Evaluation and interpretation of peak temperatures of DSC curves. Part 1: Basic principles

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The peak temperature is an important experimental value in DSC measurements. Systematic differences in this quantity can occur depending on the measurement conditions and the origin of the peak. The article explains the reasons for these differences and discusses the possibilities for correcting them. If proper attention is paid to the points concerned, samples can be more reliably compared and more meaningful data is obtained.

Introduction

The determination of different characteristic values of peaks is one of the most frequent evaluations performed in DSC. Some of these quantities are shown in the curve in Figure 1. For example, the integral is determined by integrating the area under the peak and yields the transition enthalpy, Δh. Equally important are the onset temperature, T_{on}, (especially with the melting of pure materials) and the temperature of the peak maximum (the peak temperature, T_m) because they are directly related to characteristic values of the material under investigation. For example, with pure substances, the onset temperature is the melting temperature. However, if peaks are broad, the onset temperature cannot be precisely determined and it loses its physical meaning. The peak temperature is then used to define the melting temperature.

In the case of polymers, the peak temperature, T_m, is a measure of the average melting temperature of the crystallites. With second order phase transitions, Tm is the characteristic temperature of the transition, and with mixtures, the peak maximum defines the liquidus curve in the phase diagram.

While the values measured for Δh and T_{on} are largely independent of the heating rate, β, and sample mass, m, the peak temperature is very dependent on these two parameters. Larger sample masses and higher heating rates shift the peak maximum to higher temperatures. Furthermore, in contrast to T_{on}, one notices that the peak temperature can be quite different (Figure 2) depending on whether the curve is displayed as a function of the sample temperature or the program temperature (in the STAR^e software terminology, the reference temperature). This question then arises as to what is the "true peak temperature" and what does it mean, or at least, what is the best approach for evaluating the peak. These topics will be discussed in particular in connection with melting processes in this two-part article series.

Part 1 here deals with the origin of a DSC melting peak and derives the properties of an ideal melting peak. In Part 2, these ideas will be applied and illustrated with the aid of practical examples.

Figure 1.
Typical data obtained from the peak evaluation of polyethylene terephthalate (PET).
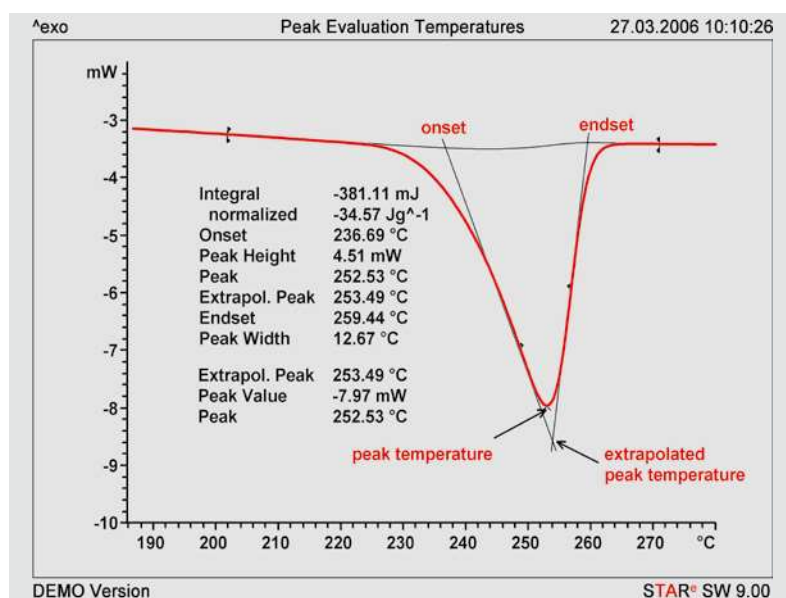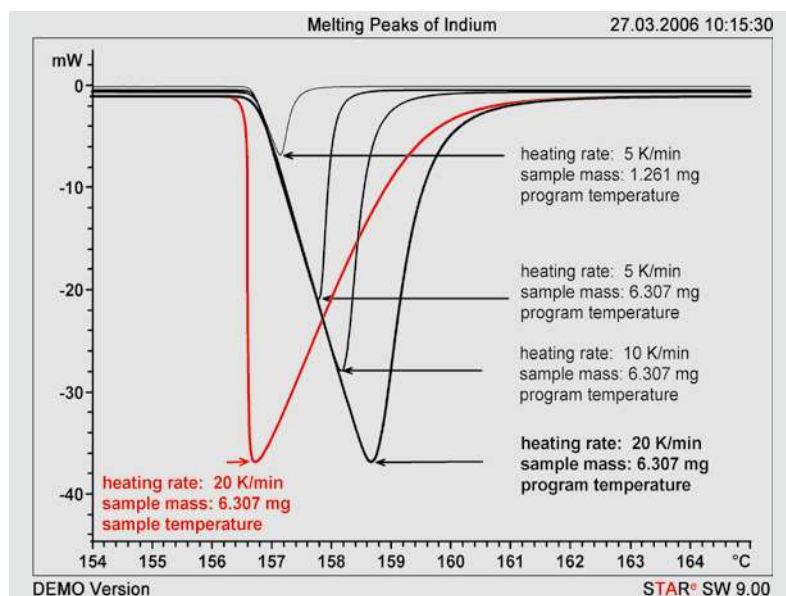

Figure 2.
Melting peaks of indium measured at different heating rates using samples of different mass. The peaks are displayed as a function of program temperature and/or sample temperature.

The ideal melting peak

The following sections discuss the influence of the sample and measurement conditions on peak temperature using a very simple model. First, the model refers to a thin sample of good thermal conductivity in which temperature gradients do not occur. The heat capacity of the sample before and after the transition is the same. The thermal behavior of the sample and reference sides of the measuring system is perfectly symmetrical. Finally, the response of the instrument to a sudden change in heat flow is a pure exponential function.

The DSC is adjusted using calibration samples whose heat capacity can be neglected. The heat capacity and the thermal contact of sample and reference crucibles are identical. In this case, the instrument is calibrated and adjusted so that the temperature at the DSC sensor corresponds to the sample temperature, T_s. If no thermal event occurs, the measurement quantity, T_s, is the true sample temperature $T_{s,t}$.

Origin of DSC peaks

If a sample of specific heat capacity, c_p, and mass, m, is heated under ideal conditions using a linear temperature program given by the equation

$$T_p = T_0 + \beta t \tag{1}$$

where T_0 is the start temperature, β the heating rate, and t the time, the sample temperature follows the program temperature with a small shift proportional to the heat capacity of the sample and the heating rate (see Figure 3).

If the sample melts at the temperature T_f, the true sample temperature remains constant while the program temperature increases linearly. An increasingly large difference develops between the true sample temperature, $T_{s,t}$, and the program temperature, T_p. This temperature difference is the "driving force" for the heat flow Φ_m that flows into the sample to melt the material given by the equation

$$\Phi_m = \frac{T_p - T_{s,t}}{R_f} \tag{2}$$

where R_f is the thermal resistance between the sample and the DSC furnace
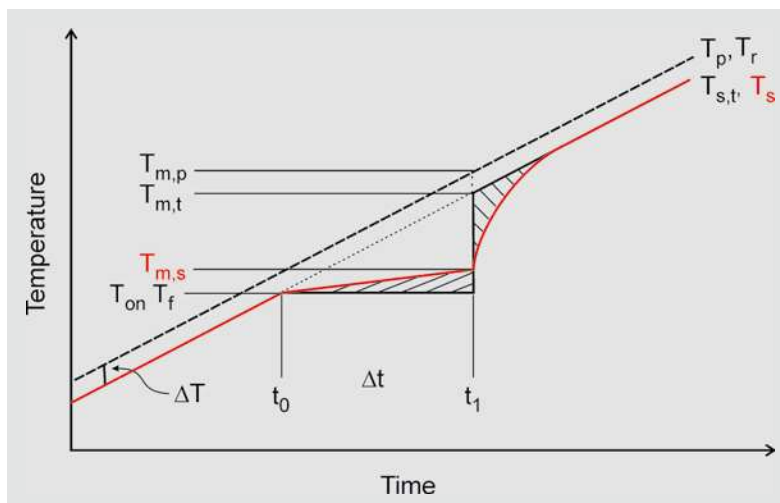
sensor. If, after a time Δt, enough heat has been transferred to the sample to completely melt it, the sample temperature jumps to the corresponding equilibrium value, $T_{m,t}$. For the enthalpy of melting:

$$\Delta t \, (\Phi_m - \Phi_{bl}) = m \, \Delta h \tag{3}$$

$$T_{m,t} = T_f + \Delta t \, \beta \tag{4}$$

whereby $\Phi_{bl} = m \, c_p \, \beta$ is the baseline of the peak.

The course of the true sample temperature corresponds to the black curve in Figure 3. The larger the thermal resistance between the sensor and the sample, the longer the melting process lasts.

The true sample temperature, T_s, cannot be measured because the sensor is not in direct contact with the sample. T_s is measured at the DSC sensor, which is separated from the sample by the thermal resistance, R_s. Since R_s is less than R_f, the measured sample temperature during melting is not constant but increases with time. The apparent heating rate of the sample temperature during the melting process is proportional to R_s. The course of T_s is shown by the red curve in Figure 3. When the sample has melted after a time, Δt, the T_s signal decays to the steady state value. The two shaded areas between the true sample temperature and the measured sample temperature are of equal size.

The sample temperature, T_s, is measured at the sensor. The measured heat flow, Φ_s, as a function of sample temperature

is proportional to the temperature difference between sensor and sample:

$$\Phi_s = \frac{T_s - T_{s,t}}{R_s} \tag{5}$$

The proportionality factor is the reciprocal of the thermal resistance between the sample and the sensor.

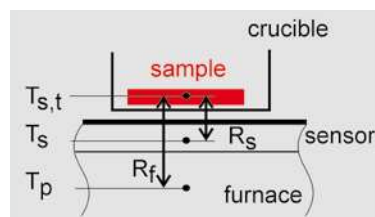The difference between the quantities used in equations (2) and (5) is illustrated in Figure 4.

In the model under discussion, the reference temperature, T_r, is equal to the program temperature, T_p. The measured signal of the heat flow into the sample is proportional to the difference between the reference temperature and the sample temperature:

$$\Phi = k(T_r - T_s) \tag{6}$$

where k is a calibration factor. This has a negative sign if ICTAC terminology is used (energy supplied to the sample has a negative sign; exothermic processes have a positive sign). In the physical definition, an endothermic heat flow is positive. Unfortunately, the ICTAC terminology is widely used in thermal analysis.

The heat flow curves obtained from the curves of the reference and the sample temperatures in Figure 3 are shown in Figure 5. It turns out that the difference between the peak and onset temperatures

is relatively small if the curve is evaluated as a function of sample temperature.

Factors influencing the peak temperature

Peak presentation as a function of the program temperature

The following three equations describe the change with respect to time of the true sample temperature, the measured sample temperature and the program temperature from Figure 3 during the melting process (i.e. between times t_0 and t_l):

$$T_{s,t} = T_{on} \qquad (7)$$

$$T_s = T_{on} + \frac{R_s}{R_f} \beta (t - t_0) \qquad (8)$$

$$T_p = T_{on} + \beta (t - t_0) + \Delta T \qquad (9)$$

Inserting of equations (7) and (8) into (5) yields the equation $\Phi = \beta (t - t_0)/R_f$ for the heat flow between the onset temperature and the peak temperature. Figure 5 shows the corresponding curve. The slope, $1/R_f$, of the melting peak in this region is constant.

The peak width is mainly determined by the distance between the peak onset and the maximum. Peak broadening occurs under the following conditions:
• poor heat conduction behavior (e.g. due to a larger crucible).
• a larger sample mass.
• a higher heating rate

This means that the peak temperature is not a characteristic value for the sample material, in contrast to the onset temperature and the normalized area.

After reaching the peak maximum, the heat flow signal decays to the value determined by the heat capacity of the liquid. To a good approximation, this region of the peak corresponds to an exponential decay function.

Influence of the experimental parameters on the peak temperature

To show how the peak temperature is influenced by R_f, m and β, the simplest case is discussed in which the exponential decay after the peak maximum is negligibly small. This approximation simplifies the following description. The resulting peak is shown in Figure 6a. The peak area, A, is given by the equation

$$A = \frac{\Phi_{max} (T_m - T_{on})}{2} \qquad (10)$$

From Figure 6a, it can be seen that for the slope of the peak

$$1/R_f = \Phi_{max}/(T_m - T_{on}) \qquad (11)$$

From thermodynamic considerations, the peak area is given by

$$A = \beta \, m \, \Delta h \qquad (12)$$

By combining equations (10) and (12) and insertion into equation (11) one obtains

$$\frac{(T_m - T_{on})^2}{2 \, R_f} = \beta \, m \, \Delta h \qquad (13)$$

Mathematical rearrangement then yields

$$T_m = T_{on} + \sqrt{2 \, R_f \, \Delta h} \sqrt{m \, \beta} \qquad (14)$$

If the peak temperature is plotted against the square root of the product of heating rate and sample mass, a straight line is obtained whose slope depends on the thermal resistance and the specific transition enthalpy. A diagram of this type is shown in Figure 6b.

This relationship between the heating rate and peak temperature was first derived by Illers [1]. He used a more realistic model for the melting peak. Practice shows that equation (14) is valid for a broad range of materials and heating rates. The Illers diagram can be used to determine the peak temperature extrapolated to a heating rate and mass of zero. This value is also independent of parameters such as the type of crucible and DSC. The peak temperature $T_{m,0}$ ex-

Figure 5.
Schematic diagram showing a melting peak as a function of the sample temperature (red) and the program temperature (black).
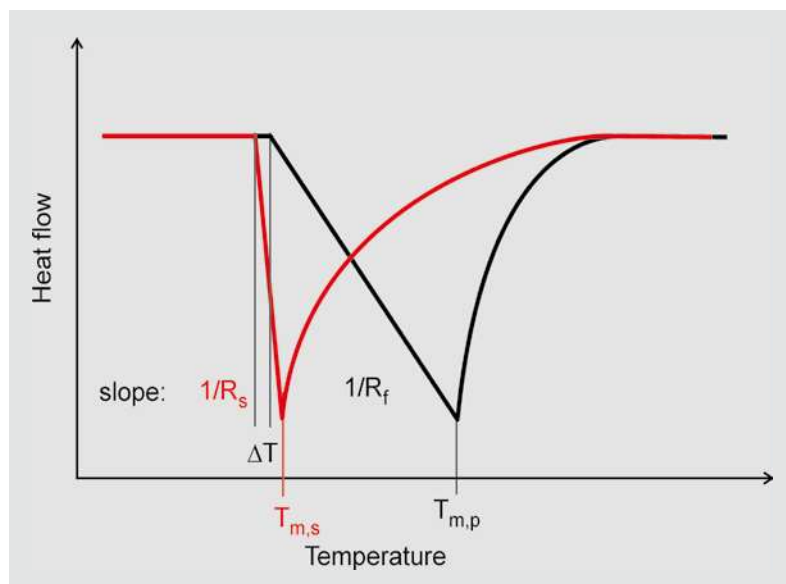

Figure 6a).
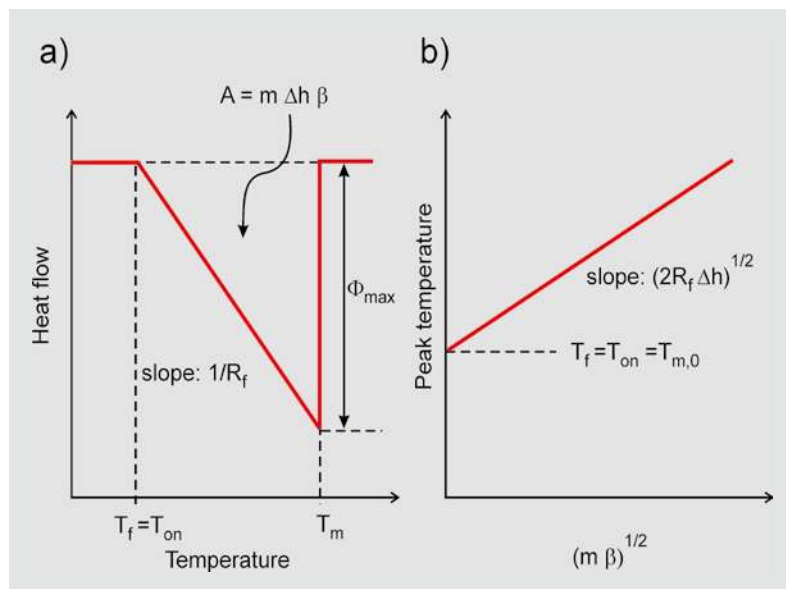Peak without decay after the peak maximum to derive equation (14);

Figure 6b).
Illers diagram.

trapolated to a heating rate of zero is the equilibrium melting temperature of the crystallites that melt at the peak temperature during the measurement.

Peak presentation as a function of the sample temperature

It can be seen in Figure 3 that the measured sample temperature, T_s, hardly changes during the actual melting process between t_0 and t_1. In the ideal case, it remains virtually constant.

From equations (5), (7) and (8), one obtains the slope of the heat flow curve in the melting region, $1/R_s$ (Figure 5). If the thermal resistance between the sensor and the sample is sufficiently small, the peak temperature is almost equal to the onset temperature (Figure 2). The dependence of the peak temperature on sample mass and heating rate also follows in equation (14). However, in this equation, R_f must be replaced by R_s. In the Illers diagram, one then obtains a correspondingly smaller slope.

Conclusions

During a melting peak, differences occur between the program temperature and the measured and true sample temperatures as a result of the corresponding heat transfer processes. The resulting temperature gradients give rise to the peaks measured in the heat flow curve.

The peak temperature, T_m, depends on the measurement conditions (heating rate, sample mass, heat transfer) and is not a direct measure for a material property. If you want to compare this quantity meaningfully for different samples, the measurements must be performed at the same heating rate using samples of similar mass contained in the same type of crucible. The peak temperature extrapolated to a mass and heating rate of zero is obtained using the Illers diagram. This quantity is independent of the experimental conditions and corresponds to the equilibrium melting temperature of the crystallites present.

The temperatures of the peak evaluation (onset and peak temperatures) differ depending on whether the evaluation is performed as a function of the program temperature (STAR^e terminology: reference temperature) or the sample temperature. The evaluation of the peak as a function of the sample temperature yields results that are closer to the true sample temperature.

In the STAR^e software, the DSC curves can be displayed using the program temperature (reference temperature) or the sample temperature. The evaluation mode can be set in the results mode. This means that the evaluation of a measurement curve displayed as a function of the reference temperature can also provide the corresponding sample temperatures.

In Part 2 of this series, a number of real measurement curves will be discussed.

Literature
[1]   K.-H. Illers, European Polymer Journal, 10 (1974) 911-916.

List of symbols used

Symbol	Description
A	Peak area
R_f	Thermal resistance between sample and furnace
R_s	Thermal resistance between sample and sensor
T_0	Start temperature
T_f	Melting temperature
T_m	Peak temperature
$T_{m,p}$	Program temperature at the peak maximum
$T_{m,s}$	Measured sample temperature at the peak maximum
$T_{m,t}$	True sample temperature at the peak maximum
$T_{m,0}$	The peak temperature extrapolated to a heating rate and mass of zero
T_{on}	Onset temperature
T_p	Program temperature
T_r	Reference temperature
T_s	Measured sample temperature
$T_{s,t}$	True sample temperature
c_p	Specific heat capacity of the sample
k	Calibration factor
m	Sample mass
t	Time
t_0	Measurement time at beginning of melting
t_1	Measurement time at peak maximum
ΔT	Temperature difference between T_p and T_s
Δh	Specific transition enthalpy
Δt	Time interval in which the sample actually melts
Φ_{bl}	Baseline of the peak
Φ_m	Heat flow referred to program temperature or time
Φ_{max}	Peak height
Φ_s	Heat flow referred to the measured sample temperature
β	Heating rate