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.

$$\frac{dH}{dt} \quad Cp\frac{dT}{dt} \quad f(T,t)$$

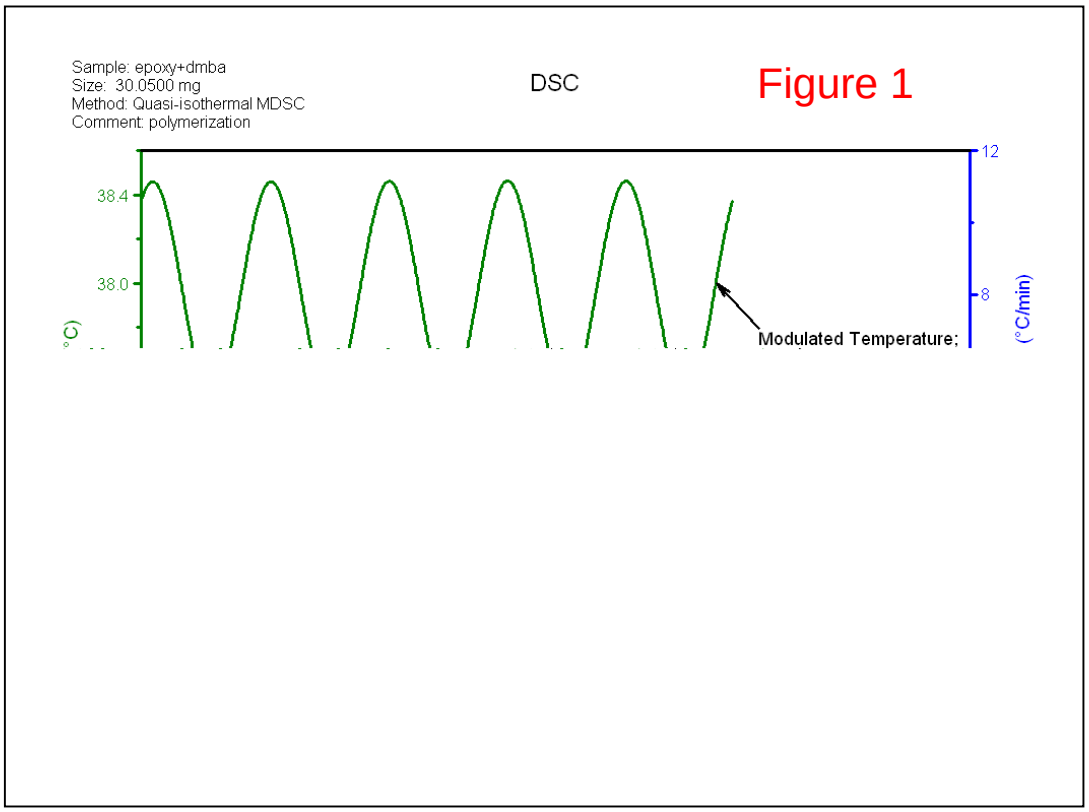
Where:

dH/dt = heat flow (mW or W/g) rate as measured by the DSC
Cp = sample heat capacity (J/ºC)
dT/dt = heating rate (ºC/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 ating [(aTJ 9.0003 Tc -9

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 °C) is applied to a constant average temperature. Figure 1 shows both the temperature and heating rate from a 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.

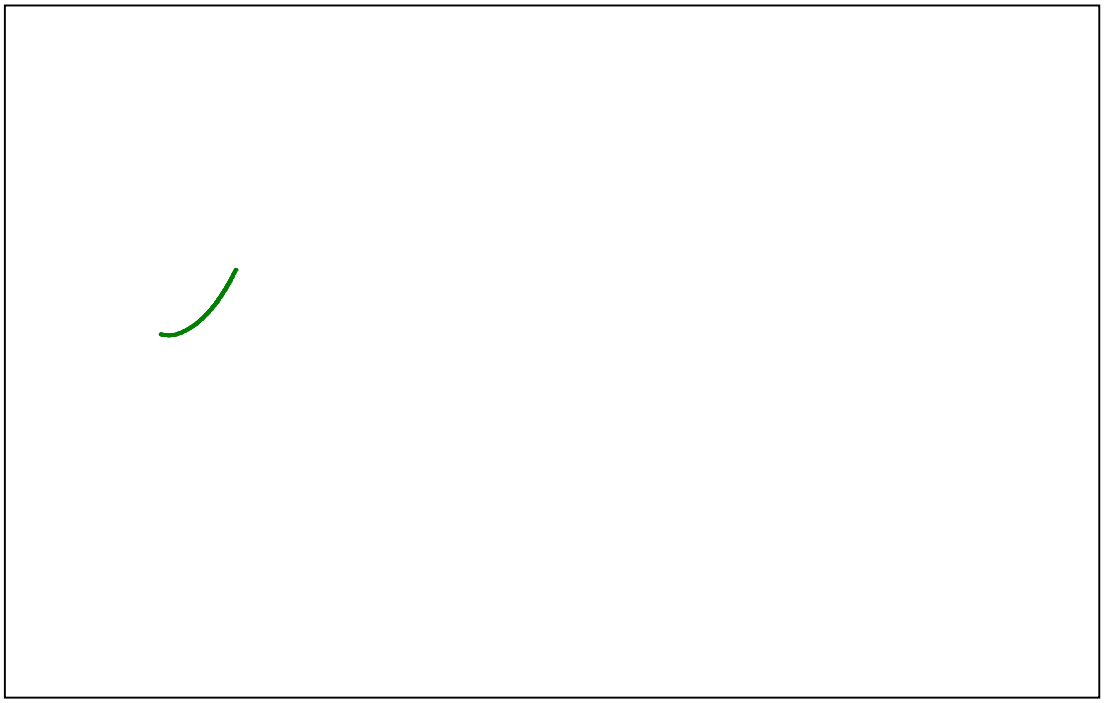
EXPERIMENTAL CONDITIONS

There are two different types of quasi-isothermal experiments and it is easy to select MDSC experimental conditions for both. 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 38ºC
2. Modulate +/- 0.5ºC 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 ºC 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 ºC, the reaction begins again and there is an additional 31 J/g of reaction.



Note that it is not possible to see or m

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 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 nature 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:

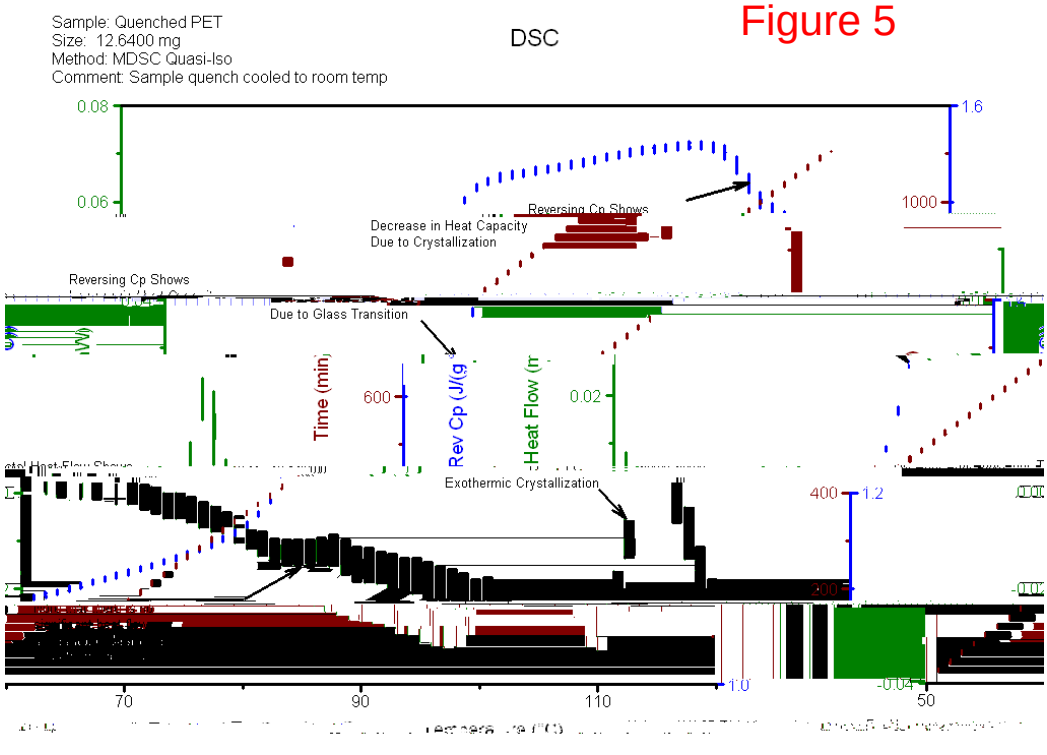
- Except for the first few minutes of the experiment, the Total heat flow signal only changes by about 30 microwatts over almost 20 hours and most of that is due to the exothermic crystallization. This is an example of extremely good baseline stability.

- 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.

Figure 4

Figure 5



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