TA Instruments

Thermal Analysis & Rheology

Heat Capacity Measurements
Using Quasi-Isothermal MDSC™

L. Thomas & S. Aubuchon

Introduction

Heat capacity (or its mass normalized relative, specific heat capacity) is a measure of the energy required to raise the temperature of a material. Measurement of heat capacity, a structure sensitive property, can readily be achieved using conventional differential scanning calorimetry (DSC) between -100 and 725°C. The measurement is made by heating a test sample at a fixed heating rate over a designated temperature range. The resulting heat flow response, normalized for sample mass and heating rate, is directly proportional to specific heat via:

$$Cp = \frac{EQ}{RM} \qquad (1)$$

where Cp = Specific Heat Capacity
E = DSC Calibration Factor
Q = Heat Flow
R = Heating Rate
M = Sample Mass

In fact, this measurement has become so widely accepted that an ASTM Test Method E1269 has been developed based on this DSC approach.

Modulated DSC™ (MDSC), which is an exciting new extension to conventional DSC, also provides the ability to obtain heat capacity information but has several additional benefits compared to measurement by conventional DSC including:

- **Better accuracy and precision -** MDSC separates nonreproducible experimental artifacts from the measurement.
- **Unique information -** MDSC provides Cp results at low heating rates and even under "isothermal" conditions.

It is this latter benefit, measurement of Cp under "isothermal" conditions, which will be explored in this paper.

Theory

In conventional DSC, Cp is generally calculated from the difference in heat flow between a blank (empty pan) run and a sample run under identical conditions including heating rate. Using that approach, equation (1) becomes:

$$Cp = K_{Cp} \text{ x } \frac{Q\,(\text{sample}) - Q\,(\text{blank})}{R} \qquad (2)$$

where K_{Cp} = Cp cell 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 (R_1 and R_2). Using that approach, equation (1) becomes:

$$Cp = K_{Cp} \text{ x } \frac{Q\,(\text{sample at } R_2) - Q\,(\text{sample at } R_1)}{R_2 - R_1} \qquad (3)$$

where $R_2 > R_1$

Curves 1 and 2 in Figure 1 show typical results for sapphire, whereas Curve 3 represents sapphire run at a faster heating rate. The Cp values at 50°C calculated from those curves using equations (2) and (3) are 14.7 and 14.5 mJ/C respectively.

In MDSC, Cp is determined by dividing the modulated heat flow amplitude by the modulated heating rate amplitude. The validity of this approach is proven by considering the curves in Figure 2 where 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 1. The direct correspondence of the resultant heat flows at the extremes of the modulated heat flow curve and curves 2 and 3 from Figure 1 shows that equation (3) applies. Note, however, that modulated DSC only requires one experiment to give results compared to multiple conventional DSC experiments.

Furthermore, the modulated heating rate amplitude and the resultant modulated heat flow amplitude in MDSC are dependent not only on the underlying heating rate but also the modulation amplitude and period. As a result, the modulated heating rate, the modulated heat flow, and therefore Cp can have finite values even when the underlying heating rate is zero (i.e., under "quasi-isothermal" conditions).

Figure 1. **Sapphire Heat Capacity - Conventional DSC**

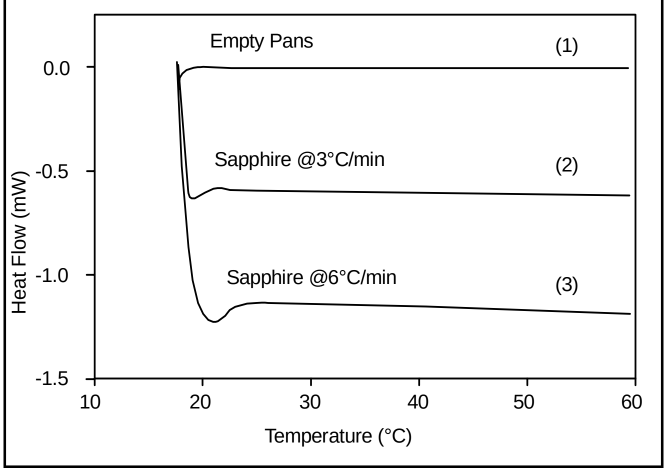
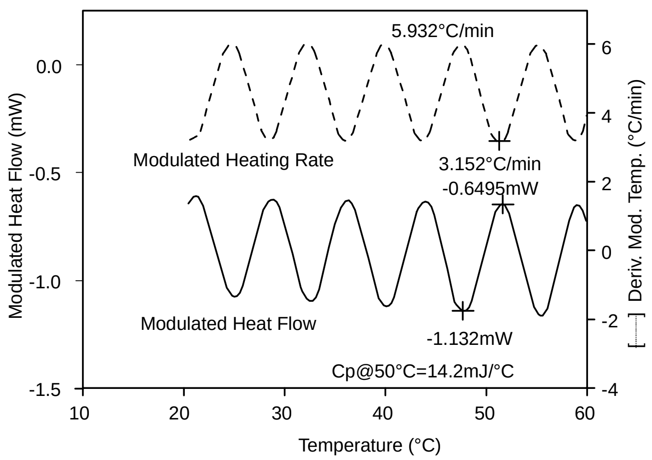


Figure 2. **Sapphire Heat Capacity - Modulated DSC**



Applications

Improved Cp Measurement in Metals

Heat capacity values for most metals are low relative to other materials such as polymers. Therefore, minor experimental variations have a significant effect on the accuracy of the results obtained. As Figure 3 shows, however, with MDSC™ quasi-isothermal measurements, it is possible to obtain good accuracy over a broad temperature range even with low heat capacity metals.

Figure 3. Copper Heat Capacity - Modulated DSC

Temp. (°C)	Cp (MDSC) (J/g/°C)	Cp (Liter.) (J/g/°C)
-154.3	0.2462	0.2812
-102.4	0.3116	0.3401
-51.5	0.3432	0.3656
-1.1	0.3639	0.3783
49.2	0.3737	0.3877
99.3	0.3784	0.3971
199.4	0.3863	0.4128
249.4	0.3977	0.4187
299.5	0.4175	0.4284

Increased Tg Accuracy & Precision

Glass transitions in polymers are measured by DSC based on the change in heat capacity that occurs. The size of this change, and hence the ability to detect the glass transition, increases as the heating or cooling rate increases. Unfortunately, in addition to affecting sensitivity, the heating/cooling rate also affects the shape and temperature of the transition. This phenomenon is illustrated in Figure 4. The solid curves represent the results of multiple heating and cooling cycles on polystyrene. These show excellent reproducibility on either heating or cooling but significant differences between the increasing and decreasing temperature profiles even at 1°C per minute. The dashed curve, on the other hand, represents the Cp values obtained using a series of MDSC quasi-isothermal steps. In this case, the same values are obtained when approaching the glass transition from either lower or higher temperature. MDSC, therefore, provides the steady-state glass transition shape and temperature.

Figure 4. Polystyrene Glass Transition

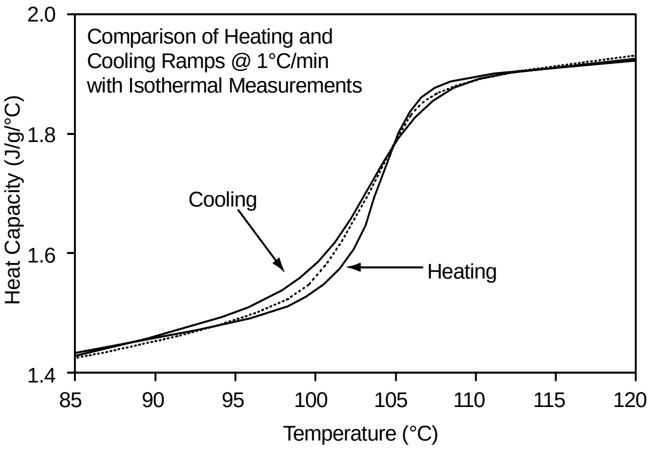
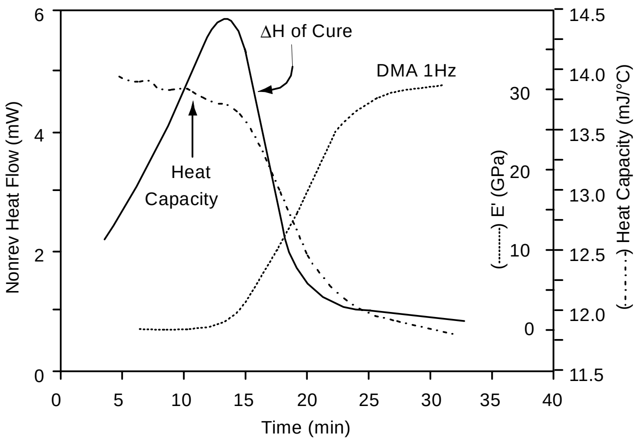


Figure 5. Isothermal Epoxy Cure



Heat Capacity During Cure

The measurement of heat capacity during the isothermal cure of thermosetting polymers is impossible by conventional DSC, not only because no heating rate exists but also because the exothermic heat flow associated with curing occurs simultaneously. Conversely, MDSC separates the nonreversing (kinetic) curing process from Cp and allows both to be quantified. Figure 5 shows results for an epoxy resin. As expected, the heat capacity decreases during cure as the material's free volume decreases 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. [Publication TA 219 describes similar results and their use for generating temperature-time transformation cure diagrams.]

Heat Capacity During Cold Crystallization & Melting

Determination of the heat capacity changes during cold crystallization (Figure 6) and melting (Figures 7 and 8) illustrate two more situations where modulated DSC provides information not available from conventional DSC. During cold crystallization heat capacity first increases due to increased molecular mobility above Tg, but then decreases as the rearrangement to a more stable crystalline form occurs. In this region, the primary benefit of MDSC is its ability to separate Cp from the exothermic kinetic crystallization process. However, quasi-isothermal measurement improves reproducibility.

On the other hand, the measurement of Cp during melting, using modulated DSC with an underlying heating rate greater than zero, is complicated by the fact that two "apparently reversing" phenomena (Cp and melting) contribute to the modulated heat flow amplitude and hence create an artifically 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 theoretical predictions. This latter measurement is still relatively new and more work needs to be done to determine its practical limits.

Figure 6. Heat Capacity Change at Cold Crystallization

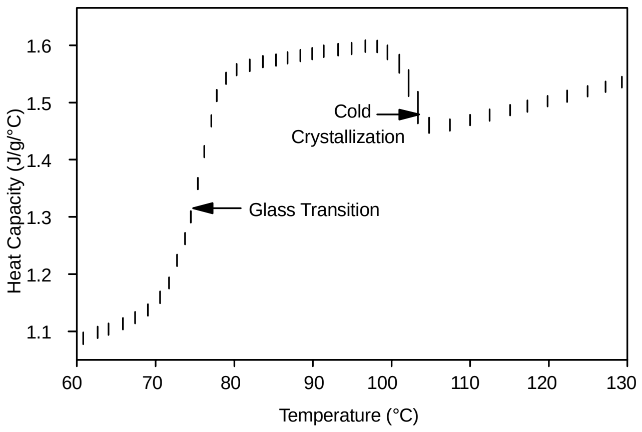


Figure 7. Slow Cooled PET

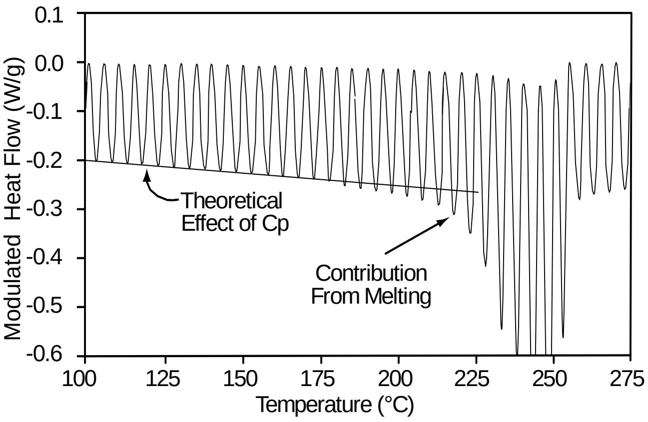
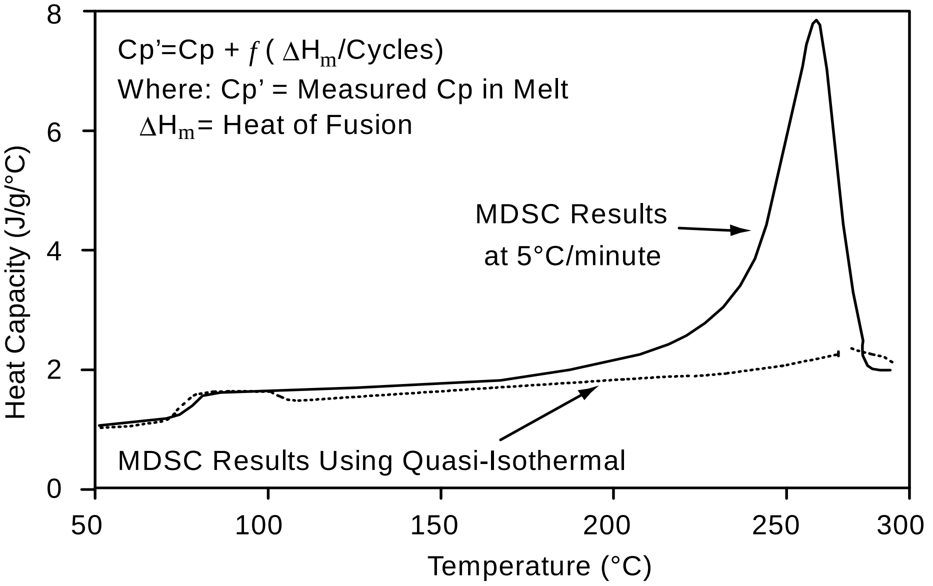


Figure 8. Cp in Melt Region by MDSC



For more information or to place an order, contact:

TA Instruments, Inc., 109 Lukens Drive, New Castle, DE 19720, Telephone: (302) 427-4000, Fax: (302) 427-4001
TA Instruments S.A.R.L., Paris, France, Telephone: 33-01-30489460, Fax: 33-01-30489451
TA Instruments N.V./S.A., Gent, Belgium, Telephone: 32-9-220-79-89, Fax: 32-9-220-83-21
TA Instruments GmbH, Alzenau, Germany, Telephone: 49-6023-30044, Fax: 49-6023-30823
TA Instruments, Ltd., Leatherhead, England, Telephone: 44-1-372-360363, Fax: 44-1-372-360135
TA Instruments Japan K.K., Tokyo, Japan, Telephone: 813-5434-2771, Fax: 813-5434-2770

Internet: http://www.tainst.com

TA *Instruments*
Thermal Analysis & Rheology
A SUBSIDIARY OF WATERS CORPORATION