Benefits and Applications of the Power Compensated Pyris 1 DSC

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Introduction

The PerkinElmer Instruments Pyris 1 DSC represents the culmination of DSC design and encompasses nearly 40 years of technological advances in the field of differential scanning calorimetry. The instrument combines the features and benefits of the unique power compensated design coupled with the new advanced technology derived from the aerospace industry. The high performance Pyris 1 DSC is a technological advancement in the field of calorimetry and thermal instrumentation and follows the tradition of innovation and leadership that has characterized PerkinElmer Instrument’s continual developments in the field of thermal analysis.

DSC

Differential scanning calorimetry measures the heat flow into or from a sample as it is heated, cooled or held under isothermal conditions. Applications of DSC include the characterization of polymers, fibers, films, thermosets, elastomers, composites, pharmaceuticals, foods, cosmetics, as well as organics and inorganics. DSC provides valuable and important information on the following important properties of materials:

- Glass transition or Tg
- Melting points or Tm
- Crystallization times and temperatures
- Heats of melting and crystallization
- Percent crystallinities
- Oxidative stabilities
- Compositional analysis
- Heat capacities
- Heats of cure
- Completeness of cure
- Percent cure
- Purities
- Thermal stabilities
- Polymorphism
- Heat set temperatures
- Recyclates or regrinds

Many applications of DSC can be demanding as the needs of the market require high levels of sensitivity and resolution. To meet this needs, PerkinElmer Instruments has the state-of-the-art Pyris 1 DSC with unique power compensated design.

Power Compensation Principle

The Pyris 1 DSC is the only differential scanning calorimeter on the market that offers true power compensated measurements. With the power compensated principle, the sample and reference materials are each held in a separate, self-contained calorimeter, with its own heater element. When an exothermic (heat...
Heat Flux DSC and power compensated DSC designs.

Figure 1. Heat flux DSC and power compensated DSC designs.

Heat Flux DSC Cell Design.

Power Compensated DSC System Design.

Figure 2. Results on two transitions of azoxyanisole demonstrating high resolution of power compensated DSC.

Insert shows enlarged view of high resolution between main melting transition and liquid crystalline transition at 135°C.

Yielded) or endothermic (heat absorbed) change occurs in the sample, power or energy is applied to or removed from one or both of the calorimeters to compensate for the energy change occurring in the sample. The power compensated DSC system is maintained in a "thermal null" state at all times. The amount of power required to maintain the system in equilibrium conditions is directly proportional to the energy changes occurring in the sample. The Pyris 1 DSC therefore provides a true measure of the calorimetric properties of the sample since the fundamental measurement with the power compensated DSC is energy flow.

In contrast, the more common heat flux DSC instruments have the sample and reference in a single furnace. Thermocouples measure the temperature differential (not energy differential) between the sample and reference platforms. With the heat flux DSC devices, the fundamental measurement is temperature differential rather than the more thermodynamically pure energy flow. With the heat flux DSC units, the temperature differential is converted to energy flow via a mathematical equation and is a more indirect approach as compared to the pure energy flow measurements obtained via the Pyris 1 power compensated DSC.

Low Mass Furnace with Power Compensated DSC

One major advantage of the power compensated design over the heat flux DSC cell is that the masses of the individual furnaces of the power compensated system are much lower than that of the heat flux. The mass of the power compensated furnace is only 1 g as compared to 100 to 200 g for most heat flux devices. The thermodynamics and physics of the low mass furnace translates into an extremely fast response times (due to less thermal inertia,) and the ability to achieve much faster heating and cooling rates (500 C/min) as compared to the more sluggish and massive heat flux DSC furnace. The fast heating and cooling rates are a benefit when attempting to generate...
an amorphous or glassy polymer or material when cooling from the melt.

The faster response time of the power compensated DSC also provides a much higher degree of resolution as compared to heat flux DSC devices. Resolution is a measure of the DSC to separate out closely occurring transitions. This is important for applications such as polymorphism of pharmaceuticals and food oils/fats, detection of heat set temperatures of polymers and fibers, characterization of liquid crystalline materials and the study of the melting properties of blends.

The DSC results displayed in Figure 2 demonstrate the high level of resolution obtained from the Pyris 1 power compensated DSC. The plot shows the melting characteristics of azoxyanisole, which has two closely spaced transitions, about 10 °C apart. The high resolution of the Pyris 1 DSC provides excellent separation of the two transitions provided by the outstanding resolution characteristics of the power compensated design.

**Platinum Resistance-Thermometer (PRT)**

Another outstanding design feature of the Pyris 1 DSC is the use of the platinum resistance thermometer (PRT) for the measurement of temperatures. Most heat flux DSC devices used lower cost and lesser performing thermocouples for the measurement of sample temperature. PerkinElmer chose to use the more expensive PRT for the temperature measuring system because of its outstanding performance in terms of linearity and reproducibility. Thermocouple systems tend to have a non-linear response, which must be accounted for via software corrections to prevent transitions from appearing in the DSC curves. The chromel thermocouple, for example, yields a significant non-linearity near 160 °C due to a solid-state transformation.

One of the essential points in the consideration of a DSC instrument is the temperature sensing device used to measure temperature, as the DSC can really be no better than the inherent properties of the temperature sensor. The Pyris 1 DSC utilizes the highest performing temperature sensor device, the platinum resistance thermometer, in contrast to other DSC devices which use lower cost, and lesser performing thermocouples.

**Applications: Proof of Performance**

The very broad capability of the Pyris 1 DSC for characterizing materials is illustrated by these representative application examples. These examples demonstrate many of the benefits inherent in the high performance Pyris 1 power compensated DSC system.
One of the most demanding, but useful, DSC tests for polymers or oils is the isothermal crystallization test. This test is performed by melting a semi-crystalline thermoplastic (such as PET, nylon, HDPE, polypropylene, PEEK, PBT) and then cooling as quickly as possible to a temperature somewhere below the melt, but well above the polymer’s Tg. The polymer will then recrystallize under isothermal conditions and the resulting exothermic transition provides useful information on the characteristics of the given polymer. Information can be obtained on molecular weight distribution, presence of recyclates or regrinds, nucleating agents and the presence of copolymers. The information obtained from the isothermal crystallization test is a valuable screening tool or quality assurance test for polymer feedstocks to ensure uniform consistency of the feedstock.

To properly perform the isothermal crystallization test requires a DSC instrument that can cool very quickly (500 C/min) to allow the observation of the complete crystallization transition. The low mass furnace design of the power compensated DSC allows for the necessary rapid cooling to perform outstanding isothermal crystallization measurements. One of the most demanding materials for isothermal crystallization studies is high density polyethylene (HDPE). Because of its extremely fast crystallization times, most DSC instruments cannot adequately measure the crystallization exotherm after the polymer has been melted and cooled. However, the fast response time of the Pyris 1 DSC permits the crystallization of HDPE to be studied as is shown in Figure 3.

Isothermal measurements are also important for photocure materials such as dental resins and electronic photoresists. Many photocured resins react and crosslink very rapidly when exposed to UV radiation. The very fast response time featured with the Pyris 1 DSC ensures that the photocure exothermic transition will be successfully observed.

**Determination of Polymorphism of Pharmaceuticals and Foods**

The high resolution of the Pyris 1 DSC is very important for the assessment of polymorphism of pharmaceuticals and foods. Polymorphism refers to the development of unstable crystalline states for a given material. For pharmaceuticals, the characterization and understanding of any polymorphic forms is important as different polymorphic forms can exhibit different solubilities and affect the uptake of the active drug when ingested. One crystalline form may exhibit slow release while another polymorphic form may yield fast release of the drug.
For food products, such as cocoa butter and chocolate, polymorphism is important as it relates to the textural properties of the chocolate when eaten. Fats can yield different polymorphic forms, depending upon the processing or tempering of the cocoa butter or chocolate and this will affect the edible properties of the material. A high resolution DSC instrument is required to examine the effects of polymorphism on fats and chocolate as the melting of the polymorphs occurs over a very narrow temperature range (typically between 0 and 30°C). Shown in Figure 4 are the results obtained on two different chocolate batches exposed to identical processing conditions. The differences in the polymorphic forms shows that the polymorph associated with chocolate sample 4 has a greater level of crystallinity. The Pyris 1 DSC has the necessary high degree of resolution to detect the differences between the two chocolate samples.

**Determination of Heat Set Temperatures**

DSC can be used to determine heat set temperatures associated with polymers, especially fibers. Heat setting involves running the fiber bundle over a hot plate or through a steam tunnel in order to stabilize the dimensional and mechanical properties of the fibers. The heat set processing results in the generation of a small amount of an imperfect crystalline phase with a melting point which is significantly lower than the polymer’s main melting peak. Heat setting can have a major effect on the end use properties of fibers including dye uptake and shrinkage. Streaking of carpet yarns is oftentimes due to improper heat setting. DSC provides valuable information on the heat setting step as the melting of the imperfect crystals formed during processing can be observed by a high performance DSC instrument.

Superba heat set treated nylon 6 fibers can be especially difficult to characterize by DSC as the heat set peak is small and is near the main melting transition. A DSC with a high degree of resolution is required for the successful characterization of Superba heat treated nylon 6 yarns. Shown in Figure 5 are the results generated from the Pyris 1 DSC on a sample of nylon 6 yarn processed using the Superba treatment.

The results displayed in Figure 5 have been enlarged in the region below the main melting peak at 222°C. The Tg of the crystalline fibers as well as the heat set peak at 196°C are clearly observed with the high performance Pyris 1 DSC.
Low Temperature Measurement of Tg

Some elastomers, such as silicone rubbers, have very low glass transition temperatures near \(-120^\circ C\). This requires a DSC instrument with high performance in the subambient regions. Many DSC devices require some time to thermally equilibrate, under dynamic heating conditions, once a run is initiated. Typically, the equilibration time is 2 or 3 times once the run is started. This means that starting a subambient DSC experiment at \(-150^\circ C\) and heating at a rate of 20 C/min would not allow the instrument to achieve a flat baseline response until a temperature of about \(-110^\circ C\) was reached. Even at a slower heating rate of 10 C/min, most heat flux DSC devices would not achieve a flat baseline response until the temperature reached \(-125^\circ C\). Given that the Tg of silicone rubbers is at \(-120^\circ C\), this does not provide a good response going into the transition.

In contrast, the design of the power compensated Pyris 1 DSC allows the instrument to achieve thermal equilibration in a much shorter time period. Even when heating at 20 C/min from \(-150^\circ C\), the Pyris 1 DSC yields a flat baseline response at \(-145^\circ C\). Displayed in Figure 6 are the DSC results obtained from the Pyris 1 DSC on a silicone rubber sample.

The Pyris 1 DSC provides outstanding results on the silicone rubber sample even when heating at the relatively fast rate of 20 C/min. The instrument yields a very flat baseline response going into the Tg at \(-122^\circ C\) making the transition easily identifiable and easily analyzed. The DSC results also reveal the crystallization of the silicone at \(-82^\circ C\) and the melting of the portion that underwent crystallization at \(-41^\circ C\). The Pyris 1 DSC yields outstanding results over the entire temperature range from \(-145\) to \(20^\circ C\).

**Better Heat Capacity Data**

The heat capacity, Cp, of a sample represents its ability to store heat. The heat capacity is important for research studies as it is more thermodynamically quantitative as compared to the usual heat flow that is generally presented with DSC results. The heat capacity – temperature relationship of materials is related to entropy, S, and this can be a valuable quantity when attempting to characterize and understand the properties of materials.

The heat capacity can also be important for process control reasons for it is directly related to the heat required to bring a large quantity of material up to some desired temperature. Additionally, it is important to know the heat capacities of a slurry or liquid when it is transferred through pipes at an industrial facility. Many plant upsets have been caused by not factoring in the effects of the heat.
The power compensated design of the Pyris 1 DSC performs true energy measurements on a sample and this is important for the accurate and reproducible assessment of heat capacities. One critical test of a DSC instrument to yield accurate heat capacity values is to examine the effects of changing the sample mass. Many DSC instruments will provide reasonable heat capacity values when the sample mass is constant. However, when the mass is changed, the heat flux DSC devices will yield inaccurate Cp values where the measured Cp is significantly lower than the true value at higher sample masses. The heat capacity is a mass independent quantity and the DSC should be able to provide accurate and reproducible Cp values over a wide range of sample masses. The power compensated Pyris 1DSC provides this ability as is demonstrated by the Cp results obtained on two samples of sapphire standards with masses of 29.7 and 129 mg. As the results in Figure 7 demonstrate, even though the mass difference between the two sapphire standards was 100 mg, the Pyris 1 DSC was still able to yield accurate, reproducible heat capacity values.

**Studies of Very Weak Transitions: Protein Denaturation**

One key aspect of a DSC instrument is its real-life sensitivity. Oftentimes, instrument companies provide outstanding ‘paper’ specifications on the performance of a DSC, especially with regards to sensitivity. The true measure of a DSC instrument in terms of sensitivity is its ability to be able to detect very weak transitions. The Pyris 1 DSC provides very high, real-life sensitivity.

This can be seen in the results obtained on a dilute (2.5%) protein in aqueous solution. Proteins undergo thermal denaturation when heated from ambient to 100 C, and this reflects the unfolding of the protein in solution. The denaturation event is low energy and can be difficult to detect with most DSC instruments. The analysis is further hindered by the fact that protein must be heated relatively slowly (2 C/min) due to the kinetics of the unfolding process. The use of slower DSC heating rates decreases the effective sensitivity of the measurement. The transition is there, but disappears into the background noise level of the DSC instrument. However, the high sensitivity provided by the Pyris 1 DSC permits the protein denaturation to be detected.

In order to enhance the analyses of materials in solution (such as proteins or starches), PerkinElmer offers high volume, stainless steel capsules that contain the water and provide outstanding results on solutions.

Displayed in Figure 8 are the DSC results generated for the denaturation
event of a protein in solution using the high performance Pyris 1 DSC.

**StepScan DSC for Better Sample Characterization**

The Pyris 1 DSC features StepScan DSC for improved and enhanced sample characterization. The technique uses a series of heat-hold steps which permits the separation of DSC results into reversible (‘fast’) or irreversible (‘slow’) signals. The StepScan approach removes irreversible or kinetic thermal events (e.g., enthalpic relaxation, stress relief, crystallization, deabsorption of moisture) from the reversible glass transition event and makes it much easier to observed and analyze Tg.

The advantage of StepScan DSC over temperature modulated DSC (TMDSC) is that StepScan uses pure heating and isothermal repetitive segments rather than a sine wave. The use of a sine wave does imply that short term cooling must be applied to the DSC sample during a measurement and this can potentially complicate the analyses. Additionally, the input of a pure time-temperature sine wave does not necessarily result in a pure heat flow sine wave response from the sample. The resulting output sine wave can be distorted (due to experimental factors such as thermal gradient effects, phase lag, problems due to cooling, etc.), and the distortions cannot be handled by the TMDSC data analysis software. This can potentially result in erroneous data.

In contrast, StepScan DSC does not employ a sine wave, but, rather, uses the more straightforward and pure heating and isothermal segments. There are no problems with distorted sine waves and with Fourier transform deconvolution with StepScan DSC.

StepScan DSC requires a DSC instrument with a fast response time to rapidly achieve pure isothermal conditions after the application of a short heating period (2°C step increment at a rate of 10 C/min). This is not possible with the heat flux DSC devices with their massive furnaces. However, it is possible and eminently practical with the power compensated Pyris 1 DSC. The fast response time of the Pyris 1 DSC permits StepScan DSC experiments to be conducted significantly faster than equivalent TMDSC experiments. In general, the time required for a StepScan DSC experiment is about 3 times less than an equivalent TMDSC experiment.

Uses of StepScan DSC include:
- The characterization of nylon polymers where the deabsorption of water can make the detection of the water plasticized Tg difficult
- The detection of the weak Tg’s associated with pharmaceutical freeze-dry formulations.
- The clear and unambiguous measurement of Tg where the glass transition is obscured with an enthalpic relaxation peak or other irreversible transition
- More precise heat capacity data with the use of small steps

Figure 9 shows the StepScan DSC results obtained from a sample of nylon 6 fibers that were completely saturated with absorbed water. The plot shows the StepScan DSC heat flow signal (blue curve), the Thermodynamic Cp signal (in red) and the IsoKinetic Baseline response (in green or the curve at the minima of the StepScan heat flow). The Thermodynamic Cp reflects the reversible transitions taking place and the water plasticized Tg, which is reversible on the time scale of the DSC experiment, occurs at ~19.6 C. The water deabsorption peak, which is irreversible on the time scale of the experiment, is observed between 0 and 50 C for the nylon 6 fibers. The separation of the DSC results into the Thermodynamic Cp and IsoK responses allows the plasticized Tg to be observed for the saturated nylon 6 fibers.

**Purity Analysis**

For the pharmaceutical industry, one important application of DSC is the assessment of purities of organics. The PerkinElmer Pyris software does feature Purity Analysis software which performs an automated determination of the purity of organics and pharmaceutical materials, based on the van’t Hoff approach. The Purity Analysis software also features special multiple linear regression analysis, which handles the purity calculations for pharmaceutical samples which undergo degradation during melting.

The power compensated DSC provides the best possible results for purity analysis since the assessment of purities is fundamentally based upon the shape of the melting curve. The fast response time and subsequent unparalleled resolution of the Pyris 1 DSC yields the most accurate possible determination of the true melting response of organic and pharmaceutical materials. With the power compensated DSC, the shapes of the melting peaks are narrow and intense, as theory would dictate. Because of this, there is no danger of distortions of the overall shape of the peak and ‘smearing’ of the partial areas of melting. Displayed in Figure 10 are the Pyris 1 DSC melting and purity results obtained on a sample of phenacetin (purity of 99.96%). The x-axis scaling covers only 7 C, and it may be seen that the melting peak yielded by this high purity sample is narrow and intense with the Pyris 1 DSC.

**Characterization of Thermosets and Cure Kinetics**

The Pyris software features kinetics software for the determination of the cure kinetics associated with thermosetting resin materials, such as epoxies. The software handles both isothermal cure studies as well as dynamic heating assessments. The high sensitivity and high resolution of the Pyris 1 DSC yield outstanding results on thermosetting resins, even highly filled composite samples.
Displayed in Figure 11 are the DSC data generated on a glass filled epoxy resin material used for electronic applications. The DSC results show the following important characteristics of the cure of the epoxy material:

- Tg or softening temperature
- Onset of cure
- Maximum rate of cure (peak maximum)
- Completion of cure
- Heat of cure

Using the PerkinElmer Pyris Kinetics software, the cure kinetics associated with the epoxy resin material can be easily determined. The kinetics data is useful for process optimization and process control purposes, as it provides information on the resin’s degree of cure as a function of temperature and time. Figure 12 shows the predictive isothermal cure curves for the epoxy resin generated by the PerkinElmer Pyris Kinetics software. The curves show the percent cure of the epoxy resin as a function of cure time at temperatures of 160, 150, 140 and 130°C.