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Practical Uses of Differential Scanning Calorimetry for Plastics

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INTRODUCTION

Although differential scanning calorimetry (DSC) is used in many different industries, its application and use in the plastics industry is widely accepted. It is used to characterize materials for melting points, softening points, and other material and material-reaction characteristics such as specific heat, percent crystallinity, and reaction kinetics. This chapter addresses the practical uses of DSC in the plastics industry, focusing on the most common tests and experiments. Advanced analysis will be mentioned briefly, but not reviewed in detail. For the best results and the most reproducible data, consider all of the suggestions about operational variables discussed, and you will experience successful and reliable thermal analysis.

DEFINITIONS OF THERMAL ANALYSIS TERMS

Differential scanning calorimetry is an analytical technique that measures the heat flow to or from a sample specimen as it is subjected to a controlled temperature program in a controlled atmosphere. In other words, a DSC

heats or cools a material and energy is either absorbed or released as the material experiences physical or chemical changes.

Heat is a form of energy. Heat is not temperature. It is measured in joules. This is an important factor when doing DSC work, because the material is heated or cooled and, in some DSCs, the energy is measured directly. Often the process engineer will want to know the amount of heat required to melt a material or how much heat is given off by a material as it cools in the mold.

A *joule* (J) is the amount of work done when the force of 1 newton (1 N) acts through the distance of 1 m. Although the joule is mechanical in nature, it is a suitable form for heat energy. Heat flow is measured in joules per second.

Temperature is the degree of heat measured on a definite scale. The centigrade scale is internationally accepted.

A watt (W) is the power expended when 1 J of work is done in 1 s of time. Heat flow is measured in watts or milliwatts. A *milliwatt* (mW) is 1000th of a watt.

A *calorie* is the amount of heat required to raise 1 g of water by 1°C.

Heat flow is measured in milliwatts. Heat flow is the flow of energy measured by the DSC as it heats or cools the sample specimen.

Enthalpy, H , is the “heat content” of a material. The absolute enthalpy of a material cannot be measured directly; however, a change in enthalpy, ΔH , can be measured directly by DSC. The change in enthalpy of a material is either a gain (endothermic, such as melting) or a loss (exothermic, such as curing or recrystallization). This information is very helpful for process engineering.

Specific heat or *heat capacity* is the amount of heat required to raise the unit mass of a material 1° in temperature. *Note*: Specific heat and heat capacity should be assumed to be equal for engineering purposes.

$$C = \frac{Q}{m \Delta T}$$

where

C = specific heat

m = mass of materia

Q = heat added

ΔT = change in temperature

Heat of fusion is the amount of heat per unit mass needed to change a substance from a solid to a liquid at its melting point. A melting transition is an endothermic reaction, which is represented as a peak on a DSC thermal

curve. The heat of fusion is the amount of energy added to the material divided by its mass. It is determined from a thermal curve by calculating the area under the melting peak. This is important information for process engineering as a plastics processing system is designed.

$$H_f = \frac{Q}{m}$$

where

H_f = heat of fusion

m = mass of material

Q = heat added

Mass is often incorrectly interchanged with weight because the mass of a material is determined by using a balance and weighing the sample. Most thermal software does this by using the sample weight in the above equations. As a practical matter, remember that weighing the mass of the sample will directly affect the DSC's specific heat measurement and heat of fusion measurement. It is best to use a microbalance (accurate to six decimal places of a gram) for weighing.

APPLICATIONS

Glass Transition Temperature

The glass transition temperature is the softening region of a plastic. It actually refers to the amorphous region of semicrystalline materials or to amorphous materials; it is the molecular motion of the material as it is heated that makes the material pliable and no longer brittle.

The glass transition temperature is represented graphically in the thermal curve as a shift in the baseline. It is a change in the heat capacity of the material as the amorphous regions melt. For the easiest identification of glass transition temperature, use a large sample specimen and quench the material from just above the melting temperature to below the glass transition temperature region. Faster quenching creates larger shifts in the baseline (see [Figs. 1 and 2](#)).

The calculation of the glass transition temperature can be done in several different ways. The most common calculation is the half- C_p or half-height of the shifted baseline. The limits are set up on the flat portion of the preshifted and postshifted baseline with the calculation construction lines extrapolating the baselines as shown in [Figs. 1–3](#).

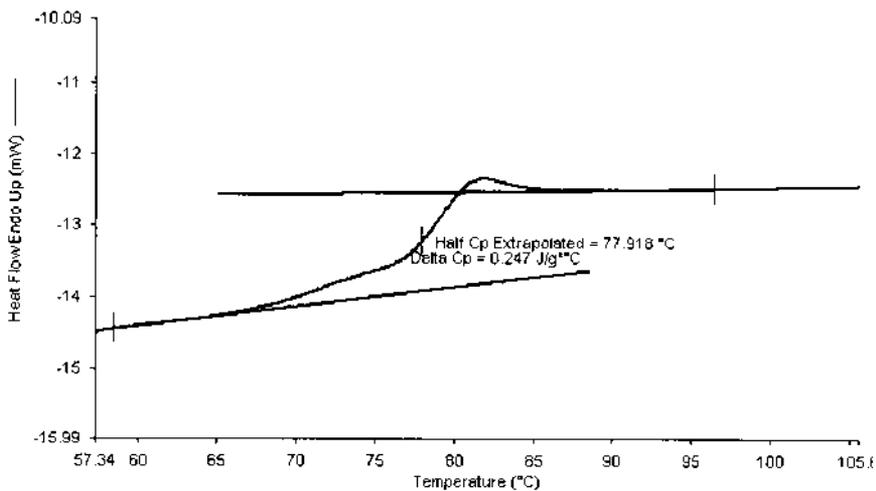


Figure 1 Thermal curve of PET after quenching (cooling at 200°C/min) with a glass transition temperature calculation using the half-height (half- C_p).

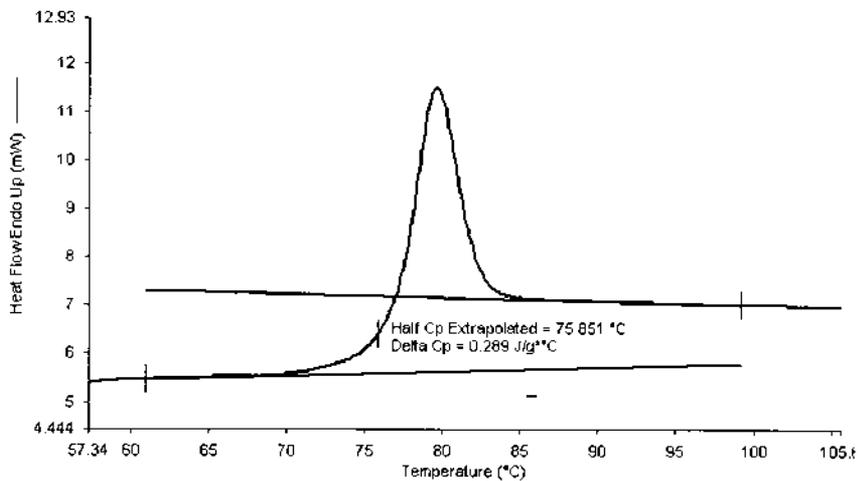


Figure 2 Thermal curve of polystyrene with a glass transition calculation.

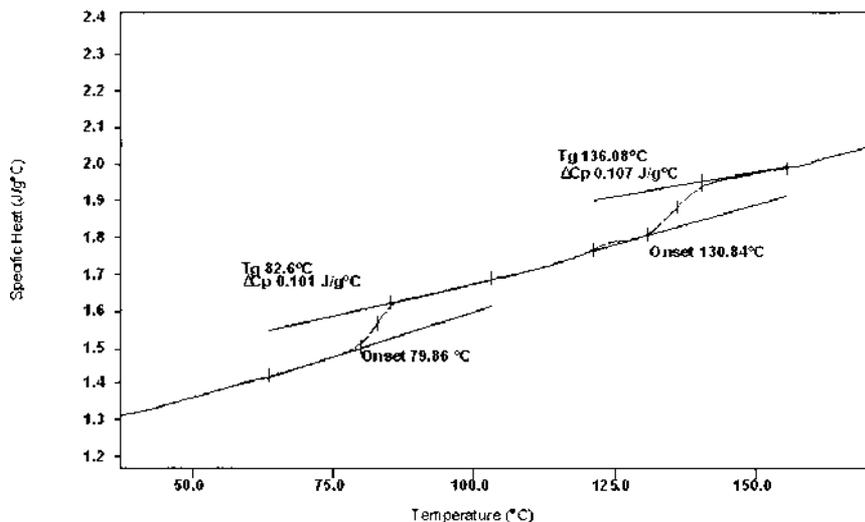


Figure 3 This material exhibits two glass transitions (T_g). The T_g is calculated by establishing the calculation limits and extrapolating the pre- T_g baseline and the post- T_g baseline and calculating the half-height as the T_g . This is the most common representation of the T_g .

Melting Temperature

Melting temperatures of different materials are identified as different portions of the thermal curve. During calibration the melting temperature of the calibration reference materials (usually a pure metal such as indium) is identified as the onset temperature of the melting peak (Fig. 4).

Because plastics process engineering has defined the minimum process temperature of a plastic (its melting temperature) as its peak temperature on a thermal curve, the melting temperature of a plastic is sometimes confused with the melting temperature of a nonplastic. Figure 5 shows the melting peak of polyethylene.

The melting temperature is calculated by setting the calculation limits before and after the peak, keeping them on the flat portion of the baseline. This will give the most reproducible results (Fig. 5).

Enthalpy of Melting

The area under the melting peak represents the amount of energy required to melt the polymer. This is the heat of fusion of the material or how much

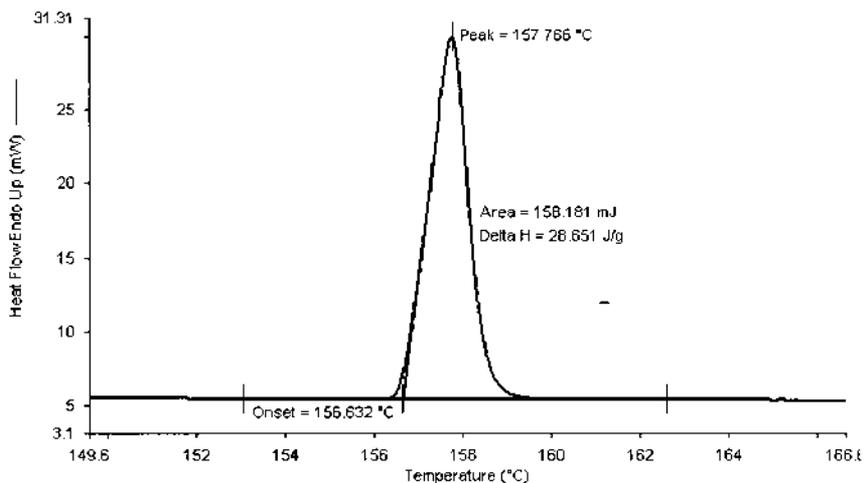


Figure 4 Thermal curve of indium melting with a peak area calculation including the onset temperature and peak temperature.

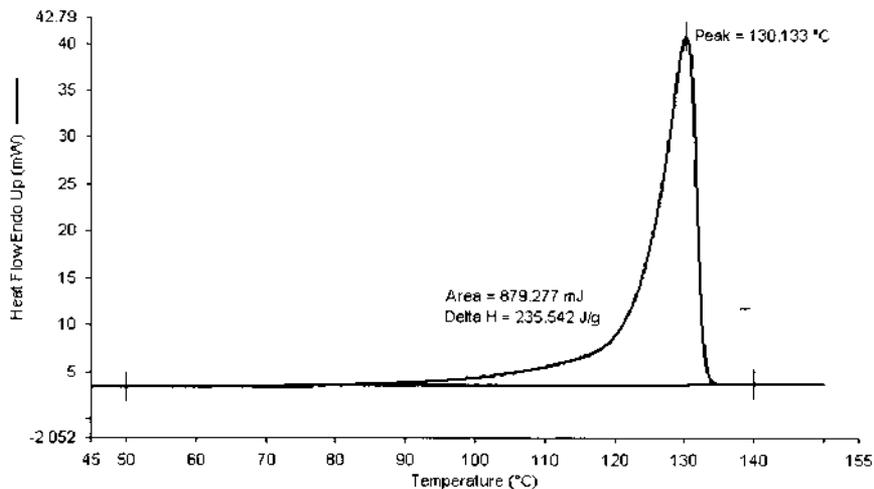


Figure 5 Thermal curve of polyethylene melting with the peak area calculation including the peak temperature.

energy is required to melt the material. The ΔH or change in enthalpy is expressed in normalized terms of joules per gram (J/g). Because this term, has the sample weight as the denominator, accurate sample weighing is important. Melting is an endothermic reaction, that is, it is a reaction that absorbs energy. The calculation of the peak area is very helpful in process development and material characterization. The peak area can also be used to identify the percent crystallinity of the material. This is explained later.

The peak area calculation is used with the limits of the calculation on the flat portion of the baseline before and after the melting peak. Some thermal analysts use the horizontal flat portion of the first derivative curve as a guide to set the peak calculation limits (Figs. 4 and 5).

Curing Studies

Curing of a resin material is an exothermic event, which means that energy is released as the material goes through the transition. This is the opposite of melting, which is an endothermic event. Curing studies may be conducted as DSC scanning experiments or DSC isothermal experiments.

Rates of reaction of both these types of curing experiments are very useful to polymer scientists. There are several different kinetics software packages available to characterize materials. There are scanning kinetics, isothermal kinetics and model-free kinetics calculations. Each has its own unique application or is best suited for certain applications. Figure 6 depicts the thermal curve of an epoxy cure with a second curve superimposed representing the percent area as the reaction advances.

In curing studies, the glass transition temperature will vary depending on the degree of cure of the material. Remember that the glass transition temperature is the softening region of the material. If the cure reaction is more advanced in sample A than in sample B, the glass transition temperature will be higher for sample A than for sample B.

Recrystallization Temperature upon Cooling

Recrystallization studies are useful for process engineers who want to optimize the process by identifying the recrystallization temperature of the material in the mold. A simple recrystallization study is accomplished by running a multiple-step temperature programmed (heat-iso-cool) experiment, in which the material is heated slightly above its melting temperature and held there for a minute or so, then cooled in a controlled fashion at a certain scanning rate such as 20°C/min. The temperature of recrystallization of the material can be identified by using the onset temperature calculation (Figs. 7 and 8).

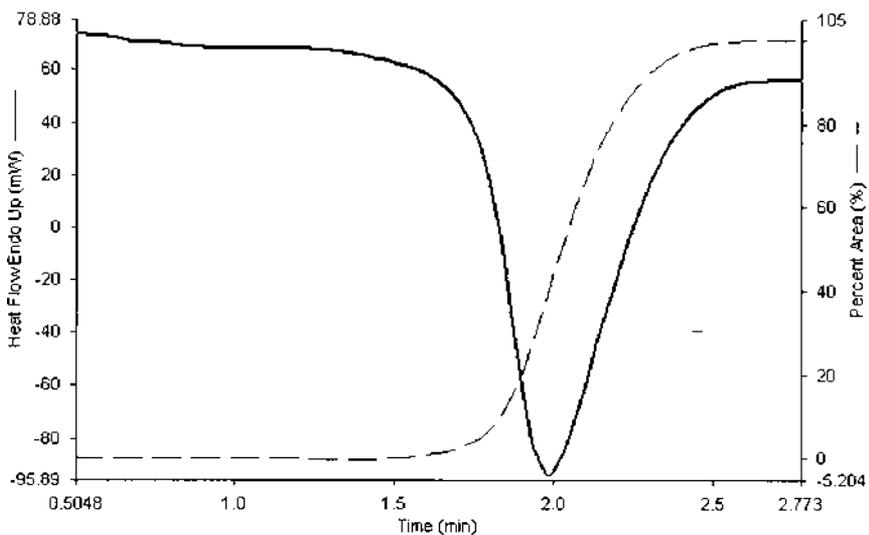


Figure 6 An epoxy cure is an exothermic event as depicted by the heat flow curve. The second curve with the dashed line is the percent area curve, which relates directly to the percent reacted assuming the epoxy is 100% cured.

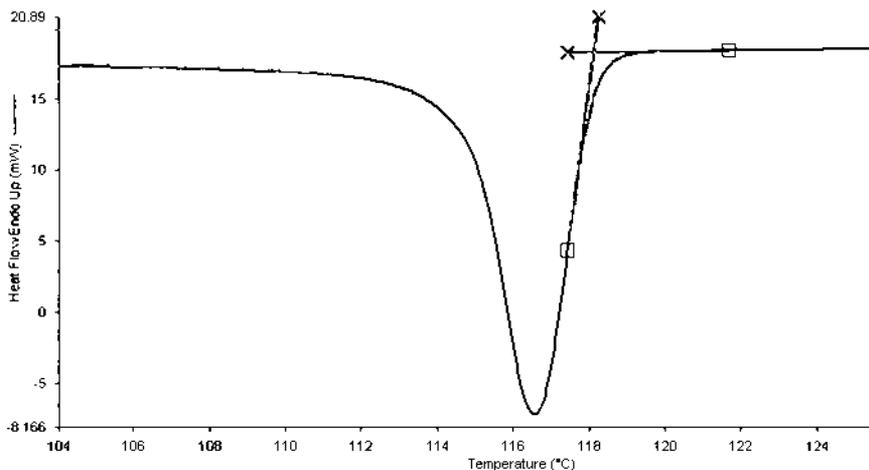


Figure 7 The limits of an onset calculation of this recrystallization-upon-cooling curve are identified and the construction lines are adjusted correctly. Many analysts use the peak of the first derivative curve (not shown) to identify the left limit in this case.

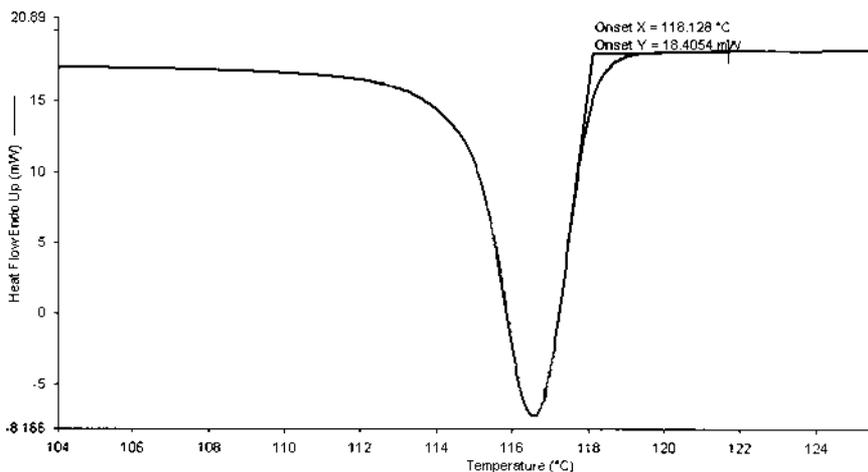


Figure 8 The onset of recrystallization upon cooling is calculated.

Note that for best results when conducting cooling experiments, calibrate the calorimeter upon cooling. This will correct for instrumental effects and sample supercooling phenomena.

Recrystallization Time

Recrystallization time is very useful for the development of processing times for recrystallization upon cooling from the melting temperature. Recrystallization time is measured in an isothermic experiment in which the material is cooled to a predefined temperature and then held there isothermally until the recrystallization is complete. The time it takes to recrystallize is measured. A slight shift in mold temperature often saves time, thus increasing manufacturing throughput. The sensitivity and temperature control of a power-compensation DSC is ideal for this experiment (Fig. 9).

This type of experiment is also used to identify the curing cycle of an epoxy material. Although an epoxy material is usually mixed at room temperature (or at subambient temperature), it is heated to an elevated curing temperature and examined isothermally. At the selected isothermal temperature, the material is examined with regard to the length of time it requires to cure fully.

Oxidative Stability Testing

The investigation into the effectiveness of antioxidant additives in a material is easily done by DSC. This a test that determines the length of time that a

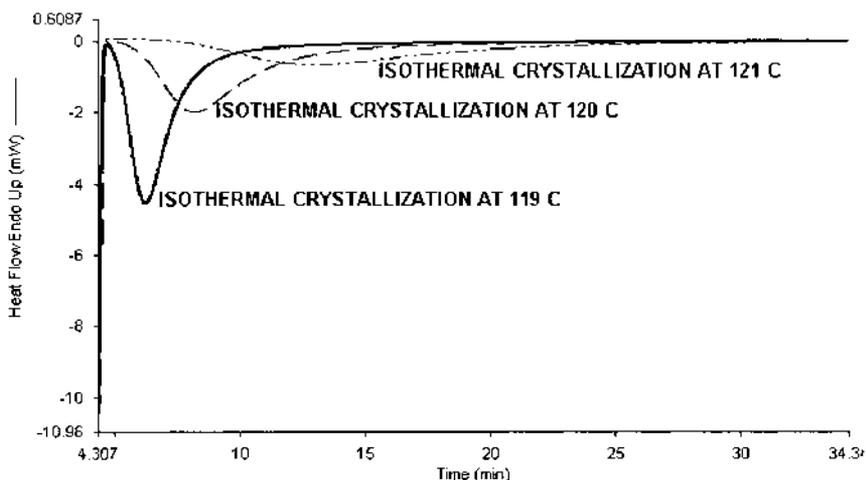


Figure 9 The three curves displayed are the same sample quickly cooled to slightly different temperatures and then held isothermally until fully crystallized. This is an example of the type of resolution power compensation DSC is known for. This information may have been used to optimize a process.

polymer can withstand an oxidative environment at an elevated temperature. This test is regularly done for cable and wire insulation materials, among others.

A brief overview of this test is that the sample is prepared and installed in a calorimeter that has been purged with oxygen. The sample is heated to 200°C and held isothermally at that temperature. The time it takes the material to decompose is measured. Decomposition is indicated by an exothermic downturn of the baseline. The extrapolated onset is calculated to determine the amount of time it took for decomposition. The longer the time, the more effective is the antioxidant (Fig. 10).

There are two very important considerations when conducting this test: (1) very accurate temperature calibration and (2) consistent and accurate purge gas flow rate.

For more information on this test, refer to ASTM Publication STP1326, "Oxidative Behavior of Materials by Thermal Analytical Techniques."

Effects of Additives in Plastics or Treatments of Plastics Can Be Analyzed by DSC

Additives will affect the thermal characteristics of a material. The glass transition temperature (T_g), the melting peak, or the recrystallization

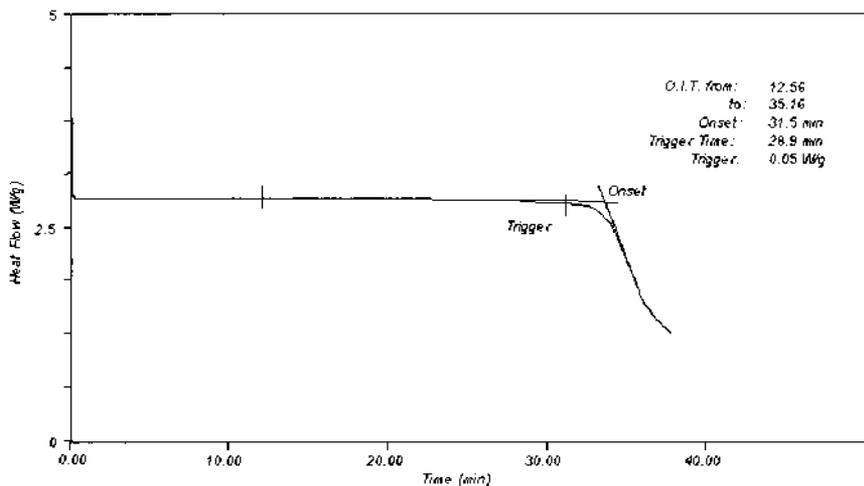


Figure 10 The calculated extrapolated onset temperature determines the oxidative induction time.

point may shift due to the additive's effect on the material. Some general categories of additives are plasticizers, antioxidants, stabilizers, reinforcements, fillers, impact modifiers, cross-linking agents, foaming agents, flame retardants, lubricants, and antistatics.

One of the most common thermal laboratory practices is to analyze a virgin material, then add plasticizer of a known percentage to the untreated material and measure the effects of the additive by comparing the T_g or other thermal characteristics of each specimen. [Figure 11](#) compares untreated and treated polypropylene samples.

Temperature-Dependent Crystallinity

Temperature-dependent crystallinity is a relatively new data calculation of a temperature scan of a material. PerkinElmer Instruments LLC has the exclusive rights to this software package, which was developed by Vincent B. F. Mathot of DSM, The Netherlands, and Gosse van der Plaats of the Netherlands. Note that it does not matter what instrument you use to collect the data, just that it is in ASCII format so that it can be imported into this standalone software package.

Before the temperature-dependent crystallinity calculation was available, the estimate or calculation of the percent crystallinity of a semicrystalline material was more subjective. The melting peak area of a semicrystalline

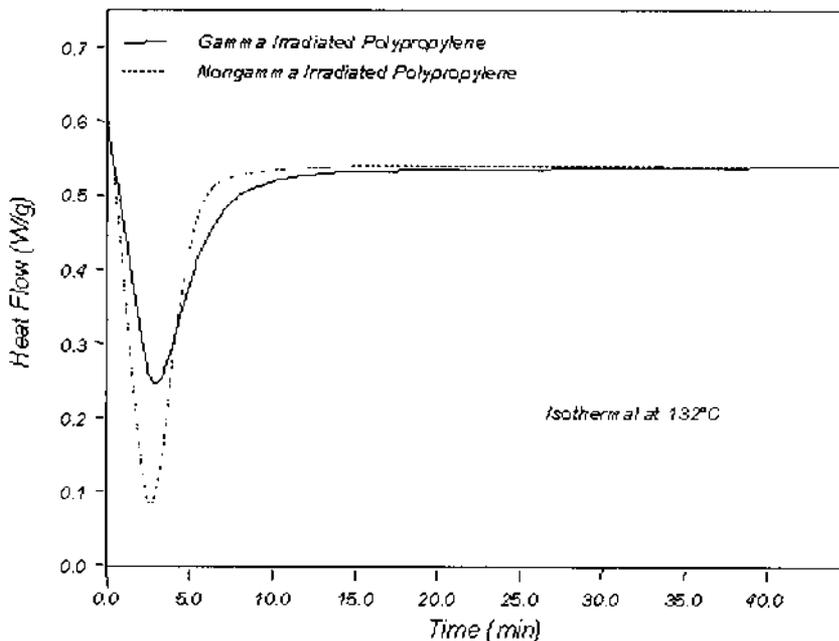


Figure 11 A recrystallization of two polypropylene samples; one is gamma-irradiated and the other is untreated. Notice the differences of endsets (where the exothermic peak returns to the baseline), the peak temperatures, and the areas.

material was compared to the melting peak area of a 100% crystalline structure. A simple ratio was done of the two and the percent crystallinity was assumed. The subjectivity arises from the placement of the calculation limits chosen by the analyst. Many times they are in error or are not reproducible. Temperature-dependent crystallinity calculations eliminate many of these errors and are more reproducible.

Temperature-dependent crystallinity software analyzes the percent crystallinity of a material during a DSC scanning experiment. As the material changes during heating, the calculation may be done on any portion of the thermal curve through the melt. It extrapolates the postmelt baseline down to the lower temperature limit, which is usually in the glass transition region. This extrapolation is a reference line; deviations in the thermal curve are compared to it and to published theoretical crystallinity values. The crystallinity values of the material are then presented in tabular form.

Understanding the percent crystallinity in a material will be helpful in designing products, prolonging product life, or designing new processes (Figs. 12 and 13).

QA/QC Applications

Some mechanical tests of materials are now being correlated to DSC testing. Examples of these are abrasion testing and impact testing. They are now being tested by both mechanical means and by DSC. A material that passes the mechanical test should be characterized by DSC and likewise the failed products being characterized by DSC. The differences in the materials characterization by DSC are noted and used in collaboration with the mechanical test findings. Generally the DSC testing is faster and more reproducible.

Routine QA/QC material testing is now being automated so that the samples are accurately prepared and encapsulated by the thermal analyst, but loaded into an autosampling system for analysis and data calculations with automatic tolerance testing. That is, the software automatically identifies the sample as a passed or failed sample. This type of automation

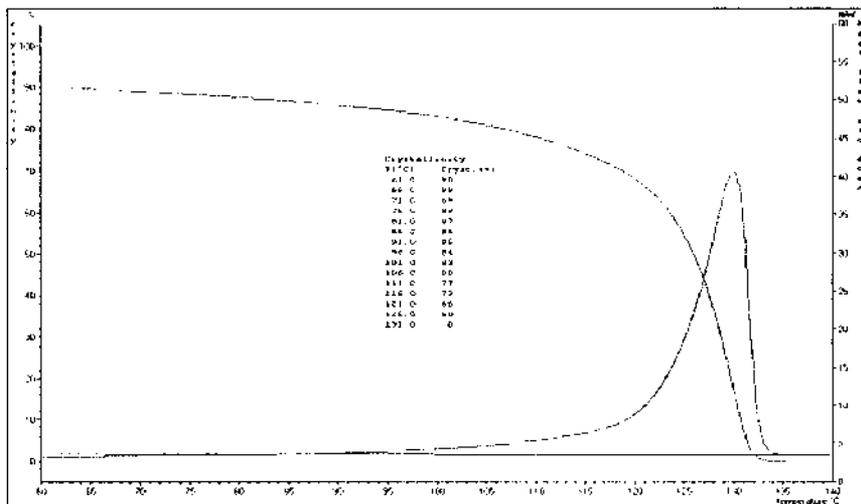


Figure 12 Temperature-dependent crystallinity is determined for most common polymers by using a simple software package that employs user-defined limits for the calculation on the DSC heat flow curve. The resultant temperature crystallinity curve is produced with the percent crystallinity table.

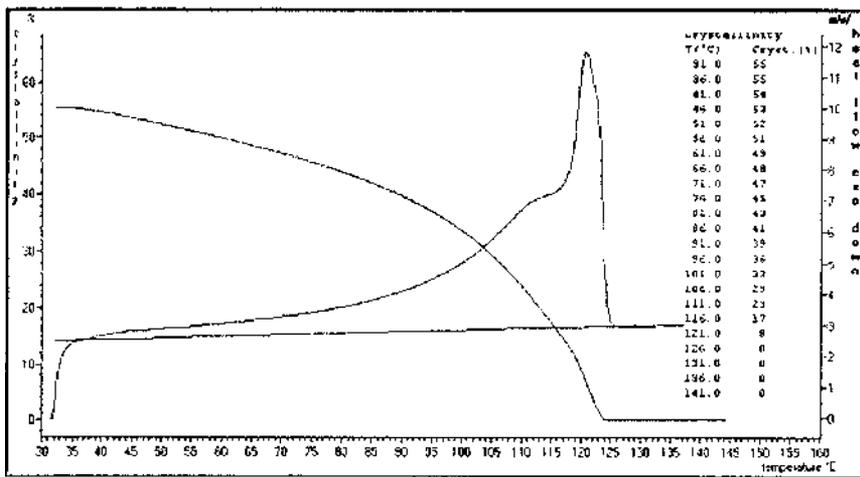


Figure 13 An example of temperature-dependent crystallinity showing the postmelt extrapolated baseline. The table indicates the change in crystallinity as the material is heated. This information may be useful for determining processes and the material's useful working range.

system addresses the needs of business today by providing not only higher throughput, but also a simple handling of samples and data. [Figures 11](#) and [14](#) show examples of QA/QC comparisons.

A BRIEF HISTORY OF DIFFERENTIAL SCANNING CALORIMETRY

Early civilizations stumbled over the effects of temperature on materials. Since those early stages, there have been significant advances that are worth mentioning.

The current DSC evolved from the first thermal analysis done by Sir Roberts-Austen, who, in 1899, invented differential thermal analysis (DTA). His investigations were of clays and silicate materials. DTA was used as a laboratory setup that measured the temperature difference between a sample specimen and an inert reference material.

Currently there are two DSC designtypes that are used to characterize plastics. They are power-compensation DSC and heat flux DSC. The power-compensation DSC measures the heat flow directly to or from the sample specimen, while the heat flux DSC measures the change in temperature between the sample specimen and an empty reference pan and then uses

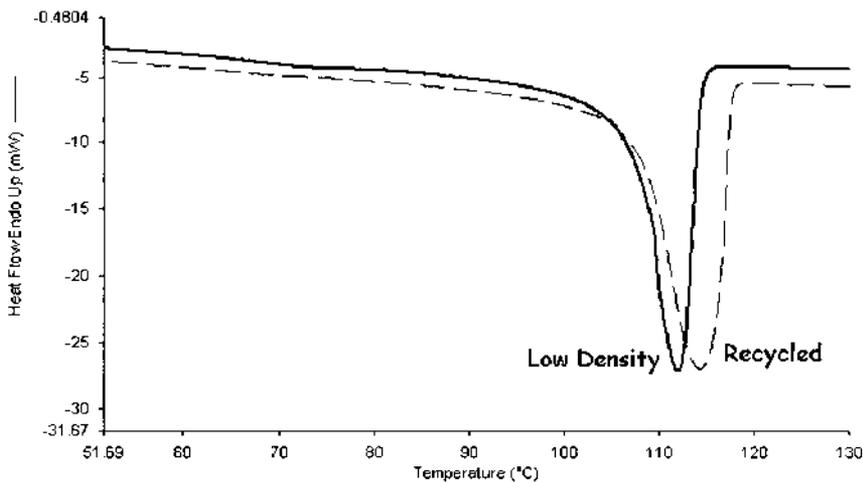


Figure 14 A comparison of two types of polyethylene upon cooling.

algorithms to calculate the heat flow. They both serve the plastics industry well.

Heat flux DSC and power-compensation DSC are used to analyze most polymers. The difference between them, besides the temperature-sensing device, is the speed and accuracy at which they can heat and cool a sample specimen. The power-compensation DSC has the ability to heat and cool at very fast rates (up to 500°C/min), while the heat flux DSC effectively heats or cools at slower rates (up to 30°C/min). Their differences in heating/cooling are due to the design of the calorimeters and the heat transfer characteristics of each. For a heat flux DSC diagram, see [Fig. 15](#).

Because of the fast cooling rates, the power-compensation DSC is typically used for materials that are difficult to analyze or that require fast cooling rates (quenching). Depending on what analysis is, desired, quenching may be required to condition the sample in such a manner that the next heating scan will produce the desired results consistently. Power-compensation DSC has the best temperature control and energy sensitivity of all calorimeters. [Figure 16](#) is a power-compensation DSC diagram.

DSC OPERATING VARIABLES: REPRODUCIBLE EXPERIMENTS AND TESTS

The best way to ensure that material investigations that are reproducible and accurate is to be aware of the operational variables that will affect your analysis. For best results, none of these variables should be overlooked:

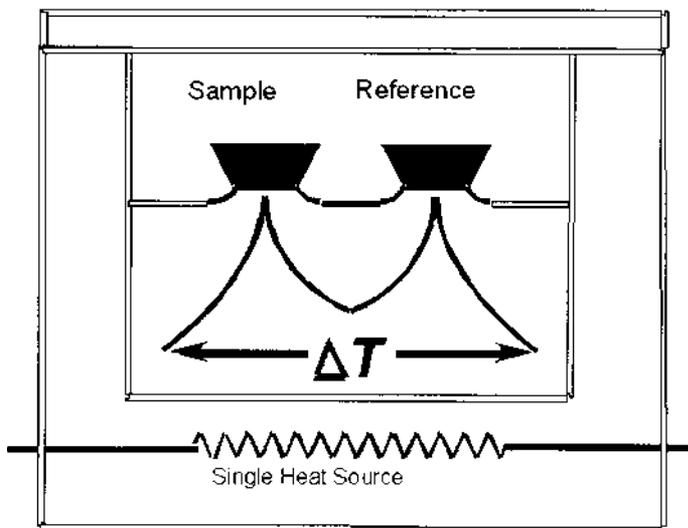


Figure 15 Heat flux DSC utilizes a large, single heating element that heats both sample and reference materials. It should be operated slowly, at about $10^{\circ}\text{C}/\text{min}$ to minimize thermal lag. It utilizes thermocouples to sense the temperature difference between the sample and the reference.

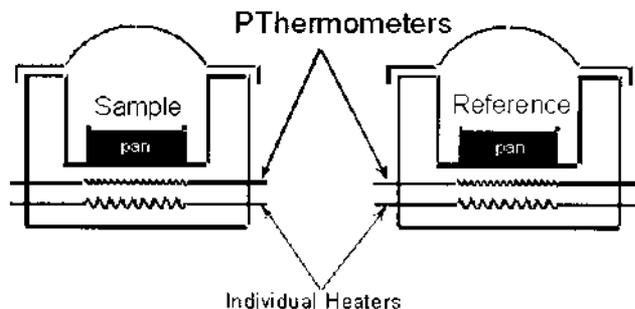


Figure 16 Power-compensation DSC schematic depicting individual platinum heaters and sensors. Power-compensation DSC is typically used for very exact calorimetry work which demands accuracy as well as precision. It is used for fast quenching experiments such as subtle T_g determination as well as melting studies and specific heat studies. It is also used for routine analysis.

- Cleanliness of the instrument
- Instrument coolant
- Calibration parameters
- Sample pan selection
- Sample size
- Sample preparation
- Sample encapsulation
- Sample atmosphere
- Temperature range of interest
- Scanning rate

The operating variables of the DSC will affect the results. The point of DSC experiments is to have reproducibility from today's experimental run to next week's experimental run. These operational variables are important; if they are not checked they will lead to nonreproducible results.

Checking Instrument Calibration

The first instrument variable to verify is that the analyzer is calibrated correctly. This is easily done by running an encapsulated calibration reference material and evaluating its melting temperature and the transition energy required to melt that material. A typical reference material used for calibration is indium. The melting temperature of indium is 156.61°C. It is 99.999% pure, which translates into very accurate temperature calibration and energy calibration (ΔH), which is the integrated area under the melting peak (Fig. 4). This test may be done regularly—daily or weekly, or when deemed necessary.

To see if the analyzer is calibrated correctly, compare the results of an indium run (run under the same conditions as the sample—same scan rate, etc.) to the expected or theoretical values of indium. Let's say that your calibration check reveals that the onset temperature of indium is 159.0°C. Is this value out of tolerance? The acceptable tolerance range for any analyzer is chosen by the operator. Indeed, 159.0°C might be acceptable for someone who is doing a very broad review of materials. On the other hand, it might be out of tolerance and totally unacceptable for more precise material characterization work.

Assuming that the instrument calibration check is not acceptable and the DSC requires recalibration, the first thing to do is to clean the analyzer.

Cleaning a DSC

Visual observation of the DSC furnaces, lids, and covers should be done. If you see contamination in the furnaces, remove the covers or swing them out of the way and remove all sample pans from both the sample and reference

sides of the calorimeter. Then, with the furnace open to ambient air, heat it to 600°C. This will burn off the organic contaminants. If volatile gases evolve during cleaning, you may want to hold a small exhaust line above the furnace to evacuate the volatile gases safely out of the laboratory.

Cleaning the remaining furnace covers must also be done. If you have a power-compensation DSC, flame the platinum covers and reshape them before installing them into the furnaces. Check the underside of the swing-away cover, and if there are any blemishes or stains from volatiles, clean them away with an appropriate solvent, followed by an isopropyl alcohol rinse, followed by a water rinse, and air dry.

If you have a heat flux DSC, the cover over the sample area should be cleaned in the same manner as the swing-away cover described above. Never use abrasives on the sample area components or furnaces. If there is a persistent stain that heat or solvent cannot remove, then call the instrument manufacturer and follow its recommendations.

Now reassemble the clean DSC and run the indium sample again. Sometimes cleaning the DSC is all that is required to return the instrument to working order. Check the indium onset temperature of melting against the expected values and determine if the DSC still needs recalibration.

If the DSC is still out of calibration, you must recalibrate it.

Getting Ready to Calibrate the DSC

There are certain things that remain to be checked on the instrument.

1. Check the sample purge gas. If you are using bottled gas, now is the time to check whether the tank should be replaced. It is best not to let tanks run to empty. If 100–300 psi is left in the tank, replace it.
2. Check the coolant that you are using and replenish it, if required.

Calibrating the DSC

When calibrating a DSC or any other thermal analysis analyzer, the previous calibration values that are applied in the software should be erased. This is easily done via the software by restoring defaults. Defaulted values are calibration settings that the factory sets as a common value for all DSCs produced. If you don't restore defaults, you will be calibrating incorrectly by installing your calibration factors on top of previous calibration factors. To understand exactly how your calibration software operates, refer to the instrument documentation provided by the manufacturer.

Today's calorimeters have a furnace calibration routine that is separate from the temperature and enthalpy calibration routines. Follow the manu-

facturer's recommended sequence of which order to perform these routines. The first thing to identify is the temperature range of interest that you will be working in. Let's use the example of -10 to 200°C for your temperature range of interest. Based on this information the furnace calibration should bracket this range. That is, set up the furnace calibration with limits equal to these or slightly beyond these limits.

A general overview of temperature calibration and enthalpy calibration (heat of fusion) is best if DSC operational basics are understood before calibration is begun.

1. Use the same sample pans that you will use when running your samples.
2. Set the sample purge gas so the flow rate, in milliliters per minute, is exactly the same as when you run your samples.
3. Use the same instrument coolant as you will when you run your samples.
4. Use the same scanning rate as you will use when you run your samples.

The instrument should be thermally equilibrated and stable before calibration. This is accomplished by turning on the purge gas, coolant, and instrument 45 min before calibration. The analyzer should be equilibrated at load temperature, which is usually set to 25°C .

The next thing to do is to select two calibration reference materials that melt within the experimental temperature range. It is best to use the purest materials available. Materials that may be commonly used for this temperature range (-10 to 200°C) are distilled water and indium. (Note that there are many other subambient calibration materials. Water was chosen to explain how to run a liquid sample.) The melting of these materials is well documented and reliable. At room temperature, water is a liquid and indium is a solid. Each sample will have to be prepared slightly differently.

We will make the assumption that the sample pans selected are proven to be best for the samples that will be run. In this case we will use standard aluminum pans. For the liquid sample we will not crimp the sample pan and for the indium sample we will crimp the sample pan.

We will use the indium and water to calibrate temperature, and indium to calibrate energy.

To run the water sample, place an empty uncrimped sample pan on the reference side of the calorimeter. This is always the right side of the analyzer. Using a pipette or an eyedropper, fill another sample pan halfway with distilled water and place it on the sample side of the analyzer. Weighing the water sample is not necessary because we are only using the melting onset temperature, which is unaffected by sample weight. Install the furnace

covers and cool the analyzer to -25°C ; let it equilibrate for 5 min. The distilled water is now a solid that can be used as a melting standard.

Set up the method as you would for the samples that you will run, using the same scanning rate (usually 10 or $20^{\circ}\text{C}/\text{min}$) and experiment with temperature limits of -25 and 25°C . This temperature span should be large enough to encompass the melting peak of the distilled water. Begin the run and observe the melting.

After the run is over, calculate the melting temperature of water. This is easily done by calculating the peak temperature and including the onset temperature. In Fig. 4, an indium melt, observe that the limits of the calculation are set on the flat portion of the baseline before and after the melting peak. Use the onset temperature as the melting point of water.

Now return the analyzer to the load temperature (25°C) and remove the sample and reference pans. Preparing indium for a calibration run takes a little more time than preparing the distilled water because you will crimp the sample and weigh it accurately before using it.

Using the same type of standard aluminum pans, crimp one empty pan and lid together and place them in the reference side of the calorimeter. This point is a good time to check the calibration of the weighing balance and calibrate it if required. For the sample side of the calorimeter, we will tare the weight of the sample pan and lid in the balance before encapsulating the indium in the pan.

Indium is supplied as a $\frac{1}{8}$ -in. diameter wire. It is soft enough to use a razor blade to slice off a thin slice of the indium. The ideal indium sample will weigh between 6 and 10 mg and lay flat on the bottom of the pan. Take the sliced piece of indium and smear it against a clean work surface with a handle of a forceps or tweezers until it is a thin foil. Then cut a small rectangle of indium from that foil and weigh it. Keep trimming it until it is the desired weight. Place the indium in the sample pan, flat along the pan bottom, and encapsulate it per the manufacturer's instructions. Record the weight and enter it into the method being used. Install the crimped sample in the calorimeter on the left side (sample side). Indium melts at 156.61°C , so set up the method to begin and end approximately 25° below and above this temperature. Once the analyzer contains the sample and reference crimped pans and it is equilibrated at the initial starting temperature of the experiment, begin the run.

Again, calculate the peak area of the indium melt and include the onset temperature in the calculation (Fig. 4). Observe that the limits of the calculation are set on the flat portion of the baseline before and after the melting peak. Use the onset temperature as the melting point of indium and use the normalized peak area (ΔH) as the enthalpy value for indium. Indium is the purest material available for calibration of a DSC and should always be

used for the energy or heat flow calibration. Even if indium is not in the temperature range of interest for your analysis, it should still be used for the energy calibration.

Now enter the calculated and expected values for distilled water and indium into the calibration software per the manufacturer's instructions and apply them to the DSC. The analyzer is now properly calibrated and ready to run sample specimens.

Sample Size

For the very best results, the sample weight should be the same from run to run. The sample shape and preparation should be the same. The sample should cover the entire bottom of the sample pan and ideally should weigh more than 3 mg. Of course, the sample weight is dependent on the density of the material and there might be times where you will struggle to reach 2 mg of sample; 3 mg is only a guideline.

Sample Preparation

DSC sample specimens can have different physical forms: thin films, thick films, composite sheets, powders, chunks, pellets, liquids, or highly aerated foams. Sample preparation is important because a poor choice of sample preparation tools can actually change the crystalline structure of the sample. An example of this is the use of a saw, which creates friction during cutting that translates mechanical energy into heat energy, which may change the structure of the polymer.

Thin films are easily prepared for encapsulation. Typically, a cork borer or a clean paper punch is used to punch several sample specimen disks from the larger thin film sheet. These disks should be sized to fit snugly in the sample pan and cover the bottom of the pan. They should be stacked until the sample specimen mass is more than 3 mg. Other tools that can be used for thin film preparation are scissors or razor blades. If irregularly shaped thin film sample specimens are prepared, then cover the bottom of the sample pan and stack them evenly in a similar fashion as the disks.

Thick films are prepared in the same manner as thin films; razor blades are frequently the first choice as a cutting tool. Razor blades are much better than other mechanical cutting devices, because they do not introduce heat energy into the sample during preparation.

Composite sheet material sample specimens are prepared for the DSC by means of shears, saws, and nibblers. These tools all generate heat that may be detrimental to the sample specimen. Many times, however, there is no other choice. A wise choice is to use cutter coolant during preparation.

Choose a coolant, such as a water-based coolant, that will not react with the sample.

Powders are the simplest to prepare for DSC analysis. Each powder particle is usually the same size in diameter or mesh. Carefully scoop the powder into the sample pan using a spatula. Cover the bottom of the pan and fill the sample pan halfway or enough to reach 3 mg.

Chunks and pellets are samples that are larger than a powder and irregular in size. The best way to prepare irregular chunks is to use a razor blade and slice the chunks into smaller chunks. Smaller chunks are better than larger chunks, as are small slices of a pellet as opposed to a large section of pellet. Uniform heating of the sample is the main concern. A large solid sample can be compared to an iceberg, in that an iceberg melts on the outside and is cold on the inside. The ideal situation is to have small sample specimen pieces, which afford more surface area to the controlled atmosphere, so each piece will heat in a uniform manner. If large chunks cannot be avoided, then use a slower scanning rate so uniform heating of the sample takes place.

Liquids are easily run in the DSC because there are special sample pans designed for liquids. Use a pipette, eyedropper, or a thin glass rod as a dipstick to load the sample into the proper sample pan. Be aware that sometimes liquids will wick up the sides of the sample pan; if this happens, use a smaller sample or choose an alternative sample pan.

Highly aerated foams may be difficult to prepare for the DSC because of their low density. What results is a very large sample that is low in weight. To overcome this, you may have to use the largest-volume pan available and use a piece of platinum mesh as a cover. Use a tweezers to pinch the mesh in place. Avoid crushing or compressing the foam to make it fit into a standard pan or small pan, because the material's characteristics will change as a result of the mechanical energy transferred to the sample during compressing. It is not unusual to have to run a sample as light as 1 mg. A high-quality DSC can analyze foams, but not all DSCs have enough sensitivity. Usually a power-compensation DSC is required.

Sample Pan Selection

A sample specimen is encapsulated in a sample pan to protect the calorimeter from the sample during heating, and the pans provide a convenient way to handle the samples. Most sample pans are crimped or sealed after installing the sample specimen. Crimping and sealing usually enhance the heat transfer properties between the calorimeter heating element and the sample specimen. A crimper is the best choice to seal a pan, rather than tweezers or other devices, because a crimper ensures the same crimp each

time. Crimpers eliminate differences between analysts' style and provide a reproducible seal each time. Numerous sample pans and crimping assemblies are available. Sample pan selection is based on sample type and temperature range of interest. The following general categories of the pans and crimpers are discussed in more detail in this section:

Standard sample pans and crimpers

Specialty pans

DPA 7 pans

Volatile sample pans and crimpers

Vapor pressure pans and crimpers

Large-volume stainless steel pans and crimpers

Reusable high-pressure capsules and sealers

Autosampler system pans and universal crimpers

Standard sample pans are made of aluminum, gold, or copper. Aluminum standard sample pans are most commonly used for polymer analysis. They are the least expensive pans and provide for easy crimping, and they have excellent heat transfer properties. A simple, push-type, manual, mechanical crimper is used to seal them. The standard aluminum pans are used in the temperature range of -170 to 600°C . These pans are mechanically sealed, but not hermetically sealed. Use the gold or copper pans when aluminum is not appropriate for the sample specimen due to a chemical reaction, physical change, or temperature range of interest.

Specialty sample pans and covers are used when standard pans are not suitable. Specialty pans are usually used to study inorganic materials such as metals, ceramics, and soils. They are available in alumina (Al_2O_3), platinum, and graphite. No crimper press is required with specialty pans.

DPA 7 aluminum pans and covers are intended to be used with a photocalorimetric accessory. The covers are actually quartz windows that allow ultraviolet (UV) energy from the accessory light source to transfer to the sample specimen. Photocalorimetry is used to study UV-curing reactions. A crimper is not required with these pans.

Volatile sample pans are used for volatile solid or liquid samples that exert significant vapor pressure in the temperature range of interest.

Aqueous solutions can be scanned up to and through sublimation to observe solute behavior. The heats of fusion of materials which require an enclosed atmosphere (e.g., water vapor evolved in dehydration below 100°C).

The capacity of these pans is $20\ \mu\text{l}$, with an internal pressure limit of 2 atm. A simple, rotational-type, manual mechanical crimper is used to seal them. The operating temperature range is from -170 to 600°C .

Vapor pressure sample pans are similar to volatile sample pans, but they have a hole 50 μm microns in diameter in the center of the cover. These pans and covers are used for more reproducible measurements of boiling points, heats of vaporization, and sublimation temperatures. They use the same crimper as the volatile sample pans. The operating temperature range is from -170 to 600°C .

Large-volume O-ring-sealed stainless steel sample pans and covers are used with samples that vaporize or contain a volatile reaction product in the temperature range of interest. These are used when a large volume or high internal pressure limit is required. These pans have a capacity of 60 μl and an internal pressure limit of 24 atm. They utilize a rubber O-ring to seal and maintain pressure. They are sealed by a manual lever-type press. Curing reactions (phenolic or epoxy resins) and the study of dilute aqueous solutions between -40 and 300°C are some of the applications for these pans. They can also be used with large samples to detect subtle glass transition temperatures.

Reusable high-pressure capsules are used to suppress the endothermic signal resulting from volatilization of sample material or from the volatilization or decomposition of reaction by-products. They are used in any situation where the advantage of a self-generating atmosphere is to be employed. They have a capacity of 30 μl and an internal pressure limit of 150 atm. They are available in titanium or stainless steel and utilize gold-plated seals. These pans screw together with a sealer that has a slip clutch to ensure the same torque each time. The temperature range for these pans is -170 to 750°C .

Autosampler system sample pans are designed to be used with an auto-sampling system. There are several types, made of aluminum or gold. The capacity range is 10, 25, 30, 40, or 50 μl . There are pans that have a pressure limit of 2 atm, and there are also vented pans. They are sealed with a manual lever-type universal crimper that uses an interchangeable die to crimp the pan. The universal press with the appropriate die can crimp all sample pans.

Purge Gas

A purge gas is used in the calorimeter to control the sample environment. The sample environment is controlled so that each experiment is reproducible from day to day. The typical purge gas used with DSC is dry and with a purity of 99.9% pure. The purge rate should be from 20 to 50 ml/min. For general thermal analysis choose a rate between 20 and 30 ml/min and always run the DSC at that purge rate. For best results, install a gas dryer in line with the gas supply. If a gas cylinder is used, it is best not to run it dry but to replace it when 100–300 psi remains, to ensure that no contaminants will

enter the calorimeter. Nitrogen is the most commonly used purge gas with polymers in the -120 to 750°C region. Helium has a much higher thermal conductivity than nitrogen and should be used when conducting experiments beginning at -170 to 200°C . Above 200°C , helium molecules become too excited and do not enhance the analysis. Compressed air or oxygen are also used when performing oxidative stability testing such as OIT or shelf-life testing.

There are some situations in which a combination of gas sequences is required. Then a combination of gases can be programmed into the experimental method and gas switching can be done on a time basis or a temperature basis. Up to four different gases can be switched on and off.

Coolants

Always use a coolant when performing DSC analysis. It does not matter if you are above ambient temperature or not. Use the appropriate coolant to accommodate sample equilibrium in the temperature range of interest. There are commercial chillers that attach to the calorimeter that enable the DSC to operate from -120 to 750°C . Liquid nitrogen is used to achieve lower temperatures.

Selecting the Pan and Sample Size for the Experiment

Never load a sample into a sample pan and run it in a DSC without first performing a preliminary muffle furnace or hot-plate test. This simple test will determine what is the maximum sample size and best pan for the analysis without damaging the calorimeter. The desired results of this test is to choose a sample pan the sample size that will not spill out of the pan and contaminate or damage the DSC. This is accomplished by selecting the pan you think will be best for the analysis. That is usually the cheapest-priced pan. We will assume that the standard aluminum pan will be used. Then crimp 5-, 10-, and 20-mg samples in separate pans and wrap them in foil, mapping the size and position in the foil and place them in a muffle furnace. Heat the furnace up to the maximum temperature of the experiment and hold it there for a few minutes until the temperature is stable. Cool the furnace and then carefully remove the pans from the furnace and unwrap them.

Observe whether any sample bubbled out of the pans. If some did, use a smaller sample size. If all pans exhibit material flowing out of them, choose a different sample pan style and test three more samples with the new style pans.

Running a Sample Specimen: The Effects of Scanning Rates and Sample Size

There are two variables to consider after you have successfully selected the best sample pan: the maximum sample size and the best scanning rate for your analyses.

A *slow scanning rate* will yield a thermal curve that has good resolution with the baseline and a smaller peak that is sharp. Slower scanning rates are used to separate or resolve components that are close to each other in temperature. Slow scanning rates are 5°C/min or slower.

A *fast scanning rate* yields a thermal curve that has a large broad peak with poor baseline resolution. Faster scanning rates are used for subtle events that need to be magnified to see. Glass transition temperatures are usually scanned at faster rates, such as 20°C/min or faster.

A *small sample size* has an effect on the thermal curve comparable to that of a slower scanning rate. A small sample size will yield a thermal curve that has good resolution with the baseline and a smaller peak that is sharp. Small samples are used to separate or resolve components that are close to one another in temperature.

A *large sample size* has an effect on the thermal curve comparable to that of a faster scanning rate. A large sample yields a thermal curve that has a large broad peak with poor baseline resolution. Larger sample sizes are used for subtle events that need magnification, such as glass transition temperatures.

As an example, to separate two peaks, use a smaller sample at a slower scanning rate. Adversely, there might be a shoulder on a peak which cannot be resolved into two separate peaks.

Running a Sample Specimen: The Effects of Heat History

Thermal history, also known as heat history, describes the memory effect in polymers. In simple terms, polymers are affected by hot or cold temperatures and remember the last effect. This is considered a variable that should be controlled in the laboratory. Thermal history has a strong influence on the material's glass transition, melting, and crystallization temperatures. Temperature changes, both hot and cold temperatures, induce thermal stresses in the material. The extent and implication of thermal stresses to a polymer are usually unknown and uncontrolled. This variable may be of interest for those who want to know more about the sample as it was received in the laboratory or how it reacts to an uncontrolled end-use environment. Usually this is of interest, but because it is uncontrolled it is very difficult to rely on for material comparisons.

Comparison of polymers is best when a controlled thermal history is applied to each sample. To apply a controlled heat history to a polymer, the as-received heat history must be erased. This is simple done by heating the material above the melting temperature and holding the material isothermally at that temperature for several minutes. Usually the material is heated just above the melting peak, by about 10°C or so, and held for 5–10 min. Beware that no decomposition or volatilization occurs during this erasure. Now a known heat history can be applied to the sample by cooling it rapidly or slowly. When comparing samples, each sample should be subjected to the identical heat history. A simple way to accomplish this is to set up the analysis as a multiple-step *heat-iso-cool-iso-heat* experiment.

Important: Always compare first heats with first heats, and second heats with second heats. Never compare first heats with second heats, because the conditioning of each sample (heat histories) is different.

The *first heat and isothermal temperature* is used to examine the “as-received” condition of the sample and to erase the previous unknown heat history. This is done by heating the sample past its melting point and holding it at that temperature isothermally for several minutes to ensure temperature equilibration.

The *controlled cooling* step is the most important step for this analysis. Controlled cooling can be deliberately slow or fast. Controlled cooling is used to give the material a known heat history. Fast controlled cooling at 200°C/min from just above the melting peak to below the glass transition temperature or room temperature is called *quenching*. Quenching is used to trap amorphous regions of a semicrystalline material and to minimize the crystalline ordering that takes place upon cooling. Quenching is usually necessary to investigate glass transition temperatures. Slow controlled cooling at 10 or 20°C/min from just above the melting peak to the initial experimental temperature is called *annealing*. This is used to investigate crystalline melting (Fig. 17).

The *second heating* step should start after thermal equilibrium of the sample/DSC has been achieved. Equilibrium is identified when the ordinate signal (heat flow or temperature) is stable. The second heat is used to compare sample specimens that have been conditioned in the same manner. This heating is used because all samples being compared now have the same controlled heat history. In this step, the sample is heated from below the glass transition temperature through the melting temperature.

Running a Sample: Subtract a Baseline

A baseline run is a temperature scan across the temperature range of interest. It is done under the same experimental conditions as the sample speci-

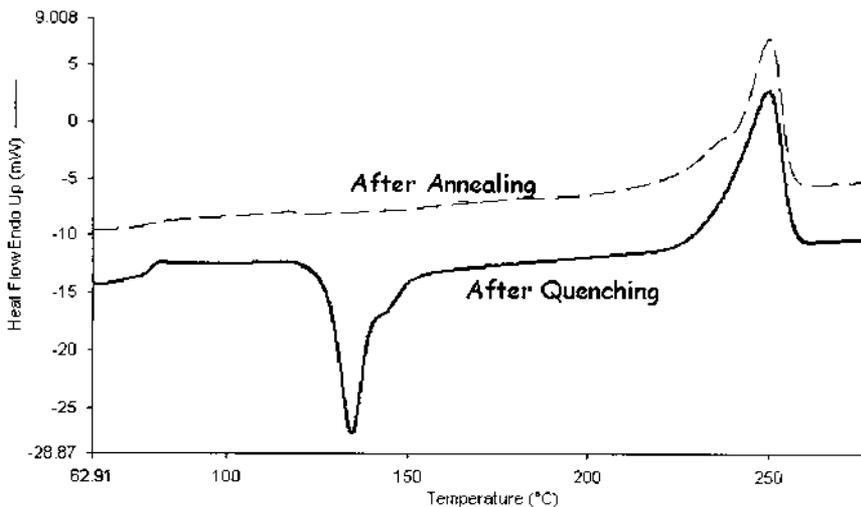


Figure 17 The thermal curves displayed are of the same PET sample subjected to different heat histories. These are different segments of the same experiment. Before quenching (cooling at $300^{\circ}\text{C}/\text{min}$) or annealing (cooling at $10^{\circ}\text{C}/\text{min}$), the sample was heated above the melting peak to remove the previous heat history and stresses.

men run, but with no sample and reference pans in the furnace or an empty sample pan on each side. This is your choice; both baseline methods are acceptable. Whichever you choose, stick with it. Remember that you always want your experiments to be run exactly the same way each time. It is best to begin and end every run with an isothermal segment of 1–2 min. This ensures that temperature equilibrium is achieved. Run a baseline before sample specimens are run and save the baseline as a separate file. Then input that file into the sample specimen method so that it is automatically subtracted from your sample specimen run, in real time. This will remove any instrumental effects of noise or baseline curvature. This is strongly recommended for all analyses.

Characterizing a Sample: What Type of Experiment Should I Run?

It is best to know as much about the material as possible before starting an experiment:

Of the polymer materials in engineering use, the plastics form the largest group by production volume. It is common to subdivide

plastics into thermoplastics and thermosets (or thermosetting resins). Thermoplastics comprise the four most important commodity materials—polyethylene, polypropylene, polystyrene and poly(vinyl chloride)—together with a number of more specialized engineering polymers. The term “thermoplastic” indicates that these materials melt on heating and may be processed by a variety of molding and extrusion techniques. Important thermosets alkyds, amino, and phenolic resins, epoxies, and unsaturated polyesters, and polyurethanes, substances that cannot be melted and re-melted but which set irreversibly. The distinction is important in that production, processing and fabrication techniques for thermoplastics and thermosets differ (Hall, 1989, pp. 1–2).

For *partially crystalline thermoplastics*, analyze the glass transition region, the melting region, recrystallization upon cooling, and isothermal crystallization.

For *amorphous thermoplastics*, analyze the glass transition regions.

For *thermosets*, analyze the glass transition regions and curing studies.

For *elastomers*, analyze the glass transition regions.

Common ASTM Tests and Test Methods for DSC

- D2471 Test Method for Gel Time and Peak Exothermic Temperature of Reacting Thermosetting Resins
- D5028 Test Method for Curing Properties of Pultrusion Resins by Thermal Analysis
- D4816 Test Method for Determining the Specific Heat Capacity of Materials by DSC
- D4565 Test Method for Determining the Physical/Environmental Performance Properties of Insulation and Jackets for Telecommunications Wire and Cable
- D4591 Test Method for Determining Temperatures and Heats of Transitions of Fluoropolymers by DSC
- D3012 Test Method for Thermal Oxidative Stability of Polypropylene Plastics Using a Biaxial Rotator
- D4803 Test Method for Predicting Heat Buildup in PVC Building Products
- D2117 Test Method for Melting of Semicrystalline Polymers by the Hot Stage Microscopy Method
- D3417 Test Method for Heats of Fusion and Crystallization of Polymers by Thermal Analysis
- D3418 Test Method for Transition Temperature of Polymers by Thermal Analysis

- D3895 Test Method for Oxidative Induction Time (OIT) of Polyolefins by Differential Scanning Calorimetry
- D4419 Test Method for Determining the Transition Temperatures of Petroleum Waxes by DSC
- E698 Standard Test Method for Arrhenius Kinetic Constants (of thermally unstable materials) Using DSC
- E1559 Standard Test Method for Contamination Outgassing Characteristics of Space Craft Materials by DSC
- E537 Standard Test Method for Determining the Thermal Stability of Chemicals by DSC
- E793 Standard Test Method for Determining the Heat of Crystallization (of solid samples in granular form) by DSC
- E1269 Standard Test Method for Specific Heat Capacity by DSC
- E1356 Standard Test Method for Glass Transition Temperature by DSC

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PETAN-58, Polyethylene: The Effect of Thermal Conditioning on Percent Crystallinity.
PETAN-78, Low Temperature Phase Transitions of Siloxane using Pyris 1 DSC.
PETAN-79, Low Temperature Phase Transitions of ABS using Pyris 1 DSC.
PETAN-82, Heat Capacity of Sapphire using the “Two Curve” Method.
PETAN-83, Measurement of the Temperature Dependent Crystallinity of Polyethylene.