# MODULATED DSC<sup>®</sup> (MDSC<sup>®</sup>): HOW DOES IT WORK?

#### **BACKGROUND**

Differential scanning calorimetry (DSC) is a thermal analysis technique which has been used for more than two decades to measure the temperatures and heat flows associated with transitions in materials as a function of time and temperature. Such measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. DSC is the most widely used thermal analysis technique with applicability to polymers and organic materials, as well as various inorganic materials.

DSC has many advantages which contribute to its widespread usage, including fast analysis time (usually less than 30 minutes), easy sample preparation, applicability to both solids and liquids, wide temperature range, and excellent quantitative capability. On the other hand, DSC does have some limitations. In order of importance these limitations are:

#### • The ability to properly analyze complex transitions

Many transitions are complex because they involve multiple processes. Examples include the enthalpic relaxation that occurs at the glass transition, and the crystallization of amorphous or metastable crystalline structures prior to or during melting. Enthalpic relaxation is an endothermic process that can vary in magnitude depending on the thermal history of the material. Under some circumstances, it can make the glass transition appear to be a melting transition. Simultaneous crystallization and melting make it nearly impossible to determine the real crystallinity of the sample prior to the DSC experiment. These problems are compounded further when analyzing blends of materials.

Conventional DSC does not allow these complex transitions to be properly analyzed since conventional DSC measures only the sum of all thermal events in the sample. Hence, when multiple transitions occur in the same temperature range, results are often confusing and misinterpreted.

#### • The presence of sufficient sensitivity

The ability of DSC to detect weak transitions is dependent on both short-term (seconds) noise in the heat flow signal and long-term (minutes) variations in the shape of the heat flow baseline. However, since short-term noise can be effectively eliminated by signal averaging, the real limitation for reproducibly detecting weak transitions is variation in baseline rectilinearity. Because of the need to use different materials in the construction of DSC cells and because of changes in the properties of these materials and the purge gas with temperature, all commercial DSC instruments have varying degrees of baseline drift and related effects.

#### • The presence of adequate resolution

High resolution, or the ability to separate transitions that are only a few degrees apart, requires the use of small samples and low heating rates. However, the size of the heat flow signal decreases with reduced sample size and heating rate. This means that any improvement in resolution results in a reduction in sensitivity and vice versa. Conventional DSC results are always a compromise between sensitivity and resolution.

#### • The need for complex experiments

Some DSC measurements such as heat capacity and thermal conductivity require multiple experiments or modifications to the standard DSC cell which increase the opportunity for error as well as the experimental time. Hence, they are not commonly made by the average user.

Modulated DSC<sup>™</sup> (MDSC<sup>®</sup>) is a new technique which provides not only the same information as conventional DSC, but also provides unique information not available from conventional DSC by overcoming most of the limitations of conventional DSC. The result is an exciting new way to significantly increase the basic understanding of material properties.

#### **THEORY**

The theory supporting modulated DSC can be easily understood by comparing it to conventional DSC. In conventional DSC, the difference in heat flow between a sample and an inert reference is measured as a function of time and temperature as both the sample and reference are subjected to a controlled environment of time, temperature, and pressure. The most common instrument design for making those DSC measurements is the heat flux design shown in Figure 1. In this design, a metallic disk (made of constantan alloy) is the primary means of heat transfer to and from the sample and reference. The sample, contained in a metal pan, and the reference (an empty pan) sit on raised platforms formed in the constantan disc. As heat is transferred through the disc, the differential heat flow to the sample and reference is measured by area thermocouples formed by the junction of the constantan disc and CHROMEL<sup>®</sup>\* wafers which cover the underside of the platforms. These thermocouples are connected in series and measure

the differential heat flow using the thermal equivalent of Ohm's Law,  $\frac{dQ}{dt} = \frac{\Delta T}{R_D}$ , where  $\frac{dQ}{dt}$  = heat flow,  $\Delta T$  = the temperature difference between reference

and sample and  $R_D$  = the thermal resistance of the constantan disc. CHROMEL<sup>®\*</sup> and ALUMEL<sup>®\*</sup> wires attached to the CHROMEL<sup>®\*</sup> wafers form thermocouples which directly measure sample temperature. Purge gas is admitted to the sample chamber through an orifice in the heating block before entering the sample chamber. The result is a uniform, stable thermal environment which assures better baseline flatness and sensitivity (signal-to-noise) than alternative DSC designs. In conventional DSC, the temperature regime seen by the sample and reference is linear heating or cooling at rates from as fast as 100°C/minute to rates as slow as 0°C/minute (isothermal).



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Modulated DSC is a technique which also measures the difference in heat flow between a sample and an inert reference as a function of time and temperature. In addition, the same "heat flux" cell design is used. However, in MDSC a different heating profile (temperature regime) is applied to the sample and reference. Specifically, a sinusoidal modulation (oscillation) is overlaid on the conventional linear heating or cooling ramp to yield a profile in which the average sample temperature continuously changes with time but not in a linear fashion. The solid line in Figure 2 shows the profile for a MDSC heating experiment. The net effect of imposing this more complex heating profile on the sample is the same as if two experiments were run simultaneously on the material - one experiment at the traditional linear (average) heating rate [dashed line in Figure 2] and one at a sinusoidal (instantaneous) heating rate [dashed-dot line in Figure 2]. The actual rates for these two simultaneous experiments is dependent on three operator-selectable variables:

- Underlying heating rate (range 0-100°C/minute)
- Period of modulation (range 10-100 seconds)
- Temperature amplitude of modulation (range  $\pm 0.01 10^{\circ}$ C)

(Note: The ranges shown here for these variables are the settable ranges. Not all values in the range produce acceptable MDSC results. See the section on *Optimization of Results* in Modulated DSC Compendium TA-210 for recommendations on the actual values to choose depending on the measurement of interest.)

In the example shown in Figure 2, the underlying heating rate is  $1^{\circ}$ C/minute, the modulation period is 30 seconds, and the modulation amplitude is $\pm 1^{\circ}$ C. This set of conditions results in a sinusoidal heating profile where the instantaneous heating rate varies between +13.44°C/minute and -11.54°C/minute (i.e., cooling occurs during a portion of the modulation). Although the actual sample temperature changes in a sinusoidal fashion during this process (Figure 3), the analyzed signals are ultimately plotted versus the linear average temperature which is calculated from the average value as measured by the sample thermocouple (essentially the dashed line in Figure 2). [Note: As in conventional DSC, MDSC can also be run in a cooling or isothermal mode rather than heating mode.]



The general equation which describes the resultant heat flow at any point in a DSC or MDSC experiment is:

$$\frac{dQ}{dt} = C_p \beta + f(T,t)$$
[1]

where:  $\begin{array}{ll} \frac{dQ}{dt} &= total \ heat \ flow \\ Cp &= heat \ capacity \\ \beta &= heating \ rate \\ f(T,t) &= heat \ flow \ from \ kinetic \ (absolute \ temperature \ and \\ time \ dependent) \ processes \end{array}$ 

As can be seen from the equation, the total heat flow  $(\frac{dQ}{dt})$ , which is the only heat flow measured by conventional DSC, is composed of two components. One component is a function of the sample's heat capacity and rate of temperature change, and the other is a function of absolute temperature and time.

Modulated DSC determines the total, as well as these two individual heat flow components, to provide increased understanding of complex transitions in materials. MDSC is able to do this based on the two heating rates seen by the material - the average heating rate which provides total heat flow information and the sinusoidal heating rate which provides heat capacity information from the heat flow that responds to the rate of temperature change.

These individual heat flow components are often referred to by different names. In the remainder of this document the terms "heat capacity component"  $[Cp\beta]$  and "reversing heat flow" will be used interchangeably. Likewise, "kinetic component" [f(T,t)] and "nonreversing heat flow" will be used interchangeably.



All of these MDSC heat flow signals are calculated from three measured signals - time, modulated heat flow, and modulated heating rate (the derivative of modulated temperature). Figure 3 shows the the latter two signals for amorphous polyethyleneterephthalate (PET). Since these raw signals are visually complex, they need to be deconvoluted to obtain the more standard DSC heat flow curves. The following sections describe that process using quenched PET as the example material. (Note: Although deconvolution is required to obtain the final quantitative results provided by MDSC, the raw signals, particularly the modulated heat flow, can still be used to obtain valuable insights as to what is occurring in the material, as well as to troubleshoot experimental conditions and to detect artifacts. Hence, it is generally recommended that the raw modulated heat flow and modulated heating rate signals be stored as part of the MDSC data file.)

# **Heat Capacity**

The heat capacity (Cp) of the sample is continuously determined by dividing the modulated heat flow amplitude by the modulated heating rate amplitude. This approach is based on the well-accepted procedures for determining Cp in conventional DSC. In conventional DSC, Cp is generally calculated (equation [2]) from the difference in heat flow between a blank (empty pan) run and a sample run under identical conditions. Curves 1 and 2 in Figure 4 show typical curves for sapphire.

$$Cp = K_{Cp} x \frac{\text{Heat Flow (Sample) - Heat Flow (Blank)}}{\text{Heating Rate}}$$
[2]

where  $K_{Cp}$  = calibration constant

Cp can also be calculated, however, by comparing the difference in heat flow between two runs on an identical sample at two different heating rates. Curve 3 in Figure 4 represents the same sapphire sample as curve 2 run at a higher heating rate. In this case:

$$Cp = K_{Cp} x \frac{\text{Heat Flow at Heat Rate 2 - Heat Flow at Heat Rate 1}}{\text{Heating Rate 2 - Heating Rate 1}}$$
[3]



In MDSC, the heating rate changes during the modulation cycle. In Figure 5, the MDSC conditions are chosen so that the modulated heating rate varies between two heating rates which are essentially the same as those chosen for curves 2 and 3 in Figure 4 (i.e., approximately 3 and 6°C/minute). Overlaying the resultant modulated heat flow curve from Figure 5 on curves 2 and 3 from Figure 4, shows (Figure 6) that taking the difference in modulated heat flow and dividing it by the difference in modulated heating rate is equivalent to the conventional DSC approach using two different heating rates and equation [3]. [Note: The heat capacity signal is actually calculated in modulated DSC based on a Discrete Fourier Transformation where the measured amplitudes of the sample temperature and heat flow modulation are compared to a reference sine wave of the same frequency. The equation used is:

$$Cp = K_{Cp} (Q_{amp}/T_{amp}) (Modulation Period/2\pi)$$
[4]

where:

For a complete description of the Discreet Fourier Transformation technique, see Press, W.H.; Flannetry, B.P.; Teukolsky, S.A.; and Vetterling, W.T., *Numerical Recipes, the Art of Scientific Computing*, 1986, Cambridge University Press, Cambridge, pp. 386-390.]

## **Reversing Heat Flow**

The heat capacity (reversing) component of total heat flow is calculated by converting the measured heat capacity into heat flow using equation [1] where  $\beta$  is the average (underlying) heating rate used in the experiment. [Note: -Cp is used in the actual calculation so that endotherms and exotherms occur in the proper downward and upward directions respectively. See Figure 7.]

Reversing Heat Flow = (-Cp) x Average Heating Rate











## **Total Heat Flow**

The total heat flow in MDSC is continuously calculated as the moving average of the raw modulated heat flow signal (Figure 8). [Note: As Figure 8 shows, the raw modulated heat flow is not corrected for real-time for temperature by the current TA Instruments MDSC software and, hence transitions appear to occur lower in temperature in this raw signal than in the calculated signals. This difference is a result of the time delay associated with "real-time" deconvolution (about 1.5 cycles).]

## **Nonreversing Heat Flow**

The kinetic (nonreversing) component of the total heat flow is determined as the arithmetic difference between the total heat flow and the heat capacity component. Figure 9 shows the three heat flows for quenched PET.

Nonreversing Heat Flow = Total Heat Flow - Reversing Heat Flow [6]