

Thermal Analysis

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HyperDSC – A Breakthrough Method for Materials Characterization

Abstract

Increasing the sensitivity and throughput of Differential Scanning Calorimetry (DSC) analysis has always been a challenge for thermal analysts in research and development. A relatively fast temperature scanning rate (20 °C/min or 40 °C/min) using traditional DSC has been sufficient

for most applications. However, DSC analysis becomes difficult when a sample size is small due to the weak signal and the number of samples that have increased as a result of the demand for high throughput. Because of the slow heating rate, some materials may experience re-crystallization during the melting process or decompose immediately after melting. This may cause difficulty in obtaining a true analysis and may also generate some additional, unexpected thermal phenomena.

HyperDSC™ is a DSC analysis technique by PerkinElmer with fast scanning rates enabling increased sensitivity and high throughput. With very fast temperature scanning rates (100-750 °C/min) in heating as well as in cooling over a broad temperature range, sensitivity and throughput have dramatically increased by a factor of ten over most conventional DSC analyses. Due to the fast scanning rate, the re-crystallization during melting, decomposition after melting, and unknown thermal behavior are either completely eliminated or significantly reduced by this method. In this study, we will present the HyperDSC technique and demonstrate the benefits of this method for several applications in polymers and pharmaceuticals.

Introduction

HyperDSC is a breakthrough method for materials characterization, providing extra sample information in seconds rather than minutes. HyperDSC can run samples as fast as 750 °C/min under control, measuring the real sample temperature,¹ whereas, for a conventional DSC method, the scan rate is normally 20 °C/min or 40 °C/min. As a result of these fast scanning rates, throughput is at least 10 times faster. To achieve these fast scanning rates, ultra low mass furnaces and small dimensions (Figure 1) are required to ensure the system is under control during the scans with rates up to 750 °C/min. This is significantly faster than any conventional heat flux DSC. The HyperDSC technique is only possible on power-compensation DSC, which measures heat flow directly and does not require complex mathematics to get premium results.

Because the DSC output is mW (J/sec), HyperDSC gives increased sensitivity with shorter scan times and smaller sample mass. The technique enhances DSC analysis and allows the measurement of small samples down to a few micrograms. Examples of small samples are very thin layers in multilayer films, coatings or very small amounts of materials for pharmaceutical development. Another major interest in the pharmaceutical industry is the study of polymorphism. The use of fast scanning rates can reveal the dependence of the polymorphic transitions and can allow better interpretation of related processes.²

In the past, the simulation of realistic conditions (like injection molding) that occur in the polymer production process represented a challenge for the polymer industry. The cooling rates in polymer processing strongly influence crystallization behavior.^{3,4} HyperDSC provides fast cooling capability and new insights in material processes. In addition to fast controlled cooling rates, polymer production also expressed a great need for fast heating rates.^{1,5} The analysis and the linking of melting behavior prior to crystallization is often a challenge. A product which is cooled down quickly and then gets analyzed with a conventional heating rate of 10 °C/min or 20 °C/min often raises questions. During slow heating re-organization processes can occur so the results do not necessarily reflect the material that exists at room temperature. Such reorganization can be prevented by heating at a high rate so that the relationship between crystallization and the subsequent melting becomes more transparent.¹

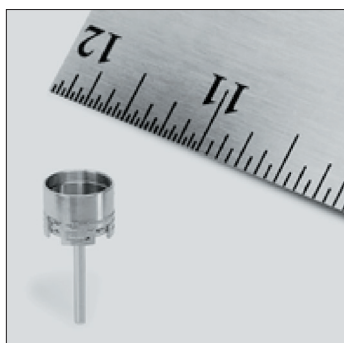


Figure 1. Sample furnace of a power-compensation DSC.

For all measurements it is important to ensure that the instrument is under control (program and sample temperature have the same slope) when using these fast scanning rates of HyperDSC.

Experimental

Several examples of different material types will be shown in this study. A PerkinElmer dual furnace (Power Compensation) DSC was used for these measurements. The DSC was calibrated for temperature and heat flow with reference materials having transitions in the range of interest. Depending on the required cooling rates, different cooling devices such as Intracooler or CryoFill (a liquid nitrogen device) were used. The CryoFill system requires Helium or a Helium/Neon mixture for sample purge which provides a temperature range from -180 °C to 500 °C with good thermal conductivity. The Intracooler configuration can also use nitrogen as purge gas.

Results and discussions

Figure 2 shows the very short transients of under 12 seconds (even shorter under helium) found at the start of a measurement in a PerkinElmer DSC 8000. This allows data to be obtained without going to extremely low temperatures to start a run. The precise time will depend upon the pan type and sample mass.

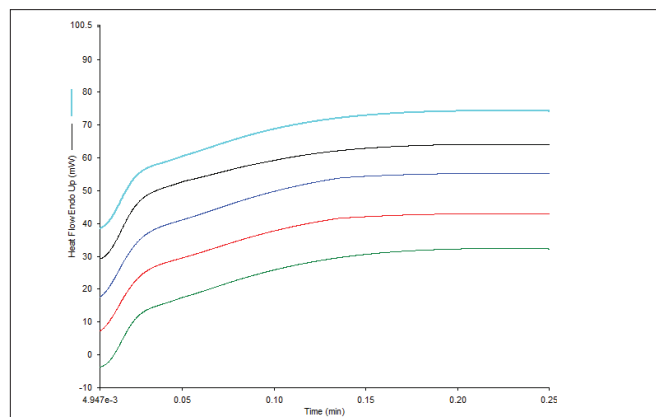


Figure 2. Start transients from different samples run in a DSC 8000 at 300°C in a Nitrogen purge. These are stable after 0.2 minutes (12 seconds). Stabilization is even faster with a Helium purge.

With classical heating rates of 10 °C/min or 20 °C/min, it is often difficult to find small transitions or to identify them as seen on the DSC curve of polypropylene generated at 10 °C/min. Increasing the scan rate to 150 °C/min raises the sensitivity and allows the easy determination of the glass transition (T_g) on this polypropylene sample as shown in Figure 3. This scan took less than two minutes compared to the 20 minutes that a classical DSC method requires. The results show that the onsets of the glass transitions line-up very nicely.

¹Diamond DSC instrument is superseded. It has been replaced by DSC 8500.

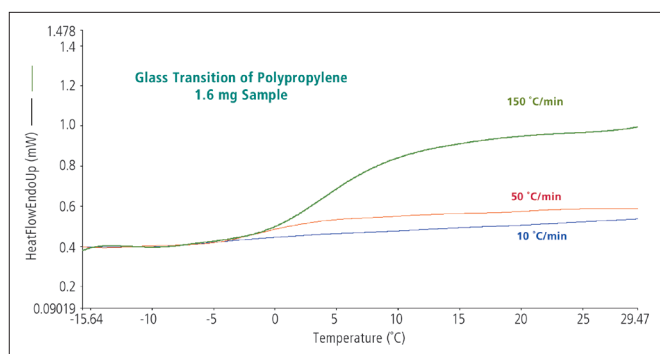


Figure 3. Polypropylene scans with 10 °C/min (blue), 50 °C/min (red) and 150 °C/min (green).

Often, to eliminate any thermal history, material is initially heated and then cooled down under control. This is a slow process using the conventional DSC approach.

Analysis is often on the second heat since the sample has a known thermal history; the first heat is influenced by cooling conditions so comparing under identical conditions can be helpful. However the reheat is no longer in the condition in which a production process delivers it. Figure 4 shows how cooling rates can impact crystallization behavior.

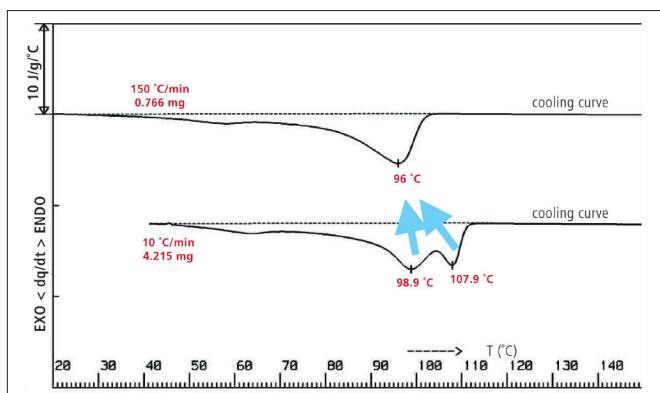


Figure 4. Polyethylene blend with different cooling rates.

Cooling a polyethylene blend at 10 °C/min shows two crystallization peaks. Increasing the rate to 150 °C/min changes the crystallization process and curve characteristic.

The next example shows the analysis of two polypropylene films. Depending on the required material properties, these films are stretched in one (regular) or two (biaxial) directions. Measuring these samples at a heating rate of 10 °C/min using traditional DSC analysis, results in very similar melting temperatures of 162 °C and 165 °C. However, if the experiment is conducted using HyperDSC, the differences are remarkable (Figure 5). The regular film shows a melting peak at 157 °C and the biaxial film at 166 °C. HyperDSC allows you to measure the real properties of the actual sample, unveiling the subtle differences which would be obscured and disappear as the sample is conditioned at low scan rates.

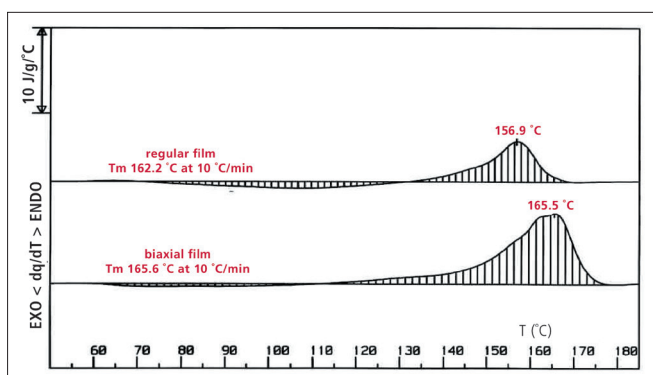


Figure 5. Polypropylene films.

Another polymorphic example where HyperDSC proves to be highly beneficial is Carbamazepine (Figure 6). In this particular case, two phase transitions are shown as the sample is heated. The first one is much smaller than the second and very difficult to see at slow scanning rates. The energy calculation of the small peak shows the same result independent of the heating rate. This indicates that the transition is not related to a polymorphic transition and was determined to be a dehydration process.

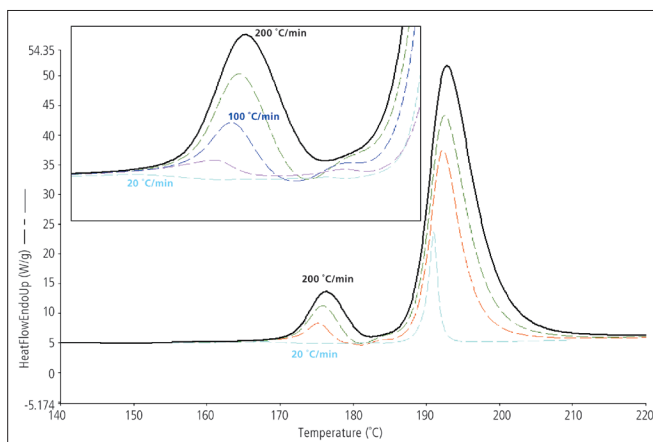


Figure 6. Carbamazepine at different scan rates.

The heat flow curve of Carbamazepine at 200 °C/min and the second derivative (Figure 7) show the transitions that are present. The second derivative at a very high scanning rate demonstrates that HyperDSC is able to pick up closely related events.

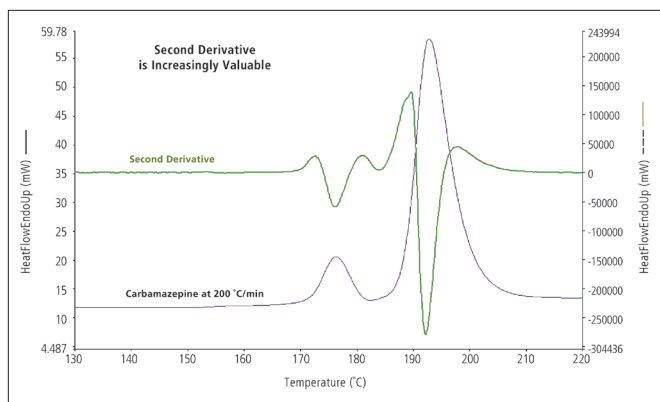


Figure 7. Carbamazepine heat flow and second derivative.

A frequent concern using HyperDSC is the loss of resolution which does reduce with increasing scan rate. The use of low sample weight and a helium purge can help to offset these issues, but Figure 8 shows the run of Dotriacontane at 250 °C/min and the second derivative. This is a very valuable tool to help resolve potentially overlapping transitions. It clearly indicates a transition not resolved in the high scanning rate heat flow curve. The information can be generated in less than two minutes and helps in the selection of samples which may provide additional information at lower scan rates.

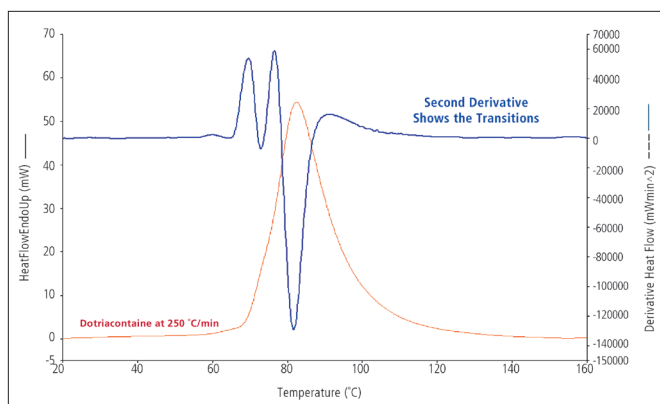


Figure 8. Heat flow of Dotriacontane, scanned with 250 °C/min.

Conclusions

HyperDSC is a very important tool for the pharmaceutical and polymer industries. It meets the urgent needs for measurements performed under process conditions. HyperDSC can also provide true information of the sample

without introducing any additional interference, such as re-crystallization or decomposition. HyperDSC helps our understanding of material properties and helps to eliminate misinterpretation of material behavior and so to improve product quality. The fast scanning rates allow users to increase sample throughput so can be a powerful tool for screening new materials.

The increased sensitivity available with this technique enhances the ability to identify weak transitions often missed with conventional DSC. All features of HyperDSC improve researchers' ability to study material characteristics. Accurate interpretation of results and fast scanning make HyperDSC the preferred tool of the pharmaceutical and polymer industries to reduce time-to-market for new products and increase manufacturing efficiency. Other markets will soon begin to discover the benefits of HyperDSC.

Acknowledgments

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