APPLICATION NOTE

Thermal Analysis

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Double-DSC Isothermal Crystallization Studies for Improved Injection Molding of Polymers

Introduction

Differential scanning calorimetry (DSC) is widely used to characterize the thermophysical properties of polymers and can be used to measure important thermoplastic properties including:

- Melting temperature
- Heat of melting
- Percent crystallinity
- Glass transition (Tg) or softening
- Crystallization
- Presence of recycled material (regrinds)
- Presence of plasticizers
- Polymer blends (presence, composition and compatibility)

In the characterization of polymer materials, DSC is most commonly used to verify the quality of the resin prior to release for processing. This avoids the potential loss of many thousands of dollars from processing a product that does not meet final quality tests, or a resin that may cause problems during processing, potentially as serious as a close-down of the processing line until the unsuitable material is removed. These routine, goods-in, quality tests are generally performed by heating the sample from ambient conditions to above the melting temperature then observing the position of the melting peak and/or glass transition.

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However, for some thermoplastics, differences in physical properties can be seen during processing, yet the melting points or glass transitions may not show any significant changes. Here, a real world example demonstrates a product quality issue where standard DSC heating and cooling was uninformative but where the use of isothermal crystallization revealed the subtle differences in material properties during processing.

For superior sensitivity, isothermal crystallization demands a fast-scanning DSC such as the PerkinElmer® DSC 8500. In this instance, without the fast-cooling capability of the DSC 8500, the differences between the good and bad batches will have remained a mystery and the customer unable to eradicate the quality issue.

Figure 1. The PerkinElmer DSC 8500.

Double-DSC Furnace Design: Power Compensation DSC

The DSC 8500 incorporates two independently controlled, low mass sample and reference furnaces. This technique is known as the power compensation approach. The very low mass of the furnaces yields a DSC with low thermal inertia and the fastest response time of any DSC instrument on the market. This double-furnace design approach and the extremely advanced electronics in the DSC 8500 allow samples to be linearly heated and cooled at rates as fast as 750 °C/min. This is extremely important when measuring isothermal crystallization behaviors of polymers.

In contrast, heat-flux DSC instruments employ a single large mass furnace. Some DSC devices use a silver block with a mass of 100 g or more. This provides a much higher thermal inertia and a slower inherent DSC response time. Single-furnace DSC instruments cannot achieve the very fast cooling and heating provided by the double-furnace instruments.

The outstanding rapid response of the double-furnace DSC 8500 may be seen in Figure 3. This plot shows the cooling performance of the DSC 8500 over a typical thermoplastics cooling range.

Figure 2. The double-furnace design pictured on the right allows very fast cooling and heating required for isothermal crystallization studies.

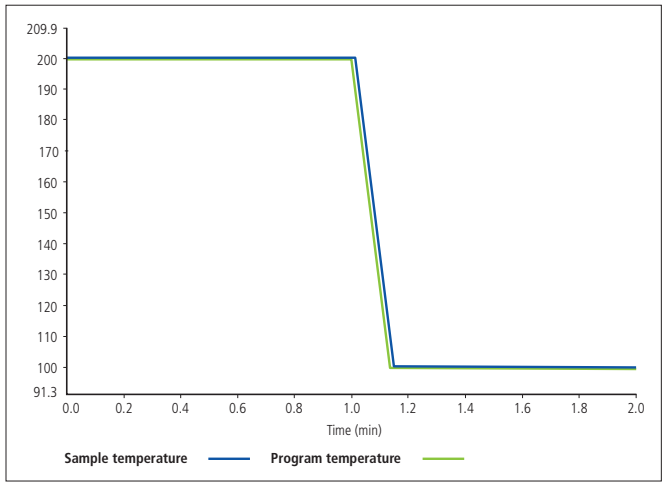

Figure 3. Sample temperature curve from DSC 8500 showing controlled cooling at 750 °C/min.

Failing thermoplastic resin in an injection molding process

In this study, an injection molder was having problems with a specific batch of polypropylene-polyethylene (PP-PE) resin used in the manufacture of automotive fuel tanks. Compared to "good" batches, the "bad" batches did not yield the desired flow properties and could not be processed into the final form. In order to prevent bad raw materials going into the molding process, the company began screening for materials that failed to have the desired flow qualities.

To the injection molder, DSC seemed an obvious candidate for this screening as it is a very easy to use and accurate tool to measure the melting point of a material. Unfortunately however, the heating curves (Figure 4) of the good and bad batches did not show any significant difference in the melting profile of the PP at 160 °C, and only a minor change in the intensity of the PE melt at 120 °C. This small change would be very difficult to screen for on a routine basis or for a less experienced DSC analyst.

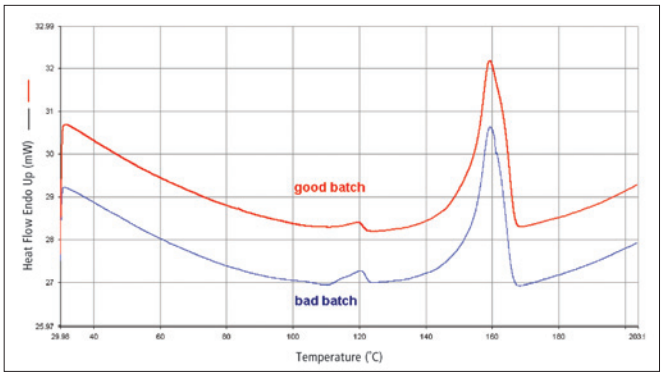

Figure 4. Standard DSC heating curve (10 °C/min) where no distinguishable differences are apparent between good and bad sample batches.

Isothermal crystallization

It is common that the standard heating curve cannot distinguish between polymer batches that perform differently during processing, yet clearly they are dissimilar because they behave differently during the manufacture of these molded parts.

One property of a plastic that will have large impact on processing or final product performance is the resin's crystallization behavior. A large number of additives are used to control and optimize crystallization behavior for a given end use or processing method. Its importance in injection molding is that if a polymer resin begins to crystallize too quickly then its flow properties are altered. With a higher viscosity, the molten resin does not fill complex molds correctly, injectors are likely to get blocked and the products and the process begin to fail. Understanding crystallization is of paramount importance to anyone involved in the processing of thermoplastics.

The primary method used to understand crystallization behavior is isothermal crystallization. A DSC instrument heats the sample until it is molten, then cools it to a constant temperature (an isotherm). Being exothermic, the crystallization of a material will be evident on a DSC curve. When the DSC is held at a constant temperature, the time of the exothermic event becomes an indicator of how quickly the material crystallizes. The intensity of the curve can be used as an indicator of how much of the material is crystallized.

The successful measurement of the isothermal crystallization of polymers requires a DSC instrument that can cool the sample extremely quickly. This is because many thermoplastics crystallize rapidly when cooling from the melt. The DSC must be able to cool and equilibrate as fast as possible in order to detect the complete crystallization exothermic peak.

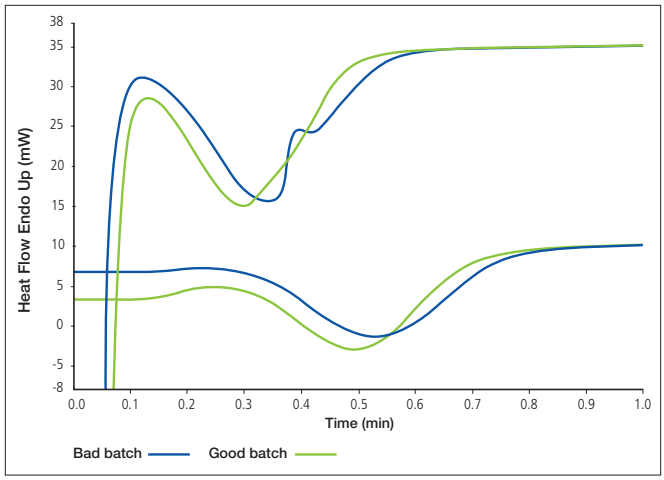

Figure 5. Isothermal crystallization results for the good and bad batches on heat flux DSC (lower curve) and DSC 8500.

In this case, isothermal crystallization behaviors of the good and bad batches were studied using both a single-furnace DSC instrument and the double-furnace DSC 8500. With the single, larger mass furnace and its longer response times, a typical cooling rate for the DSC using an intracooler-type accessory is 50 °C/min whereas the hyper-enabled double-furnace DSC 8500 is capable of reaching cooling rates of 750 °C/min.

While the standard heat-flux DSC was unable to show a clear distinction between the good and bad samples, the hyper-enabled DSC 8500 readily shows a significant difference between the two batches (Figure 5).

Summary

In this material, the crystallization of the PE-PP resin is clearly rapid. With the slower cooling rates on the heat-flux DSC, crystallization is partly underway by the time the instrument reaches its isothermal temperature. This has prevented the system from capturing the double crystallization behavior in the bad batch samples.

With its fast-cooling rates, the DSC 8500 is able to characterize this behavior and provides a detection technique for the quality testing of all future incoming raw materials.

Further analytical experimentation would be required to understand the chemical and phase changes that underlie this issue. One possibility would be to take a sample from the bad batch and combine this isothermal crystallization experiment with direct Raman spectroscopy, applying the emerging Raman-DSC hyphenated technique. The additional information offered by the Raman-DSC technique would further increase the processor's chances of getting to the root cause of batch variations and so eliminate completely the problem further down the processing line.

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