An Introduction to the Techniques of Differential Scanning

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1. Introduction

Differential Scanning Calorimetry or DSC is one of a series of analytical techniques called thermal analysis. These techniques can be used to characterize the physical properties of a wide variety of materials and how they change with temperature. The most frequently used techniques and the properties measured include:

- Differential Scanning Calorimetry (DSC) – Heat Flow
- Thermogravimetric Analysis (TGA) – Weight Change
- Thermomechanical Analysis (TMA) – Dimensional Change
- Dynamic Mechanical Analysis (DMA) – Modulus (Stiffness)
- Rheology – Viscosity (Flow)

DSC is the most important analytical tool because all transitions (change in physical properties) involve heat flow. Endothermic transitions such as melting absorb energy (J/g = Joules/gram) while exothermic transitions such as crystallization release energy. Other advantages of DSC include the ability to use small samples (1-10 mg), analyze solids and liquids, and use short test times (10-30 minutes). Sample preparation is easy and most commercial DSCs offer auto samplers and auto analysis.

The utility of DSC for characterizing a wide range of materials can be seen in Table 1 which lists the types of most frequently made measurements (properties) on those materials.

Table 1. Frequent DSC measurements

	TP	TS	EL	CH	PE	GL	ME	Bio
Glass Transition Temperature (Tg)	🗐	🗐	🗐	🗐	🗐	🗐	🗐	🗐
Glass Transition Size (ΔCp)	🗐		🗐	🗐		🗐	🗐	🗐
Melting Temperature ™	🗐		🗐	🗐	🗐	🗐	🗐	🗐
Crystallization Temperature (Tc)	🗐		🗐	🗐	🗐	🗐	🗐	
Crystallinity (J/g not %)	🗐		🗐	🗐		🗐	🗐	🗐
Heat Capacity (J/g°C)	🗐					🗐		
Oxidative Stability (Temp or Time)	🗐				🗐			
Texturing (process) Temperature (°C)	🗐							
Curing/Degree of Cure (%)		🗐	🗐					
Polymorphic Transitions				🗐				
Denaturation/Gelatinization								🗐

TP = Thermoplastics　　CH = Chemical/Drugs　　ME = Metals
TS = Thermosets　　PE = Petroleum　　Bio = Proteins/Starches
EL = Elastomers　　GL = Glasses

Heat flow is always the result of a temperature difference between two objects or two points in a single body. With DSC, the difference in heat flow rate between a sample and an inert reference is measured as both are heated or cooled (scanning) in a controlled temperature environment. The temperature difference (ΔT) between the sample and reference changes each time the sample goes through an exothermic or endothermic transition. This ΔT causes a proportional difference in heat flow rate (ΔQ). The magnitude of the heat flow rate is also a function of the thermal resistance (R) and is expressed by:

$$\Delta Q = \frac{\Delta T}{R}$$

In order to obtain the highest level of performance (sensitivity, resolution, single-run measurement of heat capacity, straight baseline, etc.), modern DSC instruments such as the TA Instruments Tzero™ technology also account for heat flow within the components of the DSC. These components have the ability to store heat (thermal capacitance) and transfer heat (thermal resistance). Instead of the simplified equation above, Tzero™ technology uses the following equation in order to more accurately measure the sample heat flow by separating it from heat flow within components of the DSC.

$$\Delta Q = \frac{\Delta T}{R_r} + \Delta T_o \left(\frac{1}{R_s} - \frac{1}{R_r} \right) + (C_r - C_s) \frac{dT_s}{dt} - C_s \frac{d\Delta T}{dt}$$

Where:

ΔQ $= Q_{Sample} - Q_{Reference}$

$\dfrac{\Delta T}{R_r}$ $=$ Principle Heat Flow Term

$\Delta T_o \left(\dfrac{1}{R_s} - \dfrac{1}{R_r} \right) =$ Imbalance in Sensor Resistance Term

$(C_r - C_s) \dfrac{dT_s}{dt}$ $=$ Imbalance in Sensor Capacitance Term

$C_s \dfrac{d\Delta T}{dt}$ $=$ Imbalance in Heating Rate During Transition Term

Figure 1 shows a cross-section of a Tzero™ DSC cell. The cell is the actual measuring chamber which would be located within an environmentally controlled cabinet complete with electronics and a cooling system. The cabinet is interfaced to a computer controller which uses software to perform experiments and analyze the resulting data.
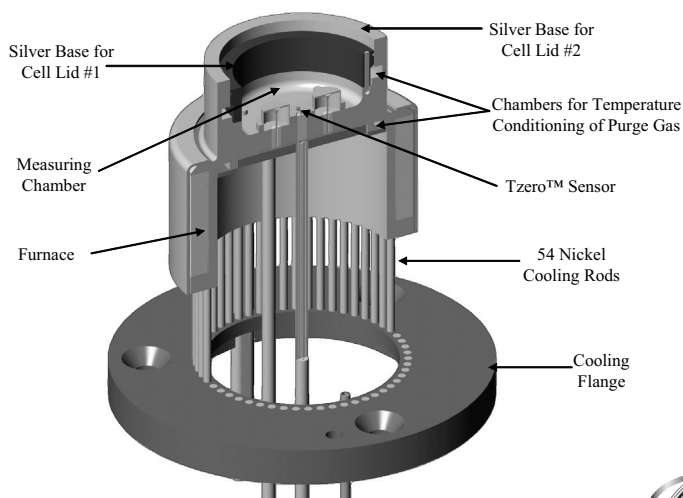

Figure 1. Tzero^{TM} DSC cell schematic

Figure 2 shows the major components of a modern DSC system.

Figure 2. Modern DSC system

A DSC system usually contains a DSC module, which can have numerous options such as Autosampler, Autolid, and MDSC®, a Refrigerated or LN2 Cooling System and a computer-based controller

2. Typical DSC Measurements

Figure 3 illustrates the most common type of report obtained from a DSC experiment, a plot of endothermic (heat absorbed) and exothermic (heat released) heat flows as a function of the sample's temperature. No one sample would contain all of the transitions shown in Figure 3. It simply is an illustration of the most common types of transitions.
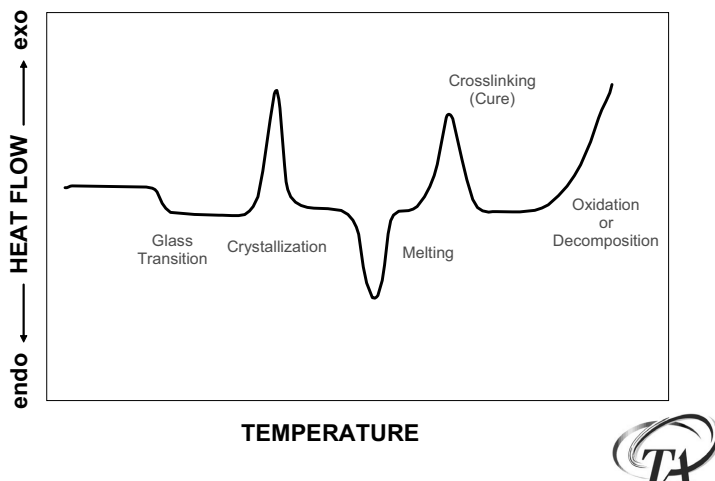

Figure 3. Transitions in a DSC curve

A brief definition/description of commonly measured transitions is provided below:

Glass Transition

A change in the physical properties of an amorphous material. One of the properties to change is heat capacity, which can be measured by DSC as an endothermic shift in the heat flow baseline as sample temperature is increased.

Glass Transition Temperature (Tg)

The temperature, usually a range, over which the properties of an amorphous material change. Below Tg, materials exhibit a glassy, rigid structure; while above Tg, they are rubbery and flexible.
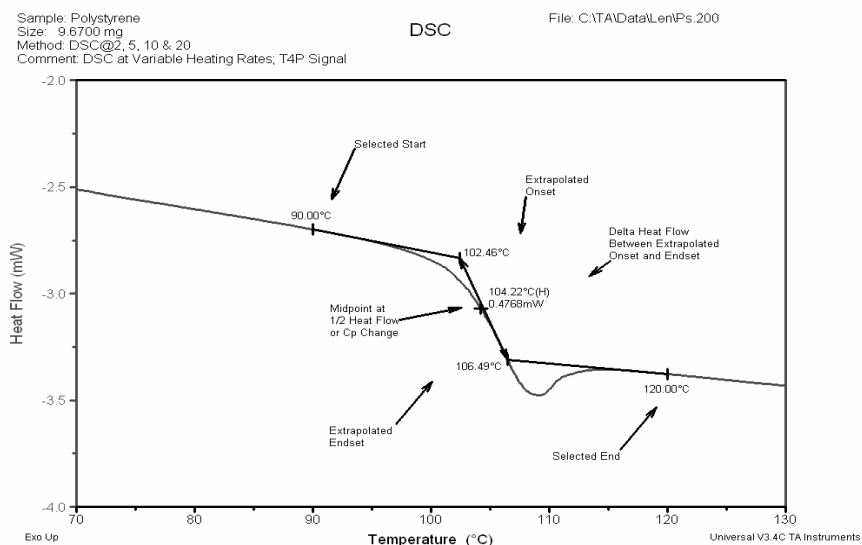
Figure 4. Glass transition analysis

Crystallization

The conversion of amorphous structure into crystalline structure. Most crystalline polymers have both types of structure and are usually referred to as semi-crystalline. Crystallization is normally seen during cooling from a temperature above the melting point, but it can also occur during heating. In this case, it is often called "Cold Crystallization."

Melting

The conversion of crystalline structure to a viscous amorphous structure. Melting occurs over a temperature range in polymers due to the molecular weight distribution and range in crystal sizes and defects within the crystal. With chemicals, the melting range increases and moves to lower temperatures as the impurity level in the sample increases. Although amorphous materials can flow at higher temperatures, due to decreasing viscosity, they do not melt.
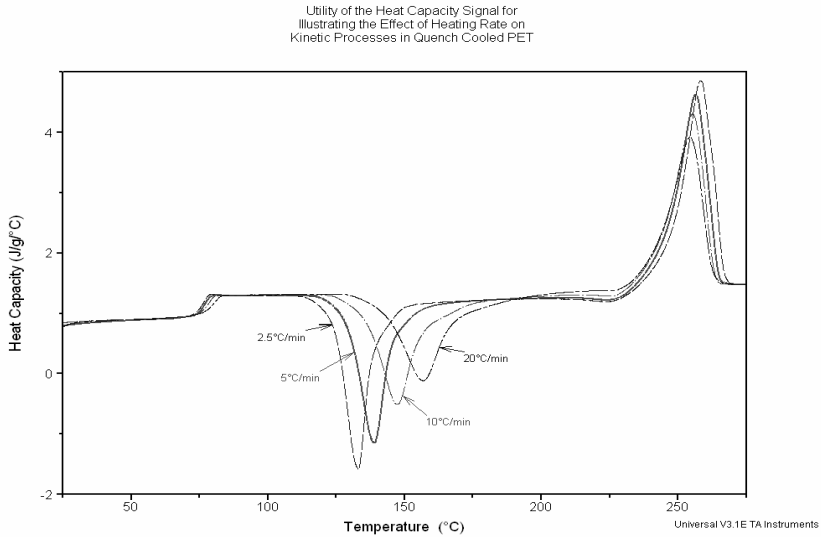
Utility of the Heat Capacity Signal for
Illustrating the Effect of Heating Rate on
Kinetic Processes in Quench Cooled PET

Fiure 5. Effect of heating rate on crystallization and melting of quench-cooled PET

Cure

A chemical reaction within a material that increases the crosslink density of the material and reduces molecular mobility. The term is usually used to define the reaction that takes place in thermosetting polymers (epoxies, phenolics, etc.). The glass transition temperature of the sample increases as the degree of cure increases.
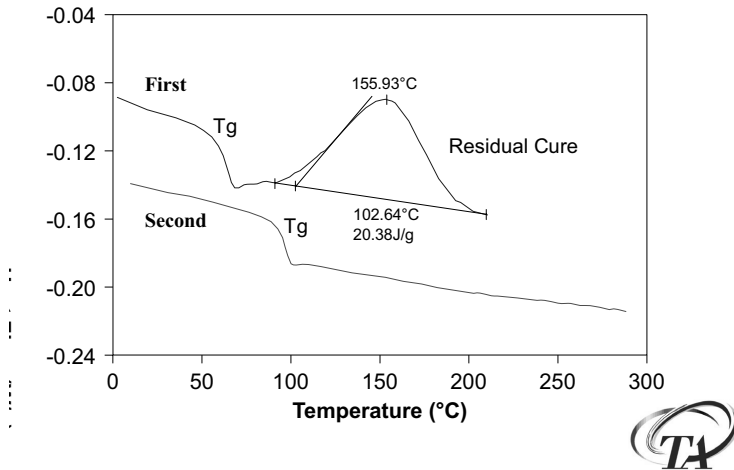

Figure 6. Thermosets.. Comparision of first and second heat

Decomposition

The breaking of chemical bonds due to heat or a chemical reaction such as oxidation. Partial decomposition usually results in a decrease in the glass transition and melting temperatures.

Other, but less common, measurements are as follows:

Oxidative Stability

A measure of the ability of a material to resist a chemical reaction between components of the material and oxygen. Tests are normally performed at elevated temperatures to reduce test time to less than one hour. Pressure DSC is the preferred technique for characterizing samples with volatile components.

Reaction Kinetics

Uses mathematical models to analyze the shape and temperature of reaction exotherms to determine kinetic parameters such as activation energy.

Purity (Figure 7)

Determines the purity of high purity (> 98%) metals and chemicals. The DSC method of determining purity is based solely on the shape of the melting curve as compared to the shape of the curve for a pure melting material. The higher the impurity level, the lower the melting temperature and the broader the melting range.
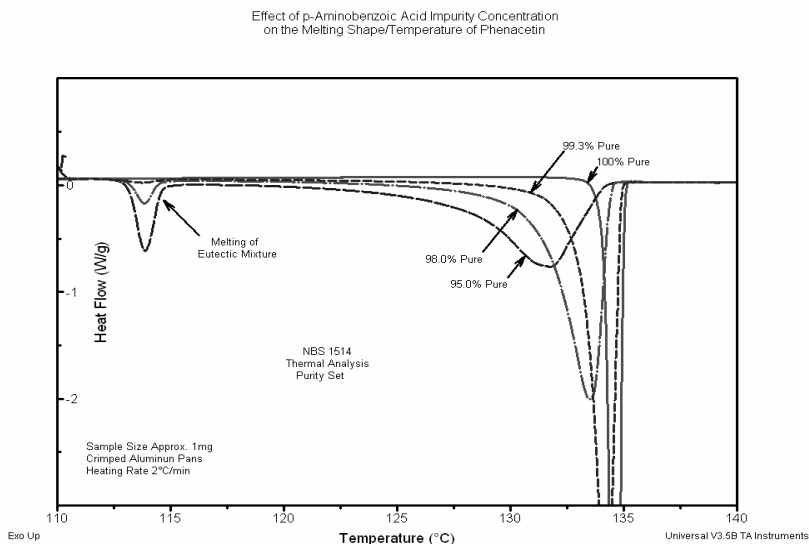

Figure 7. Melting temperature decreases and melting range increases as the level of impurity increases

Specific Heat Capacity (Figure 8)

The quantity of heat required to raise the temperature of one gram of a material by 1°K. It is measured in DSC by comparing the endothermic heat flow of an unknown with the endothermic heat flow of a standard material at a specific heating rate. A baseline scan is typically done first, which means that three separate experiments need to be performed. Modern instruments such as Tzero™ DSC and advanced techniques such as Modulated DSC® can measure specific heat capacity in a single run.
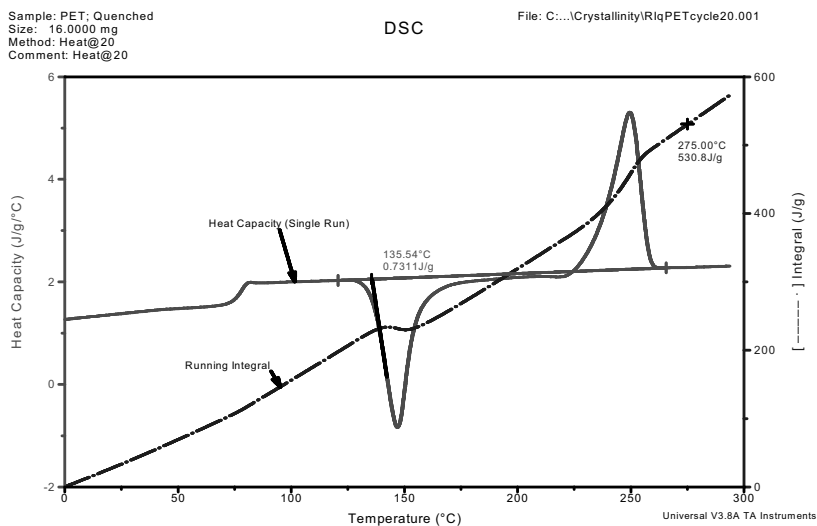

Figure 8. Engineers often need heat capacity information

3. Use of DSC in R&D, Analytical and QC/QA Laboratories

DSC in the R&D Laboratory

The goal of R&D is to create new or improved products that provide financial benefit to the corporation. Although we often think that new products improve profitability through increased market share and sales, an equally good way is to lower the cost of manufacturing a product without adversely affecting its end-use performance. The most successful new products are ones that provide the consumer with a better performing product that also has a lower manufacturing cost. Regardless of which approach you are taking, DSC is a valuable tool that will help you achieve program goals.

In developing a new product, there are at least three major elements in the development process that need to be considered.

1. Product Formulation and Costs

   In selecting materials to be used in a product, it is necessary to consider their:
   a. Cost per unit of product.
   b. Ability to meet mechanical and any chemical resistance requirements.

    c.   Aging characteristics: do properties change with time?
    d.   Manufacturing costs and sensitivity to normal process variations.
    e.   Environmental impact: are any of the components volatile, and how do you dispose of the product when it is no longer needed?

DSC can measure changes in structure that result from formulation, processing or aging. Before subjecting new materials or formulations to more extensive testing, which often requires more elaborate sample preparation or long-term oven testing, run a quick check with the DSC to see if the formulation is even a candidate for a product.

It is sometimes possible to use cheaper materials in a product through the use of additives such as fillers, plasticizers and antioxidants. Although DSC could not measure a change in color, it can determine the relative effectiveness of antioxidant concentrations and measurer the effect of plasticizer or filler level on transition temperatures.

2. End-Use Performance

Obviously, the product needs to perform the task that the consumer wishes to satisfy. This means that the product must have the physical and/or chemical properties required for its specific end-use. Those properties, and how they are measured or predicted from DSC data are as follows:

- Mechanical Strength

  In order to determine if a new or modified material has sufficient mechanical stability, it is important to define the temperature range over which the product could be used. Once that is known, DSC can identify the temperatures at which transitions or phase changes occur, which is also the temperature where physical properties can change by orders of magnitude. For example, if a rubber O-ring is to be used as a gasket between two rigid parts, it needs to remain flexible during end use. If it is rigid, it cannot fill the space between the two rigid parts as they move. By measuring the Glass Transition temperature of the material, it is possible to determine the temperature at which the properties change from rigid to flexible.

- Mechanical Stability

  Materials can be amorphous (non-crystalline), crystalline or a mixture of both. Amorphous materials tend to creep or flow over time as stress is applied to them. However, they tend to have better impact properties than crystalline materials. Although crystalline materials are usually more brittle, they have higher modulus or mechanical strength. DSC can measure the relative crystallinity of materials.

  In order to optimize both mechanical strength and stability, it is often necessary to use blends of two or more polymers or to precisely control processing to achieve an optimum level of amorphous or crystalline structure.

- Visual Characteristics

  Color, color uniformity, surface gloss, etc., are affected by the components and the distribution of the components used to make the product. But, they are also affected by thermal or oxidative degradation as well as relative crystallinity. Since sample sizes can be as small as a milligram or as large as tens of milligrams, it is often possible to sample the product to determine if a particular material is susceptible to thermal or oxidative degradation, or tends to undergo phase separation or has surface properties that differ from bulk properties.

3. Processability and Cost

   Although some materials have high strength as well as high thermal and oxidative stability, it may be necessary to heat them to higher temperatures in order to process them and this costs money. DSC is very useful in helping to determine the suitability of a particular formulation based on the following:

   a. Maximum processing temperature required.
   b. Process time, temperature cooling rate, and total energy requirements.
   c. Potential for thermal or oxidative degradation during processing.
   d. Environmental issues due to volatilization of components.
   e. Product variability due to normal processing variability.

   The goal is to produce the best product in the shortest amount of time and at the lowest cost. DSC provides many of the answers required to meet that challenge. Using DSC to determine the effect of a nucleating agent on crystallization time and temperature would be one such example of a possible cost reduction.

DSC in the Analytical Laboratory

Many companies use a central laboratory to meet the analytical needs of the company. Although there are pros and cons of having a single, central laboratory, it usually results in a better-trained and staffed laboratory that is a useful resource to materials scientists throughout the company. Support can be provided to R&D, Process Control, Quality Control/Assurance and even Marketing. A sales force loves to have proof statements about why their product is better, and the Analytical Lab can provide them through competitive product analyses.

DSC in the Quality Control/Assurance Laboratory

In order to provide consistent product at the lowest possible cost, it is necessary to monitor physical properties of both incoming raw materials as well as outgoing finished product. This way, if a problem occurs, it can be traced back to the material supplier or to the manufacturing process. The procedures used in the R&D laboratory to develop the optimum product can just as easily be used in the QC/QA laboratory. For high value-in-use products, vendor certification through DSC analyses provides a fast and reliable way to help insure product quality.

4. Introduction to Modulated DSC® (MDSC®)

Although DSC has been an extremely useful analytical technique for over forty (40) years, it has natural limitations with which most thermal analysts are somewhat familiar. These include:

- Baseline straightness limits sensitivity to detect weak transitions.

- Sensitivity increases with higher heating rates but resolution decreases as heating rate increases.

- Most modern materials are mixtures of plastics, fillers and additives which have overlapping transitions that are difficult to interpret.

- Most engineering plastics are semi-crystalline which increase in crystallinity while being heated in the DSC. Because DSC data usually makes the detection of the changing crystallinity difficult to detect, DSC crystallinity values can often be wrong by 50% or more.

- The measurement of specific heat capacity by DSC is often slow and laborious.

MDSC® overcomes these natural limitations of DSC as will be illustrated. However, MDSC® also has a limitation which results in it being a much slower technique (5-10 times). Therefore, the best approach for characterizing new materials is to always start with DSC and then switch to the MDSC® mode if one or more of its advantages are needed.

5. Operating Principle of MDSC®

With traditional DSC, a linear temperature ramp (heat/cool) is applied as a function of time. The resulting heat flow is a function of the rate of temperature change, absolute temperature, sample mass and the specific heat of the sample.

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

Where:

$\dfrac{dH}{dt}$ = Heat Flow Rate (mW or W/g)

Cp = Sample Specific Heat (J/g°C) x Sample Mass (g)

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

$f(T, t)$ = Heat Flow Rate due to Kinetic Processes (mW or W/g)

MDSC® uses two simultaneous heating rates, a linear ramp that provides the same information as traditional DSC plus a sinusoidal ramp superimposed on the linear

ramp that provides information about the sample's heat capacity. Figure 9 shows how temperature changes as a function of time in an MDSC® experiment, and Figure 10 provides the time-based derivatives (°C/min) which are the applied heating rates. Although it is beyond the scope of this paper, the applied rates can be selected to provide cooling during the modulation or have heat-only conditions. MDSC® does not require cooling during modulation but does use the change in heating rate to calculate the sample's heat capacity.
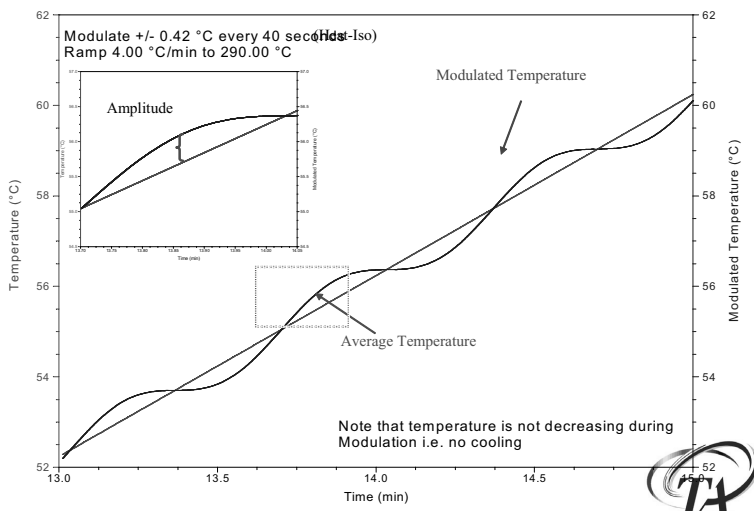
Figure 9. MDSC average & modulated temperature
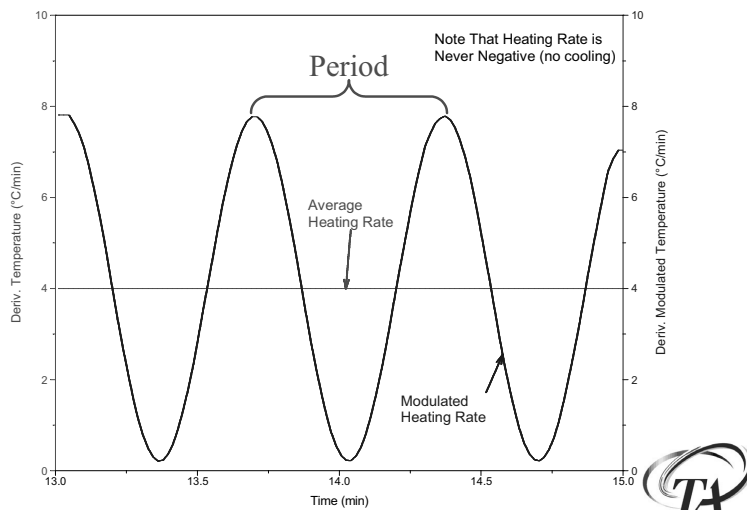
Figure 10. MDSC average & modulated heating rate

The result of the sinusoidal heating rate is a sinusoidal heat flow as shown in Figure 11. The modulated heat flow signal (MHF) is measured during the experiment and used to calculate the signals used by MDSC® for analysis of material properties. With traditional DSC, there is only one heat flow signal (Total) which is the sum of all heat flows. With MDSC®, there are three primary signals: the Total, Reversing and Nonreversing.

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

Total = Reversing + Nonreversing
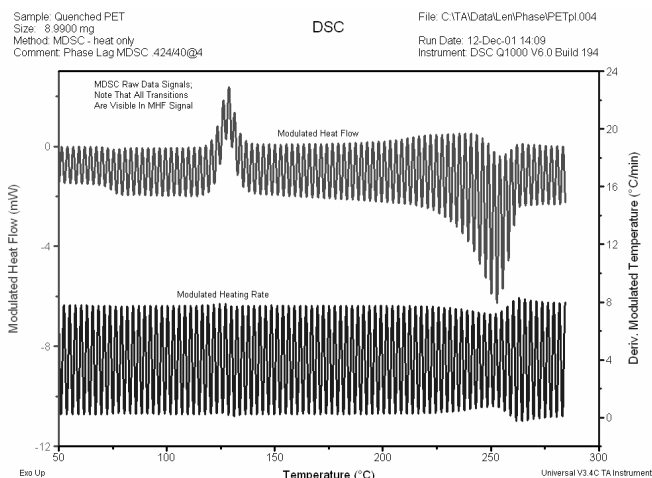
Figure 11. MDSC raw data signals

These three signals are shown in Figure 12 which is a quench-cooled sample of PET. The Total signal is calculated from the average value of the MHF signal while the Reversing signal is calculated from the ratio of the amplitudes of the MHF and modulated heating rate (MHR). The Nonreversing signal is simply the Total minus the Reversing heat flow.   All averages and amplitudes are calculated using Fournier transform analysis.

$$Total = Avg. MHF$$

$$Reversing = \frac{Amp\,MHF}{Amp\,MHR} \times Avg.\,Heat\,Rate$$
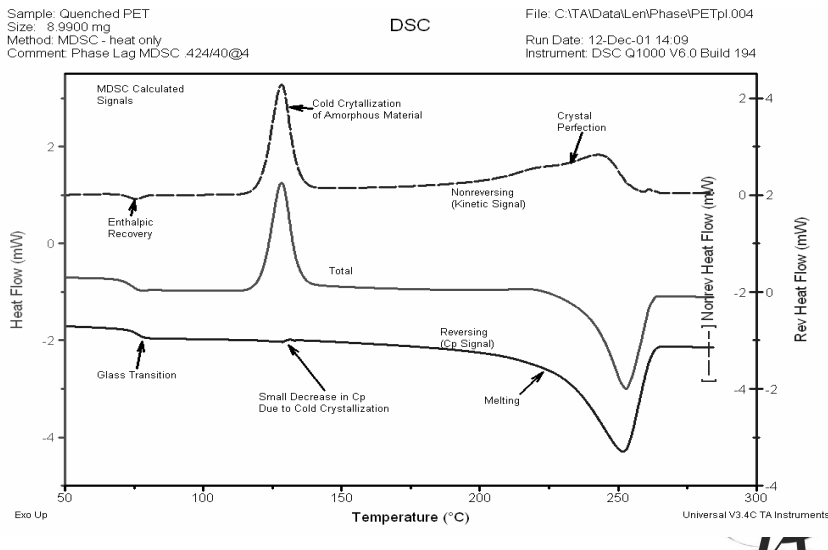
$$Nonreversing = Total - Reversing$$

Figure 12. Calculated MDSC heat flow signals

6. Applications Advantages of MDSC®

As previously stated, MDSC® overcomes the many natural limitations of standard DSC to provide superior sensitivity, resolution and separation of overlapping transitions. These benefits have been well documented in hundreds of papers since the commercialization of MDSC® in 1992. Therefore, only a few of the newer applications will be illustrated here.

Complex Polymer Blends

There is little doubt that blends of semi-crystalline and amorphous polymers are very difficult to characterize by traditional DSC. The reason is due to multiple glass transitions and often several crystallization peaks that occur while heating the sample in the DSC. Figure 13 shows DSC data on a common engineering plastic, Xenoy®, a product of the General Electric company. Xenoy® is a blend of Polybutylene Terephthalate (PBT) and Polycarbonate (PC). Except for the melting peak near 225°C, the results are very difficult to interpret.
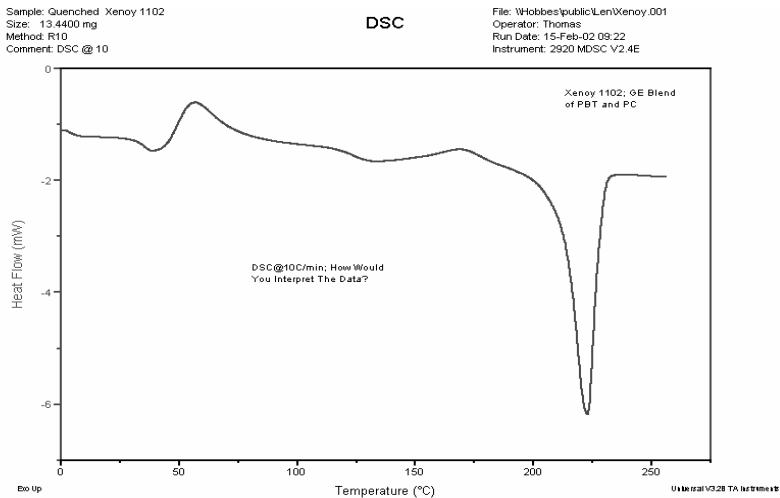
Figure 13. DSC of complex polymer blend

Figure 14 shows the same material run with MDSC®. Now it is relatively easy to measure the glass transitions of the PBT and PC and interpret the exothermic peaks near 60 and 150°C in the Nonreversing signal. Once the sample is heated above each of the glass transition temperatures, there is a step-increase in molecular mobility. This increase in mobility allows more of the amorphous PBT to crystallize.
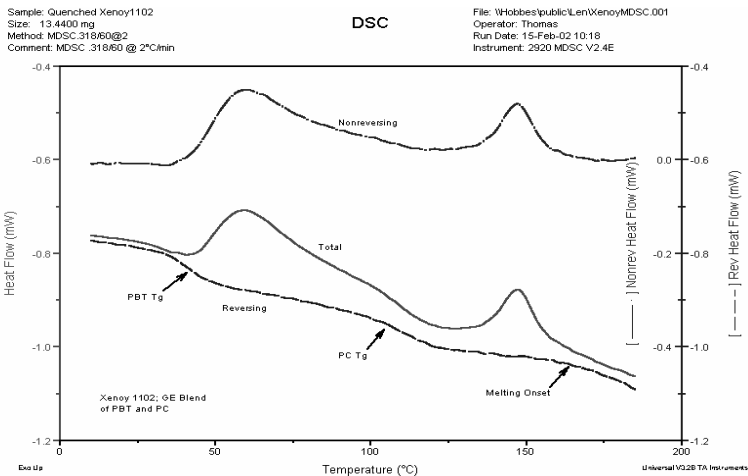

Figure 14. MDSC of complex polymer blend

Analysis of Polymer Crystallinity

Although DSC has been used for more than forty years to measure polymer crystallinity, results are often wrong by 50% or more. The reason is due to the sample's increasing crystallinity as it is being heated in the DSC and the difficulty in identifying the true heat capacity baseline in the data. Figure 15 shows DSC data on a sample of Nylon 6/6. Most DSC users would assume that baseline is best selected as shown in the blue curve. This yields a crystallinity value of approximately 50 J/g as compared to 29 J/g in the same data with the green curve. With standard DSC, it is very difficult to judge which is correct.
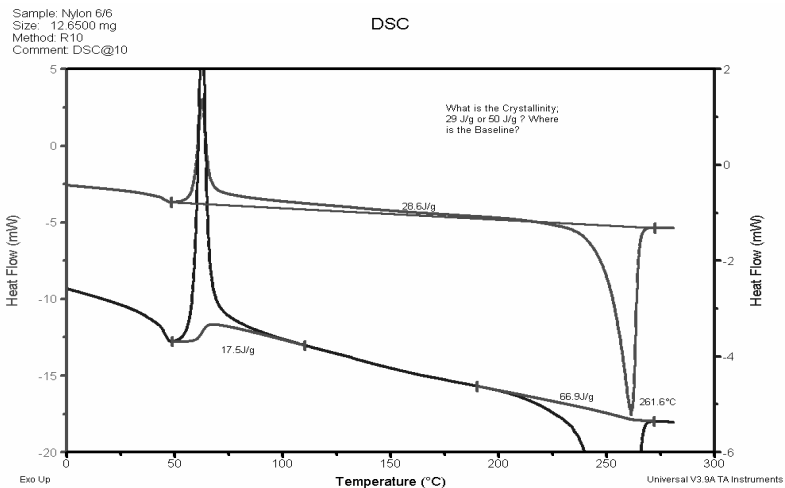

Figure 15. DSC @ 10 ºC/min on Nylon 6/6; Where is the baseline?

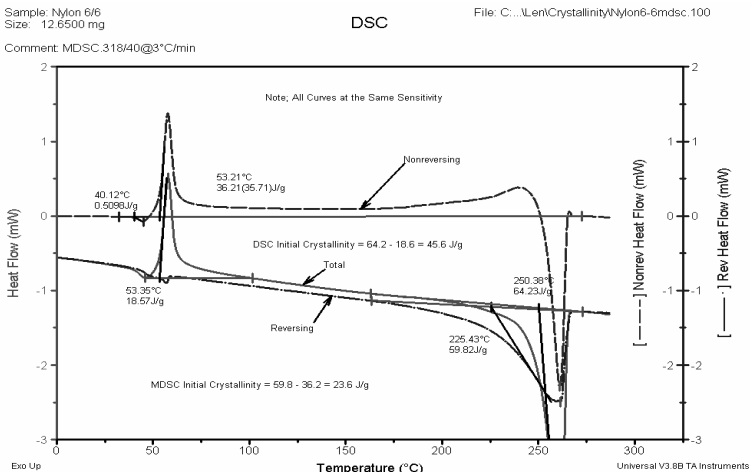Figure 16 shows MDSC® results on the same Nylon 6/6 and shows the actual crystallinity to be only about 24 J/g.

Figure 16. MDSC of nylon 6/6

Figure 17 shows MDSC® results on a sample which is a mixture of quench-cooled PET and PC. Since it was quench-cooled in liquid nitrogen, the crystallinity of the sample is known to be approximately 0 J/g. The Total curve, which is typical of the data from traditional DSC, is impossible to analyze correctly because the glass transition of the PC is not even visible. The sum of the melting and crystallization processes seen in the MDSC® Reversing and Nonreversing signals provides the expected crystallinity, and the PC glass transition is easily seen in the Reversing signal.
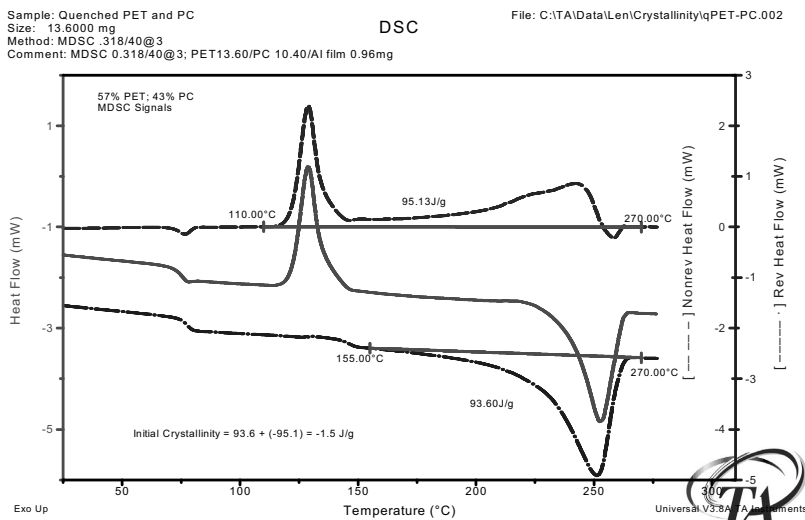

Figure 17. MSDC of 57/43 % PET/PC mixture

7. Summary

The combination of DSC and MDSC® provides an extremely useful analytical tool for the characterization of polymer structure and detection of changes (transitions) in that structure. Whereas DSC is a faster, easier to use technique, MDSC® offers advantages in sensitivity, resolution and separation of overlapping transitions.