How Tzero™ Technology Improves DSC Performance
Part V: Reducing Thermal Lag

R. Bruce Cassel
TA Instruments, 109 Lukens Drive, New Castle DE 19720

ABSTRACT

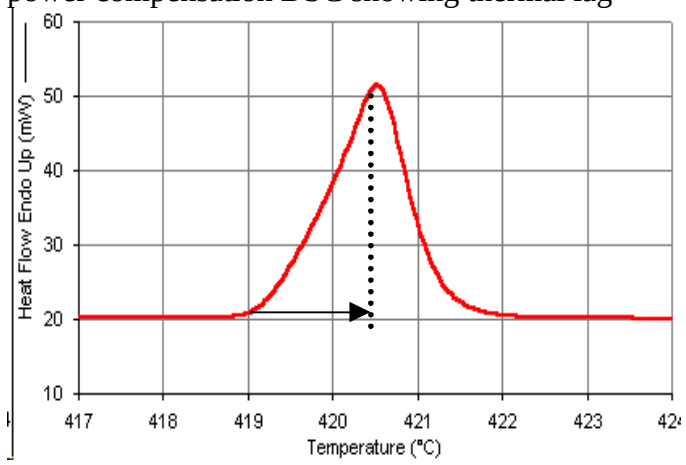
As the furnace of any DSC is temperature programmed, the temperature of the sample lags behind the programmed temperature (and behind the "sample temperature" sensor) because the heat must flow across a barrier to get to the encapsulated sample. The thermal lag is greatest when the thermal demands of the sample are greatest, such as during sample melting. The magnitude of this lag depends on a number of experimental factors, and consequently it is left up to the user to make the correction to the analyzed data through calibration.

With the availability of Advanced Tzero™ Technology from TA Instruments, the introduction of an independent T_0 sensor on the DSC disk (in addition to the sample and reference temperature sensors) provides a tool for calibration of the thermal lag characteristics of both the cell and of the pan encapsulating the sample. As a result, the sample data generated by the Q1000™ DSC contains a compensation for the thermal lag caused by the sample pan and the DSC cell. The reported temperature data is automatically corrected for these thermal lags. This measurably improves the accuracy of reporting peak temperatures for a wide range of applications.

BACKGROUND

The effect of thermal lag in DSC is well known. A DSC does not measure the sample temperature by using a sensor in contact with the sample specimen itself. Rather, the "sample temperature" is measured at a point close to the sample but using a sensor located within the cell disk or sample holder. Because the heat flow to, or from, the encapsulated sample must flow across a thermal gap before it registers on the temperature sensor, a temperature lag develops that

Figure 1 - Melting of 2 mg 99.99 % Zinc metal in a power compensation DSC showing thermal lag

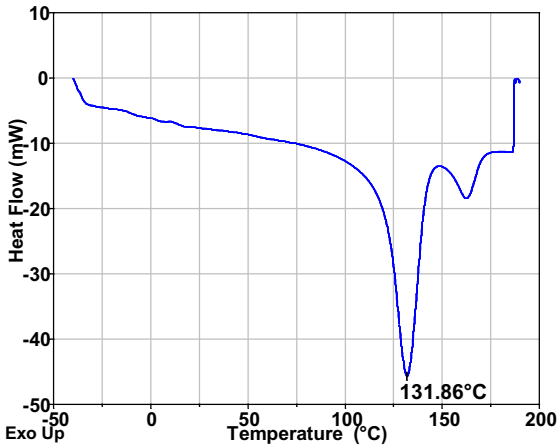


results in an error in the reported temperature. The thermal lag (ΔT_{lag}) is proportional to the dynamic signal, and can be calculated from Newton's Law of Cooling:

$$\Delta T_{lag} = (dq/dt)\, R_0 \qquad \text{(Eq. 1)}$$

where dq/dt is the heat flow displacement from an isothermal baseline, and R_0 is the thermal resistance between the sample and sensor.

Figure 2 - Polyolefin Recyclate Melting without thermal lag correction



The effect can be easily seen from the shape of a melting peak for pure materials used for DSC temperature calibration. For example, figure 1 shows the melting endotherm for zinc as it appears in the "start-up" data for a commercial power compensation DSC. From the X-axis it appears that the sample starts melting at 419 ºC and is not complete until the peak maximum at 420.5 ºC. For such a pure sample, however, the melting occurs over a few hundredths of a Celsius degree. The 420.5 ºC peak temperature demonstrates a 1.5 ºC thermal lag error in the temperature read-out. Fortunately, this thermal lag does not produce any error when one is measuring melting points (or calibrating) since the recorded point is the *onset* of the peak extrapolated to the baseline. In recognition of this fact, the ASTM method for peak determination specifically calls out the extrapolated onset as the melt temperature for pure materials (*1*).

The Problem

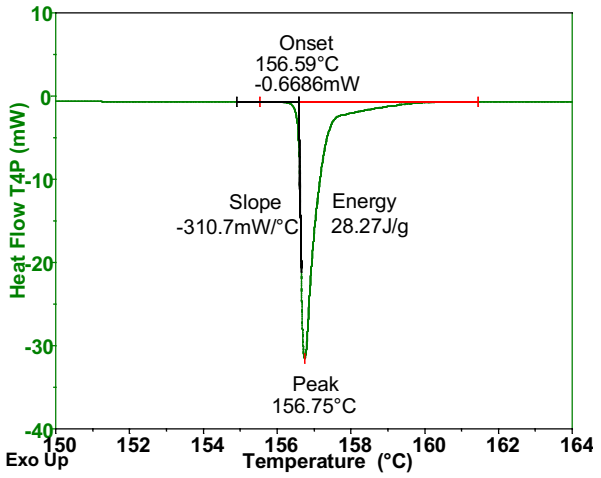
If, however, the temperature being reported is that of the maximum of the melting peak of a polymer, then the temperature of peak *maximum* is the relevant value to be reported. Without correction, the error due to thermal lag can be significant. For example, figure 2 shows the melting of mixed polyolefin recyclate with a melting peak for polyethylene (PE) and polypropylene for a heat flux DSC. The displacement of the PE peak from the isothermal baseline is 46 mW and a typical R_0 is 0.05 ºC/mW, so the thermal lag error in reporting the peak temperature is 2.2 ºC. That is, the actual temperature of the sample at the point of maximum rate of melting is not 131.86 ºC as indicated, but 129.7 ºC. This difference can be significant when qualifying a material for a difficult application or when documenting a material for legal purposes. This error is only constant if the sample sizes, pan types and heating rates are maintained constant.

One Solution

Based on the equation above, one may record the value, make a correction for this effect and enter the corrected data into one's research notebook. By determining the inverse of the leading slope of melting a pure material (such as indium, run under the same conditions as the sample) one calculates R_0. Hence, to correct PE for thermal lag one measures the peak height above the isothermal baseline and multiplies this heat flow value (units of milliwatts) times the R_0 calculated for indium using the same conditions.

Such a correction is typically applied by the data analysis software to DSC heat flow data only when making purity or kinetic measurements (*2*, *3*).

Figure 3. Indium melt using AdvancedTzero Technology: Less than 0.2 °C Thermal Lag



Advanced Tzero Technology, a Better Solution

Thermal lag is corrected in a more fundamental way with the new TA Instrument DSC cell using Advanced Tzero Technology. The new cell does not merely monitor the reference and sample sensor temperature. Additionally, it monitors *the T_0 temperature*, the on-sensor, control-point temperature. During instrument setup, a fundamental calibration is performed on each DSC cell that quantifies its unique thermal characteristics. Then, the thermal lag inherent to that particular DSC cell is measured and addressed. Further, the thermal resistance and capacitance of each pan type as a function of temperature is built into each Q1000 software thus allowing *all* thermal lags to be known and addressed automatically. All that is required of the user, to take advantage of this improved temperature accuracy, is that the sample pan weight and pan type of the sample being run are recorded. Figure 3 shows a sample of indium metal melted in the Q1000 DSC with Advanced Tzero Technology, analyzed and displayed under conditions similar to those used for the zinc sample above. The leading edge of the melt is nearly vertical when viewed on the same scale expansion as the zinc sample above. Notice the small discrepancy (0.016ºC) between the melt onset and the peak maximum, thus showing that the thermal lag has been completely addressed.

Table 1 - Indium by Conventional DSC

Rate	Onset	Max
°C/min	°C	°C
1	156.0	156.3
2	156.1	156.4
5	156.3	156.8
10	156.6	157.2
20	157.2	157.9
30	157.8	158.6

Figure 4 - HDPE melt using Advanced Tzero Technology: Less than 0.2 ºC Thermal Lag

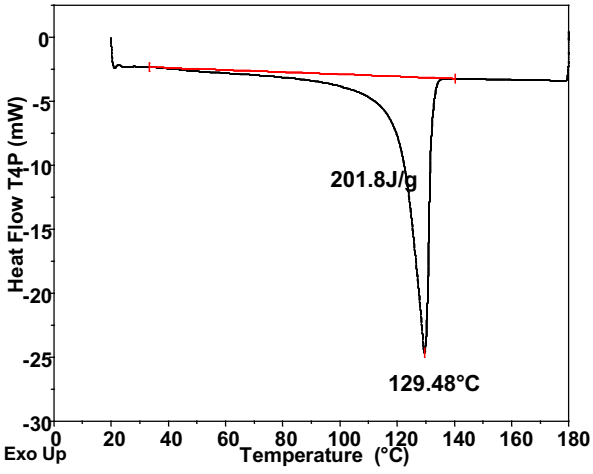


Figure 4 shows a polyethylene sample run in a Q1000 DSC with Advanced Tzero Technology. The thermal lag error for this measurement is 0.14 ºC when calculated using equation 1 and the slope of indium. Clearly, in the Q1000 the thermal lag has been reduced to a negligible level.

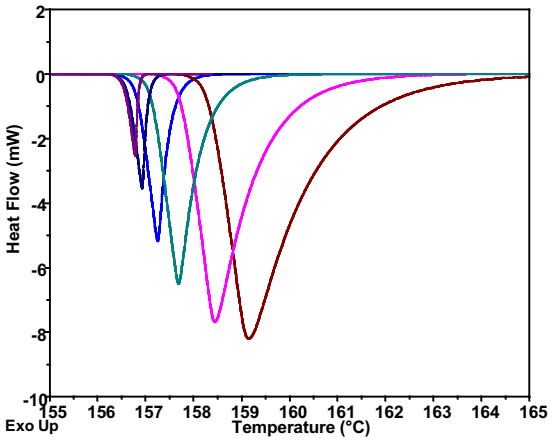
Another potential problem: scanning rate error

Table 2 - Melting Indium at several rates using Advanced Tzero Technology

Rate	Onset	Max
°C/min	°C	°C
20	156.64	156.87
10	156.60	156.78
5	156.59	156.73
2	156.58	156.68
1	156.58	156.65
0.5	156.58	156.63
0.2	156.59	156.63
0.1	156.53	156.57

A DSC is calibrated for temperature by running one or more temperature calibration standards while using the experimental conditions to be used for sample analysis. The apparent melting points of the standards are then used to calibrate the temperature scale of the output data. Because the thermal lag is proportional to the heating rate, calibration is usually performed at the same rate to be used with samples. Otherwise, there can be a temperature offset for all the data that will lead to temperature error in the reporting of calculation results. Figure 5 and table 1 show a sample of indium melted at various heating rates using a conventional DSC approach with no correction for scanning rate offset caused by thermal lag. The table shows that without some sort of correction for this problem, a 0.9 ºC error results by calibrating at 5 ºC/min and running a sample at 20 ºC/min. (Actually, it can be much larger when using other than standard crimped pans for sample encapsulation, and this error is additive to the sample-size dependent error described above.) Some DSCs provide a means to calibrate the scanning rate dependent thermal lag by requiring melting point data at multiple rates. Other DSCs build a partial correction for this effect into the software so that the error is lessened under commonly used DSC running conditions. Not only are the indium melting points (the onset data in table 1) independent of heating rate but the peak maxima are largely compensated for thermal lag as well.

Figure 5 - 1.1 mg Indium melting at various heating rates, showing uncompensated thermal lag in temperature onsets and maxima. (See Table 1.)

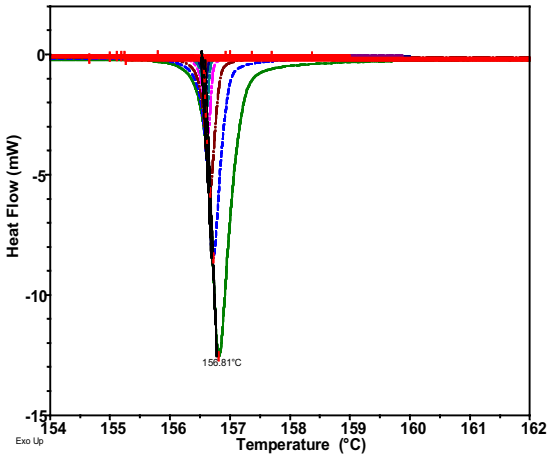


The Q Series DSC takes a different approach. By using the four term generalized heat flow equation (*4*) and calibrating using the Tzero™ signal, this technology allows the thermal characteristics of the DSC cell to be completely defined. As a result, the instrumentally caused thermal lag is largely eliminated. And by using Advanced Tzero Technology, virtually all scanning rate dependent thermal lag are eliminated. Figure 6 and table 2 show how running a sample (here a one milligram indium sample) gives melting temperature onset data that is invariant to heating rates.

When are these corrections most important?

Thermal lag error is proportional to heat flow, heating rate, and to the mass of the sample/pan system. Hence, this error becomes greatest with fast scanning rates, large sample masses, massive sample pans (such as pressure capsules), or sample specimens with especially high heat capacity, such as aqueous solutions. Thermal lag error is also proportional to R_0, so it is made worse by using pans made of poor thermal conductivity or pans making poor thermal contact. However, even in the first polymer example, using optimally coupled aluminum pans the error produced was more than two Celsius degrees. Other samples could be several times larger. Users of traditional DSCs will want to perform the indium test described above to estimate the magnitude of the thermal lag error in peak analyses that should be corrected.

Figure 6 – 1mg Indium at heating rates from 0.1 ºC/min to 20 ºC/min using a Q1000 DSC with Advanced Tzero Technology



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KEYWORDS

differential scanning calorimetry