Optimization of Flynn and Levin measurements of polymer thermal conductivity

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Abstract In this article procedures to measure specifically thermal conductivity of polymers by means of traditional differential scanning calorimetry (DSC) are discussed and an improved procedure minimizing the effect of contact resistances variability has been conceived. A pure substance, namely indium, for which the fusion temperature is known, is added to the polymer sample and used as internal reference in a unique DSC pan. Conductivity is then obtained by measuring the rate of the heat flow through the solid polymer sample during the solidliquid transition of indium. The present procedure gives uncertainties lower than those expected for thermal conductivity estimations by previous DSC methods, does not require thermal conductivity reference materials nor specimens of various thickness and may be performed routinely with an automatic sample changing device.

Keywords Thermal properties · Conductivity · Differential scanning calorimetry (DSC) · Polymers

Introduction

Thermal conductivity and diffusivity are relevant to polymer processing as these properties are essential for prediction of heat flow rates and temperature distributions in materials. Heat transport mechanisms control the morphology throughout the thickness of crystallized samples

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[1–4] that, in turn, affects the thermal and mechanical properties of the solids.

Thermal conductivity measurements show an inherent high variability due to practical limitations and various sources of inaccuracy. Therefore, high uncertainties (5-10%) may be associated with reliable methods for thermal conductivity measurements [5–8].

Moreover, the results for thermal conductivity obtained for a specific material may deviate from literature values as there may be large differences between conductivity of different samples of the same substance [9].

When two solid surfaces are brought into contact, the actual contact area is lower than the nominal area because surfaces are never actually flat. Actual contact only occurs at certain discrete spots, depending on the surface topography, whereas the non-contacting areas are vacuum filled or are filled with some medium [10]. Due to the different thermal conductivities of solids and interface materials, the heat flow through the solid surfaces may be limited, resulting in a heat transfer resistance at the interface known as thermal contact resistance [10]. Amongst materials, polymers have the lowest thermal conductivity [2, 11], that is the highest thermal resistance. The existence of contact resistances is evident for solids such as metals, whose conductivity is generally several orders of magnitude higher than that of interfaces, whereas thermal conductivity of polymers is not very different from that of interfaces. For instance, thermal conductivity of air void is assumed to be 0.0242 W m⁻¹ K⁻¹ compared to the conductivity of cay [12]. However, other sources of uncertainty affect thermal conductivity measurements of polymers since thermal conductivity is very sensitive to the microstructure [9, 13] which, in turn, depends on several parameters. Consequently, thermal conductivity of semi-crystalline polymers may be even more scattered than that of other

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materials if measurements are performed on samples with different microstructures (for instance, on samples differently processed or with various thickness).

A large number of methods have been used to measure thermal conductivity of materials, both conductors and insulators [9]. However, available methods for polymers need slabs of rather large dimensions and they often work in a limited temperature range (usually from 243 to 393 K). Techniques measuring thermal diffusivity require knowledge of density and heat capacity to calculate thermal conductivity, and these two quantities are often not known for polymer samples [5, 14, 15]. Thermal conductivity and diffusivity measurements of poor heat conductors based on differential scanning calorimeter (DSC) [7, 14, 16-20] and temperature modulated DSC (TMDSC) [8, 21] have been described, demonstrating the powerful of this technique in a non-conventional field. Indeed, DSC is widely utilized to calculate transition temperatures, enthalpies connected to physical changes and heat capacity of materials [22].

In the present article, a method for determination of low thermal conductivity by traditional DSC is proposed, which has the following advantages over conventional techniques for polymers: requirement of a very small quantity of material (few tens of mg), achievement of relatively high temperatures that are hardly accessible by other techniques, saving of time because neither particular sample preparation nor long time of analysis are required.

The method consists in placing a small weighed amount of a standard substance shaped as a thin disk onto a polymeric sheet in a DSC aluminium pan and in measuring the rate of the heat flow, during fusion of the standard substance. The diameter of the melting point standard must be lower than that of the pan to minimize the lateral heat propagation and ensure one-dimensional heat pattern, as in the arrangement used by Khanna et al. [17]. It is also necessary to scan the melting standard substance alone, to get its fusion peak in absence of the polymer. Indium (In) was chosen as melting point standard substance, and polymers polytetrafluoroethylene (PTFE), polyethyleneterephthalate (PET), polymethylmethacrylate (PMMA) and a polyoxymethylene copolymer (POMC) were used as technique demonstrators because of their thermal and dimensionality stabilities at the fusion temperature of In. This method neglects the contact resistance at the interfaces sample pan-polymer and reference material-polymer, in agreement with previous assumptions and experimental evidences [5, 7, 17–19, 23, 24]. In addition to low contact resistances between polymer-metal surfaces (because of high thermal conductivity of metals and similar thermal conductivity between air voids and polymers), the negligible contact resistance between In and polymer sheets is facilitated by In melting directly onto the polymer during the thermal conductivity measure, ensuring an intimate contact between the two phases, as shown by Hall et al. [23]. Indeed, one of the methods used to effectively minimize the thermal contact resistance consists of filling the interfacial gap with metallic materials [10]. Negligible contact resistances should entail high reproducibility of thermal conductivity measures [10, 23]. However, polymer thermal conductivity varies with morphology, which depends on crystallization conditions. In other words, the wide spread of the literature data of polymer thermal conductivity [7, 17] can be explained by the sensitivity of thermal conductivity to microstructure. Indeed, it has been recognized that thermal conductivity should be measured in a film as it processed because the measure reflects the specific physical properties of that film [5].

PTFE is an ideal polymer to prove that contact resistance to In is negligible compared with PTFE thermal resistance. Indeed, PTFE sheets of different thickness have the same morphology and crystallinity, and therefore, similar thermal conductivity values should be obtained for different thicknesses if the assumption of insignificance of contact resistances is reasonable.

The DSC measurement of the thermal conductivity of sheet materials with melting point references has already been described by a few authors [14, 17–20] but neither theoretical nor experimental approaches have been integrated to improve the precision of the method. Khanna et al. [17] used experimental conditions similar to those used in this study and assumed that the slope of the first half of the melting peak of a melting substance is inversely proportional to the thermal conductivity of the underlying polymer sheets, but utilized a different mathematical approach to derive thermal conductivity values. The procedure used by Khanna is specific for low conductivity substances, but has the disadvantage of requiring reference materials of well known thermal conductivity, whose availability is extremely limited [17].

Flynn and Levin used a mathematical approach equivalent to that described in this study, but different experimental details [18]. In their preliminary studies, they tested various melting point materials, mostly powder solids. Thereby they needed to encapsulate even the reference material alone in an aluminium sample pan, placed onto a test specimen contained in an external pan. The use of the internal pan required further assumptions for the model, namely that there was no thermal resistance between the polymer specimen and the aluminium pan and that the pan maintained the temperature of the sensor during the transition [18]. Clearly, the presence of this pan prevents the direct fusion of In onto the polymer sheets and subsequent decrease of the contact resistance. Indeed, these authors found thermal conductivities of polymers much lower than those reported in the literature and concluded that their method may require calibration with substances of known

thermal conductivity [18]. The low thermal conductivity values are instead likely due to the use of a further pan to contain the melting point reference, in contrast to the assumption of negligible contact resistances. Moreover, Flynn and Levin obtained a high scatter ($\pm 50\%$) of the thermal conductivity using polymer films with thickness from 0.246 to 1.6 mm. The analysis of data from Ref. [18] shows that the conductivity increases up to a maximum with increasing the thickness of the samples and then begins to decrease. This variation is evidently due to the change of the morphology and crystallinity of polymer films with the thickness. Samples with very high thickness also biases thermal conductivity measure because of the increase of the heat loss from lateral dimensions. Indeed, a thickness included in the range 0.5-1.0 mm must be used to obtain reproducible values of thermal conductivity.

Camirand [20] used an experimental similar approach but required measurements to be done on polymer films of different thicknesses to obtain a linear plot between the thermal resistance and the ratio between the height and cross-section area of the test specimen. The slope of the plot is considered inversely proportional to the thermal conductivity whereas the intercept at zero thickness gives the total contact resistances. Camirand observed that his method did not account for contact resistance variability from sample to sample. Moreover, the method requires that samples of different thickness have the same thermal conductivity; this assumption is not always valid for polymer films, as their morphology may change with the thickness even if crystallization occurs under the same conditions. As consequence of the changes of thermal conductivity due to morphology and crystallinity level [13, 17, 25, 26], Camirand used PTFE specimens from about 0.5 to 2 mm thickness and attributed the difference between the values obtained by his method and the literature thermal conductivity to be due to the three-dimensionality of samples and to non one-dimensional heat propagation.

Like Hu et al. [14], Camirand does not considered the contact resistances negligible but constant, and observed that this could lead to a source of error as the sum of the contact resistances varies from sample to sample [14, 18, 20]. If the bulk morphology of samples changes with various thickness, considering the effective contact resistances at the solid-solid interfaces should improve the accuracy of thermal conductivity measurements. Camirand used ten cylindrical pellets of compressed PTFE powder with different heights and constant crystallinity and found a difference between the measured thermal conductivity and the literature value of 27%. He also found empirically that a relative error less by 5% comes out by fitting the descending part of the thermal curve instead of the ascending one [20]. This method can certainly achieve a high accuracy when samples with different thickness have the same crystallinity content and microstructure, and therefore, satisfy the assumptions made by Camirand. Indeed, Camirand obtained excellent results for fused quartz, compressed PTFE and metal hydride powders. However, samples with different thickness may have different microstructures [1, 27, 28], and therefore, different thermal conductivities; consequently, the method of Camirand is not suitable to measure the conductivity of polycrystalline samples whose thermal conductivity depends on thickness, growth morphology and grain size [25]. Moreover, accuracy of the thermal conductivity coefficient of samples requires identical processing of face surfaces reference of the specimen being under test [29]. For polymers crystallized from the melt, especially at high cooling rate, it is neither that the reproducibility of the crystals size and crystallinity content is assured (crystalline materials have a higher thermal conductivity than their corresponding amorphous state [17, 26]) nor of the surface topography of samples of different thickness is assured [1– 4, 27, 30]. For instance, it is possible to have completely transcrystalline films only in a very limited range of thickness whereas thicker samples show a variable morphology from outside in [31]. Analogously, thermal conductivity of thermosetting polymers depends on the crosslink level which is very sensitive to the curing conditions [32-34] as well as properties of thermoplasticthermoset blends are highly dependent on the morphology of samples [35]. Therefore, polymer sheets of different thickness may not show a linearity in the thermal resistance against the ratio between the height and cross-section area of specimens. Another source of a small error in Camirand's method is due to the application of the ordinary least squares method on ordinate and abscissa values obtained by measurements, whereas many authors have noted that linear regression of data cannot be used to determine slopes and intercepts if the independent variable (i.e. the thickness in the Camirand's plot) is not exempt from experimental uncertainty [36].

Gubler et al. used heat conducting paste to ensure good contact and avoid air gaps but they also observed deviations from one-dimensional heat flow and a reduction of the measured resistance [5]. Hu et al., like Camirand, obtained the conductivity of polymers by the slope of the plot of the thermal resistance against the ratio between lengths and the cross sectional area of samples [14]. They used silicon grease to ensure good contact between the different materials, but they had also to determine a calibration constant to correct systematic errors [14].

Finally, the method of Hakvoort and van Reijen [19] requires the measurement of the heat fusion of the melting point standard. It also needs the DSC reference pan be filled with the polymer, and therefore, human intervention (at least in commonly available equipments) to change both

the sample and the reference pans for each thermal conductivity measure.

The present modification of the Flynn and Levin method, with the appropriate choice of the melting reference material, is suitable for any polymer using one thickness samples and achieves uncertainties lower than the accepted values for thermal conductivity determinations. It has the advantage over other similar DSC methods for thermosets and polymers crystallized by melt, because of the mutual dependences between the microstructure achieved by curing or crystallization and the thermal properties. In addition, it has at least one of the two following advantages over previous similar DSC evaluations of thermal conductivity. This method permits routine measurements with automatic changing system and avoids the need of thermal conductivity reference materials because of strict conformability between experimental conditions and data processing.

Experimental

Materials and procedures

PTFE, PET, PMMA and POMC as sheets were provided by Goodfellow (England). Indium was supplied by Mettler Toledo.

Differential scanning calorimetry was carried out by a Mettler TA-3000 endowed with a TC 10A temperature control and programming unit and a liquid nitrogen cooling system. The instrument was calibrated, at various scan rates, with pure indium, lead and zinc reference materials.

A weighed amount of polymer film was used having thickness of 0.5 or 1 mm shaped as the circular bottom of the pan. Aluminium covered pans of 40 μ L with a central pin were used.

Afterwards, a small disk of indium with radius of 0.9-1.2 mm and thickness 0.3 mm was placed onto the polymer film and the system heated from 303 to 453 K. Scan rates of 5, 10 and 20 K min⁻¹ were adopted.

Result and discussion

In the present study, DSC is used to estimate the velocity of heat propagation through an insulating material by observing the solid–liquid transition of a high purity metal with known melting point. Indium was here chosen because its melting point (429.72 K) is appropriate for thermal characterization of thermally stable polymers at a temperature above ambient.

Figure 1 shows the fusion peaks obtained at a scan rate of 10 K min⁻¹ of indium specimens in absence and in the

presence of a film of PTFE 0.5 mm thick. When only a disk of indium was placed in an aluminium pan, the quick response of the DSC equipment is demonstrated from the high slope of the left side of the fusion peak. In absence of the polymer, the heat needed to melt the metal is rapidly delivered to the sample and the DSC peak results sharp and narrow. The presence of an insulating substance, lying between indium and thermocouples, causes an increase in the characteristic time of the DSC. As a result, the DSC peak has a lower slope and becomes broad and flat.

It is well established that heat transfer analysis can be performed by using equivalent electrical parameters and related laws [24, 37, 38]. The basis of the present method is conveniently described by replacing thermal parameters with equivalent electrical quantities. In this framework the heat flow replaces the current i and the temperature the voltage V.

According to O'Neill [24], a temperature controlled calorimeter may be represented by an isothermal platform connected through a resistance R_0 (the resistance which appears at the plane of contact between the sample container and the platform and considered as the source resistance of the instrument) and a thermal ammeter to a temperature source $T_{\rm p}$. For a two-layers sample of a polymer film overlaid with a metal, a thermal transition may be easily analysed by means of the equivalent circuit shown in Fig. 2, assuming that all contact resistances between different materials (i.e. polymer-container, metalpolymer) are negligible compared with the thermal resistance R of the polymer [24]. This assumption is reasonable firstly, because polymers have very high thermal resistances [2, 11] comparable to contact resistances and the high thermal conductivity of the aluminium pans and, secondly, because indium melts during measurement and causes the effective contact area with the underlying polymer sheet to increase. During heating, fusion of indium starts at 429.72 K and a solid-liquid interface appears at



Fig. 1 DSC curves obtained at a scan rate of 10 K min⁻¹ showing the fusion peak of indium in absence (**a**) and in the presence (**b**) of PTFE. The thickness of PTFE was 0.5 mm. The slope of the tangent to the peaks is the angular coefficient of the showed linear equations



Fig. 2 Electrical circuit equivalent to the problem of heat flow in PTFE-In system placed in a DSC cell

the bottom surface of the metal in contact with the polymer. While T_p and hence the temperature of the inferior surface of the polymer increases according to the temperature programme, the temperature of the metal remains constant until the entire mass melt. A temperature gradient thus arises because of the low thermal conductivity of polymers. Assuming that the temperature gradient is constant throughout the polymer cross-sections, and that the temperature increases linearly from the top to the bottom polymer surface, the heat flow rate W measured by the calorimeter during the fusion of the metal is given by:

$$W = \frac{Ak(T - T_{\rm m})}{d} \tag{1}$$

where A is the area of the platform, k and d are the conductivity and the thickness of the polymer sheet, respectively, T is the temperature of the platform and $T_{\rm m}$ the transition temperature.

Moreover, in absence of additional resistances R that contribute to the source resistance R_0 of the instrument, from the Ohm's law and the O'Neill equivalent electrical circuit of calorimeters [24] it results:

$$W_0 = \frac{T_{\rm p} - T_{\rm m}}{R_0} \tag{2}$$

Deriving with respect to time:

$$\frac{\mathrm{d}W_0}{\mathrm{d}t} = \frac{1}{R_0} \frac{\mathrm{d}T_\mathrm{p}}{\mathrm{d}t} \tag{3}$$

This equation establishes that the derivative of the thermal power during an endothermic transition depends on the scan rate dT_p/dt and on the internal resistance of the equipment.

 dW_0/dt can be obtained by the onset slope of the straight line tangent to the DSC peak of indium. As the scan rate is known, R_0 may be obtained from the ratio between the scan rate and the derivative with respect to time of the thermal power connected to the fusion peak of pure indium.

In the presence of a poor heat conductor, an additional resistance R in series to R_0 should be included in the equivalent circuit, therefore:

$$W = \frac{T_{\rm p} - T_{\rm m}}{R_0 + R} \tag{4}$$

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\frac{\mathrm{d}I_{\mathrm{P}}}{\mathrm{d}t}}{R_0 + R} \tag{5}$$

Equation 5 establishes that the flow of heat is governed by both the thermal resistance of the polymer and the scan rate, as the time t during which the heat evolution is revealed depends on the conduction path from the substance involved in the phase transition to the thermocouples.

To calculate the thermal resistance of a polymer, the thermal curve for the fusion of indium in absence and in the presence of a polymeric film at a fixed rate is obtained, to derive graphically the slopes of the DSC peaks, and finally to solve the system of Eqs. 3 and 5 respect to R_0 and R. Finally, thermal conductivity k may be obtained by the formula:

$$k = \frac{d}{RS} \tag{6}$$

where d is the thickness of the polymer and S the area of the indium disk.

The method is described for determination of PTFE thermal conductivity in the following section.

By applying the mathematical procedure herein explained to the data derived from the DSC fusion peak of indium and showed in Fig. 1, a value of thermal conductivity of (0.34 ± 0.03) W m⁻¹ K⁻¹ is obtained for PTFE at 429.72 K. The maximum relative error on the thermal conductivity value, expressing the accuracy, was calculated according to the theory of error propagation using the rough formula:

$$|\delta k/k| = |\delta d/d| + |\delta R/R| + |\delta S/S|$$
(7)

where *k* is the thermal conductivity, *d* the thickness and *R* the thermal resistance of the polymer, *S* is the area of the indium disk, δk , δd , δR and δS are the absolute errors in the respective quantities *k*, *d*, *R*, *S*. The used absolute errors are: $\delta d = \pm 0.01 \text{ mm}$, $\delta R = \pm 0.02 \times 10^3 \text{ K W}^{-1}$ for PTFE 0.5 mm thick and $\delta R = \pm 0.07 \times 10^3 \text{ K W}^{-1}$ for PTFE 1 mm thick at a scan rate of 10 K min⁻¹, $\delta S = (dS/dr)\delta r = \pm 0.06 \text{ mm}^2$ (with $dS/dr = 2\pi r$ and $\delta r = \pm 0.01 \text{ mm}$). The absolute error δk has been obtained from (7) multiplying the relative error by the thermal conductivity *k*. It is worth noting that (7) was used, instead of the more accurate formula $|\delta k/k| = [(\delta d/d)^2 + (\delta R/R)^2 + (\delta S/S)^2]^{1/2}$, to obtain the error under the most unfavourable conditions.

thermal conductivity obtained for PTFE The $(0.34 \text{ W m}^{-1} \text{ K}^{-1})$ is higher than the literature value of 0.25 W m⁻¹ K⁻¹ determined at 296 K (datum from Goodfellow) because of the increase of the thermal conductivity with temperature [11]. Indeed, 0.34 W m⁻¹ K⁻¹ is in good agreement with the value of the thermal conductivity $(0.30-0.33 \text{ W m}^{-1} \text{ K}^{-1})$ found by Price and Jarratt at 505 K for PTFE with high crystallinity level [26], with the value found at 340 K by Chiu and Fair [7] and with the value found by Hu et al. in the interval 303–333 K [14]. The maximum relative error on the present thermal conductivity determination (a value of 0.08 comes out using formula (7)) is also relatively low. Furthermore, the repeatability of the measure performed on specimens 0.5 mm thick is high. Indeed, thermal conductivity measurements on six specimens gave a standard deviation of 0.01. To assess that the contact resistances are negligible compared to the thermal resistance of the polymer, thermal conductivity was also measured using PTFE 1 mm thick. Figure 3 shows the DSC fusion peak of indium in the presence of a bottom layer 1 mm thick of PTFE, with the relative equation of the tangent. By using the slope of the tangent line and the value of R_0 derived as described above $(R_0 = 1.45 \times 10^2 \text{ K W}^{-1})$, R can be derived from Eq. 5. Finally, the thermal conductivity k of PTFE can be calculated from Eq. 6, giving the value of (0.35 ± 0.04) W m⁻¹ K⁻¹. Therefore, the present methodology applied to PTFE of different thickness in the range 0.5-1 mm results in almost coincident conductivity values that demonstrate the reliability of the assumption of negligible contact resistances. As measurements on PTFE specimens with the same thickness show very good repeatability, the slight dependence of thermal conductivity on polymer thickness, already observed by Flynn and Levin, is ascribable only to the small difference of the heat pattern through the polymer.

The effect of the heating rate on the slope of the tangent of indium melting peak was preliminarily studied using



Fig. 3 DSC fusion peak of indium in the presence of PTFE 1 mm thick. The scan rate was 10 K $\rm min^{-1}$

three different scan rates (5, 10 and 20 K min⁻¹). It was found that a heating rate of 20 K min⁻¹ limits the repeatability of measurements and causes an increase of the error on thermal conductivity. On the other hand, a scan rate of 5 K min⁻¹ does not substantially improve the uncertainty of the results obtained at 10 K min⁻¹.

Based on errors comparison, it is advisable to use a PTFE disk 0.5 mm thick and a heating rate ≤ 10 K min⁻¹.

In principle the present method could be extended to any insulating material with a thermal conductivity less than that of In (71.1 W m⁻¹ K⁻¹). Ideal candidates are polymers, whose thermal conductivity values are in the range 0.1–0.5 W m⁻¹ K⁻¹. In practice, thermal conductivity is achievable for thermally stable polymers, including polymethylmetacrylate, polyoxymethylene and polyethyleneterephthalate sheets (see Table 1). Indeed, the values of the thermal conductivity are reproducible if specimens with the same thickness are used and the precision of the measures is lower than the achievable accuracy, whereas the results are scattered for different melt processed samples of the same polymer. This scattering is due to the different morphological characteristics and/or crystallinity level of the polymer samples. For amorphous or semicrystalline polymers, such as PET, that undergo crystallization on heating, this method does not provides the thermal conductivity of the original sample. Since it is impossible to avoid the crystallization of the amorphous part of PET before indium melting during the DSC measurement, the obtained thermal conductivity value would not refer to the original sample but to the subsequently recrystallized PET. On the other hand, a high scan rate, which might prevent PET crystallization, would bias the accuracy of the method.

Although it is not possible to obtain the thermal conductivity of the original PET sample, it is useful to compare DSC measurements on PET since they demonstrate that samples achieving different levels of crystallinity have different thermal conductivity values. In Table 1 the thermal conductivity of two PET samples achieving crystallinity of 19 and 32%, respectively, are reported.

Table 1 Thermal conductivity values obtained for POMC, PMMA and PET by melting In at 10 K min^{-1}

	Thickness/mm	Thermal conductivity/W $m^{-1} K^{-1}$	
		Measured	Literature
POMC	1	0.52	0.360 [7]
PMMA	1	0.31	0.0882 [17]; 0.134 [7]; 0.189 [18]; 0.21 [14, 20]
PET	0.5	0.22	0.256 [7]
PET	1	0.46	

The use of low melting point metallic references (such as soldering alloys and eutectic alloys composed of bismuth, lead, tin, cadmium and indium) is suggested to obtain reliable thermal conductivity evaluations at temperature lower than 430 K for polymers with a limited range of thermal stability.

Conclusions

A better theoretical and experimental approach for the measurement of thermal conductivity of polymers has been identified in a modification of the Flynn and Levine method. This improved procedure provides the determination of thermal conductivity of polymers at the melting point of indium with low uncertainty avoiding the requirements of thermal conductivity reference materials or of samples of different thickness. Moreover, the present measure of thermal conductivity permits polymer samples to be automatically processed with a sample changing robot. In principle, any pure and highly conductive substance with a first order transition at a temperature in the range of thermal stability of polymers is useful for thermal conductivity measurements. Indeed, the described method can be exploited for the determination of thermal conductivity at any temperature provided that a melting reference material showing a transition at the desired temperature (such as soldering alloys with melting point from 283 to 583 K) be available. PTFE, POMC, PMMA and PET used in this study may be replaced by any other insulating solid for measurement of the thermal conductivity in a temperature range where the material exhibits thermal stability.

References

- Fedorchenko AI, Chernov AA. Simulation of the microstructure of a thin metal layer quenched from a liquid state. Intern J Heat Mass Transf. 2003;46:921–9.
- Raimo M, Cascone E, Martuscelli E. Melt crystallisation of polymer materials: the role of the thermal conductivity and its influence on the microstructure. J Mater Sci. 2001;36:3591–8.
- Raimo M. "Kinematic" analysis of growth and coalescence of spherulites for predictions on spherulitic morphology and on the crystallization mechanism. Prog Polym Sci. 2007;32:597–622.
- Hargis MJ, Grady BP. Effect of sample size on isothermal crystallization measurements performed in a differential scanning calorimeter: a method to determine avrami parameters without sample thickness effects. Thermochim Acta. 2006;443:147–58.
- Gubler U, Raunhardt M, Stump A. Measurement technique for thermal conductivity of thin polymer films. Thin Solid Films. 2006;515:1737–40.
- Lin C, Li Z, Guo ZY. Experimental Investigation of plastic finned-tube heat exchangers, with emphasis on material thermal conductivity. Exp Therm Fluid Sci. 2009;33:922–8.

- Chiu J, Fair PG. Determination of thermal conductivity by differential scanning calorimetry. Thermochim Acta. 1979;34: 267–73.
- Blaine RL, Marcus SM. Determination of temperature-modulated DSC thermal conductivity equations. J Therm Anal. 1998; 54:467–76.
- 9. Carslaw HS, Jaeger JC. Conduction of heat in solids. 2nd ed. Oxford: Claredon Press; 1997.
- Wang AL, Zhao JF. Review of prediction for thermal contact resistance. Sci China Technol Sci. 2010;53:1798–808.
- 11. Choy CL. Thermal conductivity of polymers. Polymer. 1977;18: 984–1004.
- Al-Nassar YN. Prediction of thermal conductivity of air voidedfiber-reinforced composite laminates part II: 3D simulation. Heat Mass Transf. 2006;43:117–22.
- Rides M, Morikawa J, Halldahl L, Hay B, Lobo H, Dawson A, Allen C. Intercomparison of thermal conductivity and thermal diffusivity methods for plastics. Polym Test. 2009;28:480–9.
- Hu M, Yu D, Wei J. Thermal conductivity determination of small polymer samples by differential scanning calorimetry. Polym Test. 2007;26:333–7.
- Gaal PS, Thermitus M-A, Stroe DE. Thermal conductivity measurements using the flash method. J Therm Anal Calorim. 2004; 78:185–9.
- Brennan WP, Miller B, Whitewell JC. Thermal conductivity measurements with the differential scanning calorimeter. J Appl Polym Sci. 1968;21:1800–2.
- Khanna YP, Taylor TJ, Chomyn G. A new differential scanning calorimetry based approach for the estimation of thermal conductivity of polymer solids and melts. Polym Eng Sci. 1988; 28:1034–41.
- Flynn JH, Levin DM. A method for the determination of thermal conductivity of sheet materials by differential scanning calorimetry. Thermochim Acta. 1988;126:93–100.
- Hakvoort G, van Reijen LL. Measurement of the thermal conductivity of solid substances by DSC. Thermochim Acta. 1985; 93:317–20.
- Camirand CP. Measurement of thermal conductivity by differential scanning calorimetry. Thermochim Acta. 2004;417:1–4.
- Merzlyakov M, Schick C. Thermal conductivity from dynamic response of DSC. Thermochim Acta. 2001;377:183–91.
- Venkata R, Nagarajan K. Evolution of heat capacity measurements by temperature-modulated differential scanning calorimetry. J Thermal Anal Calorim. 2010;102:1135–40.
- Hall JA, Ceckler WH, Thompson EV. Thermal properties of rigid polymers. I. Measurement of thermal conductivity and question concerning contact resistance. J Appl Polym Sci. 1987;33: 2029–39.
- O'Neill MJ. The analysis of a temperature-controlled scanning calorimeter. Anal Chem. 1964;36:1238–45.
- Govindaraju N, Aleksov A, Li X, Okuzumi F, Wolter SD, Collazo R, Prater JT, Sitar Z. Comparative study of textured diamond films by thermal conductivity measurements. Appl Phys A. 2006; 85:331–5.
- Price DM, Jarratt M. Thermal conductivity of PTFE and PTFE composites. Thermochim Acta. 2002;392–393:231–6.
- 27. Raimo M. Analysis of layer by layer phase transformation of a polyoxymethylene copolymer film. Acta Mater. 2008;56: 4217–25.
- Binsbergen FL, De Lange BGM. Heterogeneous nucleation in the crystallization of polyolefins: Part 2 Kinetic of crystallization of nucleated polypropylene. Polymer. 1970;11:309–32.
- Vahanyan AI. A method for the thermal conductivity measurement of semiconductors. Measurements. 2006;39:447–50.
- Chan TW, Isayev AI. Quiescent polymer crystallization: modeling and measurements. Polym Eng Sci. 1994;34:461–71.

- Folkes MJ, Hardwick ST. Direct study of the structure and properties of transcrystalline layers. J Mat Sci Lett. 1987;6: 656–8.
- Pusatcioglu SY, Frike AL, Hassler JC. Variation of thermal conductivity and specific heat during cure of thermoset polyesters. J Appl Polym Sci. 1979;24:947–52.
- Gracia-Fernandez CA, Davies P, Gomez-Barreiro S, Lopez Beceiro J, Tarrio-Saavedra J, Artiaga R. A vitrification and curing study by simultaneous TMDSC-photocalorimetry. J Therm Anal Calorim. 2010;102:1057–62.
- Ferrante M, Petrini M, Trentini P, Ciavarelli L, Spoto G. Thermal analysis of light-curing composites. J Therm Anal Calorim. 2010;102:107–11.
- Sanchez-Cabezudo M, Masegosa RM, Salom C, Prolongo MG. Correlations between the morphology and the thermo-mechanical properties in poly(vinyl acetate)/epoxy thermosets. J Therm Anal Calorim. 2010;102:1025–33.
- Kalantar AH, Gelb RI, Alpaer JS. Biases in summary statistics of slopes and intercepts in linear regression with errors in both variables. Talanta. 1995;42:597–603.
- Wiener O. Die Theorie des Mischkorpers fur das Feld des stationaren Stromung. Abh Math, Physischen Klasse Konigl Sacsh Gesel Wissen. 1912;32:509–604.
- Lee SM. International encyclopedia of composites, vol 5. New York: VCH Publishers Inc; 1990, p 485.