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## **Modulated DSC<sup>®</sup> Paper #5 Measurement of Glass Transitions and Enthalpic Recovery**

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### **ABSTRACT**

This paper provides a summary of recommendations designed to permit optimization of Modulated DSC results. It also describes two important aspects (frequency dependence and enthalpic recovery) of the important glass transition measurement that can be readily determined from DSC and MDSC experiments.

### **INTRODUCTION**

Measurement of the glass transition and glass transition temperature are probably the most common measurements made with the DSC and MDSC techniques. In a previous paper in this series entitled “Optimization of MDSC Experimental Conditions” (1), recommendations were provided for selection of experimental conditions (modulation amplitude and period, and heating rate). As discussed therein, selection of experimental conditions can significantly affect measurement sensitivity and resolution. A summary of these effects is given in the following section.

### **SELECTION OF OPTIMUM EXPERIMENTAL CONDITIONS**

In general, it may be said that sensitivity increases with use of slower heating rates, and larger modulation amplitudes and periods. A larger temperature amplitude increases the amplitude of the modulated heating rate, which in turn magnifies the size of the measured heat flow signal. Also, a longer modulation period provides more time for heat transfer to occur. Although higher heating rates improve sensitivity in DSC experiments, slower heating rates improve MDSC sensitivity by providing more modulation cycles over the temperature region of the transition.

Resolution improves with slower heating rates, smaller modulation amplitudes, and slightly shorter modulation periods. The reason that smaller modulation amplitudes improve resolution is due to the way that MDSC signals are calculated (2). Since the signals are calculated over a full modulation cycle, the larger the temperature amplitude for that cycle, the more temperature averaging will occur for each data point.

### **RECOMMENDED STARTING CONDITIONS FOR MEASUREMENT OF GLASS TRANSITIONS**

These largely depend on characteristics (size, shape etc.) of the transition and are given below. After the initial experiment, conditions can be adjusted to improve sensitivity, resolution or both.

**For "Standard" Glass Transitions**

Sample Size: 10-15mg      Modulation Amplitude: 2X Table Value\*  
 Period: 40 seconds      Heating Rate: 3°C/min

**For "Hard-to-Detect" Glass Transitions**

Sample Size: 10-20mg      Modulation Amplitude: 4X Table Value\*  
 Period: 60 seconds      Heating Rate: 2°C/min

**For Tg with "Enthalpic Recovery" Peak**

Sample Size: 5-10mg      Modulation Amplitude: 1.5X Table Value\*  
 Period: 40 seconds      Heating Rate: 1°C/min

The "Table Value" (\*) indicated above is taken from the table shown below, which displays the temperature modulation amplitude, for a given period and heating rate, that would cause the heating rate to go to a minimum value of zero with no cooling. The table is supplied in the "Help" section of the "On-Line" manual and greatly facilitates the ease of the calculation for the older DSC 2910 and 2920 instruments. The latest Q Series instruments have software "templates" that calculate the modulation amplitude directly upon input of the selected period and underlying heating rate.

When measuring glass transitions or heat capacity, it is always recommended to have some cooling during temperature modulation. This is obtained by selecting a modulation amplitude larger than the value given in the table. For example, a modulation amplitude larger than 0.159 °C would cause some cooling during temperature modulation for a heating rate of 1 °C/min and modulation period of 60 seconds.

<i>H e a t i n g  R a t e</i>	Period (sec)						
	40	50	60	70	80	90	100
0.1	0.011	0.013	0.016	0.019	0.021	0.024	0.027
0.2	0.021	0.027	0.032	0.037	0.042	0.048	0.053
0.5	0.053	0.066	0.080	0.093	0.106	0.119	0.133
1.0	0.106	0.133	0.159	0.186	0.212	0.239	0.265
2.0	0.212	0.265	0.318	0.371	0.424	0.477	0.531
5.0	0.531	0.663	0.796	0.928	1.061	1.194	1.326

**This table is additive, i.e. the heat only amplitude for a period of 40 sec and heating rate of 2.5°C/min. is the sum of the values for 2.0°C/min and 0.5°C/min:**

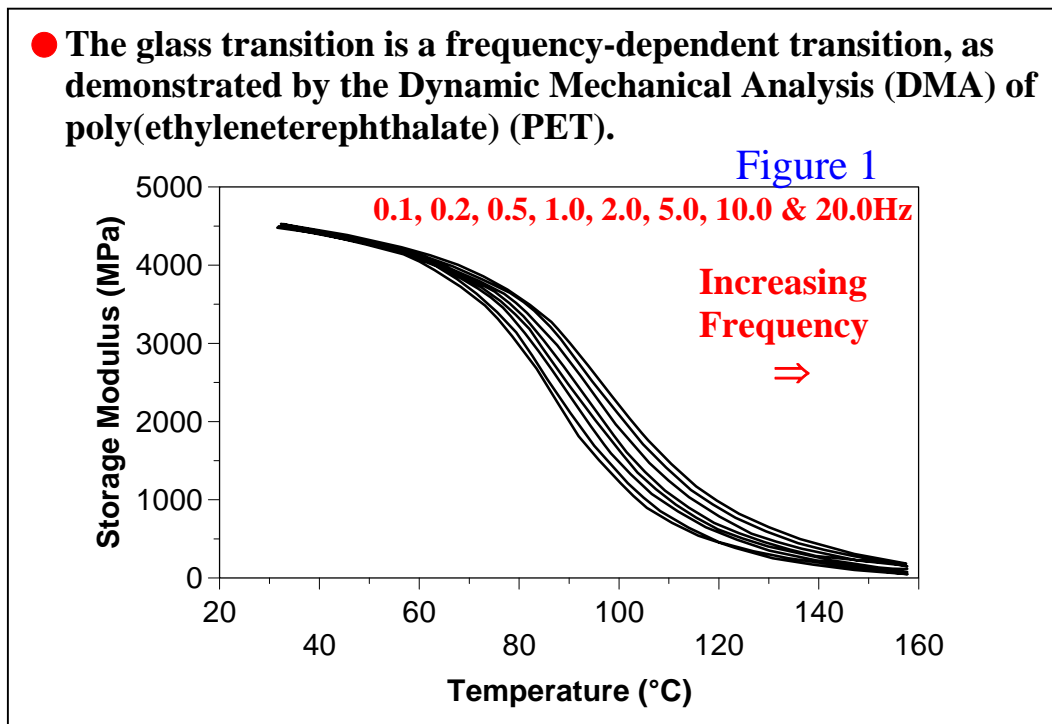
$$\text{Amplitude (40s, 2.5°C/min)} = 0.212 + 0.053 = \pm 0.265^\circ\text{C}$$

## EFFECT OF TEST FREQUENCY ON THE GLASS TRANSITION TEMPERATURE

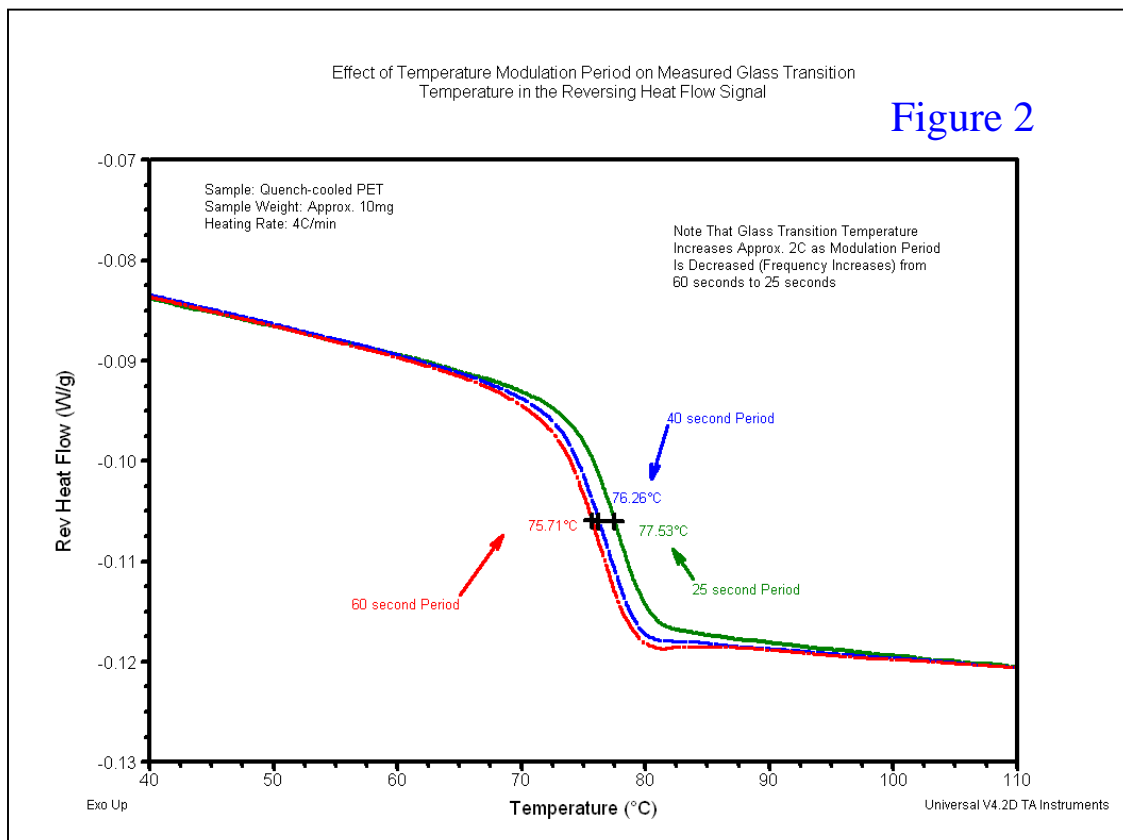
When conducting a standard DSC experiment, the analyst does not select a test frequency as one of the experimental parameters and therefore, does not need to consider the effect of frequency on the measured glass transition temperature. However, because the macro-molecular motion associated with the glass transition is a time-dependent process, the higher the heating rate in DSC, the higher will be the measured glass transition temperature. In contrast, with MDSC, the analyst selects a test frequency indirectly with selection of a modulation period, which is the inverse of frequency.

$$\text{Frequency} = \text{cycles/second}$$
$$\text{Modulation Period} = 1/\text{Frequency} = \text{seconds/cycle}$$

Thermal analysts working with other thermal-analytical techniques (e.g., Dynamic Mechanical Analysis, Dielectric Analysis or Rheology) that use a known test frequency, are well acquainted with the fact that the measured glass transition temperature increases as the test frequency is raised. This can be seen in Figure 1 for DMA results on Polyethylene Terephthalate (PET).



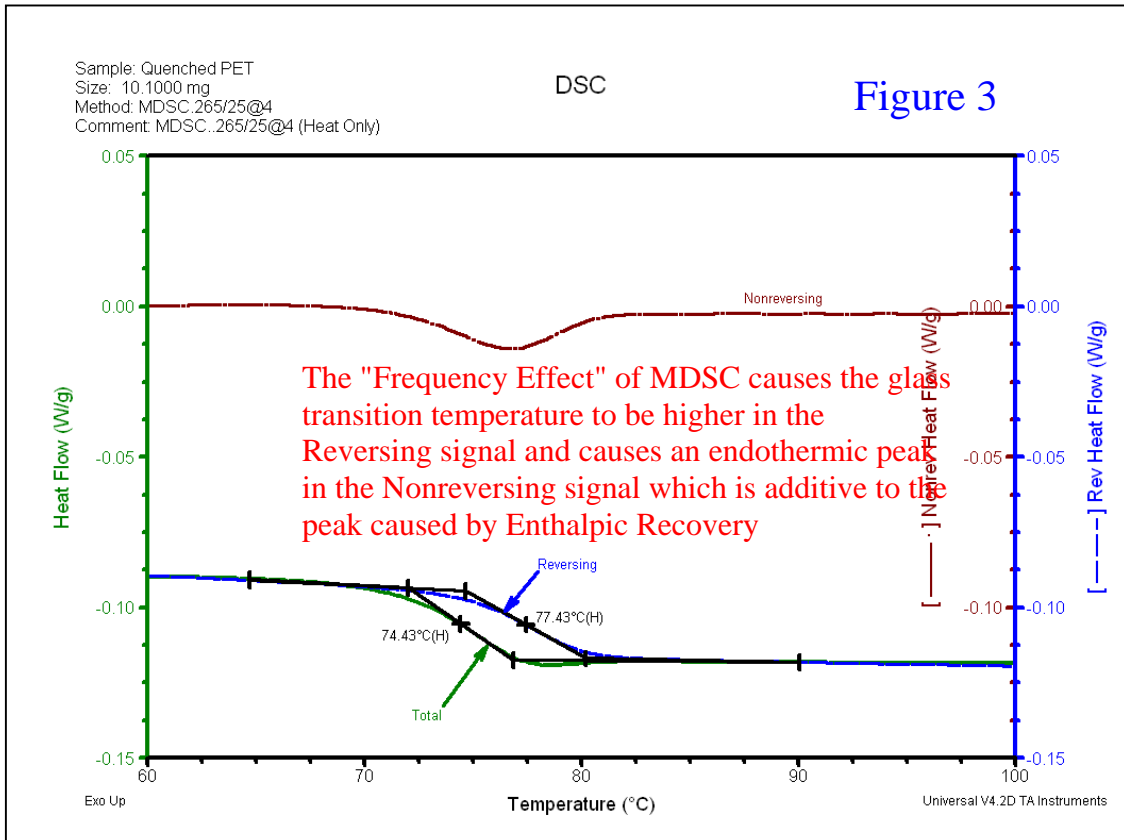
As indicated above, the MDSC user is indirectly selecting a temperature modulation frequency with selection of a modulation period. As with DMA, this affects the measured glass transition temperature. The shorter the period, the higher the test frequency and the higher is the measured glass transition temperature. This is seen in Figure 2, which is a comparison of MDSC experiments run at the same heating rate but with different modulation periods on quench-cooled PET.



Although the shorter modulation period causes a shift in the measured glass transition temperature in the Reversing Heat Flow and Reversing Heat Capacity signals, it does not affect the glass transition temperature as measured in the Total Heat Flow or Total Heat Capacity signals. The reasons for this are beyond the scope of this paper but there are two important effects of this difference in response between the Reversing and Total signals. Collectively, these effects are known as the "Frequency Effect" of MDSC and are illustrated in Figure 3.

The glass transition temperature, as measured with the Reversing signal, is at a higher temperature than that measured using the Total signal from either DSC or MDSC. The effect is only a few degrees but sometimes this can be very important when setting specifications for a proposed product.

An endothermic peak is created in the Nonreversing signal at the glass transition temperature. The area of this peak is superimposed on the endothermic peak caused by enthalpic recovery as discussed in the next section.



### MEASUREMENT OF ENTHALPIC RECOVERY

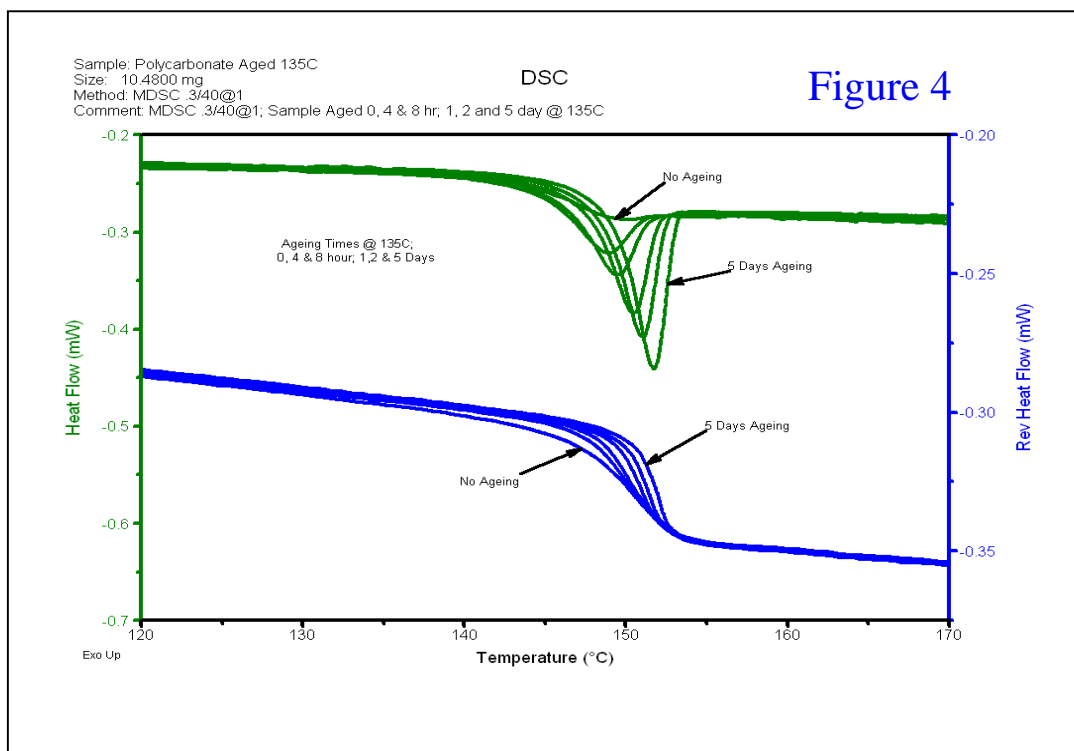
For the MDSC user, who may not be familiar with "enthalpic recovery" at the glass transition temperature ( $T_g$ ), a brief introduction is provided prior to a discussion of how to make the measurement with MDSC.

#### Background Information

Physical properties (heat capacity, modulus or stiffness, impact resistance, coefficient of thermal expansion etc.) of amorphous materials are very different from the physical properties of crystalline materials. In addition, the physical properties of amorphous materials can change with time as the sample relaxes ("enthalpic relaxation") toward an equilibrium state. This can complicate their analysis. The process of enthalpic relaxation or "physical aging" results in a decrease in the energy content of the material. Since DSC and MDSC can measure the energy (heat) content of a sample, they are excellent tools to compare differences in equilibrium between samples and therefore differences in expected end-use physical properties.

At temperatures below the glass transition ( $T_g$ ) of a material, amorphous structure has very low molecular mobility and is not in thermal equilibrium. That is, the energy content is higher than it should be and the material will gradually decrease in energy as it "ages" toward an equilibrium state. Once the material is heated above  $T_g$ , it has high molecular mobility and is in thermal equilibrium. "Enthalpic Recovery" is the recovery of energy that the sample gave-up (dissipated) as it relaxed toward an equilibrium state over time. It is seen in a DSC or MDSC experiment as the sample is heated from below  $T_g$

(non-equilibrium) to a temperature above  $T_g$ . Since equilibrium is the lowest energy state, the more energy required to heat a sample over the temperature range of the glass transition, the closer the sample is to equilibrium. The effect of this aging or enthalpic relaxation can be seen in Figure 4 for a sample of Polycarbonate (PC) that was aged at  $135\text{ }^\circ\text{C}$  for up to 5 days. The Total heat flow signal (like DSC) shows both the step-change in heat flow (heat capacity) at  $T_g$  and the endothermic recovery peak, while the MDSC Reversing signal shows just the change in heat flow caused by the change in heat capacity.

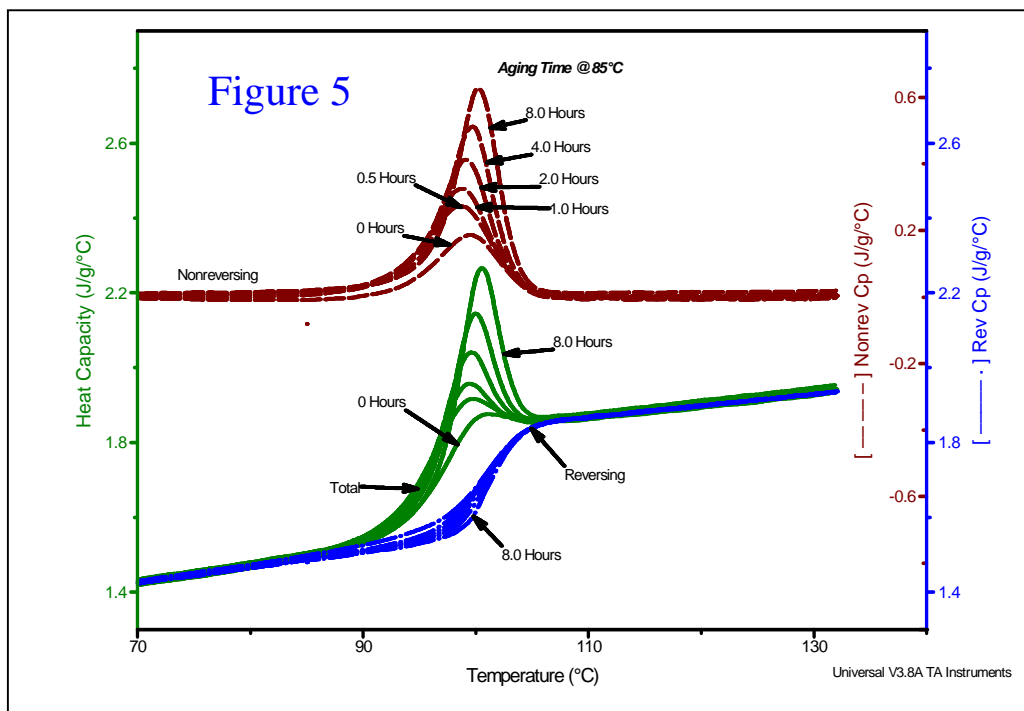


An aging temperature of  $135\text{ }^\circ\text{C}$  was used to create Figure 4 because it is relatively close to the  $T_g$  and the sample ages relatively quickly. At temperatures well below the  $T_g$  (e.g.,  $T_g - 40\text{ }^\circ\text{C}$ ), aging occurs much more slowly. If the experiment were performed with an aging temperature of  $100\text{ }^\circ\text{C}$ , the aging process would be so slow that very little difference would be seen in the samples after just five days.

### MEASUREMENT OF ENTHALPIC RECOVERY

In order to measure enthalpic recovery, it is necessary to separate the change in heat capacity (heat flow) at  $T_g$  from the endothermic peak caused by the enthalpic recovery process. This is not possible with standard DSC. With MDSC, the change in heat capacity occurs in the Reversing signal while enthalpic recovery, which is a kinetic process, occurs in the Nonreversing signal. This can be seen in Figure 5, where the MDSC signals are shown in heat capacity units on a sample of Polystyrene (PS) that was aged at  $85\text{ }^\circ\text{C}$  for up to 8 hours. It would be easy to integrate the peaks in the

Nonreversing signal and measure differences in energy content between the samples due to aging (enthalpic relaxation). As mentioned above and in MDSC Paper #3 (1), a heating rate of 1 °C/min is recommended in order to obtain sufficient modulation cycles (a minimum of 4 is recommended) over the transition region and therefore to obtain a good separation of the enthalpic recovery peak from the change in heat capacity at the glass transition ( $T_g$ ).

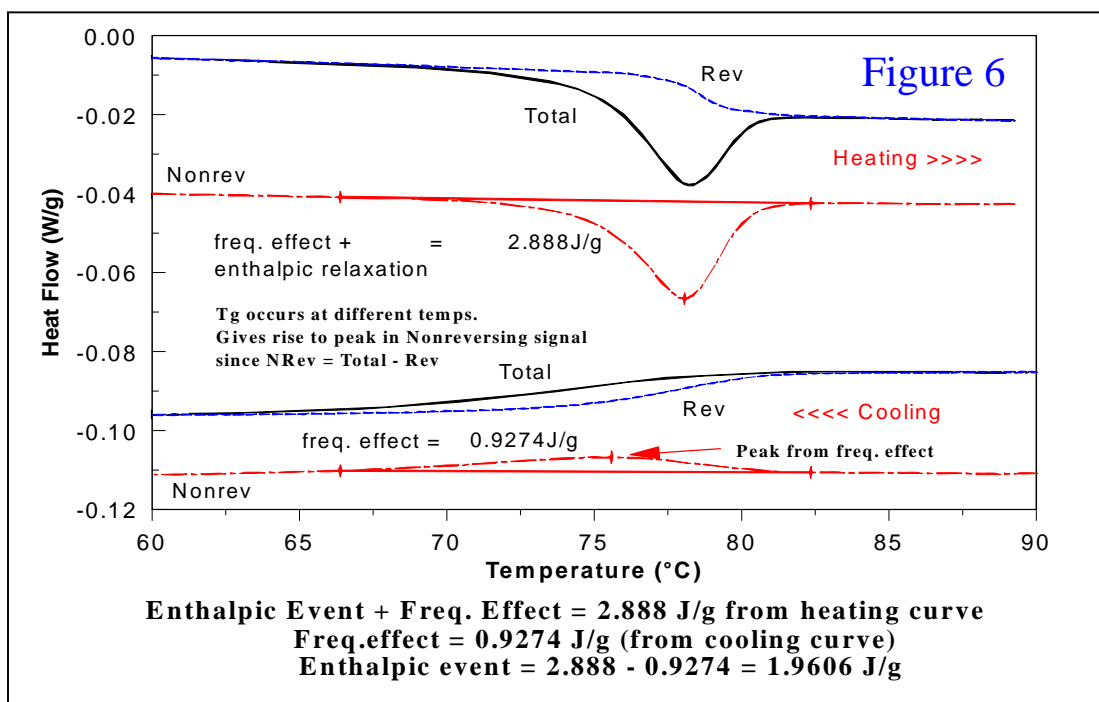


### Correction of the “Frequency Effect”

As previously stated, the "frequency effect" of MDSC causes an endothermic peak in the Nonreversing signal that is superimposed on the peak due to enthalpic recovery. In order to more accurately measure the energy caused only by enthalpic recovery, it is necessary to subtract the apparent energy caused by the "frequency effect". This can be done in one of two ways as explained below.

After measuring the peak area in the Nonreversing signal of the aged sample, the sample can be rapidly cooled back to the starting temperature and heated a second time under the same MDSC experimental conditions. The area of the peak from the second heat (non-aged sample) can then be subtracted from the first heat (aged sample) to obtain the peak area in the first heat caused by just enthalpic recovery. This is illustrated in Figure 5 where the second heat is identified as "0 Hours".

Since the "frequency effect" is seen in both heating and cooling modes, the aged sample can be heated to a temperature above  $T_g$  and then cooled under the same MDSC conditions as used for heating. Any peak area in the Nonreversing signal on cooling can only be caused by the "frequency effect". This area can then be subtracted from the peak area on heating to obtain the peak area on heating which was just due to enthalpic recovery. This is illustrated in Figure 6.



## SUMMARY

Modulated DSC is an extremely useful technique for measurement of the glass transition. Like all analytical techniques, it is important to select optimum experimental condition in order to obtain the highest quality results and to state those experimental conditions when reporting results. Because MDSC applies a temperature modulation period (inverse of frequency), the measured glass transition temperature differs between the Total and Reversing signals and increases with decreasing period (increasing frequency). Because of the difference in response to frequency between the Total and Reversing signals, it is necessary to correct for the "frequency effect" when measuring quantitative peak areas in the Nonreversing signal that are associated with enthalpic recovery.

## REFERENCES

1. Modulated DSC Paper # 3, Optimization of MDSC Experimental Conditions; TA Technical Paper (TP 008).
2. Modulated DSC Paper # 2, Calculation and Calibration of MDSC Signals; TA Technical Paper (TP 007).

## KEY WORDS

modulated differential scanning calorimetry, mdsc, dsc, glass transition, glass transition temperature, reversing signal, non reversing signal, enthalpic, recovery



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