

Modulated Temperature DSC and the DSC 8500: A Step Up in Performance

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Abstract

Modulated Temperature Differential Scanning Calorimetry (MTDSC) is a capability for determining from a single, multi-step DSC method both the specific heat capacity and the heat flow data from a kinetically controlled process (e.g., reaction or crystallization). PerkinElmer provides this capability with its StepScan™ software, which is also especially suggested for high accuracy specific heat capacity (C_p) measurement. This capability is improved with the double-furnace DSC 8500 and DSC 8000 instruments particularly by using the SmartScan™ feature which removes curvature and offset in the underlying baseline. This technical note explains the advantages of the StepScan approach and gives examples that cover common MTDSC applications.

Introduction

Among commercial DSC providers, PerkinElmer was the first to realize (in the 1970s) the advantage of a regular stepwise method to obtain accurate specific heat capacity and partial area melting data.^{1,2} Much later, in 1992, a sinusoidal technique was developed by Mike Reading and marketed by TA Instruments® under the name Modulated DSC® (MDSC®).³ This method worked by applying a superimposed sinusoidal oscillation on a DSC temperature ramp and separately analyzing the sinusoidal and non-sinusoidal response of the sample. While this technique was very time consuming and required special calibration, it allowed the separate analysis of changes in specific heat, such as what occurs at the glass transition temperature, (T_g), from other, kinetically-controlled processes, such as chemical reactions and crystallization. After the initial excitement of the new technique had died down, many laboratories found that there were relatively few cases where this separation yielded unique or superior information, although the hopeful promise of this technique continued to be heavily marketed.

Later, it was shown that a *stepwise* method was also able to perform the core application of determining a glass transition that overlaps a kinetic process, and vice versa. The generic name for all such methods is “modulated temperature DSC”, or MTDSC, and the name of the PerkinElmer® software product that supports MTDSC is StepScan.⁴ This approach is particularly applicable to power controlled DSC because of its uniquely accurate temperature control and the ability to equilibrate rapidly due to the low mass of the furnace and to its tight feed-back control.⁵ The StepScan approach also benefits from the more accurate calorimetry that derives from the direct power measurement circuitry. So it does not require an incremental MTDSC calibration, but rather is calibrated by the same indium or sapphire calibration used for standard DSC.

StepScan Benefits

- Frequency-independent MTDSC analysis
 - Separation of the glass transition from kinetic effects: curing, crystallization and volatilization
- Fastest, most accurate specific heat capacity
 - Independent of encapsulation
 - Liquids, foams, powders, fibers – no problem
- Simpler than Sinusoidal MTDSC
 - Less input parameters to choose
 - No need to calibrate for frequency, amplitude, etc.
 - No additional calibration required

Theory

In desiring to separate changes in specific heat (C_p) from heat flow due to kinetic processes we are saying:

$$\frac{dq}{dt} = C_p(T) \cdot \beta + \frac{dq}{dt}(T, t)$$

where

$$\frac{dq}{dt} = \text{total heat flow}$$

$$C_p(T) = \text{specific heat}$$

$$\beta = \text{scan rate in StepScan method}$$

$$\frac{dq}{dt}(T, t) = \text{heat flow from a kinetic process}$$

After equilibration at each temperature, the temperature is then increased or decreased by a fraction of a degree up to several degrees, and again equilibrated at this next temperature until a criterion is met. With each step change

in temperature there is a change in the enthalpy, which is evaluated by integrating the heat flow over the temperature interval, which generates C_p over that interval. After C_p equilibration (less than a minute) the continuing heat flow is representative of any kinetic process taking place. After collecting data at a series of equally spaced temperatures, the operator performs the Specific Heat calculation, which generates two curves: $C_p(T)$ and $\frac{dq}{dt}(T, t)$, the heat flow due to a kinetically controlled process.

How StepScan compares to Sinusoidal MTDSC

The mathematical separation performed by StepScan is simpler than that achieved using a sinusoidal modulation. StepScan is essentially similar in its calculation to standard specific heat analysis, except that each C_p determination lasts only about a minute, and these C_p analyses are performed serially over the desired temperature range.

StepScan has an important advantage in that the sample *fully equilibrates* at each temperature, thus minimizing temperature gradients in the sample before making the critical measurement.

Oscillation problems

By comparison, in *sinusoidal* MTDSC, the scan rate is continuously oscillating between heating and cooling (or between heating rapidly and heating slowly), and the sample-pan-sensor system *never reaches an equilibrium temperature*. As a result, the temperature gradients in the sample are always changing while the measurement is being made. Since these temperature lags are a function of sample size, coupling of the sample to the pan, and amplitude and frequency of modulation, the specific heat data is method-dependent and especially sensitive to sample preparation. An easy way to visualize this problem with sinusoidal MTDSC is to think of a poorly coupled sample (e.g., a foam, or a pellet) oscillating sinusoidally around an average temperature. Because of thermal lag, the material in the middle of the sample will not experience the same temperature amplitude experienced by that part of the sample touching the pan, therefore its full heat capacity will not be measured. In fact, the only temperature oscillation that can be measured is that of the sensor which is under the floor supporting the sample pan. Therefore, even the coupling to the pan affects how much the sample temperature will oscillate and therefore how much heat flow is produced and reported as specific heat. Therefore, with sinusoidal MTDSC calibration against a known C_p standard, such as sapphire *using identical conditions*, is required for C_p accuracy. This is a particular problem for liquids, fibers, foams, powders and pellets where there may not be a convenient standard that is physically similar to the material being measured. It is not surprising that sinusoidal MTDSC has not become a commonly used practice in most thermal analysis laboratories.

TAKE-AWAY – StepScan MTDSC does not suffer from these problems because the calculation is performed at the point of equilibration where the completeness of equilibration is guaranteed by the selection of a criterion, and at which point the temperature gradients are negligible.

SmartScan improves StepScan

Previously, to quantitatively analyze the kinetic process using StepScan in a PerkinElmer Diamond DSC or Pyris™ 1 DSC, a baseline run under the identical method would have to be subtracted, thus doubling the time required for this analysis. (When only changes in the specific heat were of interest this step was not required.) Now with the DSC 8500 or DSC 8000, running an empty pan baseline may not be required for kinetic analysis if the SmartScan feature is in use. That is, with SmartScan the baseline is characterized as part of the instrument calibration procedure, and once done, the baseline of the analyzer is seen to be essentially linear over a wide range of conditions, namely, scan rate, and temperature limits. When running StepScan with SmartScan the baseline that would have been obtained from a separate baseline StepScan run is automatically subtracted as the data is taken. The

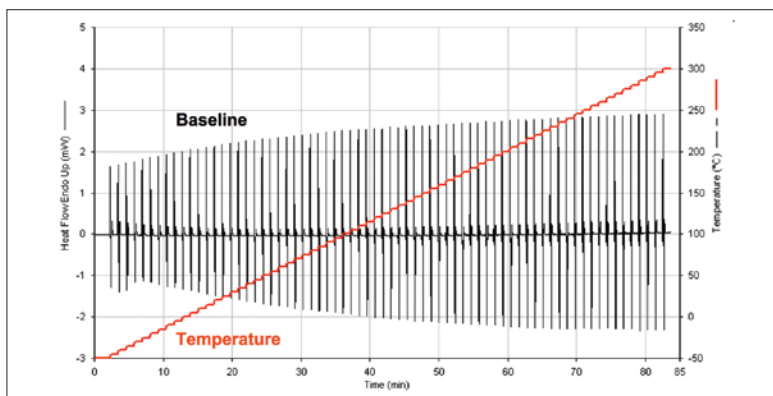


Figure 1. StepScan baseline when using SmartScan. (Not required since isothermals are near zero milliwatts).

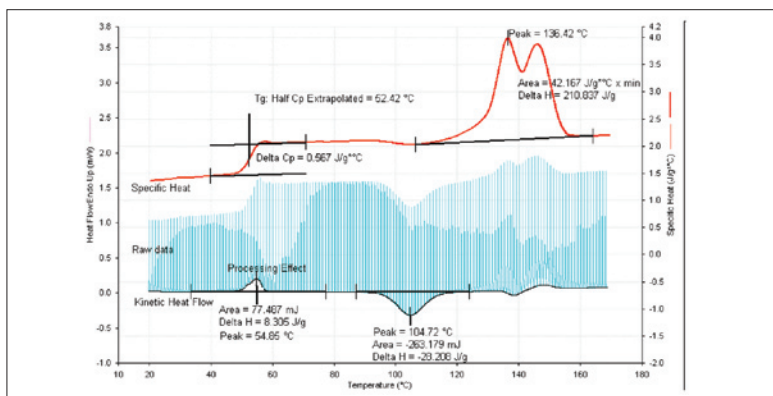


Figure 2. StepScan analysis of Lactosorb® facial tranche plate (from Lorenz® / Biomet Microfixation®).

result is a curve that represents the response of the sample specimen alone, with instrumental effects removed. If a StepScan baseline were run it would be seen to give a series of transients that return to zero milliwatts with each isotherm. An example of a DSC 8500 StepScan baseline is shown in the Figure 1.

Examples

The measurement of the glass transition has been one of the staple applications in the field of thermal analysis.⁶

Semicrystalline Polymers

The first example is that of a material used in resorbable plates used in reconstructive surgery. The plates have unique properties of strength, malleability and resorbability. The material, a polyester copolymer of 85% polylactic acid and 15% polyglycolic acid, is in the amorphous state. It is stiff enough to support in vivo screw attachment and yet will be entirely resorbed within 15 months. When a sample is scanned by a standard DSC it displays a large processing peak at the glass transition, which would be expected to correlate with mechanical properties which are critical for its first few hours in an aqueous environment during implantation. This peak can be easily resolved from the glass transition using StepScan as can be seen in Figure 2. This scan also shows partial crystallization above the glass transition and melting of crystallinity. These parameters can be measured separately on the specific heat curve or the kinetic curve generated by StepScan analysis. It should also be noted that similar information can also be obtained using a heat-cool-heat approach and a rapid heating rate.

TAKE-AWAY – From this, it can be seen that a complete separation can be achieved between the glass transition measurement and the overlapping, kinetically-controlled effects (process ordering and crystallization), and that each can be independently analyzed to obtain the required parameters – all without the added complexity and calibration required for sinusoidal MTDSC analysis.

Epoxy

The second example is the curing of epoxy adhesive, in this case, one that is used for such demanding applications as muffler and motor repair where high temperature post-cure stability is required. The primary and hardener were mixed and a small quantity transferred to a DSC pan which was immediately cooled to a subambient temperature to quench the reaction. The Pyris method used was the default method provided under the StepScan option. The criterion was made smaller to favor Cp accuracy over method brevity. The raw data, specific heat and kinetic curves can be seen in Figure 3 along with calculations. The glass transition region appears very broad because the mobility, hence, the position within the Tg interval, is changing as the cure progresses. If the reaction were quenched at various times in the middle of the curing reaction and the sample cooled and reheated rapidly it would be seen that the Tg is shifting to higher and higher temperatures as the cure progresses. The kinetic curve reflects the curing kinetics unaffected by the heat flow effect of the change in specific heat. In general a higher Tg corresponds to a greater degree of crosslinking. In this case (as in most other cases) similar, and more accurate information about the kinetics of reaction can be obtained using conventional DSC by scanning at a constant slow rate through the reaction (where the Cp change at Tg is a small effect) or by performing isothermal kinetics.⁷ The determination of degree of cure and residual heat of curing can also be obtained quickly and accurately by conventional DSC.

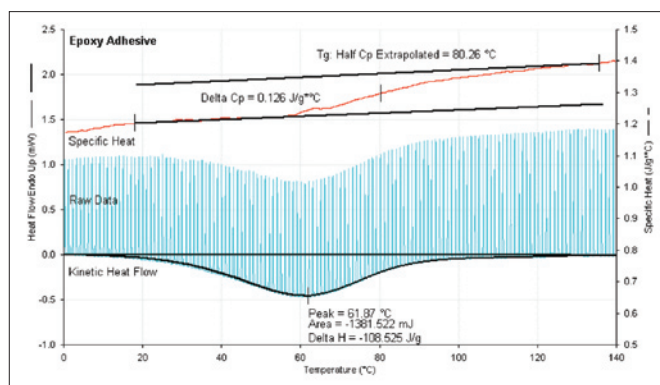


Figure 3. StepScan Analysis of an Epoxy Adhesive.

TAKE-AWAY – This example shows StepScan's ability to remove the glass transition heat flow displacement from the kinetics data, and to isolate and analyze a broad glass transition in the middle of a major curing reaction. Moreover, StepScan works equally well with samples in difficult encapsulations where sinusoidal MTDSC is likely to have extensive calibration issues that are avoided by StepScan by only analyzing data at thermal equilibrium.

Polymorphism

The third example is that of elucidating the polymorphic forms of pharmaceutical materials. MTDSC has been described as able to characterize the transitions that take place when a material that is initially in a high free energy state – such as when shock cooled into the amorphous state or crystallized into a metastable polymorphic form – is heated and allowed to relax into lower free energy states by way of solid-solid transitions or melting followed by crystallization. The material often used to illustrate this is the anti-seizure medication, carbamazepine. Figure 4 shows the StepScan analysis of carbamazepine after it has been shock-cooled from above the melting point of its highest melting polymorph into the amorphous form. Heating this form in the DSC indicates the glass transition of the amorphous form, crystallization into a crystalline polymorphic form, which then melts. While the MTDSC approach does help isolate the changes in specific heat and the kinetics of crystallization it doesn't answer the fundamental questions posed of polymorphic systems. Namely, what are the relative free energies of the different polymorphic forms as a function of temperature?⁸ The free energy curves will quantify the relative stability of the different polymorphic forms at production temperatures, storage temperatures and use temperatures. Since free energy is a predictor of solubility and stability this is exactly the information needed. Behme showed how this data could be obtained for carbamazepine using a DSC to first place the sample in each of the polymorphic forms and then determine the heat of fusion of each form – even for the case where an unstable polymorph immediately re-crystallizes into a more stable form.⁹ This standard DSC technique is benefited by fast scan rates, rapid equilibration, nimble temperature control and accurate calorimetry – all trademarks of power controlled DSC.

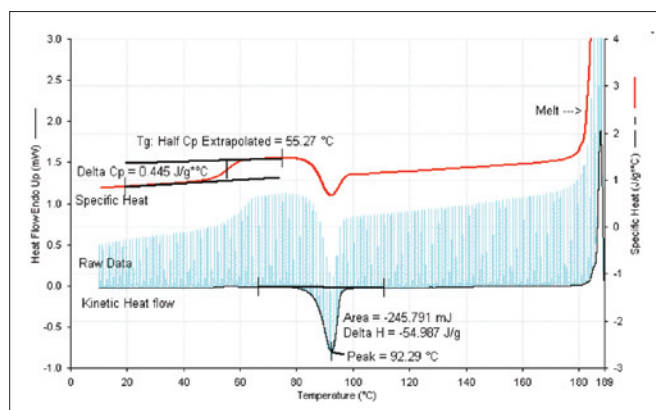


Figure 4. StepScan Analysis of carbamazepine shock cooled from the melt.

TAKE-AWAY – Fast scan techniques are generally recognized as a better way to analyze polymorphs. However, to the extent that MTDSC may cast light on a polymorphic system, StepScan is able to help interpret the transitions. Moreover, the fast equilibration time allows power-controlled DSC to jump quickly to the exact starting temperature and to shock cool samples without removing them from the DSC.

Detecting dilute amorphous phases

In most cases the best way to amplify a weak glass transition is to use a standard DSC method using a fast heating rate, if possible after first quenching the sample then cooling slowly through the expected Tg temperature region. However, because the glass transition is detected by a change in the heat capacity it should also be possible to use the high accuracy capability of StepScan to detect and quantify weak, broad or irregular shaped Tg transitions. The advantage of StepScan is that any extraneous thermal effects not involving the change in specific heat will not be observed on the specific heat signal. For example, frequently processing conditions or thermal history will result in irregular peaks or distortions in the heat flow data from standard DSC methods. These effects may make the positioning of the baseline tangents uncertain. In the case of a Tg observed on the StepScan specific heat signal, the transition will usually be more regular shaped and less ambiguous to analyze. In Figure 5 we see the glass transitions of the amorphous nylon phase and the styrene acrylonitrile phase with a volatiles/moisture peak removed from the Tg determination and appearing instead on the kinetic heat flow curve.

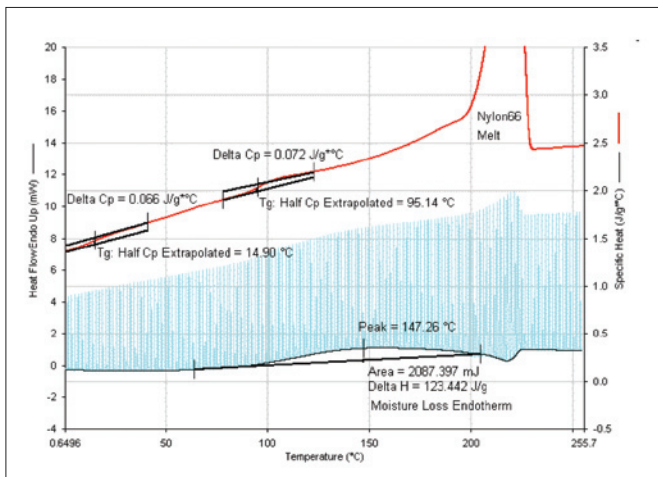


Figure 5. StepScan Analysis of a Nylon66-ABS Blend.

In Figure 6 we see detection and measurement of a low concentration of amorphous sucrose in a sample of finely milled crystalline sucrose. The extensive milling produces a fine crystalline powder but also a measurable amount of amorphous content. This ability to detect a small amorphous content in a crystalline phase has utility in the pharmaceutical industry where an amorphous phase impurity is more soluble, is more unstable and can lead to crystallization into a different crystalline form. Figure 7 shows the same data converted to heat flow units and sloped to better visualize the glass transition.

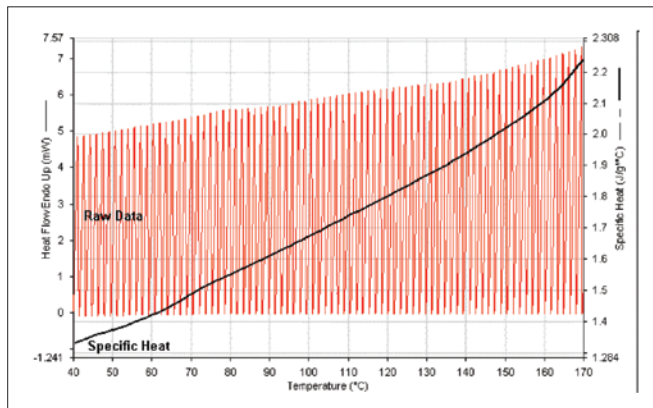


Figure 6. Determination of amorphous content in sucrose showing the raw StepScan data and calculated specific heat.

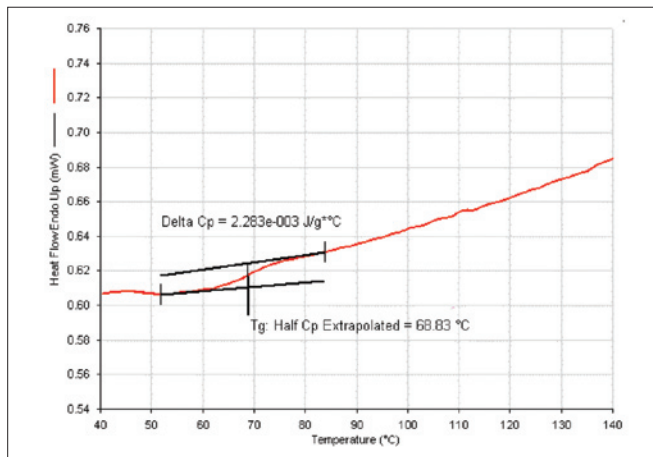


Figure 7. Conversion of specific heat data to Heat Flow units with scale expansion and slope change. Delta Cp indicates a change of 0.00283 J/g °C, which is ~1.1% amorphous content.

TAKE-AWAY – StepScan allows weak glass transitions to be more accurately analyzed by isolating the change in specific heat capacity from other thermal effects that can obscure the transition or complicate the positioning of tangent constructs.

Summary

While the excitement of MTDSC has now died down there are still cases where this approach is a useful one for simultaneously analyzing the glass transition and a kinetic phenomena, such as curing, crystallization or reorganization. In these cases, the use of SmartScan will have advantages over sinusoidal MTDSC programs because it avoids the calibration problems and it results in more reliable specific heat data.

As for extracting weak glass transitions, for example those of a small amorphous phase of highly crystalline thermoplastics like polyethylene, or for determining the small amorphous content of essentially crystalline materials, the method of using fast scan rates is likely to be more sensitive, and certainly much faster.¹⁰

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