal conductivity of polymers and other materials with similarly low values with an accuracy of about ± 10 to $\pm 20\%$.

A procedure for doing this was published in 1985 by Hakvoort and van Reijen. In this method, the melting behavior of a pure metal on top of a cylindrical sample or disk is measured.

To simplify sample handling, we have modified the method by containing the metal in a crucible. The thermal conductivities of 11 polymers were measured and the results compared with literature values. The values we obtained were on average about 4% lower than literature values. This deviation is small if you take into account the general measurement uncertainties associated with thermal conductivity measurements.

Introduction

Hakvoort and van Reijen [1] proposed an interesting method to determine the thermal conductivity of solid materials. This consisted of putting a pure metal (e.g. indium or gallium) on the upper circular end surface of a sample in the shape of a right circular cylinder or disk, and then placing the disk

(without a crucible) directly on the DSC measuring sensor. During heating, the metal reaches its melting point and the temperature remains constant while the metal melts. The temperature of the upper end surface of the disk is thus known at this instant. The temperature of the lower end surface of the disk and the heat flowing into the disk are measured by the DSC. The thermal conductivity of the sample can then be calculated from the temperature difference between upper and lower end surfaces of the disk and the heat flow.

Besides DSC, many instruments are nowadays available that have been specially designed to determine thermal conductivity. The advantage of DSC, however, is that the specific heat capacity can also be measured with the same instrument. This allows the thermal diffusivity ($\lambda/(\rho c_p)$) of a material to be determined. The method outlined above using the metals has recently been reintroduced to determine the properties of composite materials [2] and new materials [3].

In the following article we will describe a simple DSC method that allows the thermal conductivity of polymers to be rapidly determined typically with a measurement uncertainty of 10%.

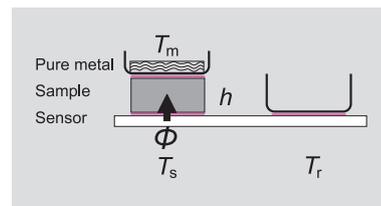


Figure 1. Schematic diagram of the sample arrangement on the DSC sensor. h : is the height of the sample cylinder; ϕ the heat flow that flows from the sensor into the sample; T_m the temperature of the metal melt, T_s the sensor temperature under the sample; T_r the temperature of the reference sample.

The reference crucible is empty. A crucible of the same type containing the pure metal is placed on the sample. The spaces between the crucible-sample and sample-sensor interfaces are filled with heat transfer oil (red lines).

Theoretical background

Under stationary conditions, the heat flow, ϕ , through a body with a thermal resistance, R_s , is proportional to the temperature difference, ΔT :

$$\phi = \frac{1}{R_s} \Delta T \quad (1)$$

The thermal resistance, R_s , of the material is given by the material-dependent thermal conductivity and the geometry of the body:

$$R_s = \frac{h}{\lambda A} \quad (2)$$

Here λ is the thermal conductivity, A the cross-sectional area, and h the length of the body.

With cylindrical samples of diameter, D , and height, h ,

$$A = \frac{\pi \cdot D^2}{4} \quad (3)$$

Figure 1 shows the setup used to determine the thermal conductivity of a material by DSC. The heat flow from the sensor to the pure metal depends not only on the thermal resistance of the sample, but also on the thermal resistances at the sensor-sample (R_1) and sample-metal (R_2) interfaces.

Equation (1) must therefore be rewritten as follows:

$$\phi = \frac{(T_s - T_m)}{R_1 + R_s + R_2} \quad (4)$$

To ensure that the thermal resistances R_1 and R_2 were reproducible, the spaces at the interfaces were filled with heat transfer oil. It can therefore be assumed that R_1 and R_2 are independent of the sample if the same sample cross-section is always used.

$$R_T = R_1 + R_2 \quad (5)$$

R_s and hence the thermal conductivity of the sample can only be determined if ϕ , R_T , T_m and T_s in eqs 4 and 5 are known. The value of T_m during melting is known because a pure metal is used. The values of ϕ and T_s are obtained from the DSC measurement, and R_T can be determined by performing several measurements. If R_T is much smaller than R_s , then R_T can even be neglected and λ can be determined from a single melting curve.

Combining eqs 1 and 2 gives eq 6:

$$\lambda = \frac{\phi \cdot h}{\Delta T \cdot A} \quad (6)$$

Equation 6 is valid only during melting. ΔT is then the difference between the temperature T_s at a time t and the melting point of the metal (i.e. the temperature of the beginning of melting, T_{onset}). The corresponding heat flow ϕ is the difference between the heat flow at the same time t and the heat flow at the beginning of melting (see Figure 2).

$$\frac{\phi}{\Delta T} = \frac{\phi_t - \phi_{onset}}{T_t - T_{onset}} = S \quad (7)$$

S is therefore the slope of the linear side of the melting peak.

Polymer		Literature value	Selected comparison value	Comments
		$Wm^{-1}K^{-1}$	$Wm^{-1}K^{-1}$	
Cork		0.07	0.07	
Polystyrene	PS	0.13 to 0.16	0.16	
Polyvinylchloride	PVC	0.15 to 0.21	0.16	
Acrylonitrile-butadiene-styrene	ABS	0.16 to 0.18	0.17	
Polypropylene	PP	0.12 to 0.22	0.17	
Polymethylmethacrylate	PMMA	0.10 to 0.20	0.20	
Polyamide	PA 66	0.23 to 0.33	0.24	Moisture influence
Polytetrafluorethylene	PTFE	0.25 to 0.26	0.25	
Polyethylene terephthalate	PET	0.15 to 0.29	0.27	Crystallinity
Polyethylene low density	PE	0.32 to 0.48	0.32	Density 0.914
Phenol-formaldehyde thermoset	PF	0.3	0.30	

Table 1. Samples and literature values of the thermal conductivity (data from different sources according to the literature list).

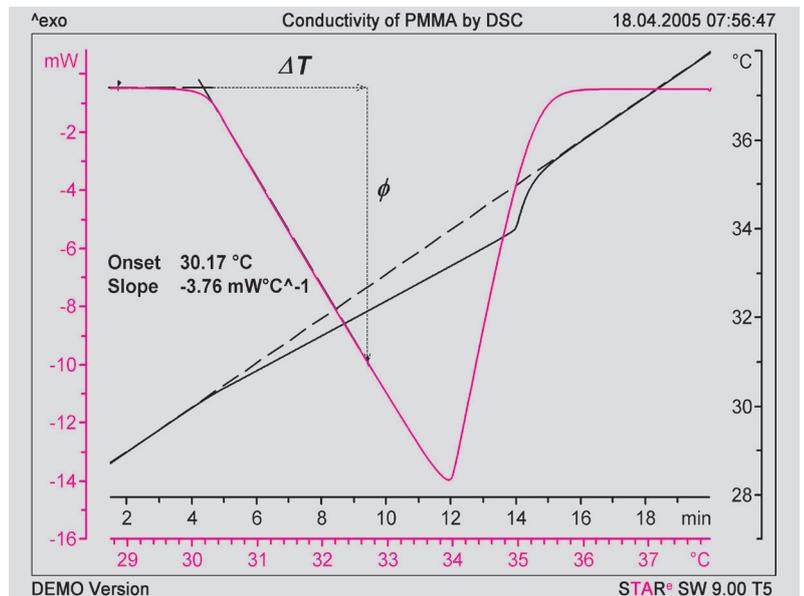


Figure 2. The red curve shows the DSC curve of PMMA (mounted as in Fig. 1) as a function of sample temperature (T_s); the black curve the measured sample temperature at the lower end surface of the sample; and the dashed line the program temperature (reference temperature).

Rearrangement of eqs 4 to 7 yields eq 8:

$$\frac{1}{S} = R_T + \frac{h}{A\lambda} \quad (8)$$

If two samples of the same material but with different cylinder heights are measured, λ can be calculated according to eq 9.

$$\lambda = \frac{\Delta h}{A\left(\frac{1}{S_2} - \frac{1}{S_1}\right)} \quad (9)$$

where Δh is the difference of the cylinder heights ($h_2 - h_1$), S_1 is the slope of the

DSC curve of the small sample, and S_2 the slope of the DSC curve of the large sample.

If several samples of different heights are used, the thermal conductivity and R_T can be determined from linear regression of $1/S$ and h/A , according to eq 8 [3].

Experimental details

Pure gallium (29.8 °C) is ideal for measuring thermal conductivity close to room temperature. The gallium sample has to be cooled down to at least 10 °C for it to

Sample	Lit. values	h	D	S	λ Direct	Difference to lit.	λ Difference	Difference to lit.
	$\text{Wm}^{-1}\text{K}^{-1}$	mm	mm	$\text{mW}\cdot\text{K}^{-1}$	$\text{Wm}^{-1}\text{K}^{-1}$	%	$\text{Wm}^{-1}\text{K}^{-1}$	%
					eq. 6		eq. 9	
only crucible		0	5.80	90.10				
Cork	0.07	1.576	6.28	1.54	0.078	11.9	0.081	15.4
PS	0.16	0.862	6.06	5.09	0.152	-4.9	0.161	0.7
PVC	0.16	1.399	6.16	3.26	0.153	-4.3	0.159	-0.7
ABS	0.17	1.336	6.06	3.28	0.152	-10.6	0.158	-7.2
PP	0.17	1.285	6.16	3.82	0.165	-3.1	0.172	1.2
PMMA	0.20	1.363	6.00	3.76	0.181	-9.6	0.189	-5.7
PA	0.24	1.364	6.25	4.95	0.220	-8.3	0.233	-3.0
PTFE	0.25	1.049	6.14	5.10	0.181	-27.7	0.192	-23.4
PET	0.27	0.382	4.99	10.49	0.205	-24.1	0.232	-14.1
PF	0.30	1.432	6.40	6.00	0.267	-10.9	0.286	-4.6
PE-LD	0.32	1.352	6.20	6.38	0.286	-10.7	0.308	-3.9
Mean value						-9.3		-4.1
Standard deviation						10.5		9.6

Table 2. Thermal conductivity (λ) of different polymers. “ λ Direct” was determined from single measurements using eq 6. “ λ Difference” was determined according to eq 9 from two measurements: the measurement with a sample and the measurement without a sample (only crucible with gallium). The difference with respect to the literature value (Table 1) is given as % of the literature value.

crystallize. Our measurements were performed using a DSC822^e equipped with an IntraCooler.

Other temperatures require different metals (e.g. indium). In some cases, it might be possible to use very pure organic substances. However, they must not sublime, must not exhibit polymorphism, and must melt and crystallize reproducibly when used several times.

Crucible preparation

Hakvoort and van Reijen placed the pure metal directly on the sample disk. To simplify sample handling, we enclosed the metal in a 20- μL light aluminum crucible without a lid (Figure 1). Since gallium readily reacts with aluminum, the inside surface of the crucible was coated with a thin film of lacquer (10 to 30 μm). This was done by completely filling the crucible with a solution of a clear lacquer in a suitable solvent (about 10-fold dilution). We used so-called “Nitrohartgrund” (a nitrocellulose wood primer) and nitro thinner. The solvent was evaporated by slowly heating to 80 °C and the amount of resin remaining in the crucible determined by backweighing. Afterward, sufficient pure

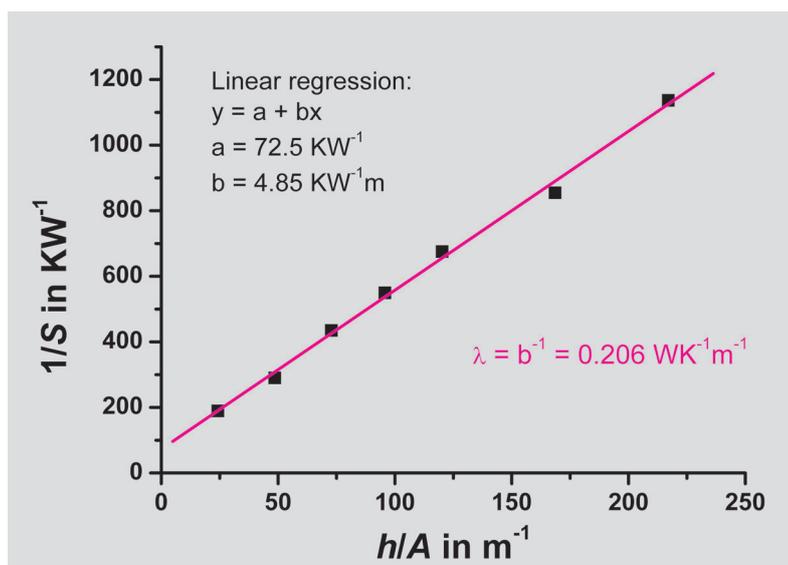


Figure 3. Measurement of different numbers of PTFE disks approx. 0.47 mm thick placed on top of one another, plotted according to eq 8.

gallium (about 80 mg) was weighed into the crucible so that the bottom of the crucible was completely covered when the gallium melted. The crucible can be used several times. It is advisable to periodically check whether the melting enthalpy and melting temperature remain constant. Any change in the values would indicate alloy formation (a possible second peak) and/or oxidation.

Polymer samples

A number of different polymers and materials available in the form of films or sheets were chosen as test materials for our studies. Disks with a height of 0.5 to 1.5 mm were punched out from these materials. The circular end surfaces were carefully polished with fine emery paper so that the height could be accurately determined to at least 10 μm and the diameter to 20 μm . The diameter of the

samples was the same as that of the bottom of the crucible (6 mm). Table 1 shows the materials used with the literature values for their thermal conductivities.

Some literature values vary markedly. A possible reason for this is that the thermal conductivity of polymers also depends on their degree of crystallinity, density, moisture content, filler content and the presence of other additives. Table 1 therefore lists the range of values found and the comparison value chosen for the measurements. Many authors quote accuracies of plus or minus a few percent for their λ values. However, the large scatter in the literature values shows that one must reckon with greater measurement uncertainty when determining thermal conductivity.

Sample preparation and measurement method

To achieve the best possible reproducibility for the thermal resistances, the spaces at the crucible-sample and sample-sensor interfaces were filled with the minimum amount of a heat transfer oil to provide complete contact between the surfaces. First, oil was applied to the upper face of the sample and the crucible placed on top of it. This essentially fixed the crucible in place and allowed it to be precisely oriented. A very small amount of oil was then applied to the lower face of the sample. The sample with the crucible on top was then carefully placed on the sensor. An empty crucible was used on the reference side.

The temperature gradients over the sample were kept small by using a low heating rate (0.5 K/min). The purpose of this is to minimize the possibility of alternative routes for heat flow (that would escape measurement). The following temperature program was used: Heating from 28 to 38 °C at 0.5 K/min, followed by cooling to -5 °C at 10 K/min to ensure that the gallium solidified again after the measurement. Purge gas: nitrogen 50 mL/min to prevent oxidation of the gallium.

Evaluation

The slope, S , is determined by plotting the DSC curve against sample temperature (T_s) (see Figure 2, red coordinates). The curve of the sample temperature is also displayed (black coordinates, but is not used in the calculation). When determining the onset temperature, you must make sure that the tangents lie exactly on the DSC curve. The slope S of the second tangent can be read off directly in the result block.

Results

Table 2 summarizes the measured thermal conductivities. The results in column “ λ Direct” were determined using eq 6 with just one measurement each time. The values in the column “ λ Difference” were calculated using eq 9. Here, for simplicity, the slope of the melting peak without sample (only crucible, $S_1 = 90 \text{ mW}\cdot\text{K}^{-1}$) was used. The difference method (eq 9) provides a marked improvement in accuracy, especially for

higher conductivities. The mean values and standard deviations compared with the literature values give a good indication of the accuracy and the reproducibility of the methods.

A measurement series with PTFE cylinders of different height shows that the linear relationship in eq 8 is obeyed (Figure 3). To obtain different cylinder heights, up to nine individual disks were placed on top of one another and the spaces between filled with oil. These measurements show that the degree of scatter of the individual measured values is small. The thermal conductivity of $0.206 \text{ Wm}^{-1}\text{K}^{-1}$ calculated from the slope of the regression curve differs only slightly from that found using the difference method ($\lambda = 0.192 \text{ Wm}^{-1}\text{K}^{-1}$).

Conclusions

The determination of the thermal conductivity of polymers can easily be performed by DSC; the measurement uncertainty is usually less than 20%. The value of -4% obtained for the deviation of the measured values from the literature values is comparable with the result of the interlaboratory study based on ASTM Standard E1952 (-6% mean measurement deviation with a repeatability, r , of 12%). The standard procedure is based on several temperature-modulated DSC measurements. It requires an accurately known reference substance and the evaluations involve complex mathematical calculations. Despite the significantly greater amount of time and complexity

of the ASTM E1952 procedure, the thermal conductivity values measured are not more accurate than those obtained with the simple method used here. Furthermore, only two polymers were measured in the interlaboratory study of the E1952 Standard. Here, in contrast, eleven different materials were measured and a much broader thermal conductivity range was determined.

The sample cylinder or disk should be about 1 to 3 mm in height and must have the same diameter as the bottom of the crucible containing the pure metal. In the molten state, the metal must completely cover the bottom of the crucible. If gallium is used as the reference metal,

the aluminum crucible must be coated internally with a lacquer in order to prevent alloy formation. The spaces between the sensor and sample and the sample and crucible are filled with oil so that thermal resistances are as reproducible as possible. Furthermore, the end faces of the sample disks must be flat.

The DSC should be adjusted in the usual way with just the crucible and the metal (i.e. without the cylindrical sample) so that the enthalpy of melting and the melting temperature agree with literature values.

In general, we recommend that you perform the determination according to eq 9, using a measurement with and without the sample.

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