PRODUCT NOTE

Thermal Analysis

Advantages of the DSC 4000 for Sample Characterization

Introduction

For over 40 years, PerkinElmer has offered the highest-quality thermal analysis products, and is recognized as a worldwide leader and innovator of thermal analysis instrumentation. We are continuing this tradition with the high-performance, heat-flux DSC 4000. The instrument provides outstanding responsiveness for the successful characterization of a wide range of samples and applications.

PerkinElmer®
For the Better

DSC

Differential scanning calorimetry (DSC) 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
- Heat-set temperatures
- Recyclates or regrinds
- Oxidative stabilities
- Oxidation induction time (OIT)
- Compositional analysis
- Heat capacities
- Heats of cure
- Completeness of cure
- Percent cure
- Purities of drugs
- Thermal stabilities
- Polymorphism
- Protein denaturation

DSC 4000

Though disk-type heat-flux DSCs are commonly used in routine analysis, many cannot stand up to the demands and rigors of daily testing. For example, the thin-sheet metal disks frequently used in many DSCs are fragile and easily damaged or corroded by oxygen and/or the decomposition off-gases of samples.

The DSC 4000 was designed to be both tough and reliable, while still providing high performance. The instrument utilizes a precision-machined sensor disk of hardened nickel chromium to form a strong thermal pathway or link between the sample and the low-mass furnace. This provides a reduction in noise and an increase in sensitivity.

The DSC 4000's low-mass furnace (30 g) provides faster heat-up and cool-down times. Additionally, the low-mass furnace provides better thermal equilibration and thermal control between the program and actual sample temperature. In contrast to the relatively low-mass DSC 4000 furnace, other heat-flux DSC devices use furnaces with masses of 200 g.

The DSC 4000 features an optional, reliable 45-position autosampler for unattended, 24-hour operation. The autosampler features high-technology shape-memory alloy-metal grippers for more reliable sample pick-up and long-term operation.

Many DSC methods call for specific gas-flow rates while some call for the switching of purge gases during the course of the experiment (e.g., oxidative induction times). The DSC 4000 features a built-in purge-gas flow controller, which both monitors and controls the purge flow rates. When a method is recalled for use, the purge-gas flow rate is automatically adjusted to the particular flow rate called for by the application or test protocol. [DSC methods can be easily stored and recalled with the Pyris™ Manager software].

The built-in gas controller of the DSC 4000 allows for the automatic switching between any two gases (e.g., nitrogen to oxygen). The gas switching is particularly critical for the DSC OIT (oxidation induction time) test for polyolefins where it is critical to switch between nitrogen and oxygen at a specified point and to maintain a constant purge-gas flow rate. This is easily accomplished with the built-in gas controller featured with the DSC 4000.

DSC 4000 – Proof of Performance

The DSC 4000 offers the following desirable features:

- Unparalleled baseline stability
- High sensitivity
- High resolution
- Temperature control

The heat-flux design of the DSC 4000 coupled with its low-mass furnace provides for outstanding baseline stability or reproducibility. This is important to ensure that consistent results are obtained.

Displayed in Figure 1 (Page 3) are the results obtained from the DSC 4000 by running the empty DSC cell (baseline) for 10 separate experiments. The very good overlay of the data demonstrates the excellent reproducibility obtained using the DSC 4000 instrument.

In addition to baseline reproducibility, two other essential performance criteria for a DSC instrument are sensitivity and resolution. Sensitivity is the ability of the DSC instrument to pull a weak transition from the background noise, while resolution is the ability of the DSC to separate out two closely spaced transitions.

The very high sensitivity provided by the DSC 4000 may be seen in the results obtained on a very low-mass sample of indium. A 0.1 mg sample of indium was heated at a rate of 10 ˚C/min and these results are displayed in Figure 2 (Page 3).

The results shown in Figure 2 demonstrate that the DSC 4000 has very high sensitivity as the sample mass used here was about 100 times less than the typical DSC sample mass.

DSC resolution and sensitivity is often tested using 4, 4' azoxyanisole as proposed by the Netherlands Thermal Analysis Group (TAWN). Azoxyanisole is an organic material, which yields two closely occurring transitions at 122 and 135 ˚C. The first is the main melting transition while the latter is a much smaller, liquid-crystalline transition. The ability of the DSC to resolve the two events is a measure of the DSC's resolution. Analyzing the liquid-crystalline endotherm of a very small sample of the azoxyanisole at a very slow heating rate is a measure of the DSC's sensitivity.

The resolution of the DSC may be assessed according to the TAWN by heating a 4.5 mg sample of azoxyanisole at a rate of 20 ˚C/min under a nitrogen purge. The results obtained are shown in Figure 3, where we see the DSC 4000 provides excellent resolution as demonstrated by its ability to separate the two transitions. The sensitivity test was performed by heating a 0.25 mg sample of azoxyanisole at a very slow rate of 0.10 ˚C/min and analyzing the smaller, liquid-crystalline transition at 135 ˚C. All of these factors combined together are a demanding test of the real-life sensitivity of the DSC. The results of the sensitivity test are displayed in Figure 4.

The DSC 4000 yields outstanding sensitivity as the results on azoxyanisole demonstrate.

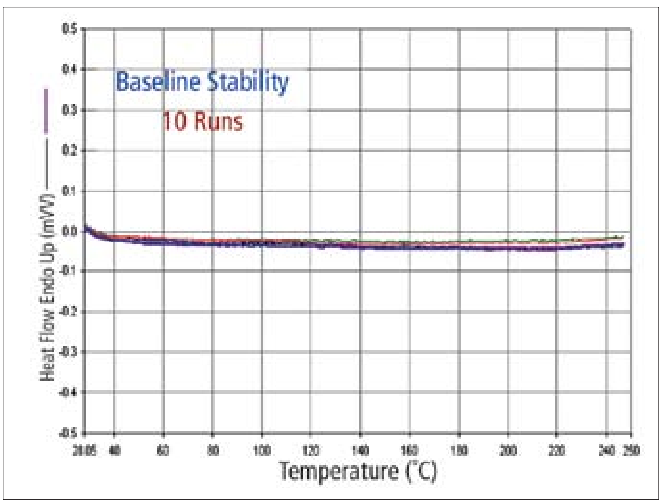

Figure 1. DSC 4000 results of ten baseline experiments.

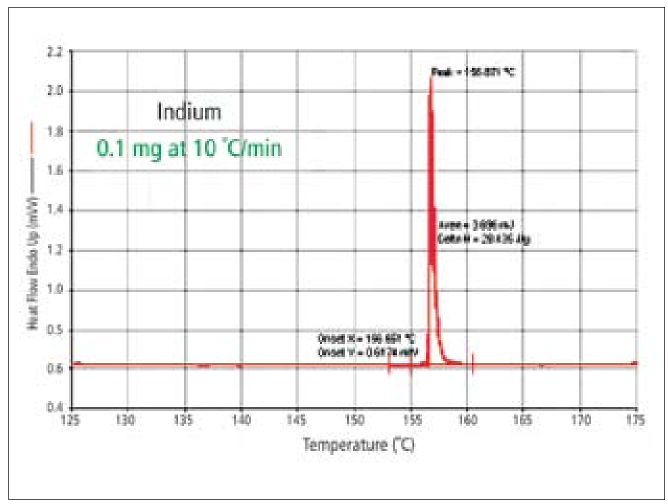

Figure 2. DSC 4000 results obtained on 0.1 mg sample of indium.

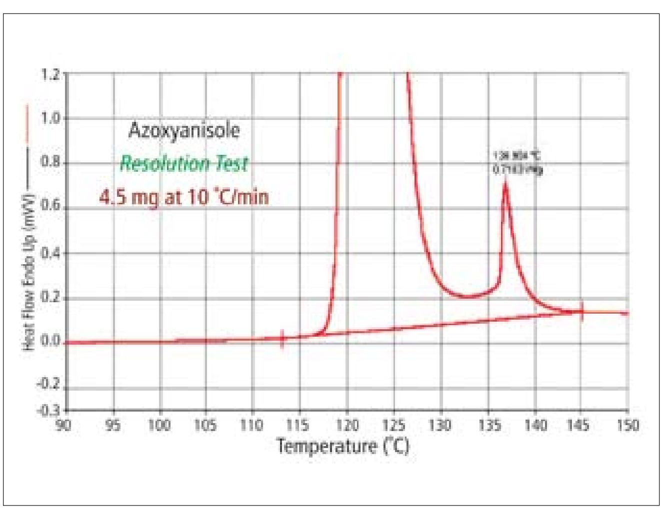

Figure 3. DSC 4000 results obtained on resolution test for azoxyanisole.

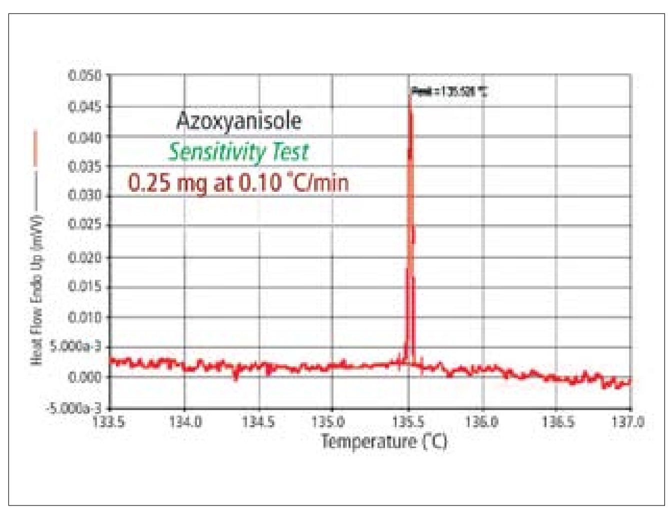

Figure 4. DSC 4000 results obtained on sensitivity test for azoxyanisole.

DSC for Polymer Crystallinities

One major application for DSC is the assessment of crystallinities of thermoplastic polymers. The crystalline content is related to essential properties including:

- Impact resistance
- Stiffness
- Optical clarity
- Barrier resistance
- Creep or cold flow
- Stability

The DSC 4000 yields excellent results on the crystallinities of polymers because of its outstanding baseline stability, sensitivity and reproducibility. The Pyris Player software allows for automated analysis of polymer crystallinities and permits automated 'pass/fail' analysis.

Displayed in Figure 5 are the DSC results obtained on a sample of high-density polyethylene. The sample was heated from room temperature through its melt at a rate of 10 ˚C/min. The test specimen yields a heat of melting of 191 J/g, which translates to a percent crystallinity of 66.9%. This information is valuable for process optimization and control as well as for QA/QC purposes.

In another example, a sample of HDPE was contaminated with some polypropylene during regrind for recycling purposes. The DSC results on the contaminated HDPE are shown in Figure 6.

The level of polypropylene contaminant contained in the sample of HDPE recyclate is estimated to be 7.5% based on the relative heats of melting of the polypropylene and the HDPE components in this sample. The DSC 4000 provides the high degree of resolution and sensitivity to be able to successfully detect, separate and analyze the two components.

DSC 4000 for Testing Recyclates

Providing the high degree of sensitivity required to detect subtle changes, the DSC 4000 can measure the transitions that occur in polymer recyclates and regrinds. Figure 7 (Page 5) shows the DSC results obtained on an ABS recyclate containing some polyvinyl chloride (PVC) contaminant. The presence of the PVC contaminant causes the occurrence of the extra glass transition (Tg) at 65 ˚C. The identification of the PVC contaminant is critical as the evolution of hydrogen chloride off-gases during processing could lead to major problems.

DSC 4000 for Uniform Product Consistency

The DSC 4000 provides excellent temperature control, and this is important when performing heat-cool-reheat DSC experiments. An example is the use of DSC for testing of PTFE hydraulic lines for aircraft. It is important that the PTFE used in hydraulic lines has the proper level of crystallinity. Over-sintering of the PTFE during production can lead to the generation of a line with too high a crystallinity and brittleness. If the PTFE is under-sintered, the PTFE in the hydraulic line may not exhibit good stability leading to premature failure. The DSC results on the PTFE provide excellent information on the level of crystallinity obtained by PTFE polymer during processing.

In this example, a sample of the PTFE was heated (as received), cooled and then reheated to determine the product uniformity and consistency. The DSC results are shown in Figure 8 (Page 5).

The first-heat results represent the material's properties due to its particular thermal history. If the heat of melting is too high, then the polymer is over-sintered and must be rejected. The occurrence of the two melting peaks is reflective of the annealing step.

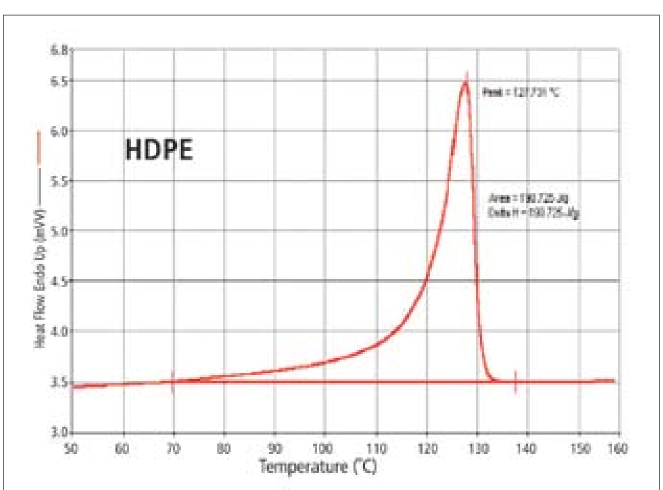

Figure 5. DSC 4000 results on the melting of HDPE for assessing percent crystallinity.

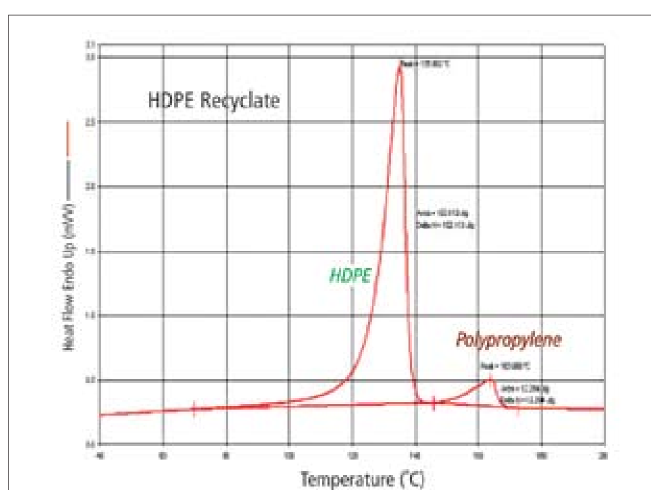

Figure 6. DSC 4000 results on the melting of a HDPE recyclate containing PP contaminant.

When the polymer is cooled back to room temperature and reheated, it now has a new, uniform thermal history, which can be used to assess the chemistry of the polymer. The DSC 4000 yields high-quality results on the PTFE heat-cool-reheat test.

DSC 4000 for Biotech Applications

The DSC 4000 delivers the high level of sensitivity and resolution required for the demanding applications in the pharmaceutical R&D market. Displayed in Figure 9 are the DSC results generated on a tablet of acetaminophen. These results are those obtained by heating a specimen acquired from a tablet of acetaminophen and heating, cooling and reheating at a rate of 10 ˚C/min.

The DSC results are clearly different from the first heat (as received tablet) and second heat, and this represents the polymorphic nature (different crystalline states) of the drug. It is important to characterize the polymorphic properties of pharmaceutical materials as different polymorphs have different dissolution rates when ingested. The DSC 4000 provides excellent resolution for the clear detection of the crystallization exotherms of the polymorphs during the second heat.

In another biotech application, the DSC 4000 has the high level of sensitivity necessary to observe the very weak thermal-denaturation event associated with proteins in aqueous solution. When in solution, the protein will unfold when heated to sufficiently high temperatures and undergo denaturation. The shape, temperature and heat of the protein-denaturation event provide valuable characterization information on the shape factor associated with the given protein. Figure 10 shows the DSC 4000 results generated on the thermal denaturation of two different proteins (2.5% concentration) when heated at a rate of 2 ˚C/min.

The detection of the protein-denaturation event is a demanding test of a DSC because an instrument with a very high level of sensitivity and baseline stability is required.

The DSC 4000 provides both of these necessary performance characteristics for the generation of high-quality results on proteins.

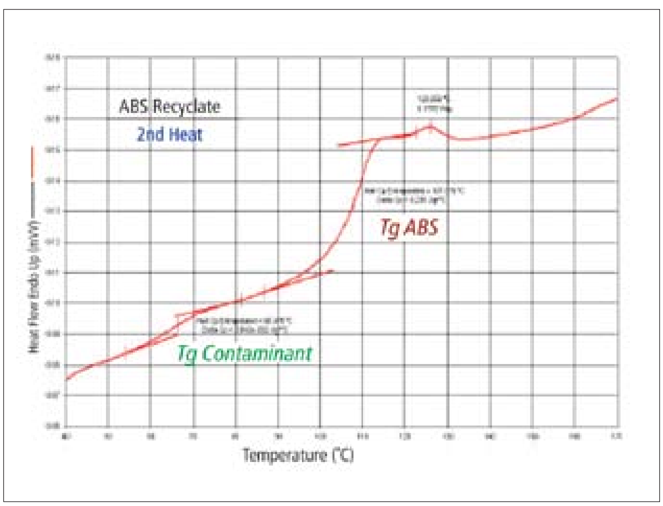

Figure 7. DSC 4000 results obtained on ABS recyclate contaminated with PVC.

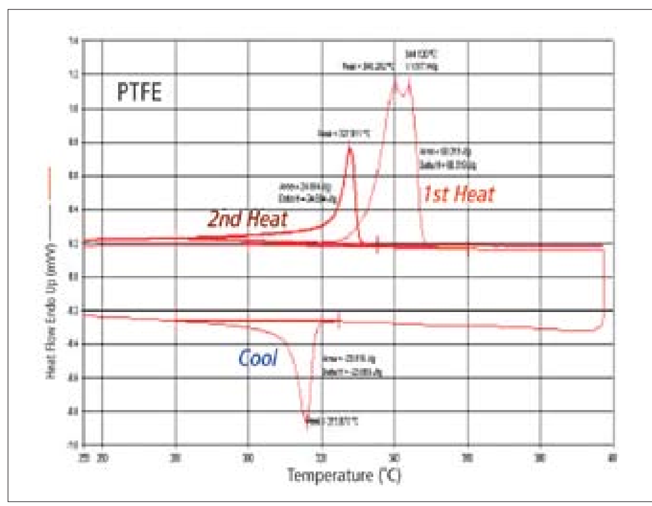

Figure 8. DSC 4000 results generated on PTFE showing heat-cool-reheat data.

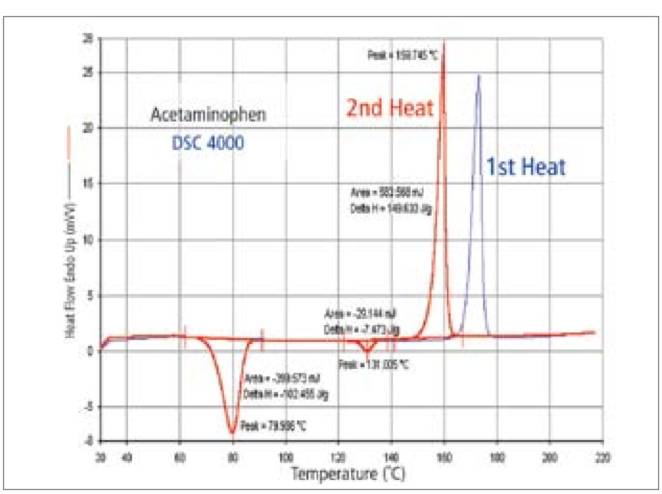

Figure 9. DSC 4000 results obtained on tablet of acetaminophen showing polymorphism.

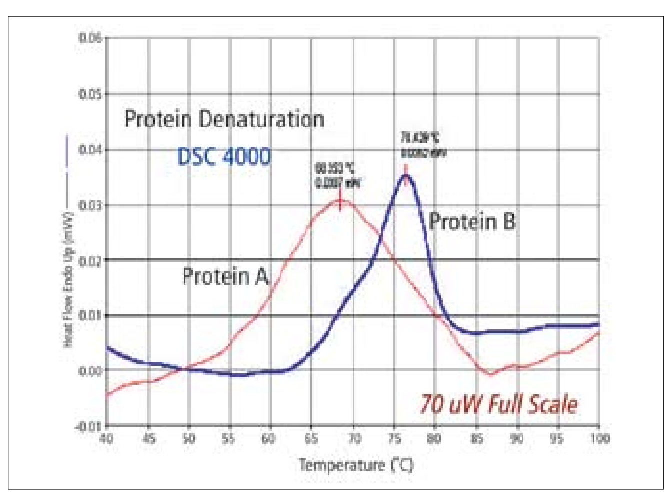

Figure 10. DSC 4000 results on the protein denaturation event of two different proteins in aqueous solution (2.5%).

Summary

The heat-flux DSC 4000 instrument provides outstanding performance in terms of:

- Reliability
- Automation
- Stability
- Resolution
- Sensitivity

The DSC 4000 meets the needs of the research scientist as well as the QA/QC engineer. It provides the flexibility and performance to handle a wide range of samples and applications including:

- Thermoplastics
- Thermosets
- Elastomers
- Adhesives
- Electronics
- Composites
- Pharmaceuticals
- Foods
- Cosmetics
- Organics

The DSC 4000, from a world leader in thermal analysis, offers both exceptional value and performance.

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