Choosing Conditions in Modulated DSC®

TN045

INTRODUCTION

Modulated DSC (MDSC®) provides a powerful enhancement to the standard DSC experiment. MDSC can simultaneously improve the sensitivity and resolution of the DSC experiment, in addition to providing heat capacity and heat flow in a single experiment. In order to obtain the maximum benefit from the MDSC experiment, however, optimal MDSC conditions must be chosen. In this paper we examine the protocol for choosing the correct MDSC conditions with respect to sample size, modulation period, underlying heating rate, and modulation amplitude.

SAMPLE SIZE

In order for the MDSC experiment to be effective, the entire sample must be capable of following the imposed temperature modulation. If any thermal gradients are present within the sample, temperature-heat flow phase-lags will be magnified, and/or steady-state conditions will not be reached. The result will be inaccurate heat capacity measurements which lead to errors in MDSC signal deconvolution. To minimize thermal gradients, use a thin, low mass sample. Keeping the sample thin minimizes the distance the heat needs to travel to keep the entire thickness of the sample in thermal equilibrium. Using a lower mass decreases the total amount of heat energy a sample must absorb due to its heat capacity. In addition, the surface area of the sample should be maximized relative to the mass. This can be accomplished by flattening solid samples in a press, or cutting multiple thin pieces if thermal or mechanical history is a concern. Flattening the sample in a press could change the sample's structure. Where thermal history is to be studied, the sample should be cut, rather than pressed. If a solid sample can be powdered, this should be done to maximize surface area. All of these suggestions will improve the thermal contact of the sample, and minimize gradients. Table 1 summarizes recommended sample sizes and preparation techniques.

Table 1
Recommended Sample Sizes and Preparation Techniques

Material	Mass	Preparation
Polymers (films)	5-10 mg (10-15 mg for Cp)	Use a single thin layer, or multiple layers to increase mass
Polymers (bulk)	5-10 mg (10-15 mg for Cp)	Flatten sample in press, or cut thin slices if thermal history is a concern
Organics, biologicals	10-20 mg	Use a fine powder, grind if necessary
Metals, inorganics	10-20 mg	Flatten or grind as necessary

MODULATION PERIOD

The ability of the sample to follow the imposed modulation depends greatly on the period which is chosen. In MDSC, program periods as fast as 10 seconds are available. However, very few samples are capable of following this rapid modulation rate. The fastest modulation rate which your sample will follow depends on the heat capacity and thermal conductivity of the sample. Most samples will easily follow modulation periods of 50 seconds or greater. A simple experiment may be run to determine the shortest acceptable period for your sample. Run an experiment at an isothermal temperature with a constant amplitude and vary the period. Program 15 minutes at decreasing periods, starting at 100 sec, 90 sec, 80 sec, etc. The measured heat capacity should be independent of period. As the period decreases, the measured heat capacity will begin to decrease. This reduction in measured heat capacity indicates that the sample is unable to follow the modulation, and represents the lower limit of acceptable periods. Figure 1 shows the results of such an experiment run using a 25 mg sample of sapphire at 100°C with a helium purge of 25 ml/min. The plot in Figure 2 shows data from the same experiment, illustrating the effect of both period and amplitude on the heat capacity calibration constant. Note that the calibration constant does not change significantly provided the period is kept at about 50 seconds and above. The plateau seen in this plot should be viewed as the "safe operating region." In other words, if the conditions are kept within this plateau, a constant value of heat capacity will be measured, regardless of varying period or amplitude.

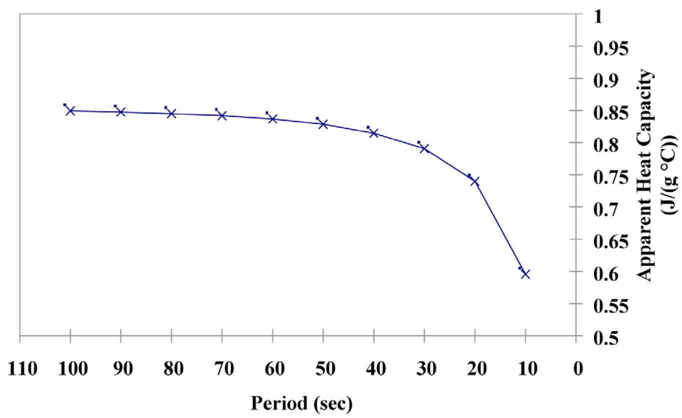

Figure 1

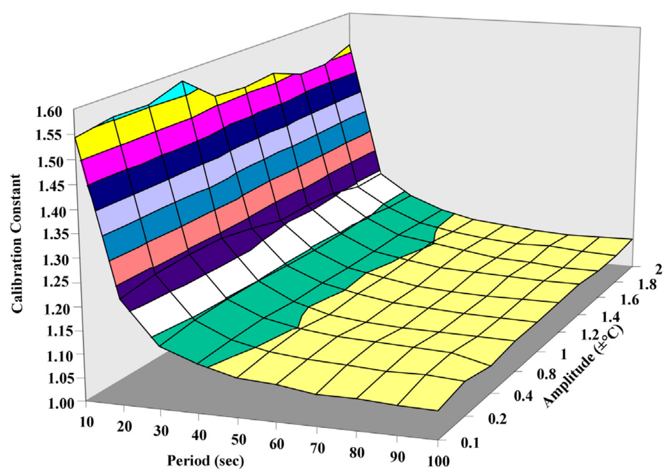

Figure 2

The purge gas used can also affect the range of acceptable periods with helium allowing faster modulation because of its increased thermal conductivity. It is critical that calibration and the period evaluation study be performed under the same purge gas, and flow rate (constancy of purge rate is particularly critical when using helium) be used for subsequent experiments. Purge affects are discussed in more detail in TA Publication #TN-44.

MEASURING TRANSITIONS

Before beginning an MDSC experiment on an uncharacterized material, a standard DSC scouting run should be performed at 5°C/min. to determine if MDSC will enhance the results. After analyzing the standard DSC data, the following questions should be addressed:

- Do I need heat capacity information?
- Is the transition a heat capacity related event?
- Is the transition masked by another event?
- Is the transition too weak or too broad to measure by standard DSC?
- Is higher sensitivity or higher resolution needed?
- Will heat capacity change as a function of time at a constant temperature (i.e., isothermal curing)?

If the answer is Yes to any of these question, then modulated DSC will help to enhance the results, and may provide more information than the standard DSC experiment alone.

Once you have decided that MDSC will improve your understanding of the data, it is important to choose the optimal MDSC modulation conditions. The first parameter to consider is modulation period. As discussed above, the period should be chosen such that the entire sample is capable of following the imposed temperature modulation. For lighter or lower heat capacity materials, this can be as low as 40 seconds. For heavier, higher heat capacity materials or those with low thermal conductivities, the period may need to be longer. Generally, a 60 second period is recommended when analyzing transitions and 100 seconds when the most accurate values of heat capacity are desired.

Next, select the underlying heating rate. This is determined using the width of the narrowest transition in the standard DSC scan. Using Universal Analysis software, by choose **Peak Width at Half-Height** in the Analysis Parameters menu. After integration, the peak width will be displayed on the plot, as in Figure 3, in which melting peak shown is 6.92°C wide.

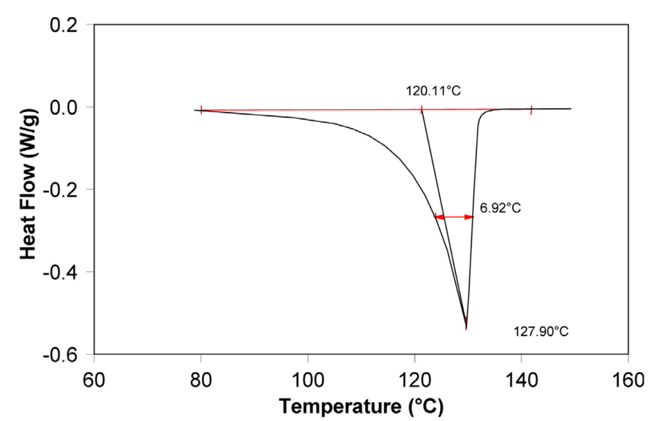

Figure 3

After determining the width of the transition, the underlying heating rate must be chosen. The combination of underlying heating rate and period must allow for at least 4–6 cycles across the width of the transition. This is required for efficient deconvolution of any kinetic events from heat capacity related phenomena. An easy way to calculate the required heating rate is shown in Equation 1:

$$\beta = \frac{T_{1/2}}{nP} 60s / \min$$

where:

$T_{1/2}$ = full width at half height
n = number of cycles
P = period

For a 40 second period, the fastest appropriate heating rate would be 2.60°C/min, therefore 2°C/min would be a reasonable rate to use. If a 60 second period is desired, "60 sec" is substituted into the denominator of the second term in Equation 1, resulting in a maximum heating rate of 1.73°C/min.

The modulated heat flow profile which resulted from an experiment with a 2°C/min underlying heating rate and a 40 second period is shown in Figure 4.

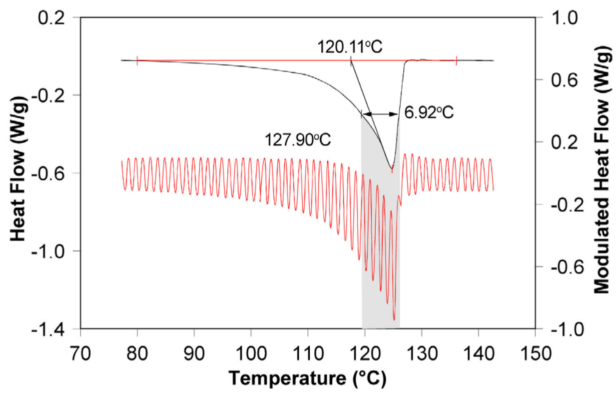

Figure 4

The shaded area represents the width of the transition, determined from the displayed peak width. Note that at the conditions used, a full five cycles are contained within the region. This confirms that acceptable modulation parameters were employed.

For the case of the glass transition, in the absence of any enthalpic relaxation event, the limits of the transition can be taken as the first deviation from baseline, and the return to baseline. For most materials, this temperature region will be sufficiently wide to allow for a multitude cycles to be contained within the transition region. Figure 5 shows the glass transition of poly(ethyleneterephthalate), analyzed under common modulation conditions of 2°C/min., with a modulation amplitude of 0.318°C every 60 seconds. Using these modulation parameters allows for a large number of cycles to be contained in the transition region (shaded area).

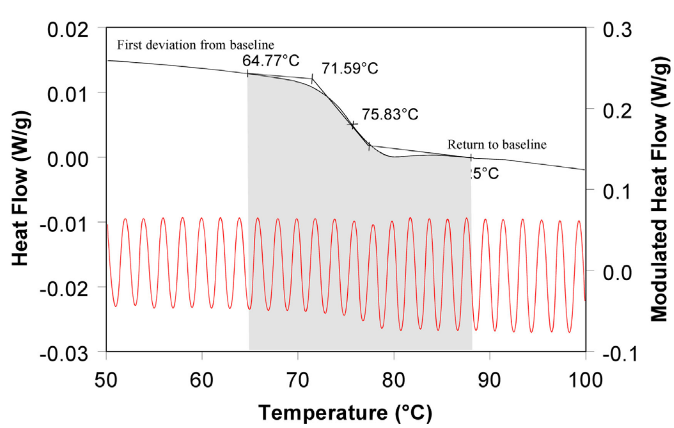

Figure 5

When analyzing a glass transition which contains an enthalpic relaxation, the transition width should be taken as the width of the relaxation peak at half-height, similar to the protocol for the melting region. Conditions should then be set which allow for 4–6 cycles to be contained within this temperature region (Figure 6). When these conditions are met, a complete deconvolution is performed, and the enthalpic relaxation is completely separated into the Nonreversing Heat Flow, with the glass transition resolved in the Reversing Heat Flow (Figure 7).

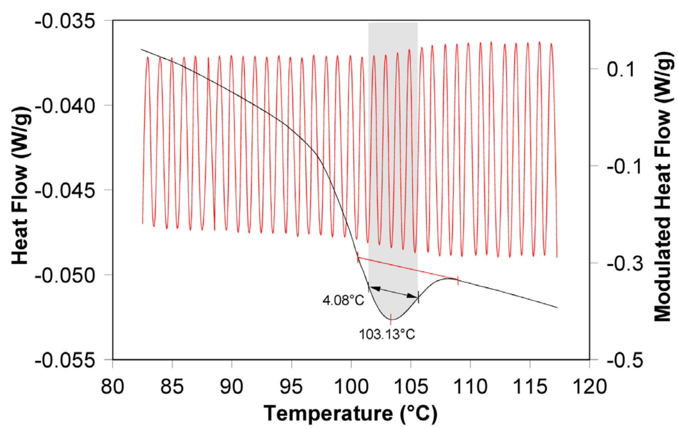

Figure 6

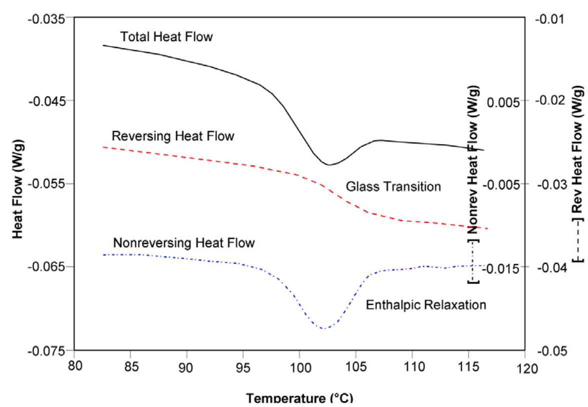

Figure 7

Allowing for 4–6 cycles across the transition is one of the most important factors when choosing MDSC conditions. Conditions which result in fewer cycles can lead to deconvolution artifacts. If you are in doubt as to the presence of artifacts, compare the deconvoluted data with the raw data. Any endothermic or exothermic events in the Reversing or Nonreversing Heat Flow signals should also be seen in the raw data. If they are not, then alternate conditions should be used to increase the number of cycles over the transition region.

MODULATION AMPLITUDE

After determining modulation period and underlying heating rate, the amplitude should be chosen. As a rule, larger modulation amplitudes provide for more sensitivity.

As seen in Figure 2, the measured value of heat capacity is not dependent on the amplitude, provided the mass of the sample is sufficiently small as to provide thermal equilibrium.

When a dynamic underlying heating rate is chosen, there are two main types of experiments available: modulated heat-cool or modulated heat-only. The temperature profiles corresponding to each are shown in Figure 8.

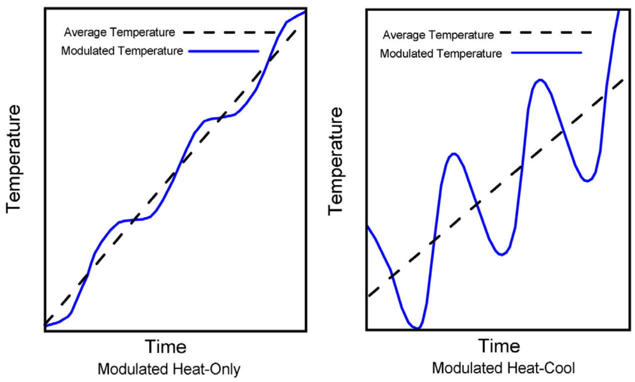

Figure 8

In the modulated heat-only profile, the modulated temperature (solid line) never decreases, i.e., the sample is never cooled. In the modulated heat-cool profile, some cooling of the sample is encountered on each modulation cycle.

For general MDSC experiments, and for the measurement of heat capacity or the glass transition, the modulated heat-cool profile is recommended. This profile provides for the best sensitivity for weak transitions and improves the precision of heat capacity measurements. The modulated heat-only profile is a special case condition and should be used when studying melting or simultaneous melting/crystallization phenomena. In these cases, cooling the sample may induce crystallization. To prevent crystallization from occurring (and potentially complicating the measurement), the modulated heat-only profile is used.

The table below can be used to determine the maximum heat-only amplitude for a given underlying heating rate and period.

Table 2

Heating Rate (°C/min)	40	50	60	70	80	90	100
0.1	0.011	0.013	0.016	0.019	0.021	0.024	0.027
0.2	0.021	0.027	0.032	0.037	0.042	0.048	0.053
0.5	0.053	0.066	0.080	0.093	0.106	0.119	0.133
1.0	0.106	0.133	0.159	0.186	0.212	0.239	0.265
2.0	0.212	0.265	0.318	0.371	0.424	0.477	0.531
5.0	0.531	0.663	0.796	0.928	1.061	1.194	1.326

If the period and heating rate were 60 seconds and 2°C/min, respectively, the maximum heat only amplitude would be ±0.318°C. Amplitudes less than this value will still provide heat-only conditions, but an amplitude greater than this value will represent a modulated heat-cool condition. This table is additive, i.e. if a value for a heating rate of 2.5°C/min. is required, adding the values for 2.0°C/min and 0.5°C/min will provide the required value. The amplitudes calculated from this table result in a minimum heating rate of 0°C/min. Use of these zero heating rate amplitudes provides additional insight in understanding the melting phenomena. The melting phenomena is discussed in more detail in TA Publication Number TA- 227.

SUMMARY

Modulated DSC is a powerful tool for materials characterization. Like any other precision technique, failure to use the optimum experimental conditions can result in sub-par performance. Following the suggestions listed in this paper should help you to design your MDSC experiment so that you derive the highest quality data.

For more information or to place an order, go to http://www.tainstruments.com to locate your local sales office information.