



Modulated DSC[®] Paper #8 Use Of Quasi-isothermal Mode for Improved Understanding of Structure Change

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ABSTRACT

MDSC provides the ability to measure heat capacity and changes in heat capacity during isothermal operation and during kinetic processes such as crystallization and chemical reaction.

INTRODUCTION

DSC has been used for isothermal experiments since its conception. The analyst selects the constant temperature and time period over which the sample will be maintained. The sample can be ramped at a heating / cooling rate to that temperature or the method can be set to jump to that temperature as fast as the DSC can heat or cool. The result is a plot of heat flow versus time. Since it is impossible to measure heat capacity at a constant temperature, it is only possible to study the rate and degree of reaction for kinetic processes by isothermal DSC. The explanation for this is easily seen in the basic equation used to describe heat flow from DSC or MDSC.

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)$$

Where:

dH/dt = heat flow (mW or W/g) rate as measured by the DSC

C_p = sample heat capacity (J/°C)

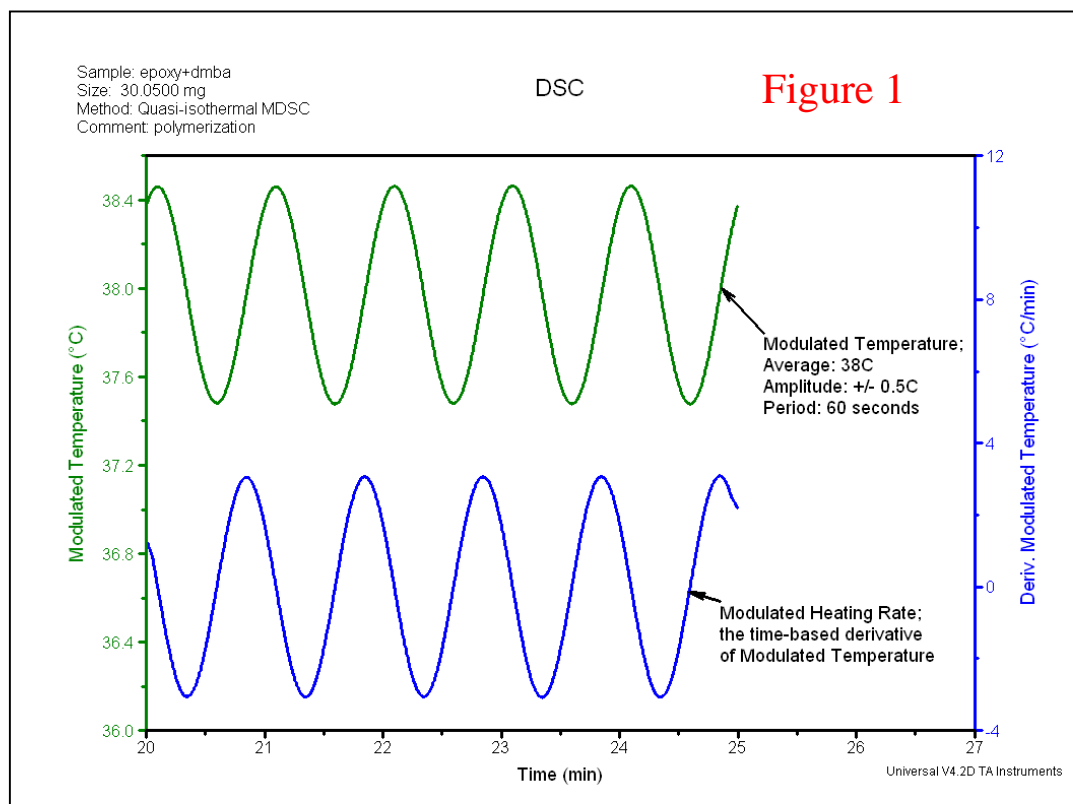
dT/dt = heating rate (°C/min)

$f(T,t)$ = heat flow (mW or W/g) that is a function of temperature and time

If a zero heating rate is used, as in a DSC isothermal experiment, the heat capacity term becomes zero, and the only measured heat flow comes from the kinetic term $f(T,t)$.

As discussed in an earlier paper (1), MDSC has a unique advantage since it uses two simultaneous heating rates. If the average heating rate is set to zero, the average temperature remains constant. The modulated heating rate can be set large for better sensitivity or small for improved resolution. Since the modulated heating rate results from selection of a modulated temperature amplitude and a modulation period, the user selects the size (amplitude) of the temperature oscillation to be superimposed on the

constant temperature and the time period (seconds) for each cycle. The term *Quasi-isothermal* describes this type of experiment in which a small temperature oscillation (typically $<1\text{ }^{\circ}\text{C}$) is applied to a constant average temperature. Figure 1 shows both the temperature and heating rate from an MDSC quasi-isothermal experiment.



Even though the average temperature remains constant in MDSC, it is possible to measure heat capacity because of the modulated heating rate.

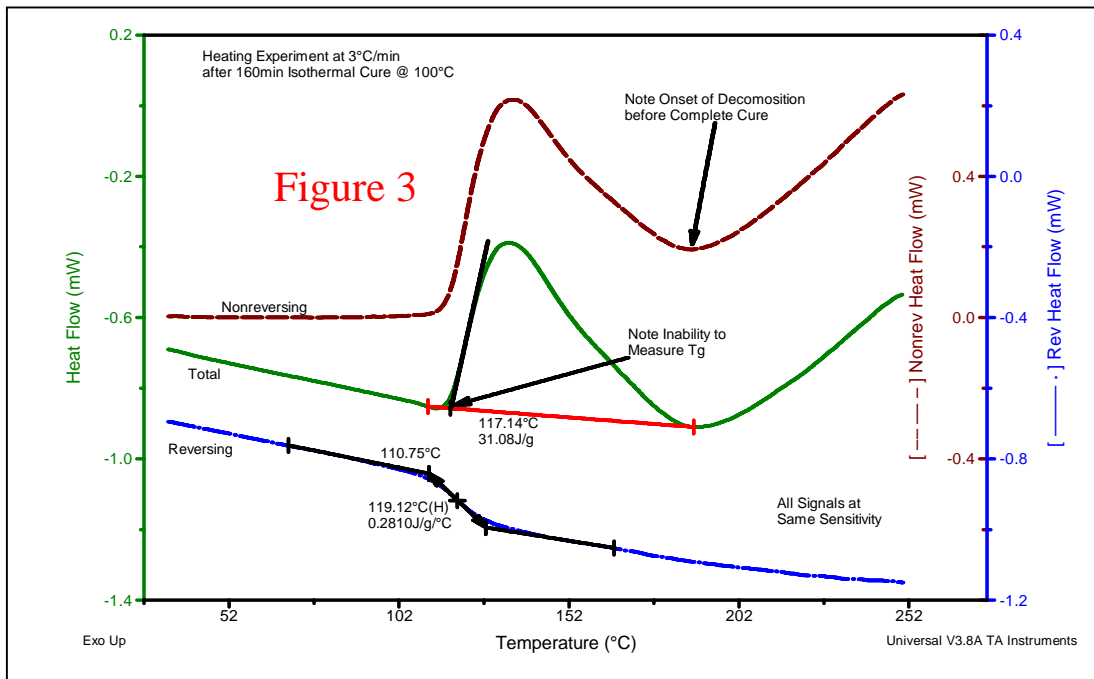
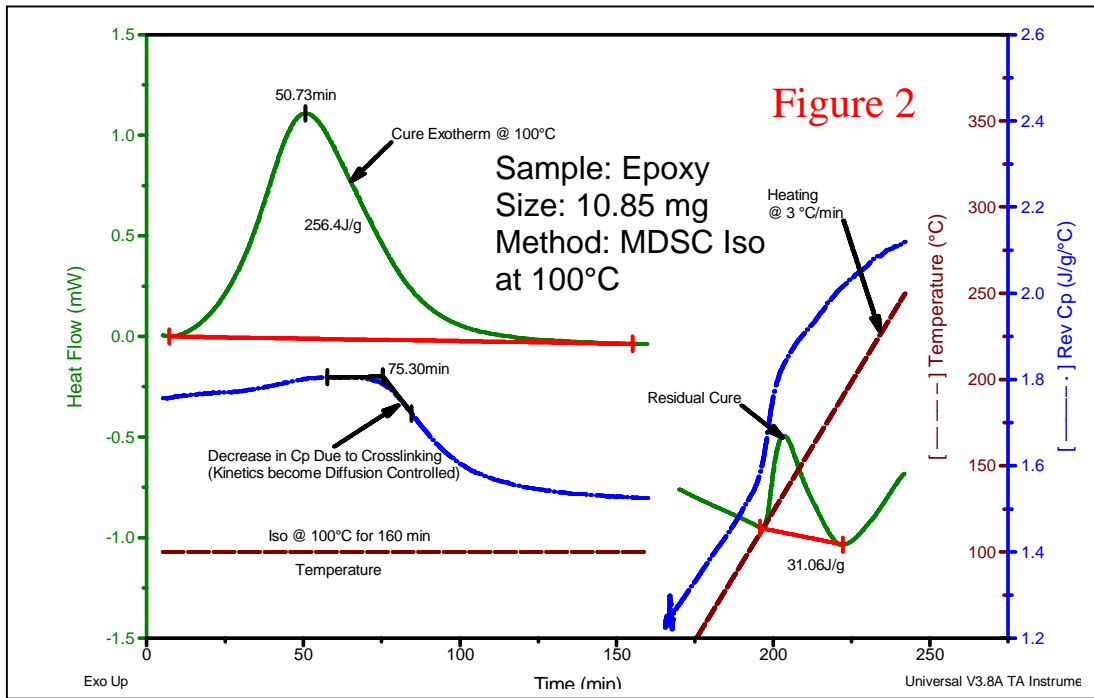
EXPERIMENTAL CONDITIONS

There are two different types of quasi-isothermal experiments and it is easy to select MDSC experimental conditions for each. The most common type is one in which a single isothermal temperature is used such as illustrated in Figure 1. A method for such an experiment might look like the following:

1. Equilibrate 38°C
2. Modulate $\pm 0.5^{\circ}\text{C}$ every 60 seconds
3. Isothermal for 160 minutes

Figure 2 illustrates a typical MDSC quasi-isothermal data on a sample of epoxy resin. The plot shows the Total heat flow, Reversing Heat Capacity and temperature versus time. The exothermic cure peak is seen in the Total signal and the amount of reaction during that time calculated in software to be 256 J/g . The Reversing Cp signal shows how the heat capacity decreases towards the end of the curing exotherm. This is a result of cross-linking of the molecules, which results in lower mobility and therefore, lower heat capacity. This decrease in mobility is what causes the reaction rate to slow as

the reaction moves from chemical control to diffusion control. This can be verified by heating the sample above 100 °C once the isothermal experiment is completed. This is seen at the end of Figure 2 and in the temperature plot displayed in Figure 3. Once the sample is heated above the start of Tg near 100 °C, the reaction begins again and there is an additional 31 J/g of reaction.



Note that it is not possible to see or measure the glass transition of the partially cured epoxy in the Total signal, which is equivalent to what would be obtained by standard DSC. The reason for this is that the endothermic glass transition is hidden by the more energetic exothermic reaction.

Important Note:

Many new MDSC users are often confused by the fact that the Reversing and Nonreversing Heat Flow signals have a value of zero during quasi-isothermal experiments. This is due to the fact that all signals that use a calculation that involves subtraction, multiplication or division by zero are automatically set to zero by the software. For example:

- Reversing Heat Flow = Reversing Cp X Avg. Heating Rate
 - Since the average heating rate is zero during a quasi-isothermal experiment, the Reversing Heat Flow is also zero

- Nonreversing Heat Flow = Total - Reversing
 - Since Reversing Heat Flow is zero, Nonreversing Heat Flow is also set to zero and the only Heat Flow signal that can be obtained during quasi-isothermal operation is the Total signal

- Total Heat Capacity = Total Heat Flow ÷ Avg. Heating Rate
 - Since the average heating rate is zero during quasi-isothermal operation, the Total Heat Capacity signal is also zero

The second type of quasi-isothermal experiment uses a series of isothermal experiments that involve a change in the average temperature at fixed time increments. It can be used to study both thermodynamic events such as the glass transition(s) or kinetic processes such as thermoset cure or crystallization. Examples of a typical method and applications are provided below.

Example of Quasi-isothermal Method With Increasing Temperature Steps

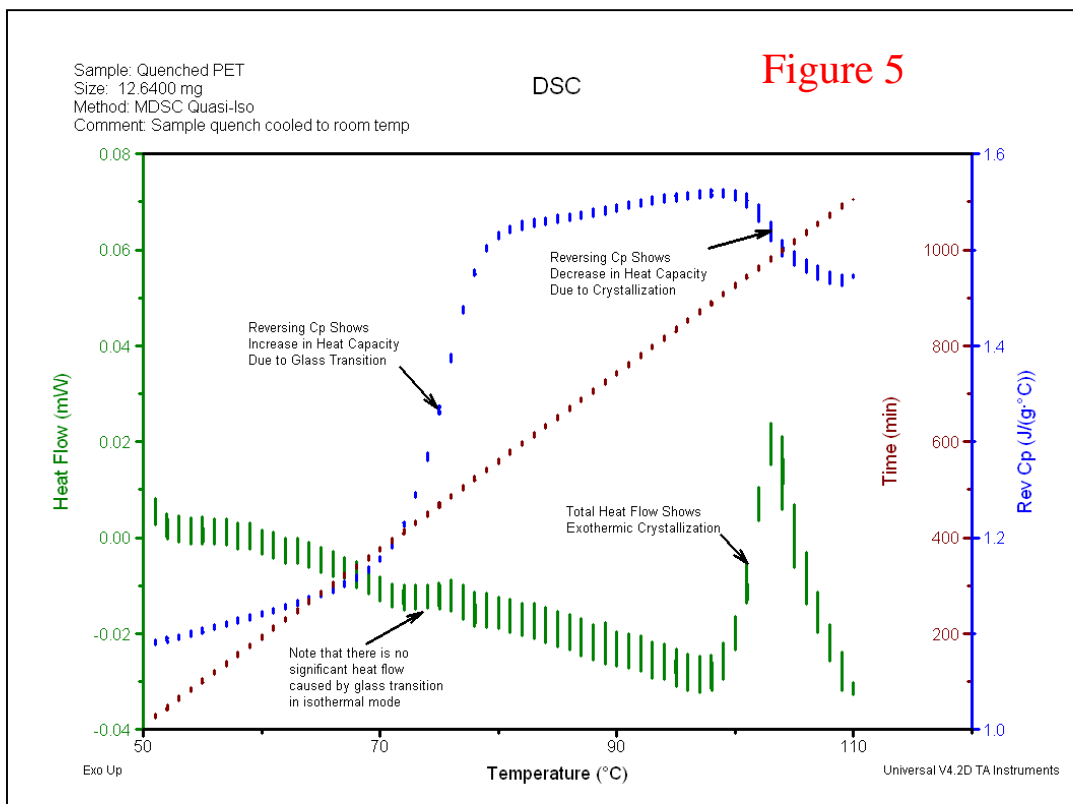
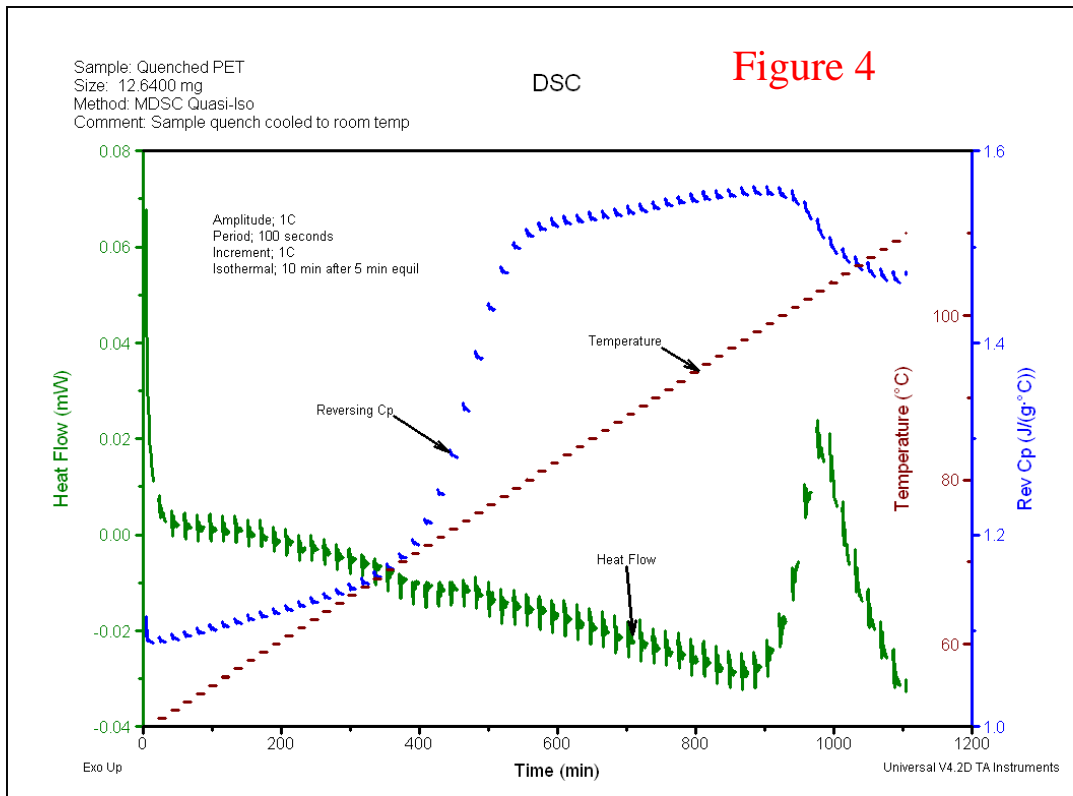
1. Data Storage *OFF*
2. Equilibrate *50C*
3. Modulate *+/- 0.5°C* every *100* seconds
4. Isothermal for *5* minutes
5. Data Storage *ON*
6. Isothermal for *5* minutes
7. Data Storage *OFF*
8. Increment *1°C*
9. Repeat Segment *4* for *100* times

An explanation for some of the segments in the above method will help the reader become more familiar with the technique.

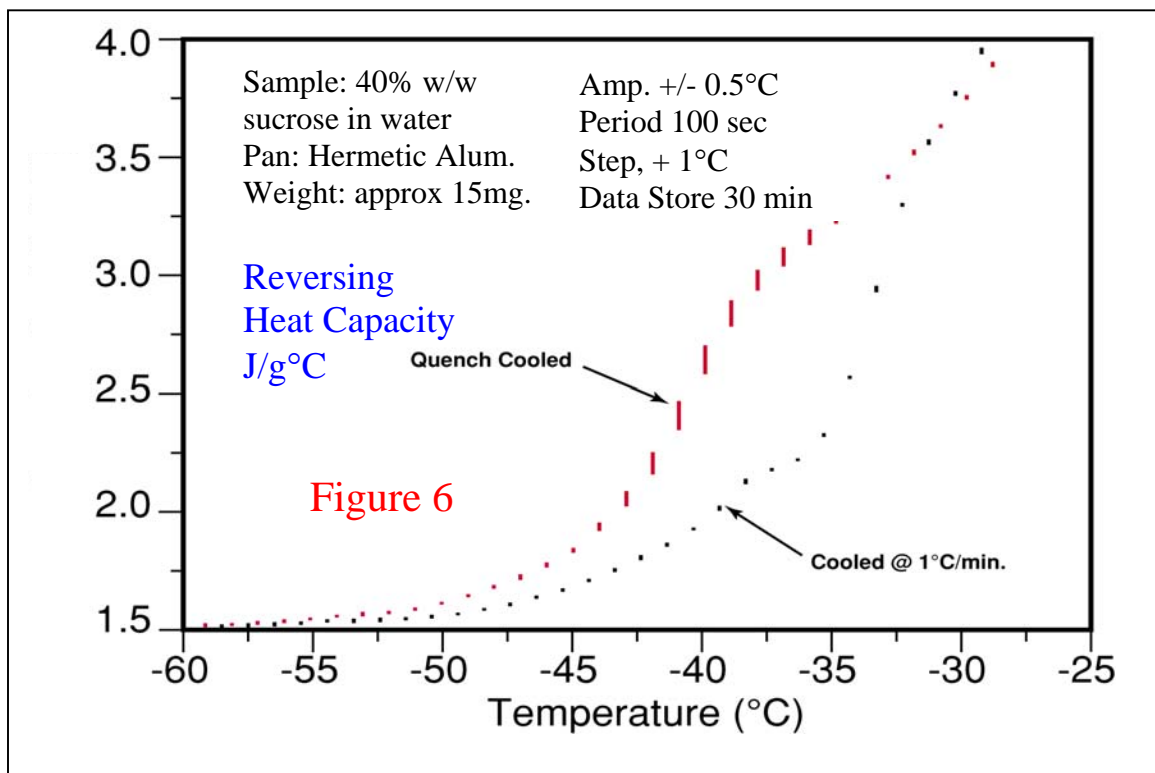
- Segments 1 and 5, Data Storage; the quality of the data can be significantly improved if data is collected only after equilibration at the set-point temperature. In this example, equilibration periods of 5 minutes are used before data storage is turned on and the data collected for 5 additional minutes at that temperature.
- Segment 3, Modulate Segment; although smaller amplitudes can be used, good sensitivity and resolution are obtained over the range of 0.5 °C to 1.0 °C. Since there is no concern with obtaining a sufficient number of cycles over a transition, a longer period (100 seconds) is recommended to insure optimum heat flow between the sample and sensor.
- Segment 8, Increment; although larger or smaller steps can be made, steps of 1 °C are a good starting point. If the mature of the sample requires decreasing temperature steps, simply use negative values (-1 °C).
- Segment 9, Repeat; this segment defines the number of steps. If a value of one (1 °C) degree is used for the increment segment then 100 such steps will result in quasi-isothermal measurements over a 100 °C range.

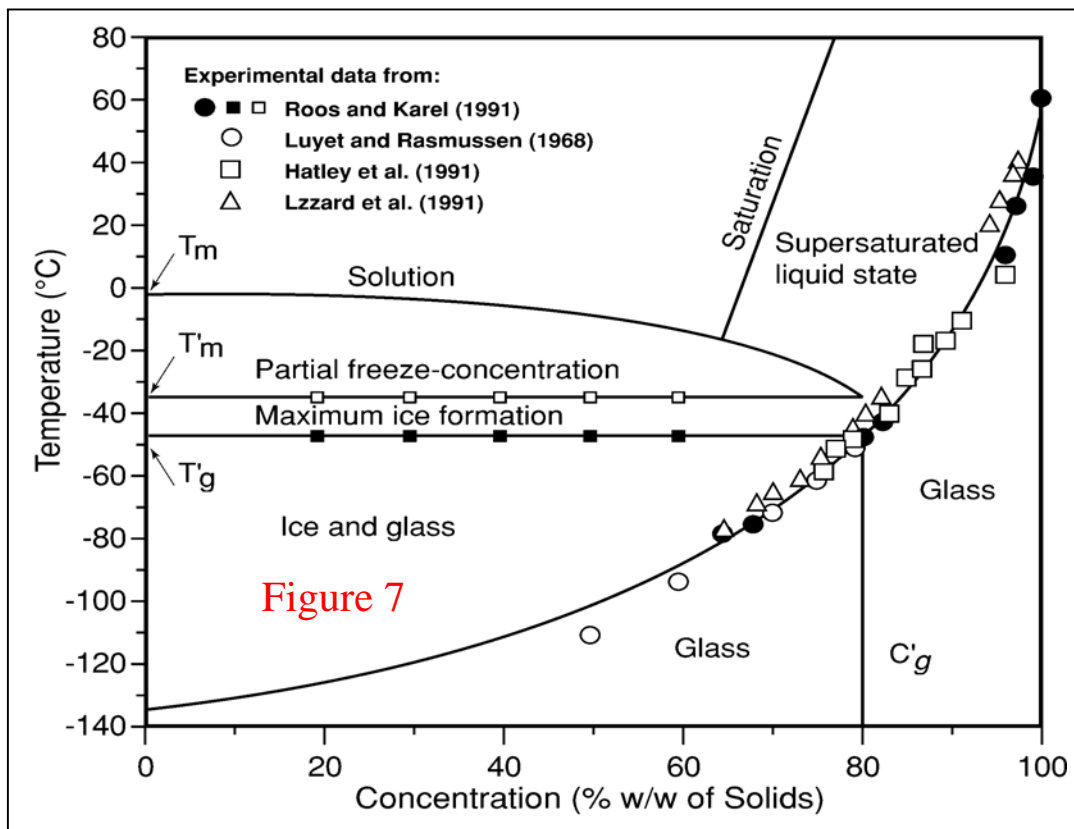
Although not specified in the method described above, a data collection rate of 1 point every 10 seconds is sufficient for this type of measurement. This compares to the recommended data collection rate of 1 point every 2 seconds for normal MDSC heating / cooling experiments. Time and temperature plots from a quasi-isothermal experiment on a sample of quench-cooled PET are shown in Figures 4 and 5. A few features from these figures deserve comment:

- Except for the first few minutes of the experiment, the Total heat flow signal only changes by about 30 microwatts over almost 20 hours and most of that is due to the exothermic crystallization. This is an example of extremely good baseline stability.
- The Reversing Cp signal is very stable in the middle of the glass transition. This is due to the fact that the glass transition is caused by a distribution of molecular motion.
- The Reversing Cp signal decreases with time during crystallization. This is due to conversion of amorphous material to a crystalline structure, which has lower molecular mobility and therefore lower heat capacity.
- The Total signal, like standard DSC, cannot measure heat capacity changes isothermally or during kinetic processes.



DSC has been used to characterize food products for many years but its utility has been limited by the complexity of observed transitions. MDSC provides numerous advantages for analysis of foods and quasi-isothermal MDSC is particularly useful in understanding structure and how that structure changes as a function of time and temperature. An example of this is seen in Figure 6, a comparison of the effect of cooling rate on the structure of a frozen sucrose solution. The quench-cooled sample shows a higher Reversing C_p and there is a single step in C_p associated with the glass transition of the frozen solution (melts above $-30\text{ }^\circ\text{C}$). The sample cooled at the low rate of $1\text{ }^\circ\text{C}/\text{min}$ has a lower heat capacity and goes through two steps. A detailed description for the difference in structure caused by the cooling rate is beyond the scope of this paper but there is additional information below that provides insight into the cause. The data for the quench-cooled sample shows that the heat capacity changes (range of values) during the 30-minute isothermal over the temperature range from -44 to $-35\text{ }^\circ\text{C}$. It was suspected that this resulted from crystallization of water that did not have time to freeze due to the high cooling rate of the quench-cooled sample. The suspicion was verified when the state diagram shown in Figure 7 was published by Roos and co-workers in a 1996 article in *Food Technology*. It clearly shows that ice forms between about -47 to $-35\text{ }^\circ\text{C}$. The conversion of water to ice would cause a decrease in C_p as seen in the MDSC results in Figure 6.





SUMMARY

As with many of the applications shown in previous papers in this series, MDSC overcomes the many natural limitations of DSC. In this case, MDSC provides the ability to measure heat capacity and changes in heat capacity during isothermal operation and during kinetic processes such as crystallization and chemical reaction. This ability is the direct result of using two simultaneous heating rates instead of the single heating rate in traditional DSC.

KEY WORDS

modulated differential scanning calorimetry, mdsc, quasi-isothermal, glass transition, foods

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