

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

ON THE DETERMINATION OF THE MELTING POINT OF SEMICRYSTALLINE POLYMER BY DSC

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Abstract

This is a study for criteria to judge the melting point of semi-crystalline polymers from the DSC endotherm for polymer melting. Beyond standard indium DSC melting results an evaluation has been made on a series of polyethylenes for which crystal sizes were measured and predicted from Raman LAM analysis. The results confirm the conclusion of Prof. Wunderlich that the DSC content of melting is the proper basis of reporting melting points.

Keywords: DSC, melting point, polyethylene, Raman-active longitudinal acoustical mode, semi-crystalline polymers

Introduction

The differential scanning calorimetry technique is widely used in the study of polymers. It can be used to study the second order glass transition, the first order melting transition and to determine the fraction of crystallinity in polymers. The data obtained from such procedures can be applied directly to the study of polymer physical properties such as phase changes, stability measurements, and thermodynamic data.

An inadequate description of experimental details is one the most serious problems in the reporting of thermal analysis. In the measurement of melting temperature for semicrystalline polymers by DSC, as indicated by Wunderlich, the characteristic temperatures are the beginning of melting, T_b , the extrapolated onset of melting, T_{onset} , or T_m , the peak temperature, T_{max} , and the point where the base line is finally recovered, the end of melting T_e . Of these, the most widely used reference temperatures are the temperature onset T_{onset} of the endothermic peak and the peak temperature T_m . For a systematic study of relative temperature changes, the choice among these two values is not critical, if all samples are measured under identical conditions, i.e. the same scanning rate, essentially the same sample size, and so on. However, for an accurate

measurement of polymer melting temperature there are further considerations necessary.

From thermodynamics, any process can be described by the following equation in terms of changes in free energy, enthalpy and entropy;

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

When a sample is heated to its melting point, the crystal begins to melt at constant temperature, and the crystal temperature will not increase further until their melting is complete. During melting $\Delta G=0$. In this case

$$T_m^o = \frac{\Delta H_m}{\Delta S_m} \quad (2)$$

where T_m^o is the equilibrium melting temperature. In the DSC instrument, the endothermic energy required to melt the sample is provided and recorded electronically. For further discussion it is worth reviewing the reported design principle and theory of the DSC. During the DSC measurement in the melting region, the thermal energy flow dq/dt can be expressed by [1, 2]

$$\frac{dq}{dt} = (C_s - C_r) \frac{dT_p}{dt} + \frac{1}{R} \frac{dT_p}{dt} \quad (3)$$

where T_p is the sample holder temperature in the DSC: This equals the program temperature. R is sample thermal resistance, C_s and C_r are the total heat capacities of the sample plus container and the reference, respectively. The first term in Eq. (3) is the baseline displacement due to heat capacity mismatch between sample and reference, and the second term is the slope of the recorded endothermic curve. Once the sample starts to melt, the baseline is no longer horizontal. Extrapolating from the baseline and peak slope, the T_{onset} of melting is obtained which is related to the melting transition temperature (T_T) by the following equation [3];

$$T_{\text{onset}} = T_T + \frac{dT_p}{dt} (\tau_x + \tau_s) \quad (4)$$

where τ_x is the power response time constant, and τ_s is the interfacial time constant between sample and container. So, T_{onset} is always higher than the actual transition temperature and depends on the scanning rate. It is obvious that at slower scanning rate the onset temperature will be closer to the equilibrium transition temperature T_T .

The time from the temperature of melting onset to the temperature for the maximum of the melting peak can be expressed as [2]:

$$\Delta t_{\max} = RC_s \left\{ \left[1 - \frac{2\Delta h}{RC_s^2 \frac{dT_p}{dt}} \right]^{1/2} - 1 \right\} \quad (5)$$

where Δh is the total heat absorbed by the sample. (For an endothermic process this value is negative.) For a sample of constant size Δt_{\max} is inversely proportional to the square root of the scanning rate. At a higher scanning rate, a lower Δt_{\max} will be obtained.

The temperature difference between the onset temperature and the peak temperature can then be obtained as follows:

$$\Delta T_{\max} = \Delta t_{\max} \frac{dT_p}{dt} \quad (6)$$

From Eq. (4) we know that the measured onset temperature is related to the transition temperature of the sample, sensitivity of the instrument and depends on the scanning rate dT_p/dt ; on the other hand, from Eq. (5) the peak temperature is influenced by the sample size, i.e. the total energy Δh absorbed. The larger the sample, the higher is Δt_{\max} or the more delayed will be the peak temperature (Eq. (6)). For a material with high thermal conductivity, such as a metal sample, R is much smaller than for polymers. Therefore, the slope of the melting peak is steeper than for a polymeric material.

The peak temperature can now be expressed as:

$$T_{\max} = T_{\text{onset}} + \Delta t_{\max} \frac{dT_p}{dt} \quad (7)$$

The Thompson-Gibbs equation describes a relationship between the melting temperature T_m and lamellar thickness of polymer crystal as following:

$$T_m = T^\circ \left[1 - \frac{2\sigma_e}{\Delta hL} \right] \quad (8)$$

where σ_e is the fold surface interfacial free energy, L is the lamellar thickness, T° is the equilibrium melting temperature of the polymer. The T_m can be estimated from a L determination or *vice versa*.

There are several ways to measure L for semicrystalline polymers, such as by electronic microscopy, measuring the melting point of samples with constant crystal morphology, small X-ray scattering, and low frequency Raman-active longitudinal acoustical mode (LAM).

LAM can directly provide the crystallite core thickness and its length distribution from the first order vibration [5–7]. The mode frequency, $\Delta\nu$ (in cm^{-1}) and length, L (in \AA), of the ordered sequence undergoing the vibration are related by the equation:

$$\Delta\nu = \frac{m}{2cL} \left(\frac{E}{P} \right)^{\frac{1}{2}} \quad (9)$$

where m is an odd number and the order of the vibration, c is the speed of light, P is the density of the crystal and E is Young's modulus of the crystal in the chain direction. Young's modulus for polyethylene crystals is known to be ~ 290 GPa [5, 8]. With the well established structural parameters, the LAM frequency-length relationship can be expressed simply as:

$$\Delta\nu = \frac{2827}{L} \text{cm}^{-1} \quad (10)$$

Crystalline thickness, thickness distribution and defects have been interpreted from the central frequency and shape of the LAM bands [9]. From the measured L , T_m can be estimated using Eq. (8).

In the present work, the influence of the measured parameters on the melting temperature in DSC is evaluated. As a check of the DSC measurements, the lamellar thickness of PE was measured both by DSC and Raman LAM.

Experiments

An Indium standard sample from Perkin-Elmer Co. was used in this study. Then the melting behaviour of an as-received series of ultra-high molecular weight polyethylene reactor powders (UHMWPE) from Union Carbide was analyzed. From solution viscosity measurements, the polymer samples were determined to have average molecular weights ranging from 0.96 to 12.4×10^6 . For Raman study, the as-received samples were compression molded into a plate 150 kg cm^{-2} thick at 150 kg cm^{-2} . To preserve the initial morphology of the reactor powder, the temperature used was 110°C , which is 30°C below the melting peak measured by DSC.

Sample melting curves were recorded on a DSC-4 Perkin-Elmer differential scanning calorimeter with nitrogen as a purge gas. The instrument was calibrated with 2.9 mg indium as standard. 156.6°C was used as the melting temperature of indium, calibrating T_{onset} on the DSC curve. An empty sample pan with a lid was used as a reference in all measurements.

Raman spectra were obtained at ambient temperatures using a microprocessor controlled Jobin-Yvon U-1000 laser Raman spectrometer. Excitation is provided by 5145 \AA radiation from a Spectra-Physics model 165-8 argon ion la-

Table 1 Scanning rate influence on indium melting temperature measured by DSC. The sample size is 4.49 mg

Scanning rate/ °C min ⁻¹	T_{melt} / onset °C	T_{melt} / peak °C	ΔT_{max} / °C	Δt_{max} / min
5	156.6	157.3	0.7	0.14
10	157.2	158.1	0.9	0.09
20	158.3	159.5	1.2	0.06
30	159.4	160.8	1.4	0.047
40	160.4	162.1	1.7	0.043

Table 2 Sample size influence on indium melting temperature measured by DSC

Sample weight/ mg	T_{melt} / onset °C	T_{melt} / peak °C	ΔT_{max} / °C	Δt_{max} / min	ΔH / J g ⁻¹	Δh / mJ
2.9	156.5	157.6	1.1	0.055	28.39	81.6
5.2	156.4	157.6	1.2	0.060	28.35	146.5
9.6	156.2	157.9	1.7	0.085	28.92	277.6
21.2	156.2	158.8	2.6	0.130	28.95	613.65
34.4	156.3	159.6	3.3	0.170	28.80	990.75

ser. In most of the Raman experiments, to prevent change in the initial morphology of the samples studied, the effective power of the incident excitation radiation at the sample is at a relatively low value of 100 mW. A 90° scattering geometry was used throughout. For quantitative LAM spectra, the background scattering was subtracted as described elsewhere [10].

Results and discussion

An Indium sample with constant weight of 4.49 mg was run first at a series of heating rates. The results are shown in Table 1. It can be seen that the onset temperature increases from 156.6 to 160.4°C, and the ΔT_{max} increases from 0.7 to 1.7°C when the scanning rate was increased from 5 to 40°C min⁻¹. In comparison with the scanning rate of 5°C min⁻¹, the temperature increments at scanning rate of 40°C min⁻¹ are 3.8 and 4.8°C for T_{onset} and T_{max} , respectively. A test of the influence of sample size on the melting temperature was also carried out at a heating rate of 20°C min⁻¹. The result are shown in Table 2. The onset temperature for 2.9 mg Indium is 156.5°C. Increasing sample weight to 34.4 mg caused this temperature to decrease slightly to 156.3°C, a difference of 0.2°C for a sample weight increase of almost ten times. The peak temperature increased, in contrast, from 157.6 to 159.6°C. These results are inconsistent

with the predictions of Eqs (4) and (5). It has to be noticed that the accuracy for temperature measurement of the Perkin-Elmer DSC-4, as given by the instrument manufacturer, is slightly less than 1°C [11].

Similar results were obtained in the thermal analysis of the UHMWPE samples. Within the same scanning rate the onset temperature is independent of sample size (Table 3). The corresponding peak temperatures are shown in the same table. When sample size was increased from 1.49 to 14.3 mg, by almost 10 times, the onset temperature remains almost unchanged, but the peak tem-

Table 3 Melting temperature of an ultrahigh molecular weight polyethylene measured by DSC

Sample weight/mg	$T_{\text{melting}} / ^{\circ}\text{C}$ (onset)	$T_{\text{melting}} / ^{\circ}\text{C}$ (peak)
1.49	137.5	142.1
4.68	137.5	142.9
6.50	137.4	143.5
9.91	137.2	143.8
14.3	137.1	145.1

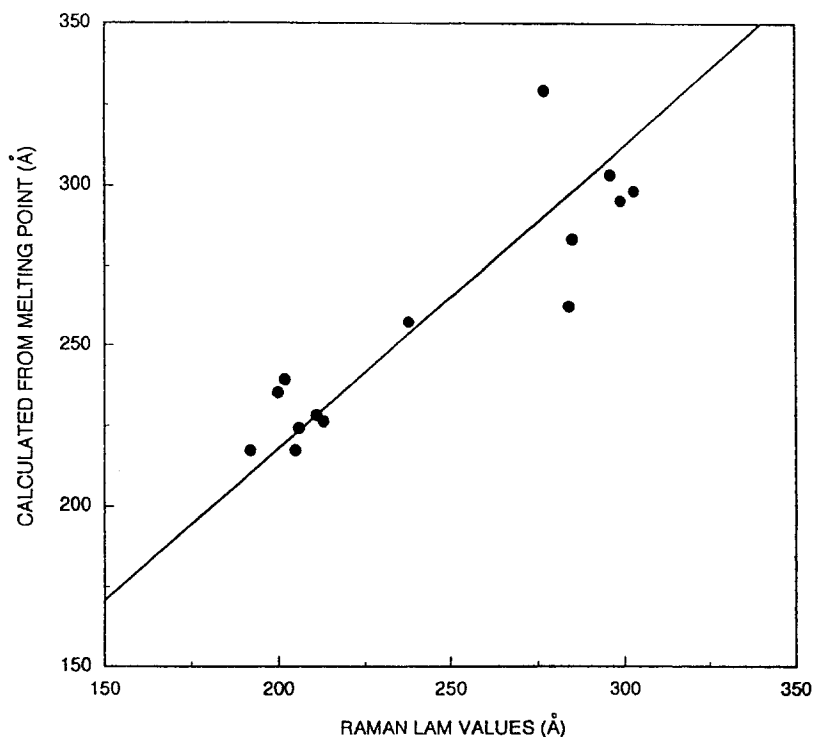


Fig. 1 Lamellar thickness of UHMW polyethylene reactor powders: LAM measurements vs. those calculated from the Thompson-Gibbs equation using DSC data

perature increased by 3.0 from 142.1°C to 145.1°C at a scanning rate of 10°C min⁻¹.

Using the measured T_{onset} , the lamellar thickness of UHMWPE samples was calculated from the Thompson-Gibbs equation. For comparison, these values were plotted together with the values obtained directly from Raman LAM in Fig. 1. Good agreement by the two different methods is observed. Results differ only by about 10%, and only at the lower values from the ideal slope of 1.0. This is remarkable in consideration of the approximations in both analytical methods. In the meantime, it also confirms that the T_{onset} is closer to the actual transition temperature.

Eysel *et al.* studied an 'official' set of temperature standards for DSC and DTA from the International Confederation for Thermal Analysis (ICTA) [12]. It was found that only the onset temperatures were consistent with the equilibrium melting temperatures for the samples provided.

For semicrystalline polymers measured by DSC, the scanning rate is important not only because of the reasons discussed above, but also during heating the poor crystals will rearrange. It is usually necessary to employ rather fast heating.

Wunderlich in his monograph indicated that the onset temperature is most reproducible if there is only a small temperature gradient within the sample and the analyzed peak is inherently sharp [13]. This is the case when a small sample size is used. The peak temperature might only be used as the melting temperature when a broad melting peak is observed.

Conclusions

From the results obtained and the above discussion several conclusions can be drawn:

1. In DSC studies, samples and standards should be run under identical conditions, such as scanning rate, sample size, the flow rate of purge gas.
2. For an accurate melting temperature measurement, a smaller sample is better and the onset temperature for the melting point is a more reasonable choice than the peak temperature as long as the melting peak is steep.
3. For semicrystalline polymer samples a sufficiently fast heating rate should be used to avoid the crystal rearrangement.

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