How Tzero™ Technology Improves DSC Performance
Part IV: MDSC® Enhancement

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INTRODUCTION

The benefits of MDSC© are well known (*1*, *2*). MDSC is used to improve the DSC analysis of glass transition, melting, crystallization and reaction phenomena. As a practical matter, it allows for the separation of overlapping processes, the measurement of specific heat capacity, thermoconductivity and enthalpy of physical aging. It has been the subject of numerous symposia, and it is said to be the most important advance in thermal analysis of the last 30 years (*3*). When using MDSC, typical heating rates are 3 °C/min or less. Faster heating rates are now possible with the Q Series™ differential scanning calorimeters that incorporate Tzero™ Technology (Q100) or Advanced Tzero™ Technology (Q1000). To understand the improvements, we need to understand MDSC.

MDSC Utility

Differential scanning calorimetry is used to characterize the thermal behavior of materials. This thermal behavior consists in 1) how much energy is required to heat the material (e.g., its heat capacity), 2) the characterization of thermodynamic transitions, such as melting; and 3) the characterization of thermally induced kinetic processes such as cross linking reactions. Unfortunately, in multiple component systems there are often multiple processes overlapping one another. For example, polymers undergo softening over a glass transition temperature range. Over this interval not only does the specific heat capacity increase, but also there may be enthalpic relaxation related to thermal history, mechanical stress relief, a loss of volatile components and/or partial crystallization. All these effects involve the release or adsorption of energy, and so affect the DSC curve. Without further information, most of these effects are not separable, and they therefore produce uncertainty in the quantitation of the thermal process.

MDSC Separations

MDSC produces two DSC experiments at once: a constant, underlying rate of increase in temperature, and a small amplitude temperature modulation. Volatilization, crystallization, stress relief, and chemical reactions proceed at a rate *determined by the absolute (underlying) temperature*. A small change in temperature caused by the modulations hardly changes the rate of these kinetically controlled processes. Specific heat capacity and melting, however, are quite different. Their DSC response is *proportional to the amplitude of the modulation*. From deconvolution of the data from a single MDSC experiment three analytical curves are produced: the *total heat flow*, which would have been obtained without the modulation; the *reversing heat flow*, which quantifies specific heat capacity and melting; and the *non-reversing heat flow*, which is the purely kinetic component. Hundreds of technical papers have been published showing how to use this technique to separate the thermal processes in a wide range of materials.

MDSC Limitations

The challenge for MDSC is the need for heat capacity calibration that is dependent on the experimental conditions, especially on the frequency of modulation. Typically, a modulation period of 60 seconds is recommended. The second challenge is the necessary to have a minimum of 4-6 complete cycles across a transition. This means that when the sample material's specific heat capacity is changing rapidly with temperature (e.g., in a transition or reaction), it is necessary to use a very low underlying heating rate. As a result, underlying heating rates of 3 ºC/min, or less are common. This results in a long test time for MDSC methods.

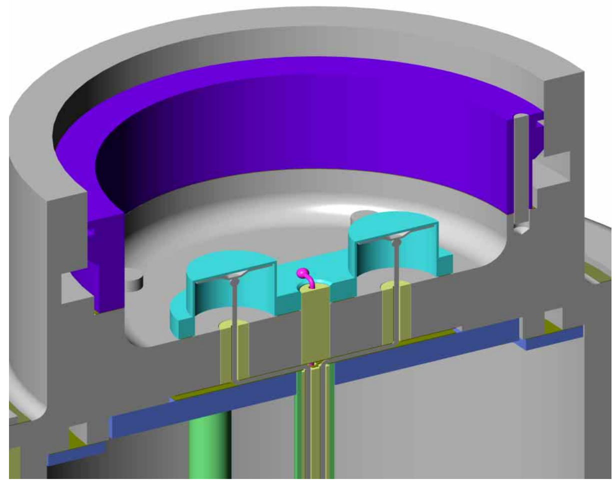
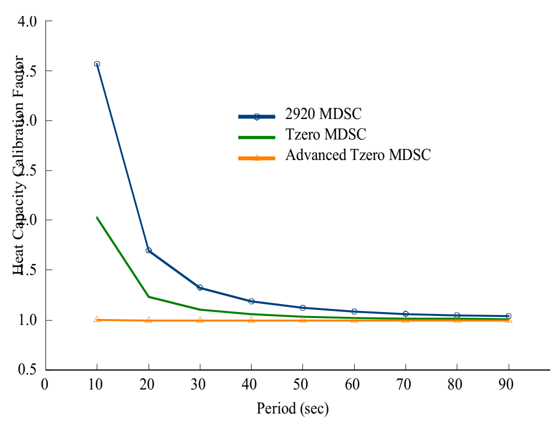


Figure 1 - Cutaway of the Qseries DSC Cell Design

Tzero™ Technology and MDSC©

The new Q Series DSC cell design dramatically changes MDSC analysis. A new T_o thermocouple separates the sample and reference positions and also is used to control the furnace. This thermocouple can be seen in figure 1 midway between the sample and reference platforms. This effectively isolates the sample and reference heat flows and allows a simple thermal model for the cell to be utilized (*4*). A special calibration procedure is used to determine the thermal resistances and capacitances in the new DSC cell. By incorporating the detailed cell description into the MDSC equations, the cell response to the modulation is addressed. Thus, by using the Tzero technology MDSC equations, the frequency dependence of the MDSC calibration curve is dramatically reduced. The practical benefit is that faster periods (40 s) and therefore faster heating rates (up to 5 °C/min) can be used resulting in a 40 % improvement in sample throughput for MDSC methods. Tzero technology is required to obtain this benefit and comes standard with the Q100 DSC.

Figure 2 - MDSC Calibration Factor



Advanced Tzero™ Technology

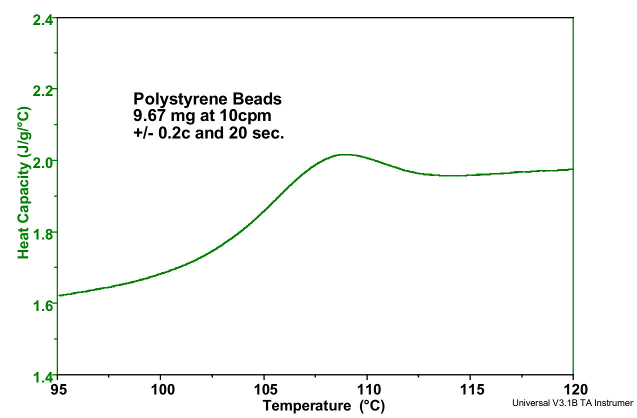
In an extension of this approach, the thermal resistances and capacitances of the sample and reference *pans* are also incorporated into the heat flow equations. This further enhancement to the heat flow relationships is referred to as Advanced Tzero

Technology (*5*). By compensating for all the resistance-capacitance lags in the system, Advanced Tzero Technology accounts for virtually all the instrumental effects. The result for ordinary DSC is unprecedented resolution (*6*), and the ability to obtain specific heat capacity data from a single DSC scan (*7*). For MDSC, this results in a calibration curve that is virtually independent of modulation frequency (see figure 2) permitting modulation periods down to 20 seconds to be used without incurring substantial calibration error. As a result of using the shorter period, underlying heating rates of up to 10 ºC/min may be used for many applications. As an example, the glass transition analysis of polystyrene in figure 3.

Benefits of Advanced Tzero MDSC

The advantages of using Advanced Tzero technology for MDSC are several. First, the use of an underlying rate of 10 ºC/min reduces experimental time to only one-third the time of traditional MDSC. This means that an MDSC experiment can be carried out in nearly the same amount of time as a standard DSC experiment. Second, signal strength in standard DSC is proportional to heating rate, while in modulated DSC signal strength is proportional to frequency. So, by increasing both the underlying rate and the frequency of oscillation, both components of the MDSC experiment are amplified. The result is higher sensitivity without sacrificing Cp accuracy. The result is accurate Cp data, and on a separate curve, quantitative analysis of kinetic events.

Figure 3 - Accurate Cp of Polystyrene by MDSC using 20 s period and 10 ºC/min



CONCLUSION

MDSC is a proven aid to understanding material behavior with a large body of literature from which to draw when selecting method parameters. The productivity and sensitivity of MDSC experiments is improved through the use of Tzero (Q100) and Advanced Tzero Technology (Q1000).

REFERENCES

1. *Material Characterization by Dynamic and Modulated Thermal Analytical* Techniques, A.T. Riga and L. Judovits (Eds.), American Society for Testing and Materials, West Conshohocken, PA, Special Technical Publication 1402, **2001**.

2. Modulated DSC is a high performance version traditional DSC in which a sinusoidal temperature profile in superimposed upon the traditional linear heating rate or isothermal operation. Fourier transformation of the resulting oscillatory separates the total heat flow into its reversing and nonreversing component parts.

3. B. Wunderlich, Y. Jin, and A. Boller, "Mathematical Description of Differential Scanning Calorimetry Based on Periodic Temperature Modulation", *Thermochimica Acta*, **1994**, 238, pp. 277-293.

4. R. L. Danley and P. A. Caulfield, "DSC Baseline Improvements Obtained by a New Heat Flow Measurement Technique", *Proceedings of the 29th Conference of the North American Thermal Analysis Society*, **2001**, pp. 667-672.

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6. R. B. Cassel, "How Tzero™ Technology Improves DSC Performance, Part II: Peak Shape and Resolution", TA Instruments Applications Brief TA298.

7. R. B. Cassel, "How Tzero™ Technology Improves DSC Performance, Part III: The Measurement of Specific Heat Capacity", TA Instruments Applications Brief TA299.

KEYWORDS

modulated differential scanning calorimetry