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Temperature calibration in the cooling operation mode of the UNIPAN-TERMAL 605 M model DSC calorimeter

Summary — A method [5] of temperature calibration of the differential scanning calorimeter operated in the cooling mode is described on the example of a UNIPAN-TERMAL 605 M DSC instrument. Such a calibration is important in studying the nonisothermal crystallization of materials that crystallize at a slow rate, *e.g.*, polymers. The result of measurement is shown to be related to the rate of temperature change and to sample mass. Application of extraneous coolant, *e.g.*, liquid nitrogen, leads to an additional effect.

Key words: differential scanning calorimeters, temperature calibration, cooling mode, effects of cooling rate, sample mass.

The method of differential scanning calorimetry has a great practical importance in the field of characteristic of polymers (e.g. [1, 2]). Heat transfer inside any type of calorimeter leads to a temperature gradient in the space between the furnace and the sample. In two types of DSC apparatus, power compensated and heat flux (Boersma) type, the thermocouple measuring the sample temperature is below the sample pan and the true temperature of the sample differs from that of the thermocouple. In the case of heating, one of the procedures (calibration) widely used to correct for this temperature difference is based on measuring the melting temperatures (onset) of pure low-molecular-weight materials at a particular cooling rate followed by comparison with the well-known (true) melting temperature. It is assumed that the true melting temperatures of low-molecular-weight standards are independent of the heating rate (superheating effect is considered negligible). The increasing interest for DSC measurements carried out in the cooling mode (*e.g.*, studies on non-isothermal crystallization of slowly crystallizing materials like polymers) makes it advisable to develop a procedure for the temperature calibration (correction) on cooling. So far only few calibration procedures on cooling have been proposed [3—6]. The situation is more complex than that in the case of heating. The true crystallization temperatures of commonly used calibrants such as indium, tin or zinc are not known exactly, and the calibration procedure similar to that used in the heating mode should be preceded by the determination of true crystallization temperatures. Recently, Martins and Cruz-Pinto [7] proposed a simple method for the determination of true crystallization temperatures in the cooling mode. They describe the difference between the temperature of a sensor below the sample pan and that of a sample at a particular scanning rate as composed of the temperature difference at zero scanning rate (so-called isothermal correction) and the difference which depends on the scanning rate. The true temperature of crystallization during cooling is determined [7] as the measured temperature of crystallization (onset) by assuming the rate-dependent component of the temperature difference during cooling to be equal in magnitude and opposite in sign to that in the heating mode (at the same absolute rate of temperature change):

$$T_t^- - T_{sh} = (T_t^+ - T_{sh}) \qquad (1)$$

where: T_t^- *and* T_t^+ *are the true temperatures in the cooling and heating modes using a particular rate, respectively, and* T_{sh} *is the temperature which would be measured in the absence of a temperature gradient at zero rate of temperature change.*

Temperature T_{sh} is related to the temperature T_m measured actually by the sample's holder sensor as

$$T_{sh} = T_m - \Delta T_0 \qquad (2)$$

where: ΔT_0 *is the so-called isothermal correction (temperature difference at zero rate of temperature change).*

Martins and Cruz-Pinto [7] assumed the isothermal correction in the heating mode to be exactly the same as in the cooling mode. The correction ΔT_0 can be determined by extrapolation of the melting temperatures measured at various heating rates to zero heating rate.

The combination of eqn. (1) with eqn. (2) allows to calculate the true temperature T_t^- in the cooling mode

$$T_t^- = 2T_m - T_t^+ - 2\Delta T_0 \quad (3)$$

from the measured temperature of transition during cooling, the measured magnitude of isothermal correction and by using the known value of the true temperature of transition in the heating mode. To have a more general relationship, Martins and Cruz-Pinto [7] introduced an additional equation for heating

$$T_t^+ = a^+ T_m + b^+ \quad (4)$$

where: a^+ *and* b^+ *are determined at a particular heating rate by using the onset temperatures of melting of two standards (e.g., indium and lead).*

With eqn. (4) introduced into eqn. (3),

$$T_t^- = T_m(2 - a^+) - 2\Delta T_0 - b^+ \quad (5)$$

In eqn. (5), the true transition temperature T_t^+ has been replaced by two parameters a^+ and b^+. The intention of such a substitution is to make it possible to perform cooling calibration by using a standard other than that used for the determination of a^+ and b^+ without knowing its true melting temperature. We will not discuss the validity of such a procedure. In our investigations, cooling calibration was performed by using one of the two standards which had been used for the determination of a^+ and b^+ in the heating mode.

The purpose of the present work is to illustrate the application of calibration procedure for cooling as proposed in [7] to the heat flux DSC (Boersma type DSC) type 605 M produced by the Polish Company UNIPAN-TERMAL.

EXPERIMENTAL

A heat flux DSC (Boersma type DSC) instrument of the type 605 M produced by the Polish Company UNIPAN-TERMAL was used. Crystallization on cooling was investigated by using indium, whereas heating experiments were performed with indium and tin. The two standards, each 99.999% pure, were supplied by Aldrich Chem. Comp.

Temperature calibration was performed according to the method proposed in [7] (eqns. 1—5). The thermal resistance of the pure metals was considered to be low enough to ignore an additional correction for thermal resistance.

Crystallization experiments were performed by using two techniques of cooling. In one, a stream of liquid nitrogen was used to achieve the same absolute values of rates as those used for heating. In the second set of experiments, cooling was performed without any additional cooling medium. In this case, the maximum attainable cooling rate in the temperature range of indium crystallization was 5 deg/min.

The temperatures of melting and crystallization taken from the registered curves were determined as the extrapolated onset of the transition obtained at the point of intersection of the extrapolated baseline and the linear portion of the transition peak.

RESULTS AND DISCUSSION

Heating mode

Figures 1 and 2 show the melting temperatures measured for indium and tin samples of various masses as a function of heating rate.

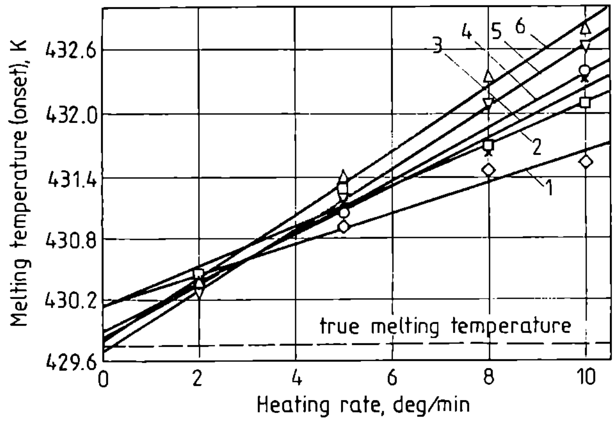

Fig. 1. Measured melting temperature of indium vs. heating rate at various sample masses (mg): 1 — 3.42, 2 — 5.11, 3 — 7.57, 4 — 10.63, 5 — 14.29, 6 — 19.40

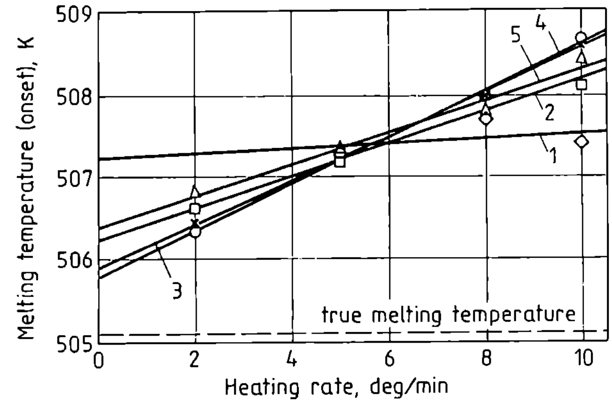

Fig. 2. Measured melting temperature of tin vs. heating rate at various sample masses (mg): 1 — 0.98, 2 — 3.30, 3 — 5.79, 4 — 7.49, 5 — 9.86

It is seen that the melting temperature measured below the pan increases linearly as the heating rate is increased. Considering the superheating effect during melting of indium and tin to be negligible [8], it is assumed that the true temperature of the sample is independent of the heating rate and is equal to 429.75 K for indium and 505.1 K for tin [8—12]. Therefore, the observed relationship between the measured temperature and the heating rate corresponds to the linear increase (with the heating rate) of the difference between the temperature measured by the sensor below the pan and that of the sample. Such a relationship has been described in many papers. For instance, in the case of DTA, Wiedemann *et al.* [11] have proposed the following relation between the measured and the true temperatures during heating at a rate v:

$$T_m = T_t^+ + v\left(\frac{R_k}{R_a + R_k} t + R_k C\right) \quad (6)$$

where: R_k *is the thermal resistance between the temperature sensor and the sample,* R_a *is the thermal resistance between the temperature sensor and the furnace, C is the heat capacity of sample, and t is time.*

The resistance R_k contains two components. The first is the thermal resistance of the sample, the second is the resistance of the system separating the surface of the sample and the temperature sensor below the sample pan. As is seen from eqn. (6), the temperature measured by the sensor below the pan should be equal to the true temperature of the sample at the zero heating rate. However, it should be noted that eqn. (6) is derived under the assumption that the heating rate is the same for the furnace and for the sample and no thermal reaction occurs in the sample [13]. Actually, even at the zero rate of temperature change, there is some difference between the temperature measured by the sensor below the sample pan and that of the sample [so-called isothermal correction, ΔT_0 in eqn. (2)]. In Figs. 3 and 4 this difference is seen to be related to sample mass. At a certain sample mass a minimum is achieved.

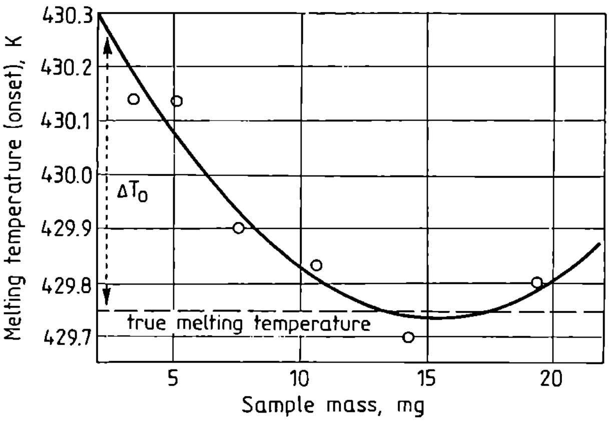

Fig. 3. Melting temperature of indium extrapolated to zero heating rate vs. sample mass

The increase in temperature error at a relatively high sample mass is probably related to the increase in thermal resistance. On the other hand, an increase in temperature error for very small samples is, in our opinion, related to the decrease in the heat signal from the sample, and the apparent delay resulting from limited sensitivity caused by heat dissipation during the flow of the heat between the sample and the sensor.

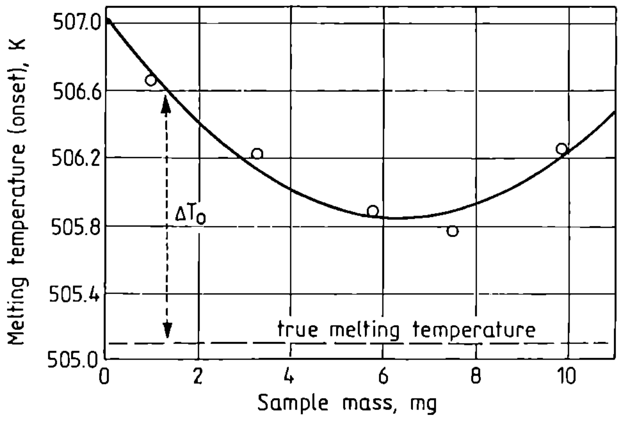

Fig. 4. Melting temperature of tin extrapolated to zero heating rate vs. sample mass

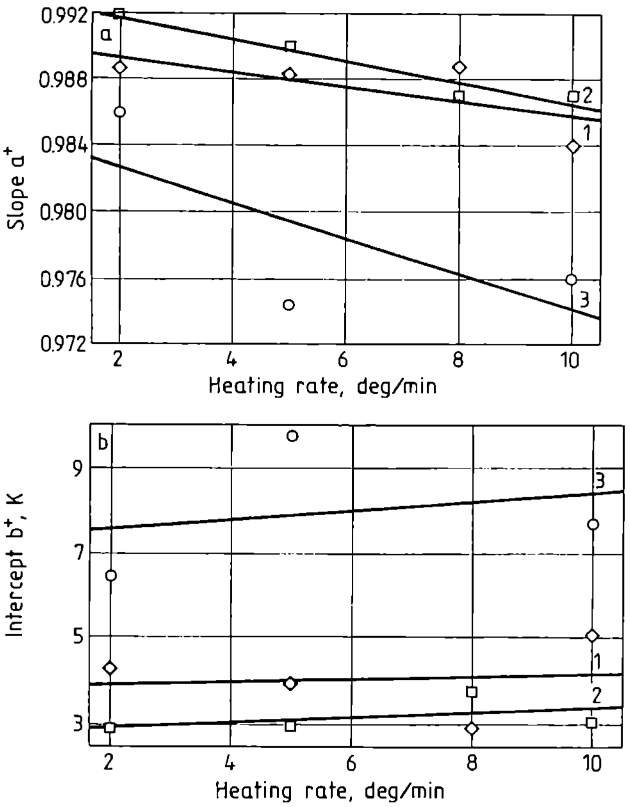

Fig. 5. Slope a^+ (a) and intercept b^+ (b) of the plot of true melting temperature T_t^+ vs. measured values T_m using indium and tin samples of various masses (mg): 1 — 3.5, 2 — 7.5, 3 — 10

Figure 5 shows the slopes a^+ and intercepts b^+ evaluated from eqn. (4) for various sample masses. Each pair of a^+ and b^+ was determined by using indium and tin with similar masses. It is seen that b^+ depends slightly on the heating rate (Fig. 5b) whereas slope a^+ is rather independent of the heating rate (Fig. 5a). Both parameters vary with sample mass.

Cooling mode

At higher sample masses the peak of crystallization was found to be slightly distorted. The distortion is related to the fact that the heat-flux DSC instrument uses only one furnace. In such a system the heat of reaction is not compensated by an additional heat from an independent furnace, the way it is in the power compensated DSC instrument, and during the reaction the temperature of the sample deviates slightly from the intended value. The resulting distortion increases as the rate of temperature change is increased. The procedure for this type of correction has been described [14].

Figure 6 shows the measured and corrected temperatures of indium crystallization. Considering the fact that the temperature measured by the sensor below sample's pan depends on sample mass, the crystallization temperature during cooling was corrected by using the parameters obtained in the heating mode applied to the same indium sample.

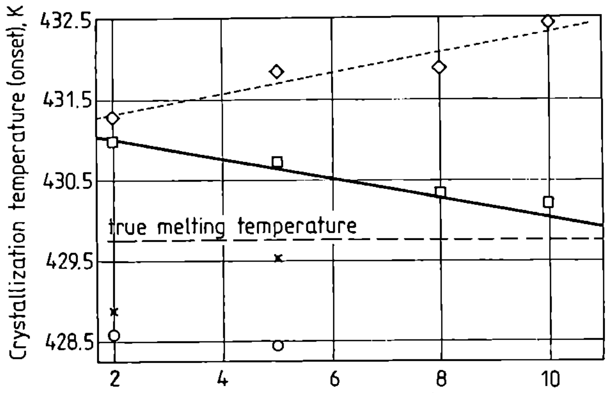

Fig. 6. Measured and corrected temperatures (onset) of indium (7.57 mg) on cooling with and without liquid nitrogen; □ and ◊ — temperatures measured and corrected, resp.; liquid nitrogen used as coolant ○ and × — temperatures measured and corrected, resp.; no liquid nitrogen used as coolant

Liquid nitrogen used for cooling is seen (Fig. 6) to have shifted the measured crystallization temperatures by about 2.4 deg above the values measured with no liquid nitrogen used. This difference is likely to be due to an additional temperature gradient introduced by the liquid nitrogen in the DSC apparatus used. According to Martins and Cruz-Pinto [7] the correction introduced into the temperatures increases the values. In the case of cooling with liquid nitrogen, the corrected crystallization temperature is higher than the true melting point. This result indicates that, in the case of the 605 M calorimeter produced by UNIPAN-TERMAL, it is necessary to add the correction for the temperature gradient introduced by the cooling medium. The application of the temperature correction for cooling without using an additional cooling medium results in the crystallization temperatures slightly below the true point of indium. Although in this case the range of cooling rates is very narrow, the corrected crystallization temperatures appear to be quite reasonable. It is known that in pure metals crystallization occurs with some undercooling. Undercoolings reported for indium are 2.2 [3] and 1.95 deg [7]. The corrected crystallization temperature has been found to rise as the cooling rate is increased (Fig. 6) [7]. This unexpected behavior has been related [7] to experimental errors but in our opinion it could be explained by some mechanisms of non-isothermal crystallization [15—17].

Figure 7 shows the corrected crystallization temperatures for indium samples of three different masses.

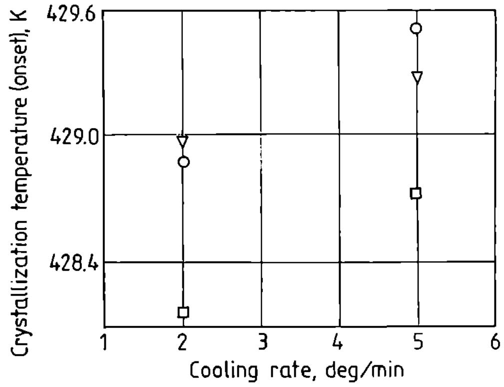

Fig. 7. Effect of sample mass on the corrected temperature of indium crystallization on cooling without nitrogen; sample mass (mg): — 3.2, ○ — 7.57,∇ — 10.63

The corrected temperatures for the 7.57 and 10.63 mg samples are seen to be very close to each other, whereas that determined for the 3.42 mg sample is considerably lower. This difference is probably due to the limited sensitivity of the instrument. As mentioned above, at low sample masses the low flux of transition heat can be responsible for a temperature error. This error is clearly seen for temperatures extrapolated to the zero rate of temperature change (Figs. 3 and 4). Comparison of data in Fig. 7 with data in Fig. 4 shows that the difference observed in Fig. 7 between the 3.42 mg sample and the samples with higher masses is equal to the temperature difference observed between the particular samples on melting at the zero temperature rate (Fig. 3) multiplied by (-2) [as seen in eqns. (3) and (5)].

CONCLUSIONS

The present results show the procedure of temperature correction for the cooling mode proposed recently [7] to be applicable under some ideal conditions. In the real instruments, and real conditions of measurements, the cooling medium applied can introduce an additional temperature gradient. Whether or not such an additional temperature gradient appears on cooling, depends on the design of a calorimeter. In the case of the UNIPAN-TERMAL 605 M calorimeter liquid nitrogen used as a cooling medium was found to introduce an additional gradient that resulted in a temperature shift of *ca.* 2.4 deg. This additional gradient should be accounted for in data evaluation. In our opinion, it is reasonable and simple to determine this additional temperature difference by comparing the transition temperature established with and without the use of an additional coolant. The other way to avoid the problem is to perform the calibration work by using the same cooling medium in the heating mode experiments as that used in the cooling mode experiments.

The present results show that results of calibration procedure can depend to some extent on the mass of the calibrant used. This is not only the problem of thermal resistivity occurring at higher sample masses leading to an additional thermal lag. An increase in temperature error was also observed at very low sample masses and is most probably related to the limited sensitivity of the instrument. We found that, in the case of the 605 M calorimeter, the optimum mass of indium and tin is between 8 and 16 mg and between 4 and 8 mg, respectively. The optimum mass range is related presumably to the thermal conductivity of the sample, its heat capacity, rate of production of transition heat, as well as to the type of the calorimetric instrument (its sensitivity).

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