

Use of multiple heating rate DSC and modulated temperature DSC to detect and analyze temperature-time-dependent transitions in materials

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Plastics are becoming more complex in order to meet the demand for lower-cost materials and improved physical properties. The result is that it is becoming increasingly more difficult to characterize the structure and resulting physical properties of plastics that are often polymer blends and composites.

Three factors that contribute to the difficulty in measuring the physical properties as a function of temperature are: 1) Multiple transitions, or changes in structure, can occur in the same temperature range. 2) The amorphous and crystalline structure of materials is a function of the thermal history (temperature and time) of the material and, therefore, can change from one sample to the next or be different based on where the sample was obtained from the much larger part (surface, center, thin section, thick section, etc.). 3) In order to measure structure, it is often necessary to heat the sample over some temperature range. Since the sample's structure can change as a function of temperature and time, it is critical to know how the sample is changing during the experiment in order to determine the initial structure, which is what would provide the actual physical properties of interest.

Differential scanning calorimetry (DSC) has been used to successfully characterize structure and transitions (change in structure) in plastics for more than 40 years. However, it often required a great deal of knowledge and skill on the part of the operator. Today, analytical chemists do not have

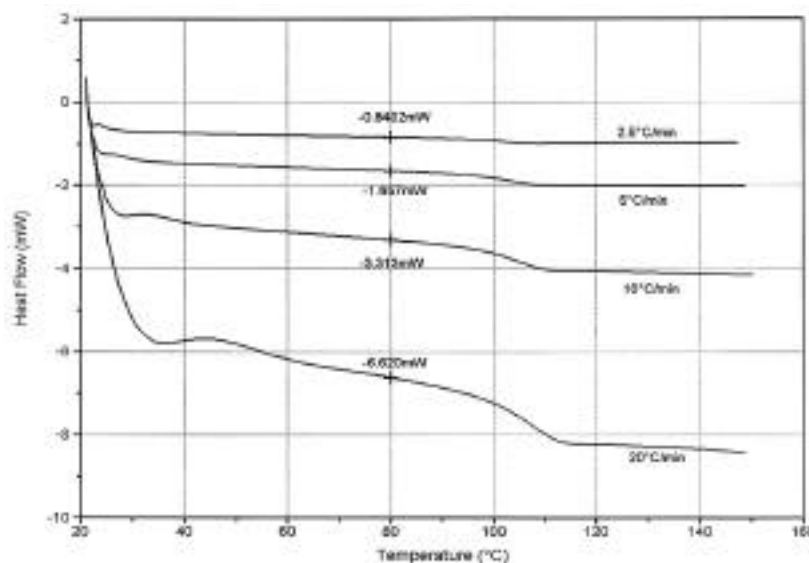


Figure 1 Effect of heating rate on heat flow due to glass transition and heat capacity.

the luxury of becoming experts on a single analytical technique, and the materials are much more complex. The result is that new approaches to using DSC or new technologies like Modulated DSC® (MDSC®, TA Instruments, New Castle, DE) are required.

Multiple heating rate DSC

In order to properly characterize complex materials, it is first necessary to determine if there are overlapping transitions. Since many transitions (evaporation, crystallization, thermoset cure, decomposition, etc.) are kinetic events, they are a function of both time and temperature. This means that the transition will shift to a higher temperature when heated at a

higher rate because it has less time at any specific temperature. As will be shown, this sensitivity to heating rate can be used to identify kinetic transitions in the sample.

The simple equation that can be used to describe the heat flow signal in DSC or MDSC experiments is provided below. It shows that one component of the heat flow signal is a function of heating rate (dT/dt), while the other component is a function of absolute temperature and time, $f(T,t)$. It is this component that will shift to higher temperatures as the heating rate is increased.

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(T,t) \quad (1)$$

where dQ/dt = differential heat flow rate (watts), C_p = heat capac-

ity (specific heat \times mass), $dT/dt =$ heat rate ($^{\circ}\text{C}/\text{min}$), and $f(T,t) =$ kinetic heat flow (watts).

The equation shows how the total heat flow increases linearly with heating rate due to the heat capacity of the sample. *Figure 1* shows this linear change in heat flow with heating rate for a common amorphous (noncrystalline) polymer, polymethyl methacrylate (PMMA). Each time the heating rate is doubled, the heat flow doubles as shown at 80°C in the four separate heating experiments on the same sample. Notice that the size (in mW) of the glass transition near 100°C also increases

when there is no kinetic component [$f(T,t)$]:

$$C_p = \frac{dQ/dt}{dT/dt} = \frac{\text{mW}}{\text{heating rate}} \quad (2)$$

This is seen more clearly in *Table 1*.

Several conclusions can be drawn from the data in *Figure 2*. The first is that the glass transition shifts to slightly higher temperatures as the heating rate is increased. This shift is the result of two different factors. The first is that the sample has low thermal conductivity and, therefore, the temperature of the center of the sample lags the temperature of the surface. The size of the tempera-

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ture lag increases with heating rate and causes the glass transition on heating to shift to a slightly higher temperature. The second factor is that the glass transition is associated with a change in molecular mobility, and this mobility has a small time-dependent or kinetic contribution. Even with both of these factors, the change in the glass transition temperature

with heating rate. For this reason, high heating rates should normally be used when trying to measure small transitions because they provide larger heat flow signals. *Figure 2* shows the data from the same four experiments. The only difference is that the scaling of all four signals was adjusted in order to normalize for the sample's heat capacity. From Eq. (1),

over a range in heating rates from 2.5 to $20^{\circ}\text{C}/\text{min}$ is slightly more than 3°C . A second conclusion that can be made from the data in *Figure 2* is that there are no other kinetic processes occurring in the sample other than the small change at the glass transition. This is evident from the fact that the curves overlap exactly in the baseline, which is due solely to the sample's heat capacity.

Table 1
Adjusting plot scale sensitivity (mW) in order to normalize for heat capacity

Heating rate (dT/dt)	Plot scale (mW)	Ratio (mW/heating rate)
$2.5^{\circ}\text{C}/\text{min}$	1.25	0.5
$5.0^{\circ}\text{C}/\text{min}$	2.50	0.5
$10^{\circ}\text{C}/\text{min}$	5.0	0.5
$20^{\circ}\text{C}/\text{min}$	10.0	0.5

over a range in heating rates from 2.5 to $20^{\circ}\text{C}/\text{min}$ is slightly more than 3°C .

An example of a completely kinetic process is the crystallization of a polymer as it is cooled from the melt. This is illustrated in *Figure 3*, where a sample of polyethylene terephthalate (PET) was cooled at four different rates from above its melt temperature. Notice how the crystallization peak has shifted by nearly 22°C as a result of cooling at $16^{\circ}\text{C}/\text{min}$ as compared to $2^{\circ}\text{C}/\text{min}$. As in *Figure 2*, the four different heat flow signals were scaled in order to normalize for heat capacity. By doing this, the baselines should overlap, except when there is a kinetic process occurring. Notice how there is complete overlap except for the crystallization peak.

Figure 4 shows four experiments at different heating rates on samples of PET that had been quench-cooled ($>500^{\circ}\text{C}/\text{min}$) from the melt. By cooling so quickly, the material does not have time to crystallize during cooling and forms a completely amorphous (noncrystalline) structure. As the samples were heated, as illustrated in the data of *Figure 4*, they showed a glass transition near 75°C , a cold crystallization peak above 120°C , and a melting peak centered near 250°C . As in the data of *Figure 2* on PMMA, the

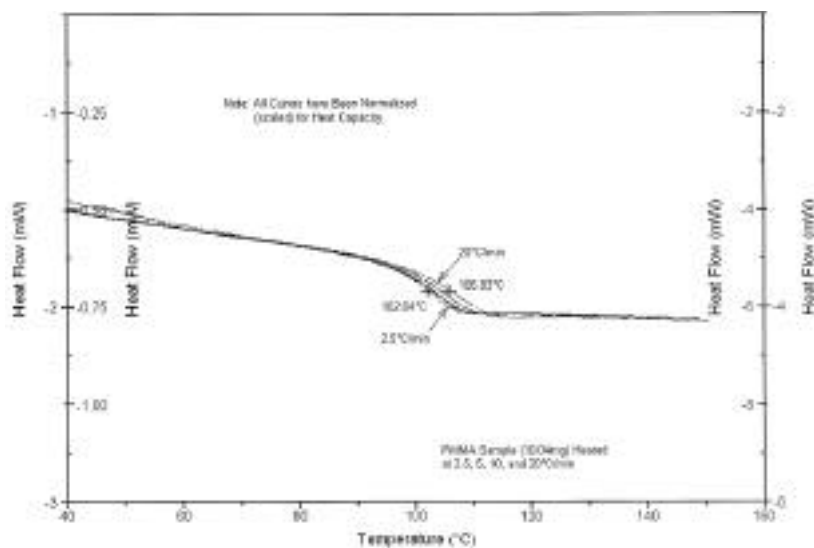


Figure 2 Effect of heating rate on glass transition and heat capacity baseline when heat flow normalized for heat capacity.

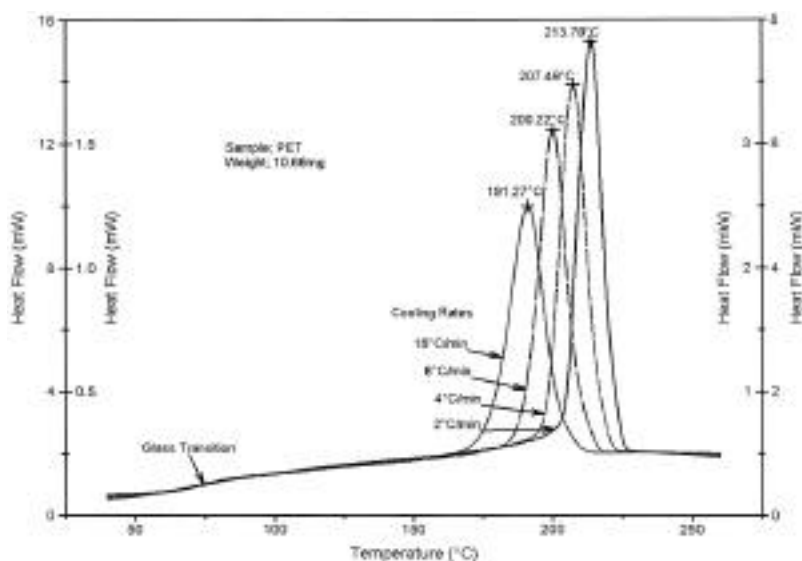


Figure 3 Effect of cooling rate on crystallization of PET.

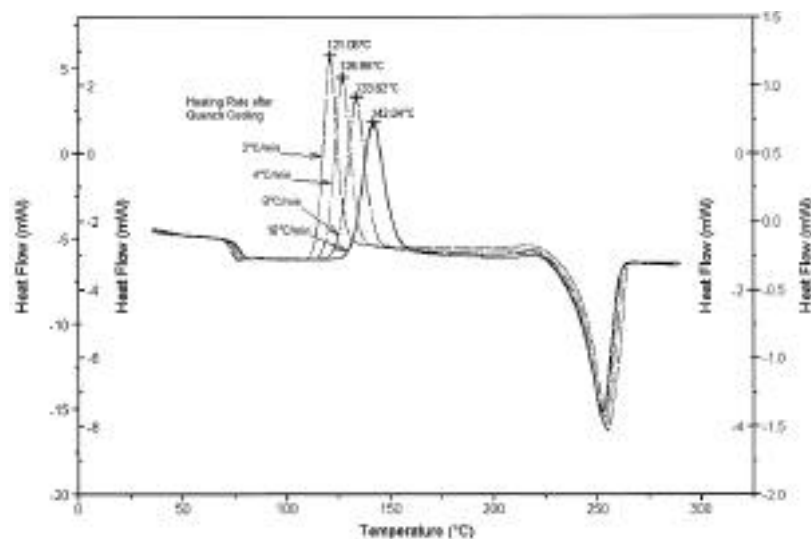


Figure 4 Effect of heating rate on temperature of cold crystallization in PET.

glass transition temperature of PET shifts to a slightly higher temperature with higher heating rates. Just as the crystallization peak during cooling shifted with cooling rate in Figure 3, the crystallization peak during heating shifts by a nearly identical amount of 21 °C for a change of 2–16 °C/min in the heating rate.

The data become most interesting above 150 °C, and an expanded view is shown in Figure 5. Even though all of the signals have been normalized for heat capacity (as described for Figure 2), the base-

lines do not overlap in the temperature region between the crystallization and melting peaks (160–220 °C). This means that there is a kinetic process occurring at this temperature, which, as will be seen from other results, is the ongoing crystallization of additional amorphous material as well as the crystal perfection (melt, crystallize, and then remelt) of small, less perfect crystals that melt below their expected thermodynamic melting point. Since crystallization is occurring in this temperature region, it will increase the size of the

melting peak to something greater than what existed in the sample prior to heating it. If the operator does not correct for this, the wrong crystallinity will be measured by DSC.

The effect of the greater crystal perfection at slow heating rates (heat flow signal is more exothermic from 160 to 220 °C) is that the melting peak for the sample heated at the lowest rate is actually higher than for the melting peak of the samples heated at a higher rate. This is just the opposite of what would be expected due to the thermal lag in the sample, but is what would be expected due to the crystal perfection process.

Modulated DSC

The technique of MDSC was commercialized by **TA Instruments** in 1992. Instead of using a single linear heating rate, as used in traditional DSC, it employs a modulated or sinusoidal change in heating rate in order to automatically separate the heat capacity baseline from the total heat flow signal. This means that it is possible to identify, measure, and quantify kinetic processes such as crystallization and crystal perfection in a single experiment.

As described earlier, the heat flow signal is composed of several parts, but traditional DSC can only measure the sum of those parts and illustrate that sum in a single signal. With MDSC, multiple signals are generated in a single experiment so that each of the components to the total heat flow signal can be shown and analyzed independently.

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(T,t) \quad (3)$$

$$\text{Total} = \text{MDSC Reversing} + \text{MDSC Nonreversing}$$

An MDSC experiment on a sample of quench-cooled PET is shown in Figure 6. The total signal is what would be obtained from a single, traditional DSC experiment. The operator would probably integrate the individual crys-

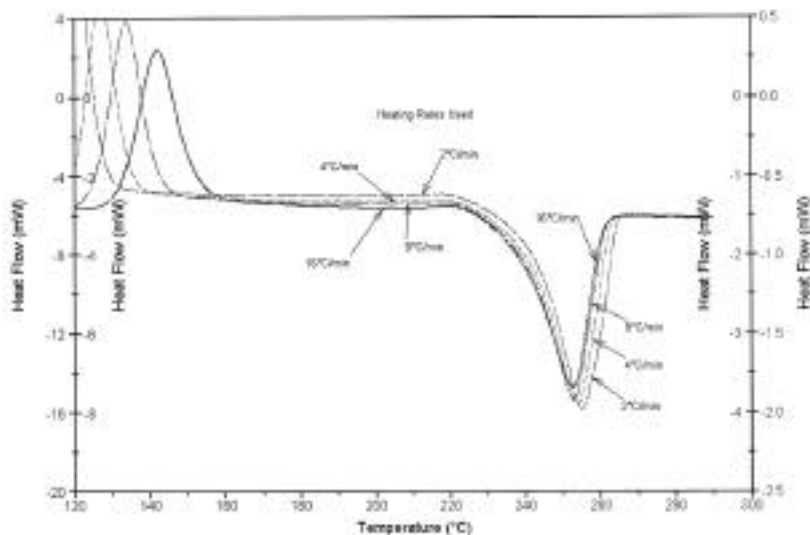


Figure 5 Effect of heating rate and crystal perfection processes on the melting temperature of PET.

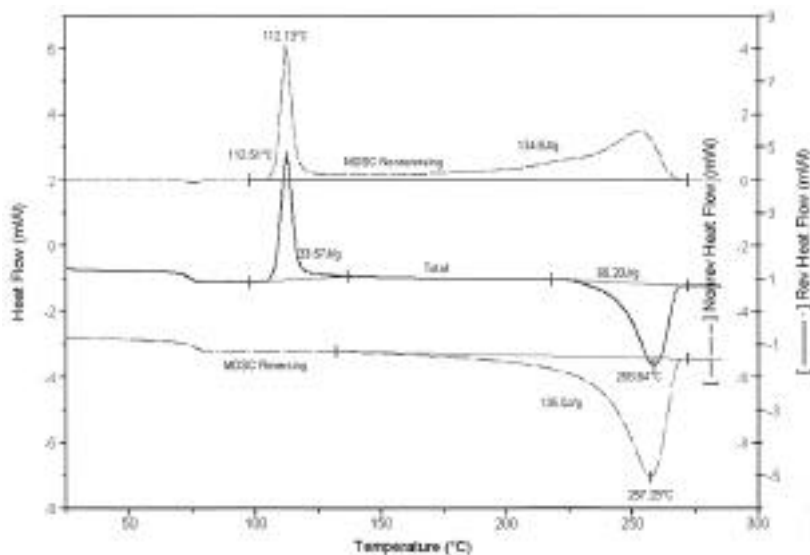


Figure 6 MDSC uses a range of heating rates in a single experiment on PET in order to separate the total heat flow into the heat capacity (Reversing) and kinetic (Nonreversing) components.

tallization (33.57 J/g) and melting (60.2 J/g) peaks and conclude that there was almost 27 J/g of crystalline structure in the sample prior to the experiment. This is a huge error, since there was zero crystallinity originally in the sample. The operator would make this mistake because he/she would fail to see the ongoing crystallization above the large crystallization peak centered at 112 °C. As shown earlier, by doing multiple DSC ex-

periments and then normalizing the heat flow signals for heat capacity, the operator would at least be aware of the additional crystallization occurring between the crystallization and melting peaks.

The MDSC Reversing signal in Figure 6 shows the glass transition as a step increase in the heat capacity baseline near 75 °C, and the melting occurring over the temperature range from 150 °C to nearly 275 °C. The total signal

does not see any melting below about 220 °C because melting is endothermic, while the ongoing crystallization is exothermic and more material is crystallizing than melting.

The MDSC Nonreversing signal is the kinetic component of the total heat flow signal. It shows clearly how crystallization starts just above 100 °C and continues until the sample is fully melted at 275 °C. To obtain quantitative crystallinity from MDSC, it is necessary to sum all of the endothermic (melting) and exothermic (crystallization) heat flows. The data show that there was 135 J/g of melting and 135 J/g of crystallization during the experiment. This means that all of the melting that took place during the experiment was the result of crystallization that occurred during the experiment and that the initial crystallinity of the sample was zero.

Summary

It is possible to detect kinetic processes in a sample by running multiple DSC experiments at different heating rates and then normalizing the heat flow signals for heat capacity. By using a sinusoidal change in heating rate, MDSC can separate the total heat flow signal into its heat capacity and kinetic components in a single experiment. MDSC provides a more accurate measurement of polymer crystallinity on complex samples because it provides a measurement of how the sample is changing during the experiment.

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