High Heating Rate Modulated DSC® Using Tzero™ DSC Technology

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BACKGROUND

Modulated DSC® (MDSC®) is nearly a ten-year old technique that has numerous demonstrated advantages over traditional DSC including:

1. Higher sensitivity for detecting weak glass transitions.
2. Higher resolution for separation of transitions close in temperature
3. The ability to separate the Total heat flow of DSC into the heat capacity and kinetic components.
4. More accurate measurement of crystallinity for polymers that change in crystallinity as they are heated.
5. The ability to measure heat capacity under quasi-isothermal conditions.

Even with all of these advantages, there are several disadvantages that prevent MDSC® from replacing traditional DSC for all applications. These include:

1. Experimental parameters are more complex since it is necessary to specify a temperature modulation period and amplitude in addition to the average rate of change.
2. Separation of the Total heat flow signal into the heat capacity and kinetic components is sometimes difficult to interpret.
3. Slow average heating rates are required in order to obtain a minimum of 4 to 5 modulation cycles over the critical region of a transition. The lower average heating rate increases the time of an MDSC® experiment by a factor of 5 to 10 over traditional DSC.

Issues 1 and 2 are reduced or eliminated with user experience and training. However, the issue of needing to use low average heating rates is a problem in many laboratories because it affects productivity.

DETAILS

Experience with the technique of MDSC® has shown that it is necessary to have sufficient temperature modulation cycles over the temperature range of the transition in order to get a good separation of the Total heat flow signal into the heat capacity and kinetic components. Ideally, the temperature modulation could be fast, on the order of 5 to 10 seconds, which would permit a heating rate of about 20°C/minute for a transition that is 10°C wide.

$$\frac{10°C}{20°C/\text{min}} = 0.5\ \text{min}\ \ x\ \ \frac{60\ \text{sec}}{\text{min}}\ \ x\ \ \frac{1\ \text{cycle}}{5\ \text{sec}} = 6\ \text{cycles}$$

The problem is that most samples cannot follow such a fast modulation due to a number of thermal resistances within the sample, pan and sensor. A practical way of determining the effect of these resistances on the measurement is to perform an MDSC® experiment at room temperature on the sample to be analysed. By doing it at room temperature, the sample properties are not changed prior to the actual measurement, which is usually over a temperature range.

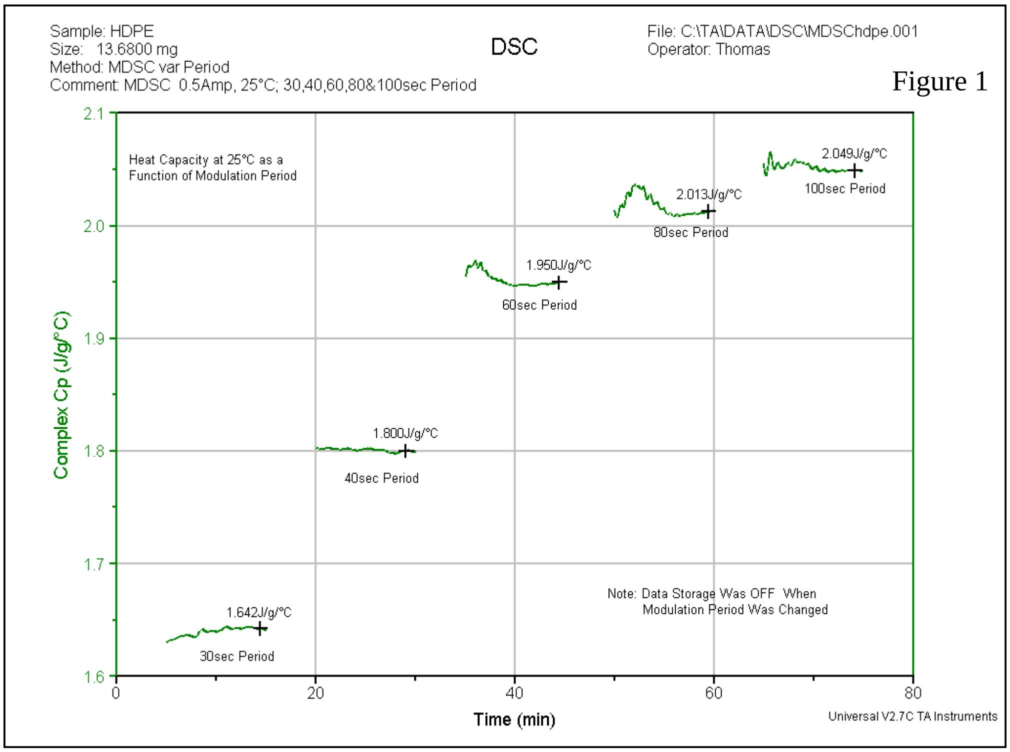

Figure 1

Figure 1 shows the effect of modulation period on a sample of high-density polyethylene. As seen in the data, the measured heat capacity for the 30- and 40-second periods is low by 15 – 20% as compared to the 100-second modulation period. This is due to the mentioned thermal resistances as well as the use of sensor temperature instead of sample or pan temperature in the calculation.

$$\text{Heat Capacity} = \frac{\text{Amplitude of Modulated Heat Flow}}{\text{Amplitude of Modulated Heating Rate}}$$

$$Cp = \frac{A_{MHF}}{A_{MHR}}$$

In the above equation, A_{MHF} becomes too small due to heat transfer problems in the sample pan and measurement sensors at short periods, and A_{MHR} is too large at short periods because pan temperature does not follow sensor temperature as well as it does at slow, long periods.

An improved MDSC® measurement is now possible with new Tzero™ DSC technology from TA Instruments. The new DSC cell and measurement principle provide improved performance due to at least 4 technical improvements:

1. Measurement of the modulated heat flow signal is made independently at both the sample and reference sensors. This eliminates any effect due to differences in phase lag between the heat flow and heating rate signals for the sensors.
2. Each sensor is calibrated for thermal resistance as a function of temperature, and this is accounted for in the calculation of the modulation heat flow signal.
3. The contact resistance between the pan and the sensor is also accounted for in the measurement. Nominal values are used based on each pan type.
4. Sample pan temperature is calculated based on the following relationship and is used in the calculation of the modulation temperature amplitude instead of sensor temperature.

$$Q_S = \frac{T_S - T_{PS}}{R_P}$$

$$T_{PS} = T_S - Q_S \times R_P$$

Where: Q_S = Sample Heat Flow
T_S = Sample Sensor Temperature
T_{PS} = Sample Pan Temperature
R_P = Contact Resistance between Sample Pan and Sensor

The benefit of these changes is obvious from Figure 2. The measured heat capacity for a typical sample of HDPE is essentially unchanged for periods of 30 – 100 seconds. This compares to a difference of more than 20% for previous technology as seen in Figure 1.

The application of Tzero™ technology to the MDSC® measurement of a glass transition is seen in Figure 3 for Polystyrene. Experimental conditions were varied from an average heating rate of 2.5 to 10°C/min. In order to achieve the same number of cycles across the transition, the modulation period was set to 20 seconds for the 10°C/min experiment and to 80 seconds for the run at 2.5°C/min. The modulation amplitudes were also varied between ± 0.2 and 0.8°C in order to obtain the same change in modulated heating rate for all experiments.

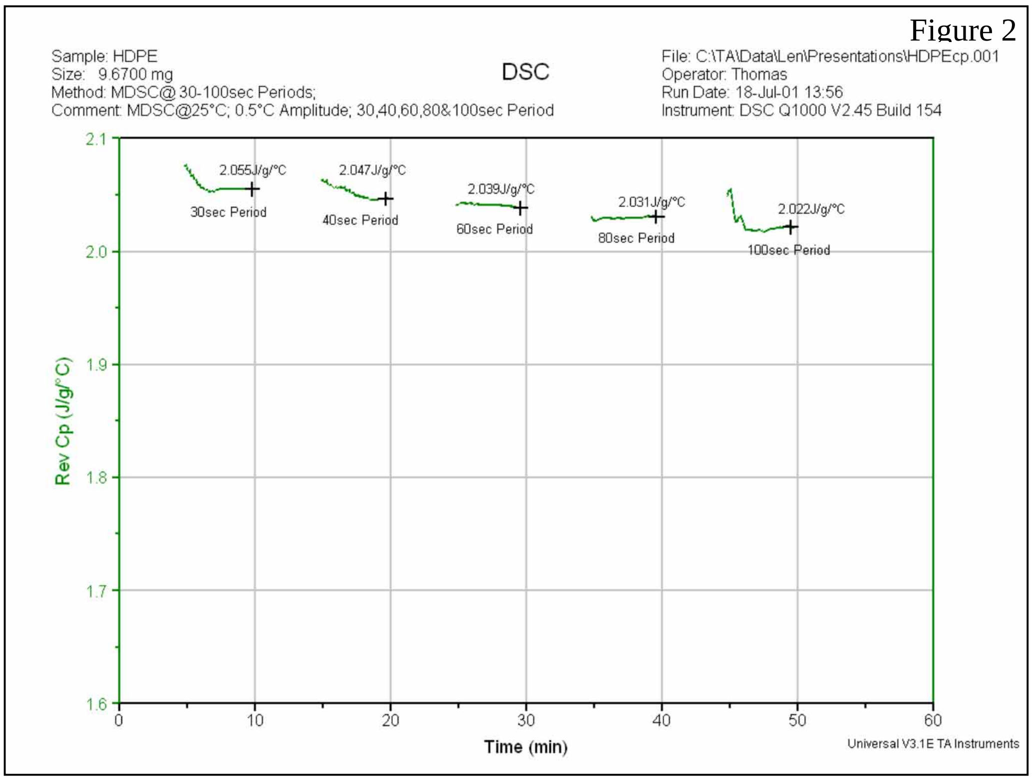

Figure 2

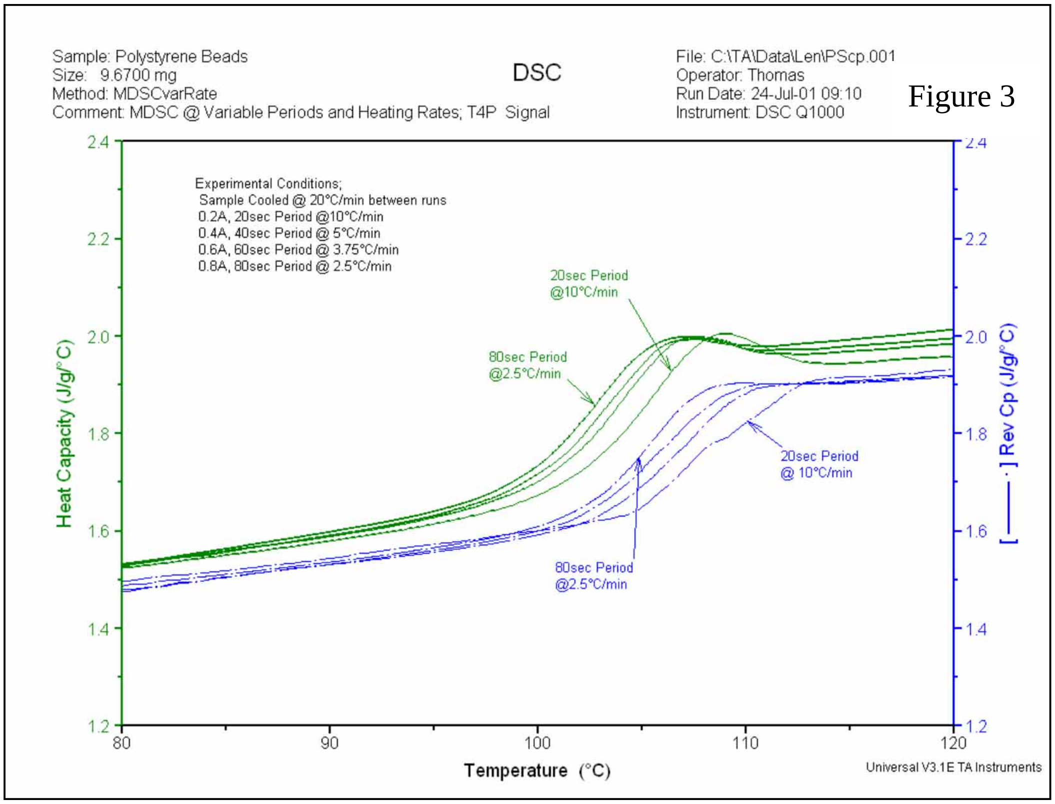

Figure 3

From the data in Figure 3, several observations can be made:

1. There is a total range in heat capacity values of approximately 5% for the Total and Reversing Cp signals. In general, higher average heating rates (10 – 20°C/min) give more accurate Total Cp values.
2. Higher average heating rates give higher values for the glass transition temperature as seen in both the Total and Reversing signals (thermal lag).
3. For a given heating rate, the Reversing signal gives a higher Tg than the Total signal. This is due to the “Frequency Effect” where the Tg is shifted to higher temperatures at higher modulation frequencies (shorter modulation periods).
4. The accuracy of the data is essentially unaffected by the modulation period with the Tzero™ DSC technology, although noise in the transition region is a little worse with a 20-second period.

SUMMARY

Tzero™ DSC provides the following benefits for Modulated DSC®:

1. Higher average heating rate.
2. Greatly reduced need to calibrate for Cp as a function of modulation period.