Practical Benefits of Using Heat Capacity Versus Heat Flow Signals

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BACKGROUND

Differential Scanning Calorimetry (DSC) has been used for over forty years to characterize transitions in materials. However, especially for the novice or periodic user of DSC, interpretation of observed events in the DSC data is often very difficult. The primary reason for the problem is that the measurement of heat flow is essentially a universal detector. Almost everything that happens in the sample (melting, crystallization, evaporation, annealing, etc.) involves either the absorption or release of heat. Since many of these processes overlap in temperature, the selection of analysis limits is difficult and often subjective.

It is only common sense that it is necessary to know at what point on the "baseline" of the data does the transition begin or end. By knowing the baseline, the proper integration limits can be selected and an accurate measurement of the heat associated with the transition can be made. The basic problem, however, is identifying the portion of the heat flow signal that represents a baseline.

Before you can identify the baseline, you need to define what it is. For the purpose of this paper, and probably all other papers, it can be defined as the heat flow signal (or heat capacity), which is the result of the heat capacity of the sample and there are no transitions or kinetic processes occurring at that point in time/temperature.

In this paper, we will focus on identifying the baseline through the use of the heat capacity signal. The relationship between heat flow and heat capacity in DSC experiments can be illustrated from the following equation:

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

Where:

$\frac{dH}{dt}$ = Heat Flow

Cp = Heat Capacity

$\frac{dT}{dt}$ = Heating Rate

$f(T,t)$ = Heat Flow due to Kinetic Processes

DSC can be used to measure the glass transition of a material because there is a step increase in heat capacity as the sample is heated through its glass transition temperature. For highly amorphous materials, the change in heat capacity, and therefore heat flow, can be quite large and the transition is easy to detect. For highly crystalline materials or for filled or blended samples, it is often hard to reliably measure Tg because any irregular shape of the instrument baseline may be confused with the small change in the baseline due to the change in heat capacity at Tg.

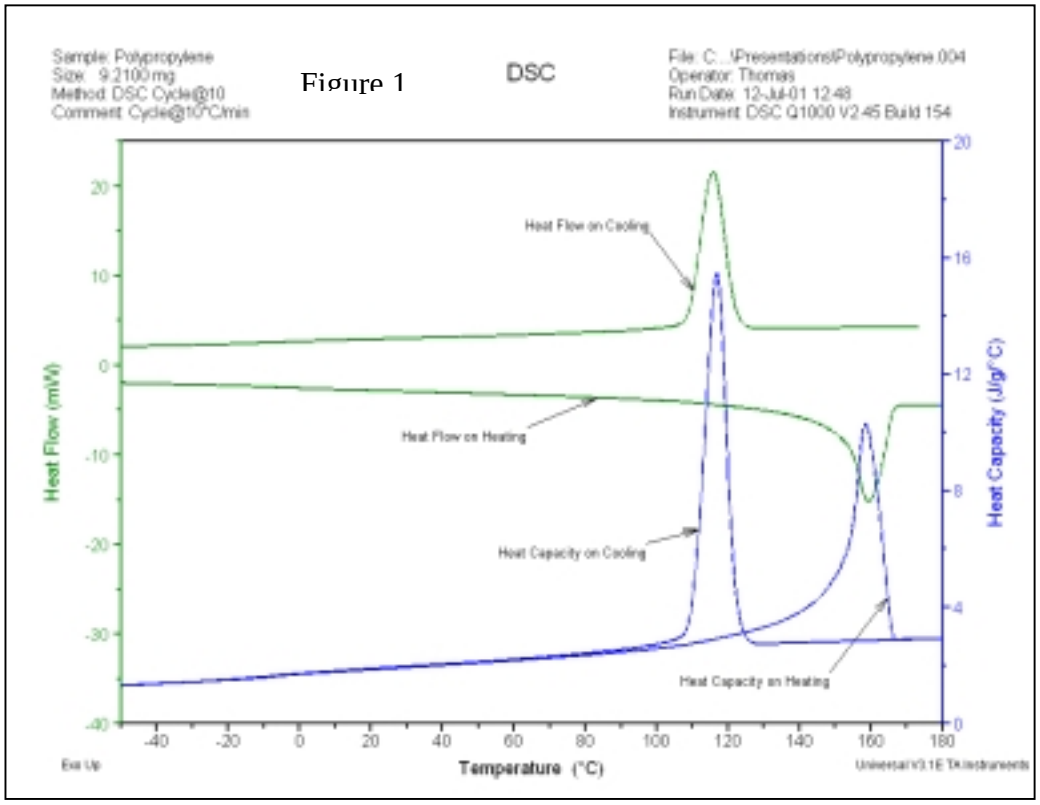


Figure 1

Figure 1 shows the heat flow and heat capacity signals for a sample of Polypropylene that had been cooled and reheated at 10°C/minute. With the data shown in the heat flow units, the heating data is endothermic while the cooling data is exothermic. This makes it difficult to compare the glass transitions on heating and cooling which are relatively small and not visible compared to the melting and crystallization peaks.

The same data is also plotted in heat capacity units. Heat capacity values should be the same in heating and cooling whenever there is no transition occurring in the sample ("baseline region"). Except for thermal lag, when the heating and cooling heat capacity values are different by a few degrees, a difference in heat capacity indicates the presence of a transition and the lack of a true heat capacity baseline.

Figure 2

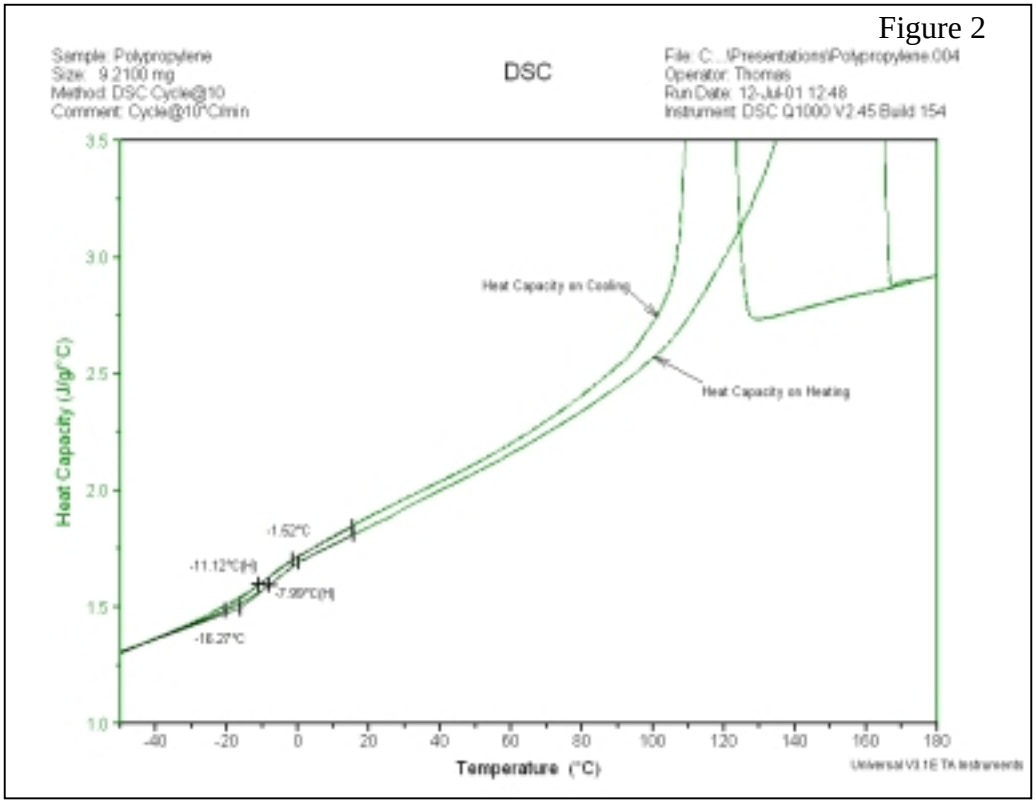


Figure 2 shows an expanded view of the heat capacity baseline region from Figure 1. Even though the glass transition is very weak due to the high crystallinity of the polypropylene, it is clearly visible in both the heating and cooling data. The shift of about 3°C in the midpoints of the glass transition is due primarily to thermal lag in the sample.

MELTING / CRYSTALLIZATION

The root cause of errors in selecting integration limits or interpreting results is that the operator simply cannot identify the heat capacity baseline of the data. Although Modulated DSC® (MDSC®) separates the onset of melting and crystallization processes very clearly, it is simply not possible for many samples to clearly identify the baseline from a single DSC experiment.

As discussed previously, the heat flow signal due to heat capacity responds linearly to changes in heating rate (Figure 3). Although the data shows some expected and unexpected effects of the change in heating rate, it is of limited value in identifying the baseline due to heat capacity.

Figure 4 shows the same data as Figure 3 except that the heat flow signals have been divided by the value of the applied heating rate. The benefit of doing this is obvious when looking at the data. The values of the heat flow signal are the same when there is no transition occurring, i.e., in the heat capacity baseline region. Note that there is no baseline region between 100°C and 270°C. Therefore, no integration limit should be selected in that range.

A disadvantage of dividing the signal by the value of the heating rate is that the measured peak areas are wrong by the same factor (heating rate) as used to divide the signal.

Figure 3

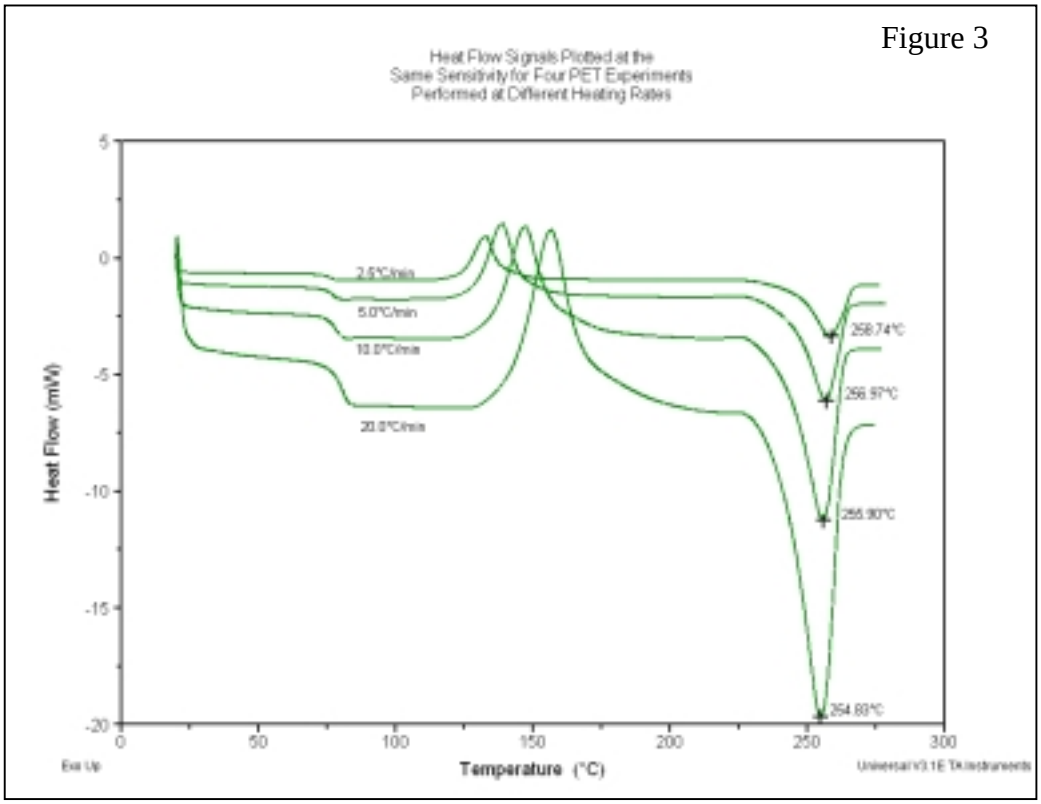
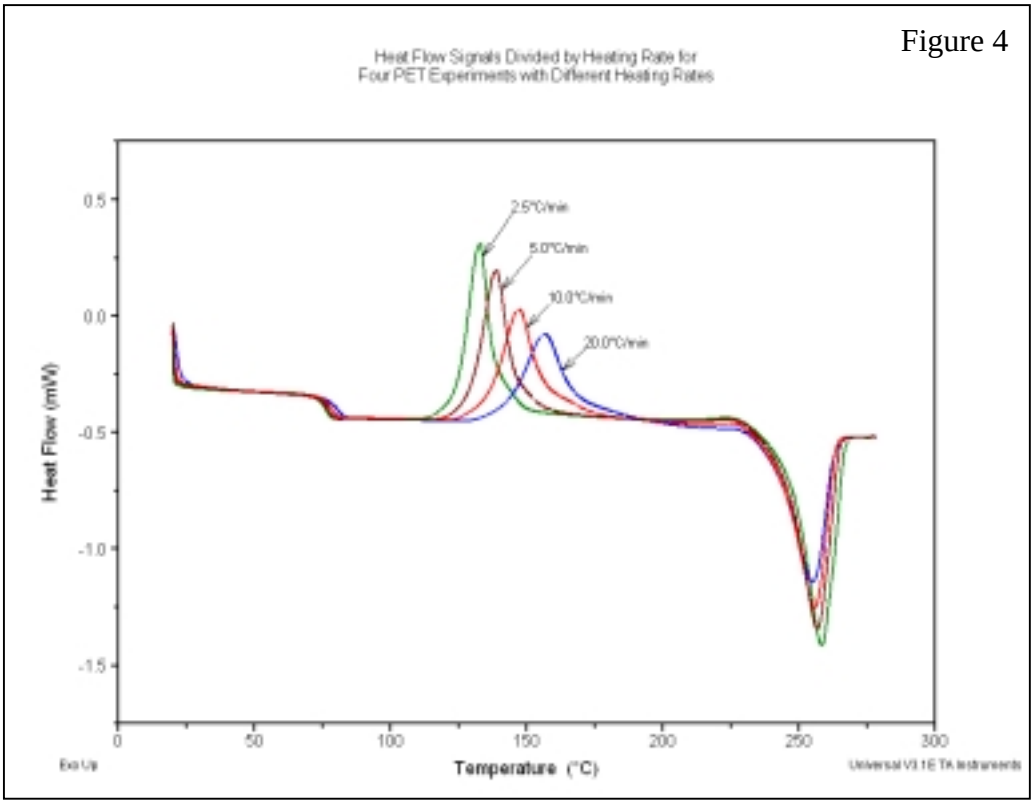
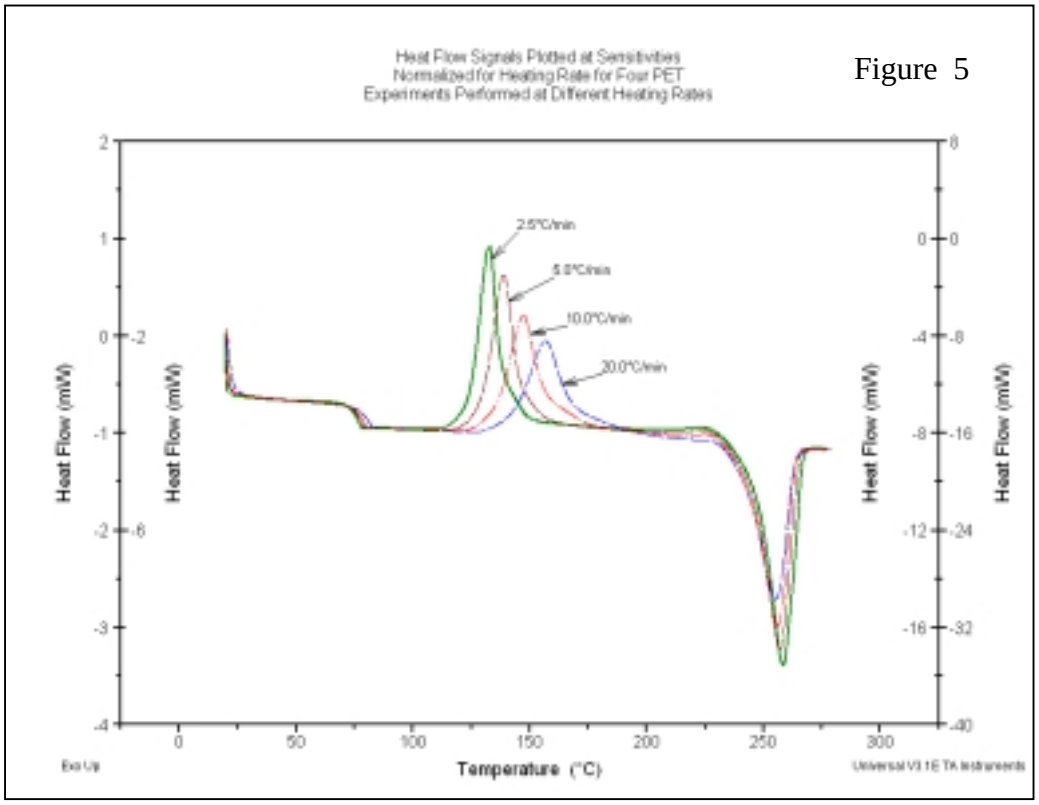


Figure 4



A solution to this problem is seen in Figure 5 where each signal has been plotted as a fixed ratio of the heating rate used. This also permits accurate identification of the baseline region but involves more effort in determining the proper scaling factors.

Figure 5



All of the above problems are eliminated when plotting data directly in heat capacity units as seen in Figure 6. All data is plotted at the same sensitivity in absolute heat capacity units. All integrated results are quantitative, and it is possible to clearly identify the heat capacity baseline.

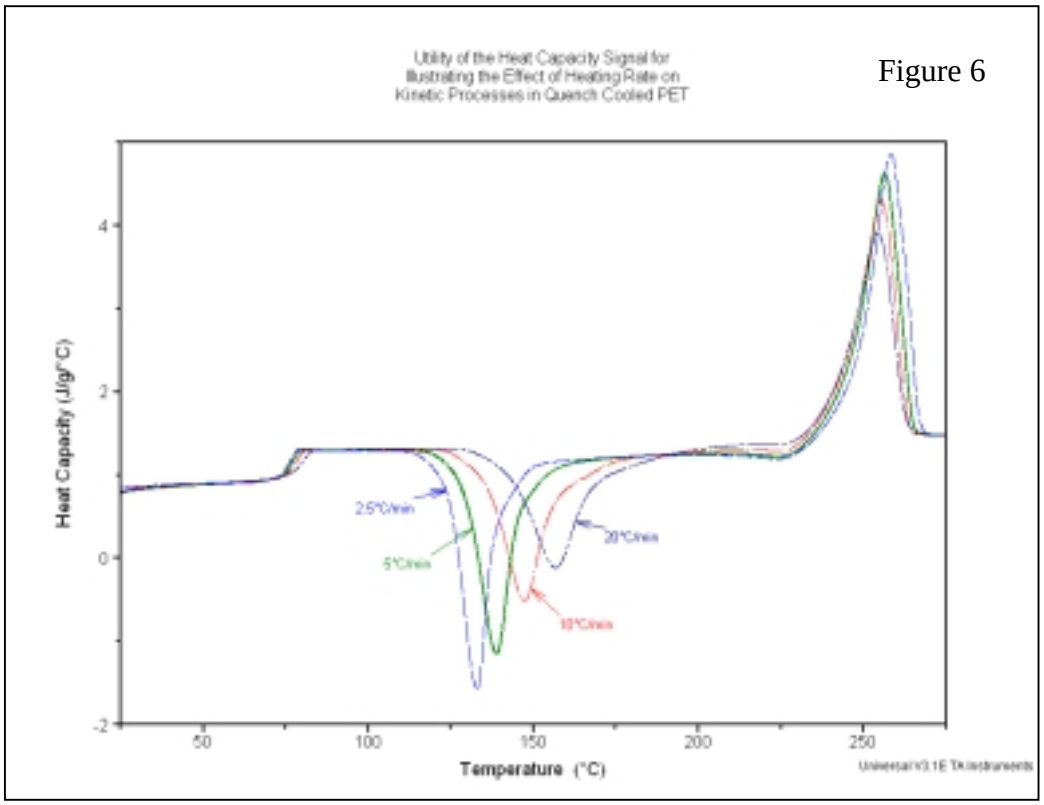


Figure 6

SUMMARY

It is highly desirable to be able to plot data in heat capacity units. This permits comparison of heating and cooling results for identification of weak glass transitions as well as experiments performed at different heating rates, which helps with selection of proper integration limits for measurement of polymer crystallinity. In order to obtain these benefits, however, it is necessary to have essentially a perfect baseline on heating and cooling with the DSC.