MODULATED DSC™ COMPRENDIUM

Basic Theory & Experimental Considerations
**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™ (MDSC™) 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 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, \( \frac{\text{d}Q}{\text{d}t} = \frac{\Delta T}{R_D} \), where \( \frac{\text{d}Q}{\text{d}t} \) = heat flow, \( \Delta T \) = the temperature difference between reference and sample and \( R_D \) = the thermal resistance of the constantan disc. Chromel and alunel wires attached to the chromel 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°/minute to rates as slow as 0°C/minute (isothermal).
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 ±0.01-10°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°C/minute, the modulation period is 30 seconds, and the modulation amplitude is ±1°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:

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

where:
- \( \frac{dQ}{dt} \) = total heat flow
- \( C_p \) = heat capacity
- \( \beta \) = heating rate
- \( f(T,t) \) = heat flow from kinetic (absolute temperature and time dependent) processes

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” \([C_p\beta]\) and “reversing heat flow” will be used interchangeably. Likewise, “kinetic component” \([f(T,t)]\) and “nonreversing heat flow” will be used interchangeably.

![Figure 3. MDSC RAW SIGNALS - QUENCHED PET](image-url)
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 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.

\[
C_p = K_{C_p} \frac{\text{Heat Flow (Sample)} - \text{Heat Flow (Blank)}}{\text{Heating Rate}}
\]

where \( K_{C_p} \) = 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:

\[
C_p = K_{C_p} \frac{\text{Heat Flow at Heat Rate 2} - \text{Heat Flow at Heat Rate 1}}{\text{Heating Rate 2} - \text{Heating Rate 1}}
\]

![Figure 4. SAPPHIRE Cp MEASUREMENT - CONVENTIONAL DSC](image-url)

- Empty Pans
- Sapphire @ 3°C/min
- Sapphire @ 6°C/min

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Heat Flow (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.00°C</td>
<td>-0.01200mW</td>
</tr>
<tr>
<td>50.00°C</td>
<td>-0.6158mW</td>
</tr>
<tr>
<td>50.00°C</td>
<td>-1.169mW</td>
</tr>
</tbody>
</table>

17.35 mg sample helium purge

50.00°C -0.1200mW
Delta 0.60mW

50.00°C -0.6158mW
Delta 1.16mW

50.00°C -1.169mW

(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.)
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:

\[ C_p = K_{Cp} \left( \frac{Q_{amp}}{T_{amp}} \right) \frac{(\text{Modulation Period}/2\pi)}{\pi} \]  

where:

- \( C_p \) = heat capacity
- \( K_{Cp} \) = heat capacity calibration constant
- \( Q_{amp} \) = heat flow amplitude
- \( T_{amp} \) = temperature amplitude


**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: \(-C_p\) is used in the actual calculation so that endotherms and exotherms occur in the proper downward and upward directions respectively. See Figure 7.]

\[ \text{Reversing Heat Flow} = (-C_p) \times \text{Average Heating Rate} \]  

**Figure 5. SAPPHIRE Cp MEASUREMENT - MDSC**

```
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Modulated Heat Flow (mW)</th>
<th>Modulated Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-1.5</td>
<td>5.932°C/min</td>
</tr>
<tr>
<td>20</td>
<td>-1.0</td>
<td>3.152°C/min</td>
</tr>
<tr>
<td>30</td>
<td>-0.5</td>
<td>-0.6495mW</td>
</tr>
<tr>
<td>40</td>
<td>0.0</td>
<td>-1.132mW</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>4.5°C/minute heating rate, ±0.4°C amplitude, 100 second period</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
```

17.35 mg sample
helium purge
4.5°C/minute heating rate, ±0.4°C amplitude, 100 second period
Figure 6. DSC & MDSC Cp MEASUREMENTS (SAPPHIRE)

Standard DSC Cp Measurement

Modulated Heat Flow used for Cp Measurement

Figure 7. REVERSING HEAT FLOW (QUENCHED PET)

HEAT CAPACITY

REVERSING HEAT FLOW

5.5 mg sample
helium purge
2°C/minute heating rate, ± 1°C amplitude, 100 second period
Figure 8. TOTAL HEAT FLOW (QUENCHED PET)

5.5 mg sample
helium purge
2°C/minute heating rate, ±1°C amplitude, 100 second period

Figure 9. ALL HEAT FLOW SIGNALS - QUENCHED PET

5.5 mg sample
helium purge
2°C/minute rate
±1°C amplitude
100 second period
**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.

\[
\text{Nonreversing Heat Flow} = \text{Total Heat Flow} - \text{Reversing Heat Flow}
\]

**TYPICAL APPLICATIONS**

Modulated DSC provides many unique measurement capabilities. Several of those are included here for illustration. However, new applications for modulated DSC continue to be found. Contact your local TA Instruments Representative for applications notes describing these additional measurements.

**Analysis of Complex Transitions**

The blending of two or more polymers is becoming a common method for developing new materials for demanding applications such as impact resistant parts and packaging films. Since the ultimate properties of blends can be significantly affected by what polymers are present, as well as by small changes in the blend composition, suppliers of those materials are interested in rapid tests which provide verification that the correct polymers and amount of each polymer are present in the blend. Conventional DSC has proven to be an effective technique for characterizing blends such as polyethylene/polypropylene where the crystalline melting endotherms or other transitions (e.g., glass transition) associated with the polymer components are sufficiently separated to allow identification and/or quantitation. However, many blends do not exhibit this convenient separation and thus are difficult to accurately evaluate by conventional DSC.

Figure 10, for example, shows the conventional DSC result for the first heat on a polymer blend (solid line) containing polyethyleneterephthalate (PET) and acrylonitrile-butadiene-styrene (ABS). There are three obvious transitions indicative of the glass transition, cold crystallization, and crystalline melting of the PET, seen at 67, 121, and 235°C respectively. However, no apparent ABS transitions are observed. Upon reheating, after cooling at a controlled rate (10°C/minute), the conventional DSC result changes (broken line). Now only two transitions are observed - a glass transition at 106°C and a crystalline melt at 238°C. Explanation of these changes on reheating, particularly the apparent shift in the glass transition temperature, is difficult based on only these results.

The MDSC results for the “as received” material shown in Figure 11 helps to resolve these interpretation issues. Phenomena such as glass transitions are reversing under MDSC, while cold crystallization is nonreversing. Hence, separation of the total heat flow into its reversing and nonreversing components separates overlapping thermal events with different behavior. The nonreversing curve in this case shows only the exotherm associated with the PET cold crystallization, as well as a weak endotherm about 70°C associated with relaxation phenomena. The reversing curve shows two transitions - the glass transition (67°C) for PET, as well as a second glass transition (at 105°C) associated with the ABS. In conventional DSC, this latter glass transition is hidden under the PET cold crystallization peak and thus only becomes visible on reheating.
Figure 10. PET/ABS BLEND - CONVENTIONAL DSC

- Heat Flow (W/g) vs. Temperature (°C)
- 67.38°C, 72.62°C (H)
- 120.92°C
- 235.36°C
- 249.75°C

- First heat on molded part
- Second heat after 10°C/min cooling (Curve shifted on Y axis to avoid overlap)

9.22 mg sample
Nitrogen purge
10°C/minute heating rate

Figure 11. PET/ABS BLEND - MODULATED DSC

- Heat Flow (W/g) vs. Temperature (°C)
- Non-reversing
- Reversing
- PET Tg
- ABS Tg

- First heat on molded part
- Total
- Non-reversing
- Reversing

8.46 mg sample
Nitrogen purge
2°C/minute heating rate, ±1°C amplitude, 60 second period
Increased Sensitivity For Detecting Weak Transitions

Weak transitions such as the glass transition are measured in DSC based on the change in heat capacity which occurs during the transition. Since this heat capacity change appears as a step change in the heat flow curve, it is important that other “baseline effects” in the heat flow curve are minimal. Unfortunately, this is not always the case. Figure 12 shows a polymer resin where the presence of moisture has such severe effects on the baseline that the glass transition is difficult to determine definitively. However, in modulated DSC these effects, which are nonreversing, are separated from the transition of interest, which is reversing.

Increased Resolution

Sensitivity and resolution in DSC are both affected by heating rate. Faster heating rates improve sensitivity but decrease resolution, while the converse is true for slower heating rates. Therefore, choosing a heating rate in conventional DSC is always a compromise. Modulated DSC eliminates this need to compromise by essentially exposing the sample to two different heating rates simultaneously - a slow average (underlying) heating rate and a fast instantaneous heating rate. The result is both good resolution and sensitivity in the same experiment. Figure 13 shows the results for sodium nitrite where an underlying heating rate of 0.05°C/minute is necessary to provide adequate resolution of the two weak heat capacity changes associated with phase transitions between 163 and 166°C. Despite this slow heating rate, the sensitivity is still sufficient to readily detect these transitions.

Direct Measurement of Heat Capacity

Heat capacity (Cp) measurement by conventional DSC is a tedious process requiring multiple experiments and considerable operator expertise to obtain results with reasonable accuracy and precision. MDSC provides the ability to measure heat capacity more directly and measure it even at slow (including isothermal) heating rate conditions. In addition, MDSC can measure heat capacity changes during certain transitions. Figure 14 shows
Figure 13. SODIUM NITRITE - MDSC

Figure 14. ISOTHERMAL EPOXY CURE - MDSC
the heat capacity change occurring during the isothermal cure of an epoxy thermoset. As expected, the heat capacity decreases during cure as the material’s free volume and mobility decrease because of crosslinking. The onset of the heat capacity decrease occurs after the exothermic peak maximum which implies that heat capacity changes more dramatically during the final stage of cure (crosslinking) than during linear polymerization (the first stage of cure). Evaluation by dynamic mechanical analysis (DMA) supports this conclusion since the modulus (E’) increases at exactly the same time as heat capacity decreases.

**Thermal Conductivity Measurement**

Thermal conductivity is a measure of the ease with which heat is transmitted through a material and is a basic material property. Materials with high thermal conductivity are called “conductors” and those with low conductivity are called “insulators”. Solid conductors (such as metals) typically have thermal conductivities in the range of 10 to 400 W/°C m while insulators (such as polymers, glasses and ceramics) have values in the range of 0.1 to 2 W/°C m. Furthermore, thermal conductivity changes as a weak function of temperature and rarely changes by a factor of ten within a general class of materials.

Conventional DSC can be used to measure the thermal conductivity of insulating materials. However, the measurement requires modification of the DSC cell and a very tedious experimental procedure. Modulated DSC provides a much better way to obtain similar information. MDSC is applicable to materials whose thermal conductivity are in the range 0.1 to 1.5 W/°Cm. MDSC measurement does not require any modifications to the DSC system. With proper calibration, accuracy and precision equivalent to accepted ASTM procedures are obtained.

**Comparative Thermal Conductivities**

<table>
<thead>
<tr>
<th>Material</th>
<th>MDSC Exp’t. (W/°Cm)</th>
<th>Literature MDSC (W/°Cm)**</th>
<th>MDSC Var. from Lit. (%)</th>
<th>MDSC Coeff. Var. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>0.14</td>
<td>0.14</td>
<td>0</td>
<td>2.2</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>0.34</td>
<td>0.33</td>
<td>3</td>
<td>2.3</td>
</tr>
<tr>
<td>Soda Lime Glass</td>
<td>0.73</td>
<td>0.71</td>
<td>3</td>
<td>7.5</td>
</tr>
<tr>
<td>Pyrex 7740</td>
<td>1.09</td>
<td>1.10</td>
<td>1</td>
<td>4.7</td>
</tr>
</tbody>
</table>

* average based on 4 measurements

**CALIBRATION**

Modulated DSC requires the same basic calibrations as conventional DSC (baseline, temperature, and heat flow). In addition, however, because heat capacity determination is a necessary first step to calculating reversing and nonreversing heat flow, a heat capacity calibration must be performed for MDSC. Note: In all calibrations, the experimental conditions (e.g., pan type, purge gas, heating rate, modulation amplitude and period) should be identical to those used in subsequent sample evaluations.

**Baseline calibration** is based on a conventional DSC experiment in which an empty cell is heated over a broad temperature range. The resultant curve is used to correct for cell heat flow imbalance between the sample and reference positions.
**Temperature calibration** is based on a conventional DSC experiment in which a reference material is heated through a well-characterized transition (e.g. indium melting). The transition temperature obtained is compared with its literature value to determine a calibration factor. At least two calibration standards which bracket the temperature range of interest are recommended.

**Heat flow calibration** is also based on a conventional DSC experiment in which a reference material is heated through a well-characterized transition (e.g. indium melting). The heat flow associated with the transition is compared with the literature value to determine a calibration factor.

**Heat capacity calibration** is based on an MDSC experiment with a known standard such as sapphire. A single calibration value is used and it should be determined near the middle of the desired temperature range (when using an underlying heating rate) and near the transition of interest (when making isothermal measurements). Alternatively, multiple calibrations which bracket the temperature region of interest can be averaged and used. Best results are obtained using 25mg (nominal) of sapphire at the same conditions as the subsequent sample runs. Note: Long periods (100 seconds) provide the best accuracy for heat capacity measurements because they provide maximum time for heat transfer through the sample.

**OPTIMIZATION OF RESULTS**

This section contains a general discussion of experimental parameters which can affect MDSC results, as well as recommended settings for those parameters in both general applications and specific situations (e.g. glass transition measurement). **These recommendations are not intended to be absolute, but rather are intended to be good starting points.**

**Recommended General Conditions**

- Prepare the sample to maximize effective heat transfer and to minimize thermal gradients
  - Spread the sample uniformly across the bottom of the pan. Use a thin film or a piece of sample with its flat side towards the pan. Do not use large irregular chunks.
  - Weigh the sample before and after the experiment to assure that no weight loss has occurred.
  - Use 5-15 mg (organics and polymers) or 20-50 mg (inorganics) samples.

- Select and prepare the sample pan to minimize gradients
  - Use standard, crimped pans if possible. Liquids and volatile materials may require hermetic pans.
  - Ensure that the bottom of the pan after sealing/crimping is as flat as possible. Lightly sanding the bottom of the pan with fine sand paper sometimes improves flatness.
  - Match weights of sample and reference pans as closely as possible.

- Select an appropriate purge gas
  A purge gas should be used in modulated DSC experiments since it helps provide uniform heat transfer in the cell. Higher thermal conductivity purge gases such as helium are recommended. Typical flow rates are 25-50 ml/minute. Purge through both the PURGE GAS (at 25 ml/minute) and VACUUM (at 50 ml/minute) ports on the DSC module. The latter purge improves modulation at higher amplitudes.

- Use a cooling accessory
  For most MDSC experiments it is necessary to have a source of cooling present so that the instantaneous heating rate fluctuations required by the chosen conditions can be achieved. A Refrigerated Cooling system (RCS), or a Liquid Nitrogen Cooling Accessory (LNCA) are two options. Since MDSC experiments are longer than conventional DSC experiments (because slower underlying
heating rates and/or “quasi-isothermal” conditions are used), the RCS, which does not consume coolant, is recommended unless its temperature range (-70 to 400°C) does not cover the region of interest.

- Select a modulation period of 40-100 seconds
  For most samples in standard crimped pans, 60 seconds is the recommended period of oscillation. Larger periods may be necessary for the larger mass hermetic pans. For higher thermal conductivity purge gases (e.g., helium), a 40 second period is sufficient for many measurements. Periods of 30 seconds or less are generally not recommended.

- Select an underlying heating rate of 1-5°C/minute
  The maximum practical heating rate for MDSC experiments is 5°C/minute. The ideal heating rate is one that provides at least 4 temperature oscillations (periods) over the temperature range of each transition studied.

- Use a modulation amplitude between ±0.5 and 3°C
  Larger amplitudes (±1.5 to 3°C) should be used when measuring weak glass transitions. Smaller amplitudes should be used for analysis of sharp transitions which are only a few ºC wide. Amplitudes smaller than ±0.03°C should be avoided since they are difficult to control.

The modulation amplitude in combination with the period determines the range of instantaneous heating/cooling rates obtained during modulation. The amplitude can be chosen to achieve heat only, heating/cooling (as in Figure 15), or heat/isothermal (see the section on recommended conditions for studying melting phenomena on page 19).

Note: Both the purge gas and DSC cell cooling capacity affect the range of achievable modulation amplitudes. Larger amplitudes and shorter periods require greater cell cooling capacity. A possible concern when using larger amplitudes, especially at low temperatures, is that some amplitude settings cannot be achieved at some periods.

![Figure 15. POLYMER COMPOSITE - MDSC MODULATED HEATING RATE](image)
• Use a data storage rate of 1 second/data point and store both the raw and deconvoluted signals.

The data storage rate in MDSC may be selected from the same range of values as for conventional DSC, namely 0.2 to 1000 seconds/data point. The default is 0.2 seconds/point. However, increasing the storage interval helps reduce the size of the MDSC files without compromising the quality of the data. This is because the data used to calculate the stored data is always collected at 0.2 seconds/data point. Data storage at 1 second/data point is recommended.

Since deconvolution of the MDSC heat capacity and heat flow signals occurs essentially in real-time (there is a 1.5 cycle delay), the option exists for not storing the raw modulated signals. Nevertheless, it is recommended that these raw signals be stored since they often provide useful troubleshooting assistance (see next section) and/or visual confirmation of specific thermal events. The list of recommended signals for storage includes time, temperature, modulated heat flow, modulated temperature, heat flow phase, heat capacity, total heat flow, reversing heat flow, and nonreversing heat flow.

Storage of all these MDSC signals, however, makes file sizes larger.

Verifying Acceptability of Conditions Chosen

Just as with conventional DSC, good reproducibility and accuracy of results in MDSC are based on the assumption that the sample is able to follow the heating/cooling regime imposed on it. Said another way, if the experimental conditions result in a modulated heating profile which the sample cannot follow, good results will not be obtained. The modulated heat flow profile (Figure 16) provides an excellent way to determine if the sample is following the modulation. A smooth, regular sine wave indicates reasonable experimental conditions.

Examination of the modulated heating rate profile or the Lissajous plot of modulated heat flow versus modulated heating rate (Figure 17), also provides an indication that reasonable experimental conditions are chosen. Note: Lissajous plots are only possible using Thermal Solutions Software.

![Figure 16. MODULATED SIGNAL INDICATES QUALITY RESULTS](image-url)
Typical Conditions for Studying Glass Transitions (The conditions described here reflect minor changes to the General Conditions described earlier and are designed to optimize glass transition results).

- 10-30 mg sample weight
- Crimped aluminum pans (matched $\pm 0.1$ mg).
- Underlying Heating Rate
  Use a rate up to $5^\circ$C/minute. Use lower heating rates if necessary to achieve at least four modulation cycles over the temperature range of the transition.
- Amplitude $= \pm 1^\circ$C
  Use larger values (up to $\pm 3^\circ$C) for very weak transitions.
- Period $= 60$ seconds
- Helium purge at $25$ mL/minute
- 1 second/data point storage rate

Recommended Conditions for Polymer Melting (Initial Crystallinity) [The conditions described here reflect minor changes to the General Conditions described earlier and are designed to optimize studies of the melt region].

In semicrystalline, broad melting polymers, MDSC has the unique ability to separate melting from simultaneous crystallization/crystalline perfection on the basis that these phenomena are reversing and nonreversing respectively. Hence, MDSC provides more accurate measurement of the onset and temperature range of melting, as well as initial crystallinity.

- 10-15 mg sample weight
- Crimped aluminum pans (matched ±0.1 mg)
- 5°C/minute Underlying Heating Rate
- Period = 40-60 seconds
  Use longest period possible to still achieve at least 4 modulations at half-height of the melting peak.
- Select the amplitude to achieve an instantaneous heating rate that varies between some positive value and zero (isothermal). The table shown in Figure 18 provides guidance in choosing that amplitude. There are two reasons for adjusting conditions to periodically achieve a 0°C/minute minimum instantaneous heating rate. First, by not cooling the material at any time during the modulation, the possibility for “artificially” affecting any crystallization phenomena observed is eliminated. Second, and more importantly, when the heating rate is zero, there is no heat flow associated with heat capacity-related (reversing) events [recall the earlier equation governing heat flow \( \frac{dQ}{dt} = C_p \beta + f(T, t) \)] and hence any heat flow observed must be the result of kinetic phenomena. Figure 19, for example, shows the modulated heat flow curve for quenched polyethyleneterephthalate (PET) with the conditions set to periodically achieve a zero heating rate. The exothermic behavior observed above the cold crystallization is associated with ongoing crystallization/crystalline perfection processes which cannot be observed by conventional DSC. The deconvoluted nonreversing heat flow (solid line) as expected corresponds exactly with the raw heat flow until steady state is lost in the melt above 230°C.
- Helium purge at 25 mL/minute
- 1 second/data point storage rate

**Figure 18. SELECTION OF AMPLITUDE FOR “HEAT / ISO” EXPERIMENTS**

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period (sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.003</td>
<td>0.005</td>
<td>0.013</td>
<td>0.027</td>
<td>0.053</td>
<td>0.133</td>
<td>0.265</td>
</tr>
<tr>
<td>20</td>
<td>0.005</td>
<td>0.011</td>
<td>0.027</td>
<td>0.053</td>
<td>0.106</td>
<td>0.265</td>
<td>0.531</td>
</tr>
<tr>
<td>30</td>
<td>0.008</td>
<td>0.016</td>
<td>0.040</td>
<td>0.080</td>
<td>0.159</td>
<td>0.398</td>
<td>0.796</td>
</tr>
<tr>
<td>40</td>
<td>0.011</td>
<td>0.021</td>
<td>0.053</td>
<td>0.106</td>
<td>0.212</td>
<td>0.531</td>
<td>1.062</td>
</tr>
<tr>
<td>50</td>
<td>0.013</td>
<td>0.027</td>
<td>0.066</td>
<td>0.133</td>
<td>0.265</td>
<td>0.663</td>
<td>1.327</td>
</tr>
<tr>
<td>60</td>
<td>0.016</td>
<td>0.032</td>
<td>0.080</td>
<td>0.159</td>
<td>0.318</td>
<td>0.796</td>
<td>1.592</td>
</tr>
<tr>
<td>70</td>
<td>0.019</td>
<td>0.037</td>
<td>0.093</td>
<td>0.186</td>
<td>0.372</td>
<td>0.929</td>
<td>1.858</td>
</tr>
<tr>
<td>80</td>
<td>0.021</td>
<td>0.042</td>
<td>0.106</td>
<td>0.212</td>
<td>0.425</td>
<td>1.062</td>
<td>2.123</td>
</tr>
<tr>
<td>90</td>
<td>0.024</td>
<td>0.048</td>
<td>0.119</td>
<td>0.239</td>
<td>0.478</td>
<td>1.194</td>
<td>2.389</td>
</tr>
<tr>
<td>100</td>
<td>0.027</td>
<td>0.053</td>
<td>0.133</td>
<td>0.265</td>
<td>0.531</td>
<td>1.327</td>
<td>2.654</td>
</tr>
</tbody>
</table>

\[
T_{amp} = H_r \star \frac{P}{2\pi \star 60}
\]

where:  
- \( T_{amp} \) = maximum temperature amplitude for "heat only" (°C)  
- \( H_r \) = Average heating rate (°C/min)  
- \( P \) = period (seconds)
Typical Conditions for Heat Capacity Measurements (The conditions described here reflect minor changes to the General Conditions described earlier and are designed to optimize heat capacity results.)

In situations where accurate heat capacity is the parameter of primary interest (rather than total, reversing and nonreversing heat flows), it is worthwhile to invest additional experimental time to ensure optimum accuracy and reproducibility.

- Sample weight: 10-15 mg polymers, 15-25 mg sapphire, 25-50 mg metals
- Crimped aluminum pans (matched within ±0.1 mg)
- Underlying Heating Rate 0-5°C/minute
  
  Generally, comparable results are obtained from any heating rate in this range. However, there are situations where a heating rate of zero (“quasi-isothermal” conditions) are desirable. For example, Figure 20 shows the heat capacity curves for polystyrene during its glass transition when heating and cooling at 1°C/minute (solid lines). The curves are different because of time-dependent hysteresis effects in the region of the glass transition. The dashed line, on the other hand, represents the heat capacity values obtained using quasi-isothermal experiments which remove this time-dependency. These values are the same whether the transition is approached from lower or higher temperature. MDSC, therefore, provides the steady state glass transition shape and temperature, as well as Cp value as a function of temperature.

Another situation where quasi-isothermal conditions are valuable is shown in Figure 21. The measurement of Cp during melting is complicated by the fact that two “apparently reversing” phenomena (Cp and melting) simultaneously contribute to the modulated heat flow amplitude and hence create an artificially high value for Cp. However, using quasi-isothermal conditions where the heat of melting is effectively spread over an extremely large number of modulations, it is possible to reduce the effect attributable to melting and obtain Cp trends which agree with theory. Note: This measurement of Cp during melting may not work for materials which rapidly crystallize (e.g., polyethylene).
Figure 20. POLYSTYRENE Tg UNDER DIFFERENT MDSC CONDITIONS

Comparison of Heating and Cooling Ramps @ 1°C/min with Isothermal Measurements

85 90 95 100 105 110 115 120
Temperature (°C)

1.4 1.6 1.8 2.0
Heat Capacity (J/g/°C)

Cooling
Isothermal
Heating

±0.5°C amplitude, 60 second period

Figure 21. HEAT CAPACITY - SLOW COOLED PET

9.55mg sample
helium purge
±0.531°C amplitude, 40 second period

50 100 150 200 250
Temperature (°C)

0 2 4 6 8
Heat Capacity (J/g/°C)

HEATED @ 5°C/MIN

ISEOTHERMAL MEASUREMENTS PERFORMED OVER 6 DAYS
Typical Conditions for Heat Capacity Measurements (cont.)

- Amplitude = ±0.5 to 1.0°C
- Period = 80-100 seconds
- Helium purge at 25 mL/minute
- 1 second/data point storage rate

Recommended Conditions for Thermal Conductivity

Thermal conductivity measurement by MDSC is based on two experiments using the same sample material but different sample thickness. In one experiment, a thin sample is used, and the experimental conditions are chosen to ensure that accurate heat capacity information is obtained (i.e., the sample follows the applied modulation). In the other experiment, a thick sample without a pan is used so that the temperature modulation occurs only in part of the sample (the side in contact with the pan) and the remainder of the sample, in effect, becomes a heat sink. [For a complete discussion of the theory associated with this measurement, see publication TA 086.]

Specific experimental recommendations include:

- Sample weight:
  - 10-15 mg (thin sample) for accurate heat capacity measurement. Sample is run in a crimped aluminum pan.
  - 100-150 mg (thick sample). Cut sample to be a right circular cylinder 3.4 - 3.8 mm high. Use of a large diameter (6.3 mm) sample is preferred to minimize heat losses through the sides of the sample. This thick sample is run directly on the DSC cell platform without a sample pan. However, an aluminum foil disk and a drop of silicone oil should be used to improve thermal contact.
- Underlying heating rate = 0. This is a quasi-isothermal measurement. Allow 10-15 minutes for equilibration before taking data.
- Amplitude = ±0.5°C
- Period = 80 seconds
- Use polystyrene to obtain the additional calibration required to compensate for heat losses through the sides of the sample.
- Helium purge at 25 mL/minute
- 1 second/data point storage rate
- Thermal conductivity experiments are generally run at specific temperatures of interest (e.g., ambient temperature). This MDSC procedure should not be used in a region above the melting or softening point of the material because the thick sample may adhere to the DSC cell platform causing contamination.
There are several additional experimental considerations which may influence the results obtained, including phase lag, frequency effects at the glass transition, and separation of reversing and nonreversing heat flow during melting. These are described here along with an indication of their impact.

**Phase Lag**

The general heat flow equation used to describe modulated DSC as stated earlier is \( \frac{dQ}{dt} = C_p \beta + f(T,t) \). This equation assumes that, in regions where the sample material has no time dependent (kinetic) phenomena, the sample responds instantaneously and directly tracks the sinusoidal heating profile. As Figure 22 shows, this means that the modulated heat flow is 180° out-of-phase with respect to the modulated heating rate [when the modulated heating rate is maximum, the resultant heat flow is most endothermic]. In reality, this assumption is not completely valid. There is actually a phase shift (lag) between the two measured raw signals due to non-instantaneous heat transfer between the DSC cell and the sample. In regions where no thermal events are occurring in the sample, this lag is due entirely to experimental effects (e.g., sample pan-to-DSC cell disk contact). In regions where the sample exhibits thermal events, this lag is a combination of experimental and sample effects. As a result, the heat capacity measured in modulated DSC is actually the complex heat capacity (\( C_p^* \)) which can be split into a component \( C_p' \) (usually considered the “real” or thermodynamic heat capacity) which is in-phase with temperature modulation and an out-of-phase, imaginary component \( C_p'' \). [The relationship between these heat capacity components is \( C_p^* = (C_p'^2 + C_p''^2)^{\frac{1}{2}} \).] To obtain a quantitative measure of \( C_p'' \), and hence \( C_p' \), it is first necessary to compensate (calibrate) for the lag associated with experimental effects. This is easily accomplished by selecting “baseline” areas outside the transition region and adjusting the phase angle to the theoretically expected 0° or zero-phase lag. Any remaining lag is then attributable to the sample and can be used to calculate \( C_p' \) and \( C_p'' \). Figure 23 shows that there is a small peak in \( C_p'' \) at the glass transition for amorphous PET. However, its resultant effect on \( C_p' \) is <1%. Figure 24 shows, furthermore, that the effect of \( C_p'' \) becomes significant for this material only in the melt where steady state is lost. Correction for \( C_p'' \) is hence currently only of interest academically. However, future work with suitable models may enable additional information about the material’s structure and behavior to be obtained from quantifying \( C_p'' \).
Figure 23. CONTRIBUTIONS TO HEAT CAPACITY (QUENCHED PET)

Figure 24. PHASE-CORRECTED HEAT FLOW SIGNALS (QUENCHED PET)
Frequency Effects

Material transitions such as the glass transition may exhibit a temperature and time dependency. This means that those transitions may shift to higher temperatures as the frequency of measurement increases. Hence, particularly in techniques such as dynamic mechanical analysis (DMA) where several decades of frequency are commonly covered, it is important to calibrate and compare materials at the same frequency.

Modulated DSC, because it involves a sinusoidal modulation, also imposes frequency effects on the collected data. Normally, those effects are of no concern provided the modulation period, which determines frequency, is constant when comparing materials. Even in situations where the period varies, frequency effects should be small because of the narrow range of useable MDSC periods (25-100 seconds). Nevertheless, there are applications where it still must be considered. For example, the separation of endothermic relaxation processes from the glass transition.

In amorphous polymers, it is common for an enthalpic relaxation to be present over the glass transition region. This relaxation, which has been described in the literature using several names including stress relaxation and volume relaxation, is endothermic and increases in size with longer aging times and increased aging temperatures. Hence, measuring the size of this relaxation is of interest because end-use applications such as wear-dated carpet fibers and packaging are affected by changes in internal polymer structure due to aging. Unfortunately, in conventional DSC overlap of the glass transition and the enthalpic relaxation is often sufficient to make interpretation difficult and measurement of the energy associated with the relaxation essentially impossible even using sigmoidal baseline treatments to account for baseline shifts. Modulated DSC, because it separates nonreversing phenomena such as relaxation processes from reversing phenomena like the glass transition, should be an ideal technique for quantifying the heat associated with the relaxation. However, the results obtained by modulated DSC are dependent on experimental conditions. The reason for this is readily explained by comparing the reversing and total heat flow curves used to generate those results as shown for polystyrene in Figure 25. The total heat flow profile is unaffected by the change in modulation period (frequency). The reversing heat flow, on the other hand, is affected, shifting as expected to higher temperatures.

Figure 25. EFFECT OF MODULATION FREQUENCY ON TOTAL AND REVERSING SIGNALS

-0.10
-0.11
-0.12
-0.13
-0.14
-0.07
-0.06
-0.05
-0.04
-0.03

Heat Flow (W/g)

-0.05993W/g
-0.05989W/g

104.68°C
106.79°C

9.5mg sample
helium purge
2°C/minute heating rate, ±0.4°C amplitude

EFFECT OF PERIOD (on Tg)
SOLID = 100 sec PERIOD
DASH-DOT = 50 sec PERIOD
DASH = 25 sec PERIOD

Temperature (°C)
Figure 26. EFFECT OF DIFFERENT MODULATION FREQUENCIES ON CALCULATED NONREVERSING (ENTHALPIC RELAXATION) SIGNAL

- REVERSING HEAT FLOW CURVES AT TWO FREQUENCIES
- ADDITIONAL NONREVERSING AREA MEASURED AT HIGHER FREQUENCY
- NONREVERSING AREA MEASURED AT LOWER FREQUENCY
- TOTAL HEAT FLOW CURVE

Figure 27. COOLING CURVES FOR RELAXATION CORRECTION

- EFFECT OF PERIOD (frequency) ON GLASS TRANSITION TEMPERATURE
- TOTAL
- REVERSING
- 103.59°C 0.05891W/g
- 105.70°C 0.05892W/g
- SOLID = 100 sec PERIOD
- DASH-DOT = 50 sec PERIOD
- DASH = 25 sec PERIOD
as modulation period decreases. Since the nonreversing heat flow is determined by subtracting the reversing heat flow from the total heat flow, this shift makes the nonreversing heat flow larger than expected. (See Figure 26). If the ultimate interest is constructing a correlation curve for comparing the area of the relaxation endotherm with other end-use properties, then this error in nonreversing heat flow can be ignored provided a common modulation period is used. Conversely, to obtain an absolute measure of the heat of relaxation requires another series of experiments. Those experiments are cooling curves at the corresponding frequencies (See Figure 27). Comparing the total and reversing heat flow curves on cooling provides a “frequency shift correction factor” which accounts for the error in the calculated nonreversing heat flow directly related to the frequency shift. When that correction is made, the accuracy and reproducibility of the heat of enthalpic relaxation measurement is excellent (Figure 28). [Note: The glass transition temperature in the reversing heat flow is also affected by the modulation period (frequency). This effect needs to be considered when comparing results.]

Separation of Reversing and Nonreversing Heat Flow

As stated earlier, the total heat flow obtained from modulated DSC is equivalent to the heat flow signal obtained from conventional DSC. In addition, the total heat flow is not affected by the selected experimental conditions, provided good modulation is obtained (see page 17). **The separation of the total heat flow into its reversing and nonreversing components is, however, affected by the selected experimental conditions especially in temperature regions where time-dependent (nonreversing) events occur (e.g., the melting region).** Figure 29 shows typical differences in the reversing and nonreversing heat flows for quenched PET in the melting region. These results were obtained under equivalent experimental conditions except for modulation amplitude. Nevertheless, despite these differences, the initial crystallinity (which is the sum of the two heat flows and therefore the total heat flow over that region) is constant and more importantly agrees well with that obtained from x-ray diffraction measurements. **Note:** The separation of the total

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Enthalpic Relaxation (Uncorrected)</th>
<th>Correction From Nonreversing Cooling</th>
<th>Enthalpic Relaxation (Corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.04 Hz (25 sec)</td>
<td>1.82 J/g</td>
<td>1.12 J/g</td>
<td>0.70 J/g</td>
</tr>
<tr>
<td>.01 Hz (100 sec)</td>
<td>1.32 J/g</td>
<td>0.60 J/g</td>
<td>0.72 J/g</td>
</tr>
</tbody>
</table>

2°C/minute heating rate, ±0.4°C amplitude
heat flow into its reversing and nonreversing components during melting is also affected by the loss of steady state (see Figure 19). This further affects the quantitative reproducibility and accuracy of these two heat flow components but does not affect the total heat flow or initial crystallinity values.

Additional theory and studies are needed before the reversing and nonreversing heat flows themselves can be correlated to specific material phenomena once steady state is lost in the melting region.

ADDITIONAL MODULATED DSC REFERENCES

The following is a compilation of technical publications from the open literature (compilation date 8/96) which may be helpful in further broadening your knowledge of MDSC and its applications. See TA Instruments Publication TN-33 for the latest additions to this list.


“Modulated Differential Scanning Calorimetry (MDSC)”, A. Boller, Advanced Thermal Analysis Laboratory, Eighth Report, University of Tennessee Knoxville, 4-8 (1995).


**FUTURE UPDATES**

By conventional DSC standards, modulated DSC is a relatively new technique, having been available about 4 years compared to 35 years for conventional DSC. As a result, it is reasonable to expect that the capabilities and applications for modulated DSC will continue to grow over at least the next decade. Please watch future issues of the TA Instruments Hotline Newsletter for announcements of these new capabilities.
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