Modulated DSC® Paper #4
Advanced Tzero™ MDSC®; Calculation of MDSC Signals, Including Phase Lag Correction

Leonard C. Thomas
TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA

ABSTRACT
This paper describes some advanced calculated signals available from MDSC® when applied to the latest Tzero™ Technolgy available in the latest Q Series DSC modules.

INTRODUCTION

An earlier paper, entitled "Modulated DSC; Calculation and Calibration of MDSC Signals" (1), presented a discussion on the basic approach that has been used to calculate MDSC signals since commercialization of the technique in 1992. With introduction of Tzero DSC technology in 2001, an improved approach to calculating MDSC signals was developed. This approach takes advantage of the unique characteristics of Tzero technology, that provides for the separate measurement of heat flow for both the sample and reference sides of the calorimeter (2,3). This ability to make two simultaneous differential measurements is the result of having a third thermocouple as part of the heat flow measuring system. This third thermocouple, called the Tzero thermocouple, is common to the measurement of the independent heat flow for both the sample and reference sides and can be seen in Figure 1, which shows a cross-section of a Tzero DSC cell.

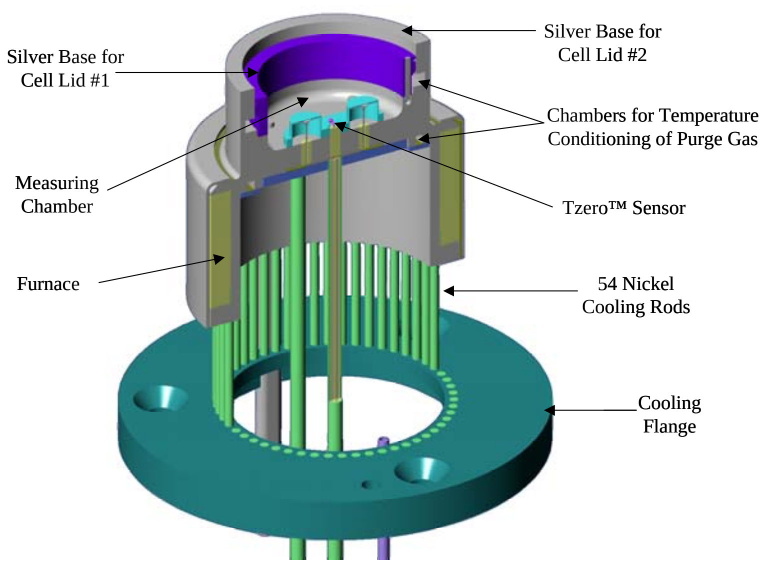


Figure 1

The ability to make two simultaneous differential measurements with Tzero technology permits separate MDSC signals to be calculated for both the sample and reference sides of the calorimeter (3). After the signals are calculated in real-time during the experiment, they are then subtracted to remove the effect of the sample pan and calorimeter on the sample results. This approach provides the following advantages over the traditional MDSC approach that uses a single differential measurement:

- The Reversing Heat Capacity calibration constant is much more stable as the modulation period is changed (4).
- The Total and Nonreversing signals have significantly improved baselines (reduced slope and curvature)
- Any difference in mass between the sample and reference pans is automatically corrected (requires user to enter pan masses into control software)
- The Phase Lag (between temperature and heat flow) correction is improved due to elimination of the effect of changes in phase between the sample and reference calorimeters

This paper will provide a brief introduction to some of the basic mathematics used by Tzero technology, but will primarily focus on the process of calculating MDSC signals including Phase Lag correction. A more complete mathematical description of Tzero DSC and MDSC signals is provided in previous published papers (2,3).

Tzero™ DSC TECHNOLOGY

Differential Scanning Calorimetry (DSC) measures the differential heat flow between the sample and reference sides of the calorimeter. Although there are differences in the DSC design, all traditional (pre-Tzero) DSC instruments <u>measure</u> the difference in temperature between the sample and reference sensors in order to <u>calculate</u> the difference in heat flow. This differential heat flow is typically plotted versus sample sensor temperature as measured with either a thermocouple, thermopile, or platinum resistance thermometer. The key point is that traditional DSC's measure only one differential temperature and one absolute temperature. With this approach, it is necessary to make numerous assumptions about the measuring system, including:

- mass (mg.) of sample sensor = mass of reference sensor
- heat capacity (J/g°C) of sample sensor = heat capacity of reference sensor
- thickness of sample sensor = thickness of reference sensor
- thermal resistance (°C/W) of sample sensor = thermal resistance of reference sensor
- mass of sample pan = mass of reference pan
- no crosstalk between the sensors

Tzero DSC technology eliminates the need for these assumptions because the thermal capacitance (heat capacity or mass) and thermal resistance of the individual sample and reference sensors are measured as a function of temperature using the dual differential measurement capability of Tzero technology and the values are included in determining heat flow as per the equation shown below. The result is a more accurate determination of heat flow associated with the sample.

$$dH/dt = -\frac{\Delta T}{R_r} + \Delta T_0 \left(\frac{1}{R_s} - \frac{1}{R_r} \right) + (C_r - C_s)\frac{dT_s}{d\tau} - C_r \frac{d\Delta T}{d\tau}$$

where:

dH/dt = differential heat flow rate (mW, mJ/s, W/g etc.)

ΔT = temperature difference between the sample and reference sensors

ΔTo = temperature difference between sample sensor and Tzero thermocouple

Rr = thermal resistance (°C/W) of reference sensor

Rs = thermal resistance of sample sensor

Cr = heat capacitance (J/g°C) of reference sensor

Cs = heat capacitance of sample sensor

dTs/dt = heating rate of sample sensor

dΔT/dt = difference in sample and reference sensor heating rates

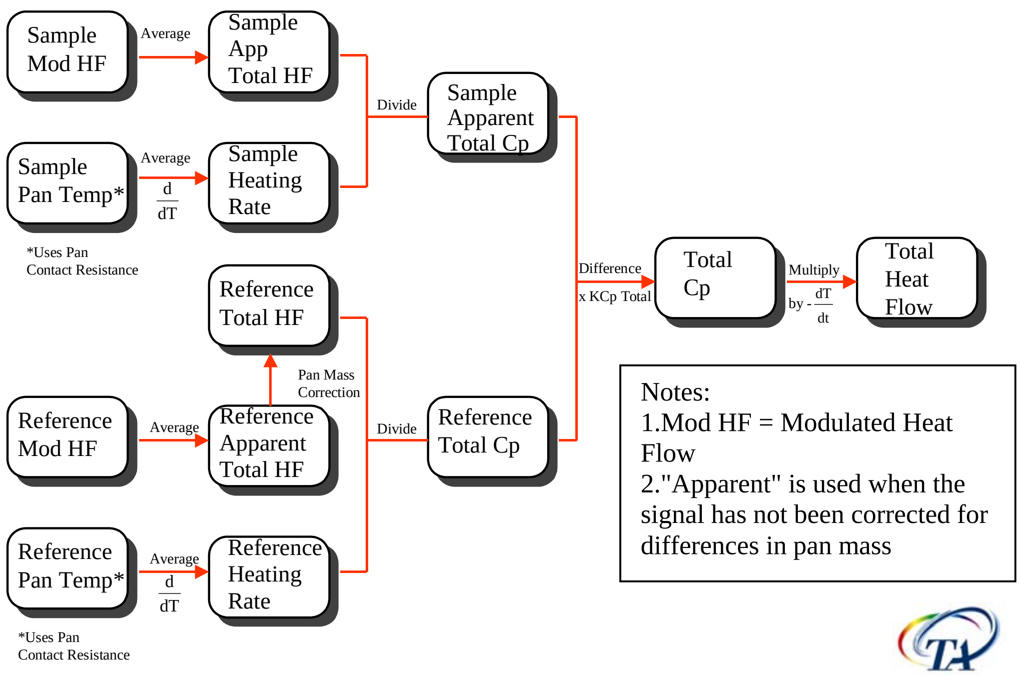
The above heat flow equation is often described as the " Four Term" heat flow equation because there are four specific components. The function of each of the components is as follows:

$-\frac{\Delta T}{R_r}$	Principal DSC Heat Flow Term
$\Delta T_0 \left(\frac{1}{R_s} - \frac{1}{R_r} \right)$	Thermal Resistance Imbalance Term
$(C_r - C_s)\frac{dT_s}{d\tau}$	Thermal Capacitance Imbalance Term
$-C_r \frac{d\Delta T}{d\tau}$	Heating Rate Difference Term

Tzero MDSC SIGNALS

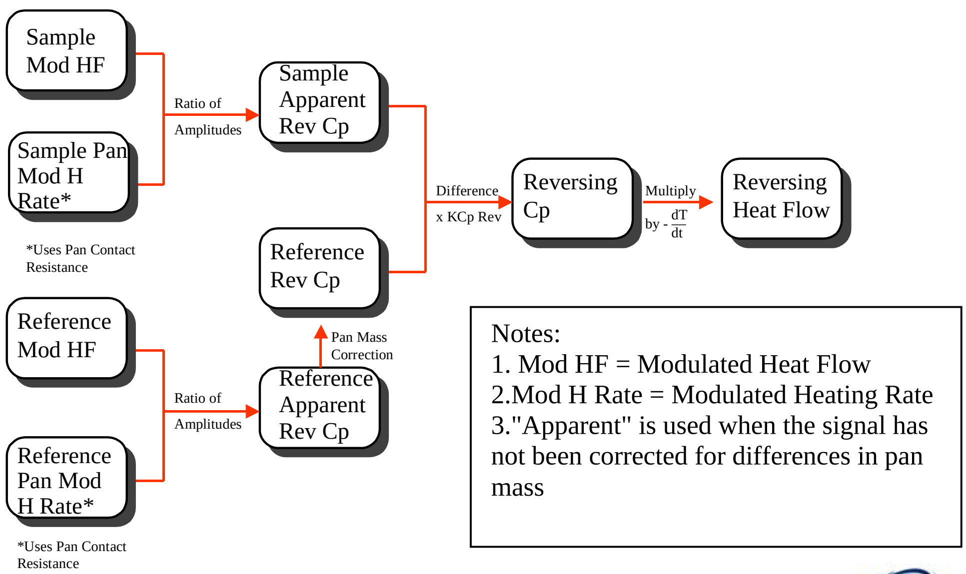
The above equation is used to calculate the DSC heat flow from Tzero technology. This equation is not used in the calculation of MDSC Tzero signals. Instead, the modulated heat flow and modulated temperature for the sample and reference sides of the calorimeter are measured independently. Once these signals are obtained, the amplitudes, average values, and phase angle between temperature and heat flow can be obtained for each. The Total, Reversing and Nonreversing signals are then calculated independently for the sample and reference sides of the calorimeter using the approach described in a previous paper in this series entitled “Calculation and Calibration of MDSC Signals” (1). After the sample and reference signals are calculated for each side of the calorimeter, they are then subtracted to obtain the heat flow due to just the sample. This process is illustrated in the flow diagrams of Figures 2 and 3.

Figure 2; Calculation of Tzero MDSC Total Heat Flow and Total Heat Capacity Signals



Brief descriptions are required about two minor points identified in both figures. The first is the comment "Uses Pan Contact Resistance". This refers to the fact that with the model Q1000 Tzero DSC, sample pan temperature is calculated using the measured sensor temperature and the physical characteristics (mass, thermal conductivity and shape) of the pan. The Q100, and older generation DSC instruments, use just the measured sensor temperature. The second comment, "Pan Mass Correction", refers to the fact that with the advanced Q1000 DSC, a difference in mass between the sample and reference pans is automatically corrected-for in the calculation of all final signals. The DSC software determines these adjustments for pan contact resistance and for mass correction once the operator enters the pan weights and the pan type prior to the experiment.

Figure 3; Calculation of Tzero MDSC Reversing Heat Capacity and Reversing Heat Flow Signals



Once the Total and Reversing signals are calculated from the measured Modulated Heat Flow and Modulated Heating Rate signals, the Nonreversing signal is calculated by subtracting the Reversing from the Total.

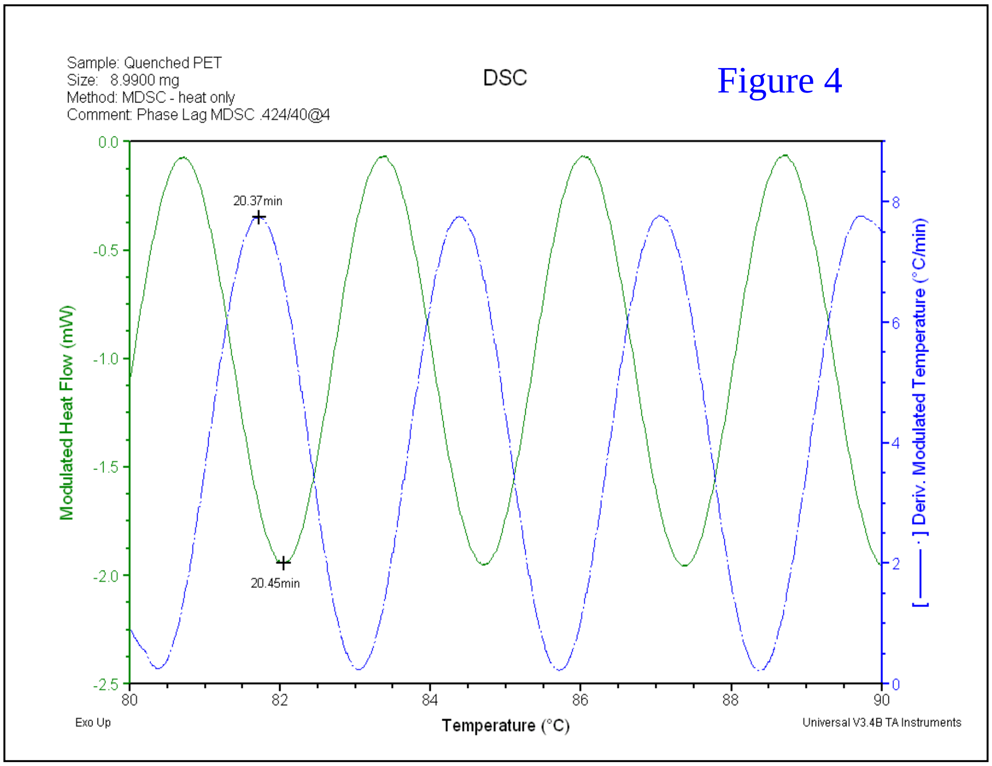
Nonreversing = Total - Reversing

PHASE LAG AND PHASE LAG CORRECTION

Phase Lag Correction has no known practical value in the measurement of transitions. However, it may be of academic interest in order to better understand the time dependence of molecular processes.

What is phase lag?

The term refers to the fact that there is a lag or time delay in the heat flow signal as compared to the heating rate. It is of possible interest because all signals are calculated over one cycle from either the average value or amplitude of two (heat flow and temperature) sinusoidal waveforms using discrete Fourier transform (DFT). Figure 4 shows the sinusoidal heat flow and heating rate signals and also reveals that there is a phase lag (20.45 - 20.37 = 0.08min) between them. That is, the maximum and minimum values for the two signals do not occur at the same time.



Because a sample absorbs and releases heat during endothermic and exothermic transitions, there can be a change in the lag between the two signals during such transitions. Since the DFT calculation occurs over a one-cycle moving average, a change in lag (phase) between the two signals can slightly affect the shape of the transition. From a practical perspective, this is of minimal importance since other MDSC experimental conditions (amplitude, period, and average heating rate) can also slightly affect the shape. In addition, sample size and heating rate also affect the shape of transitions in DSC experiments. As has been stated many times, it is important to use the same experimental conditions when comparing samples.

What is phase lag correction?

Phase lag correction is the process of correcting the shape of the transition based on the change in lag (delay time) between the two sinusoidal signals. Since this is of largely academic interest, this paper will describe the process of performing the phase lag correction and let the reader to decide on the value for his / her own application

How is phase lag correction performed?

Firstly, the analyst selects the signals of interest plus the Heat Flow Phase signal as shown in Figures 5 and 6. Note that the value of the In-Phase Heat Flow signal in Figure 6 is zero. Since it is a signal that exists only after phase correction, along with all signals listed below "Base Purge Flow" in Figure 5, its value will remain zero until the phase correction is done.

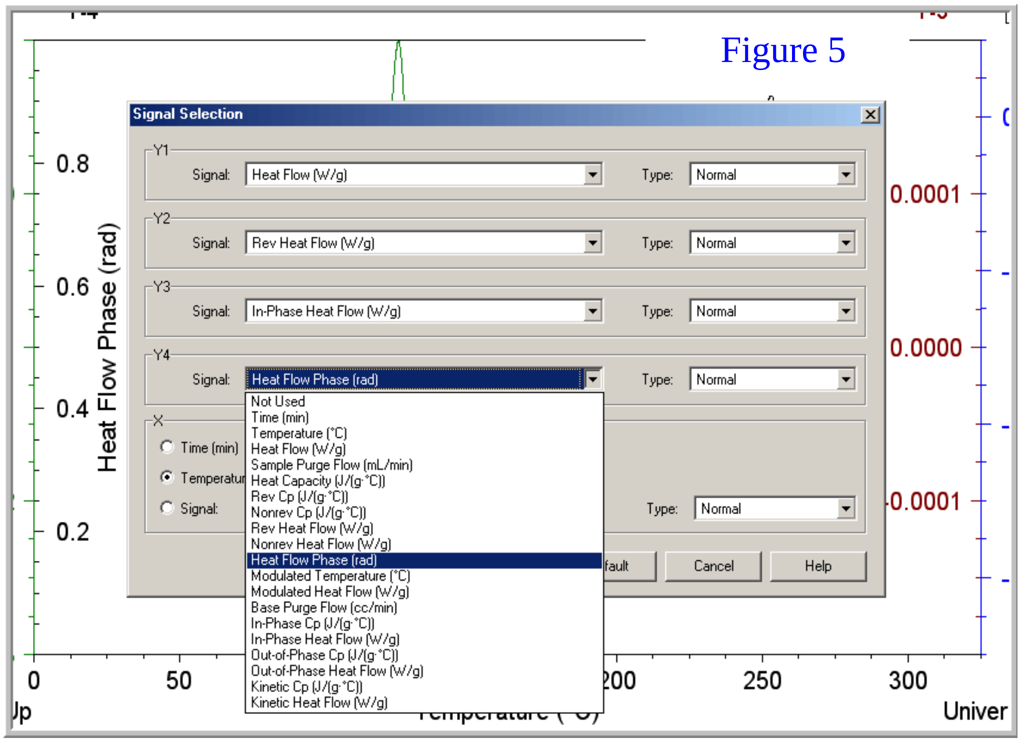


Figure 5

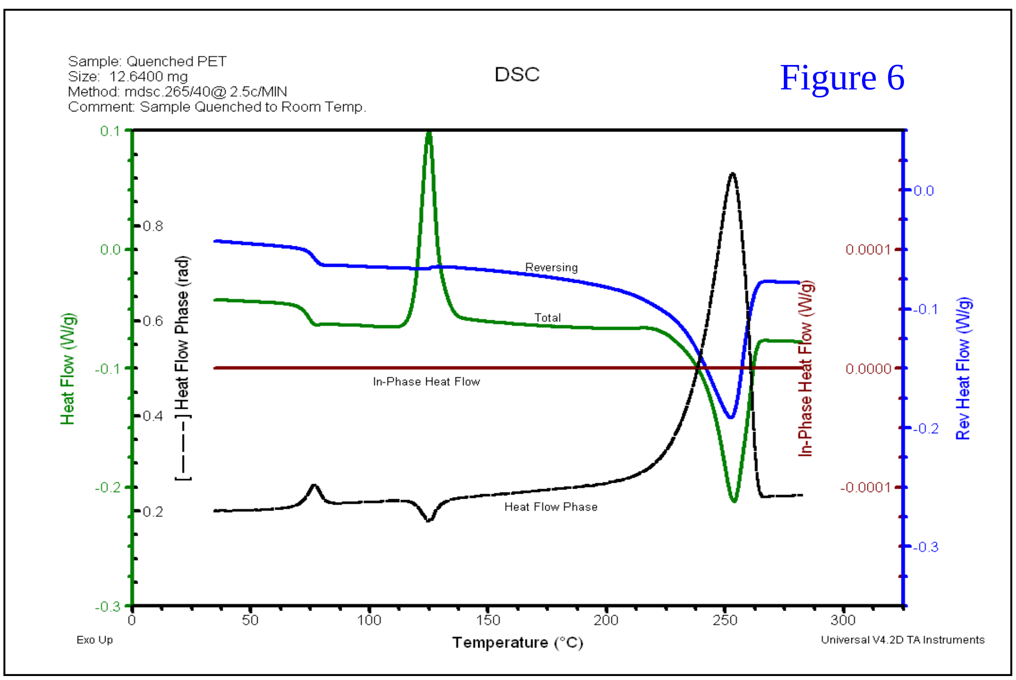


Figure 6

Secondly, once the plot of the desired signals is obtained, phase correction is performed using options (Graph - Instrument Parameters - Temperature Limits) in the Thermal Advantage software as shown in Figures 7 and 8. The analyst should select two temperatures, one below and one above the temperature range of interest, where there is no transition occurring. The software will then shift the Heat Flow Phase signal to values of zero at those two temperatures and perform phase lag adjustment using the corrected value of the Heat Flow Phase signal as shown in Figure 9. All of the phase-corrected signals are now available, including the plotted In-Phase Heat Flow signal.

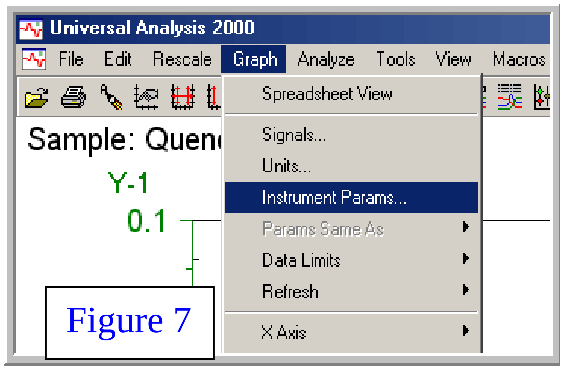


Figure 7

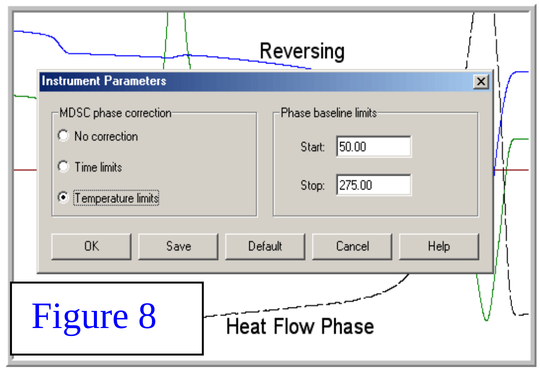


Figure 8

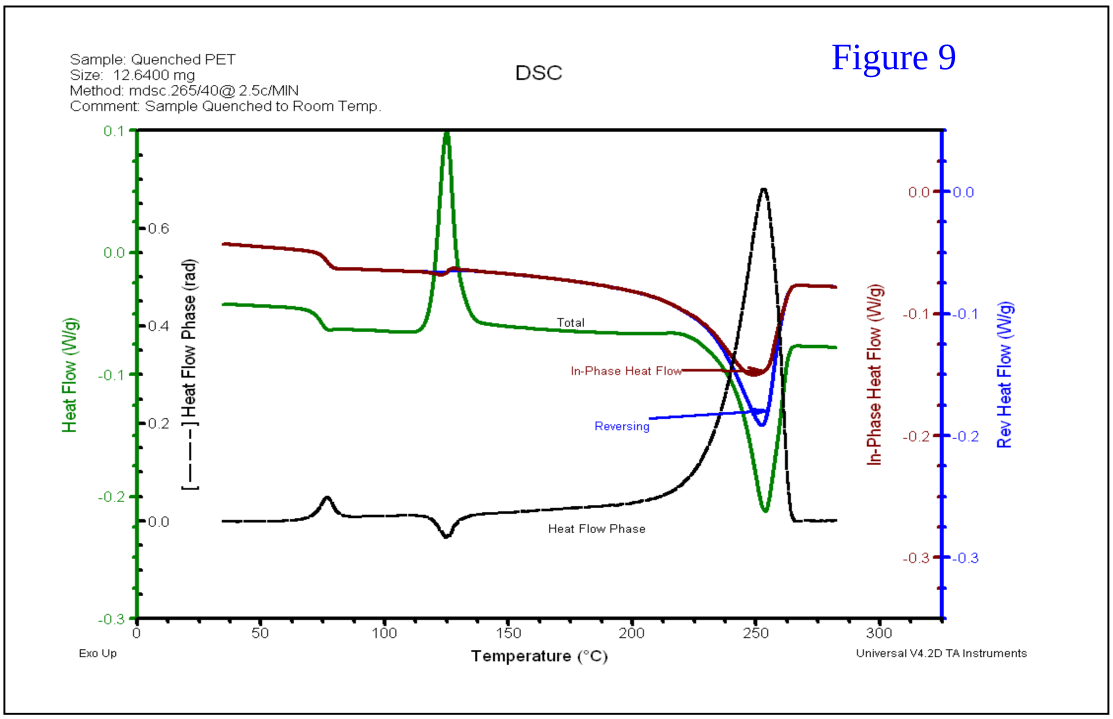


Figure 9

Note that phase-lag correction does not influence the Total signal and only affects the Reversing signal in the middle of the melting range. This minor deviation on the area of the melting peak in the Reversing signal has no effect on the measurement of Initial Crystallinity for reasons that will be further discussed in a subsequent paper entitled "Measurement of Initial Crystallinity in Semi-crystalline Polymers *(4).*

SUMMARY

Tzero DSC technology permits a more accurate measurement of phase lag between the heating rate and heat flow rate signals. During transitions in a material, heat absorbed or released by the sample causes a change in the phase lag that can have a slight affect on the calculated signals, especially in the melting region. Phase correction of the signals can be performed but the affect on most transitions is not significant and phase correction is seldom done. Although not discussed here, some researchers have shown that the Heat Flow Phase signal, which changes during transitions in materials, provides additional information or sensitivity in analyzing some transitions.

REFERENCES

1. Modulated DSC; Calculation and Calibration of MDSC Signals; TA Instruments Technical Paper TP 007.
2. New heat flux DSC measurement technique, Robert L. Danley, Thermochemica Acta 395 (2003) 201-208.
3. New modulated DSC measurement technique, Robert L. Danley, Thermochemica Acta 402 (2003) 91-98.
4. Modulated DSC; Optimization of MDSC® Experimental Conditions; TA Instruments Technical Paper TP 008.

KEY WORDS

modulated dsc, mdsc, tzero, phase lag,

TA INSTRUMENTS

United States, 109 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • Fax: 1-302-427-4001
E-mail: info@tainstruments.com

Spain • Phone: 34-93-600-9300 • Fax: 34-93-325-9896 • E-mail: spain@tainstruments.com

United Kingdom • Phone: 44-1-293-658900 • Fax: 44-1-293-658901 • E-mail: uk@tainstruments.com

Belgium/Luxembourg • Phone: 32-2-706-0080 • Fax: 32-2-706-0081
E-mail: belgium@tainstruments.com

Netherlands • Phone: 31-76-508-7270 • Fax: 31-76-508-7280
E-mail: netherlands@tainstruments.com

Germany • Phone: 49-6023-9647-0 • Fax: 49-6023-96477-7 • E-mail: germany@tainstruments.com

France • Phone: 33-1-304-89460 • Fax: 33-1-304-89451 • E-mail: france@tainstruments.com

Italy • Phone: 39-02-27421-283 • Fax: 39-02-2501-827 • E-mail: italia@tainstruments.com

Sweden/Norway • Phone: 46-8-594-69-200 • Fax: 46-8-594-69-209
E-mail: sweden@tainstruments.com

Japan • Phone: 813 5479 8418 • Fax: 813 5479 7488 • E-mail: nurayama@taij.po-jp.com

Australia • Phone: 613 9553 0813 • Fax: 61 3 9553 0813 • E-mail: steve_shamis@waters.com

To contact your local TA Instruments representative visit our website at www.tainst.com