# DSC Isothermal Crystallization Studies for Better Injection Molding of Polymers

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## Introduction

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

- Melting temperature
- Heat of melting
- Percent crystallinity
- Tg or softening
- Crystallization
- Presence of recyclates/regrinds
- Plasticizers
- Polymer blends (presence, composition and compatibility)

Most DSC experiments on polymers are conducted by heating from ambient conditions to above the melting temperature. But, for some thermoplastics, which do exhibit differences during processing, standard heating DSC may not show any significant differences. A more sensitive test, for detecting subtle, but important differences between different batches of a given thermoplastic, is the DSC isothermal crystallization test.

With this test, a sample of polymer is heated up through its melt and held under isothermal conditions for several minutes to destroy the existing crystalline structure. The sample is then ballistically cooled to a temperature below the melting temperature to allow the polymer to crystallize under tightly controlled conditions. DSC monitors the resulting crystallization exothermic peak as a function of time.

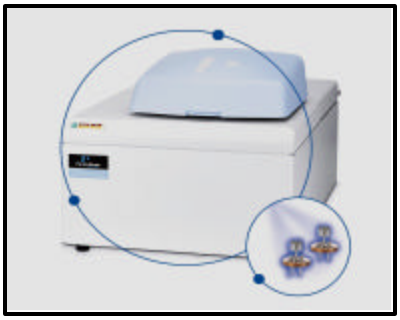
The isothermal crystallization test provides valuable information on polymers including:

- Average molecular weight
- Molecular weight distribution
- Presence of recyclates/regrinds
- Plasticizers
- Nucleating agents, pigments or other additives
- Copolymers
- Injection molding lubricants or flow enhancers

The successful measurement of the isothermal crystallization of polymers requires a DSC instrument with a very fast response time. This is because many thermoplastics can crystallize rapidly when cooling from the melt. It is important that the DSC be able to cool and equilibrate as fast as possible in order to detect the complete crystallization exothermic peak. The DSC with the fastest response time is the PYRIS Power Compensation DSC from Perkin-Elmer Instruments.

## Power Compensation DSC

The PYRIS Diamond DSC from PerkinElmer Instruments uses the Power Compensation approach. This DSC uses two independently controlled, low mass (1 g) sample and reference furnaces. The low mass of the Power Compensation furnaces yields a DSC with low thermal inertia and the fastest response time of any DSC instrument available.

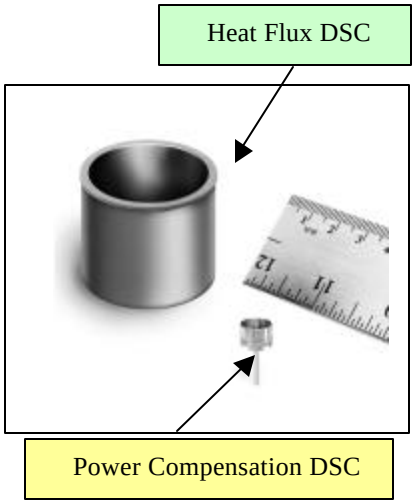


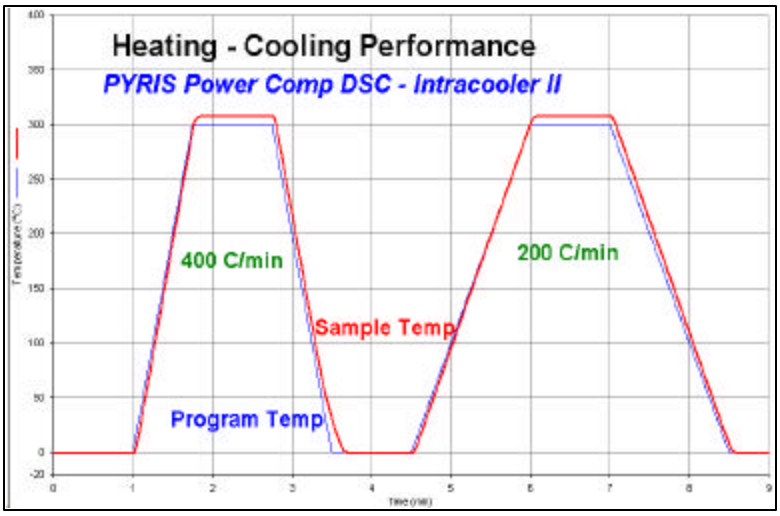
***PYRIS Diamond DSC***

The Power Compensation DSC allows samples to be linearly heated and/or cooled at rates as fast as 500 C/min. This is important when measuring isothermal crystallization times and behaviors of polymers.

In contrast, heat flux DSC instruments employ a 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. The heat flux DSC instruments cannot achieve the very fast cooling and heating provided by the Power Compensation DSC. The large difference in masses between the heat flux DSC and the Power Compensation DSC may be seen in the following figure.

PerkinElmer™ instruments.




The outstanding rapid response of the Power Compensation DSC may be seen in Figure 1. This plot shows the heating and cooling performance of the Power Compensation DSC at heating and cooling rates of 400 and 200 C/min between 200 and 0 C. The DSC was equipped with the refrigerated cooling system, Intracooler II and a helium purge was applied. The actual sample temperature (red) and program temperature (blue) are displayed as a function of time. The sample temperature tracks the program temperature very well even at the ballistic cooling rate of 400 C/min and the use of a refrigerated cooling system, rather than liquid nitrogen. No other DSC instrument can match this level of performance.

## Experimental

In this applications study, two different polypropylene-polyethylene materials (used for injection molding purposes to produce automotive fuel tanks) exhibited different processing properties. The 'good' polymer worked well during the injection molding process, while the 'bad' material did not yield the desired flow properties. The company using the polymers wished to be able to screen the materials by DSC for quality assurance purposes. The following conditions were used to analyze the polypropylene-polyethylene materials:

**Experimental Conditions**

| | |
|---|---|
| Instrument | PYRIS Power Compensation DSC |
| Temperature program | Cool from 200 C to 110 C at 500 C/min |
| Purge gas | Nitrogen |
| Sample mass | Approximately 3 mg |
| Sample pan | Aluminum auto-sampler pans |



PerkinElmer™ instruments.

## Results

Displayed in Figure 2 are the DSC heating results obtained for the good and bad polypropylene blends. No significant differences are noted between the two blends other than a slightly more intense melting peak for the good sample versus the bad. This frequently is the case between different batches of a given polymer, where standard heating DSC is unable to make a clear differentiation between the good and poor performers.

The melting of the polypropylene is observed as a dominant melting peak at about 160 C and that of the polyethylene component is obtained at 120 C. Polyethylene is frequently added to polypropylene to improve its impact properties.

Even during a constant cooling ramp from the melt, DSC does not show any significant differences between the two polypropylene materials, as is shown in Figure 3. However, these results are still very useful as they do provide insightful information on the temperature of crystallization of the polymer.

Further work on the polymers found that the DSC isothermal crystallization test was able to make clear distinctions between the good and bad polypropylene materials. Displayed in Figure 4 are the DSC isothermal crystallization results obtained on the good and bad materials at a temperature of 110 C.

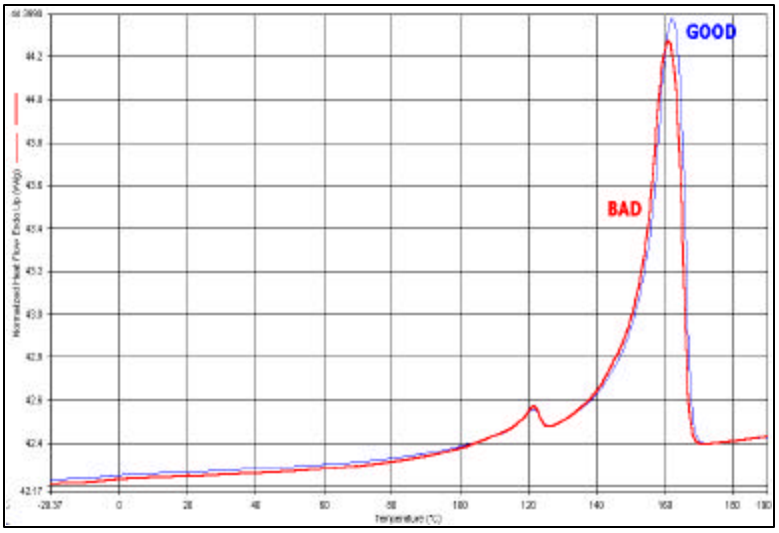



*Figure 2. DSC heating results on good and bad polypropylene-polyethylene blends*

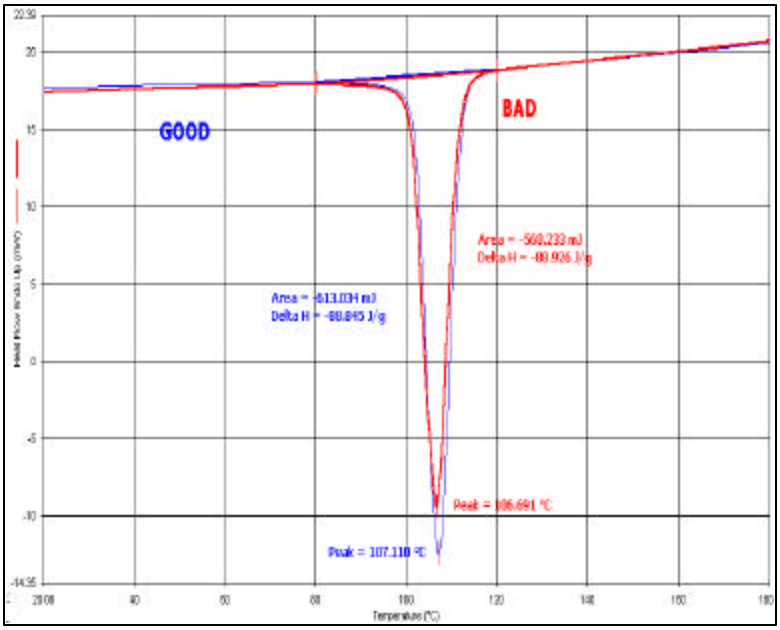



*Figure 3. DSC cooling results on good and bad blends*



PerkinElmer™ instruments.

These DSC results definitely show the very fast responsiveness obtainable with the PYRIS Power Compensation DSC. The crystallization of the polypropylene materials occurs in less than 1 minute after the isothermal target temperature is achieved. Heat flux DSC instruments could not possibly obtain these results for these polymers due to their much slower response times.

The isothermal crystallization results are quite informative as they show that the bad material exhibits two well-defined isothermal crystallization peaks. The good sample, in contrast, exhibits only a single exothermic crystallization peak. The poor injection molding of the bad polymer is most likely due to the very rapid crystallization of the first component as is reflected in the isothermal crystallization data. The difference is crystallization rates of the good and bad polymers would account for the processing differences between the two. The isothermal crystallization test, with its very high degree of sensitivity and selectivity, is able to detect these important distinctions.

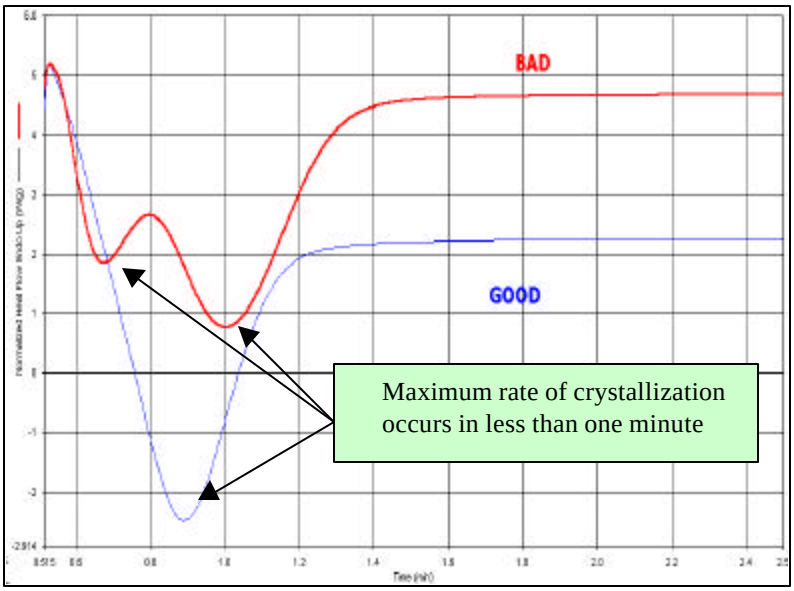



*Figure 4. Isothermal crystallization results at 100 C for good and bad polyropylene-polyethylene blends*

## Summary

Isothermal crystallization studies on polymers can frequently provide more informative characterization information. This is due to the inherently high sensitivity of this test for detecting subtle differences in the make-up of the given polymer. The successful performance of the isothermal crystallization test requires a DSC instrument with a very fast response time. The PYRIS Power Compensation DSC provides the fastest response time of any DSC on the market and allows samples to be ballistically heated and cooled at rates up to 500 C/min. The isothermal crystallization test was able to show distinct differences between two different batches of polypropylene-polyethylene blends. These results were important as the good and bad blends exhibited significantly injection molding performances.