



DSC as Problem Solving Tool: Isothermal Crystallization of Polymers

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Semi-crystalline polymers, such as nylons, PET, PEEK, PPS, exhibit both crystalline and amorphous phases or components. The level of crystallinity achieved by the polymer will have a major affect on its physical and thermal properties, including such key factors as:

- Stiffness or modulus
- Brittleness
- Optical clarity
- Barrier resistance to gases
- Cold flow or creep
- Dimensional stability
- High temperature performance

The balance between the crystalline and amorphous components which comprise a polymeric end product is a function of the chemistry of the polymer as well as the processing (cooling rates, thermal histories) used to generate the end product.

Regarding the chemistry of the polymer, various factors can affect the rate of crystallization of the polymer, once it is cooled from the melt. These include:

- Polymer chain make-up
- Additives (e.g., pigments, anti-oxidants, catalysts)
- Nucleating agents
- Plasticizing agents
- Average molecular weight
- Molecular weight distribution
- Presence of recyclates

There is need to test semi-crystalline polymers or polymer feedstocks for these particular properties, as they can significantly affect the subsequent structure or morphology obtained by the resin during processing. One of the best means of accomplishing this is through the measurement of isothermal crystallization times by differential scanning calorimetry (DSC).

DSC measures heat flow into or from a sample as it is heated, cooled or held under isothermal conditions. The DSC instrument can be used to observe the resulting crystallization of a polymer after it has been melted and cooled as rapidly as possible to some intermediate isothermal temperature. The shape and magnitude of the crystallization exotherm and the time to the peak maximum can be used as a very sensitive indicator of the resin's particular chemistry and formulation.

In performing the isothermal crystallization measurements, it is critical to have a DSC instrument which can cool a sample very quickly (e.g., 500 C/min) from the melt. The power compensated Pyris 1 DSC from PerkinElmer can accomplish this, because of the very low mass of the furnace used in the DSC cell (mass of only about 1 g). In contrast, many heat flux DSC devices have an extremely massive

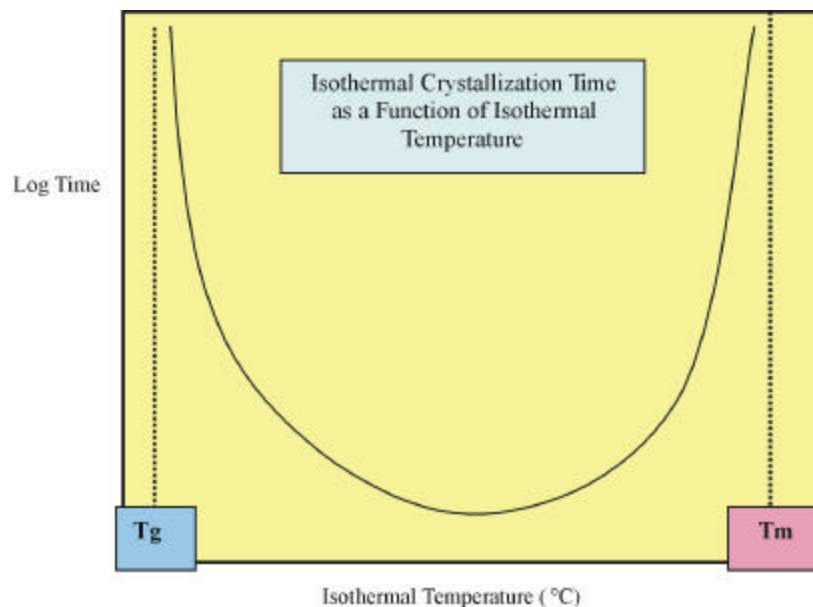
furnace (200 g) which makes this type of DSC slower to heat and cool and less responsive. The Pyris 1 DSC offers the following major advantages for characterizing polymers:

- Ability to heat and cool very quickly (500 C/min)
- Ability to achieve isothermal conditions rapidly
- Measurement of true heat flow rather than temperature differential for more accurate calorimetric determinations
- Use of PRT or platinum resistance thermometers, rather than thermocouples, for the most accurate and precise measurement of sample temperature
- Outstanding resolution
- Very high sensitivity

When performing isothermal crystallization measurements, the following approach is taken:

- Place 10 mg of polymer in crimped aluminum pan
- Use a dry nitrogen purge gas during the DSC measurements
- Heat the sample at 20 C/min to a temperature which is about 30 C above the melting peak temperature of the polymer
- Hold the sample for 5 minutes to fully melt the crystalline phase
- Quickly cool the sample at a rate of 500 C/min to the isothermal target temperature

Figure 1. Change in isothermal crystallization times with regards to DSC isothermal temperature.



- Monitor the resulting crystallization of the polymer as a function of time

The target isothermal temperature, for performing the isothermal crystallization studies, should be selected so that a well-defined exothermic peak is obtained. If the temperature is too low, the resin can crystallize extremely rapidly, and it is difficult to observe the resulting crystallization exotherm. The rate of crystallization of a polymer is governed by the proximity of the isothermal temperature to both the melting temperature, T_m , and the glass transition event, T_g .

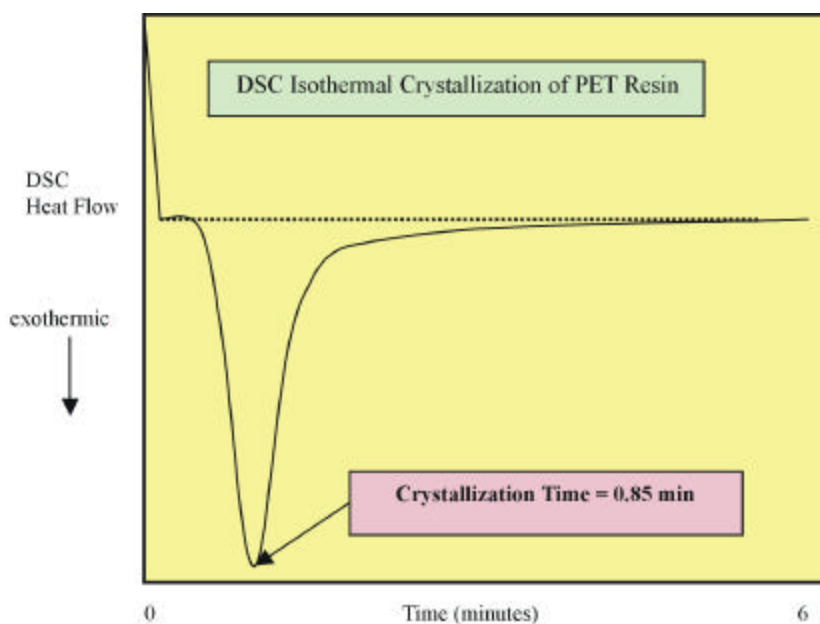
This is represented in the Figure 1, which shows the resulting rate or time of crystallization of a typical polymer as a function of the isothermal temperature.

The crystallization of the polymer from the melt is primarily controlled by two competing factors:

- Ability of the polymer to form nucleating sites
- Resin viscosity

The former is governed by entropy considerations; and, as the isothermal temperature approaches the melting temperature, it becomes increasingly more difficult for the nucleating sites to form. As a result, the time required to crystallize the polymer goes to infinity. On the other hand, if the isothermal temperature becomes too low and approaches the glass transition temperature of the resin, the viscosity of the resin becomes very high and the time that it takes for the resin to crystallize goes to infinity. In the middle, at some mid-temperature,

Figure 2. DSC isothermal crystallization results on PET resin.



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Figure 3. DSC isothermal crystallization results on samples of virgin and recycled PET resins.

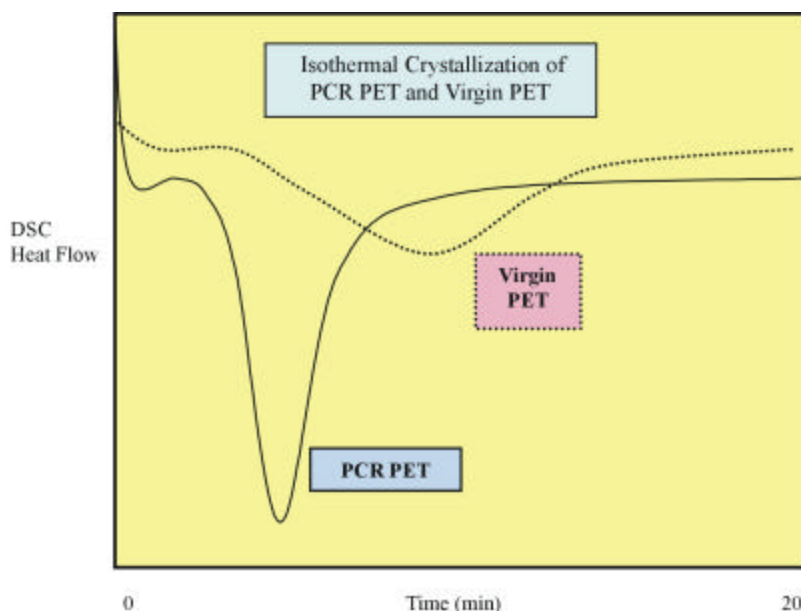
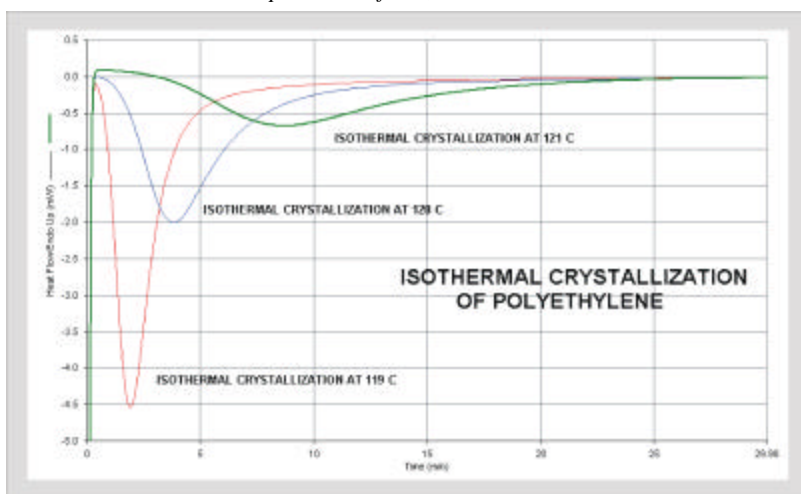


Figure 4. DSC isothermal crystallization results on polyethylene at temperatures of 121, 120 and 119°C.



the resin reaches a minimum in the U-shaped curve, where the resin will

crystallize most rapidly. It is best to avoid this minimum temperature region when performing isothermal

crystallization measurements by DSC. The ideal temperature range to perform isothermal crystallization measurements is above the minimum, but still significantly below the melting temperature. In general, polymers which crystallize relatively slowly (e.g., PET and PEEK) can be cooled to temperatures 50 C or so below the melt peak and yield a complete exothermic recrystallization peak. More rapidly crystallizing polymers (nylon 6 and polyethylene) need to be recrystallized at temperatures closer to the melt in order to generate a complete exothermic peak.

The DSC curves in Figure 2 show the isothermal crystallization of PET, which is a commonly used polymer whose end properties are strongly dependent upon the given crystallization conditions.

In this example, the PET resin achieves its maximum rate of crystallization at 0.85 minutes and this time can be used for comparative purposes.

The DSC isothermal crystallization test provides a very sensitive indicator of the properties of the chemistry of the resin material, which might not be observed by simply heating the samples in the DSC instrument.

As an example, the isothermal crystallization test can make distinctions in resin containing recyclates. The presence of the recyclates is not always clear-cut by DSC, but the high sensitivity and the distinguishing ability of this test allows for the subtle differences between virgin resin and recycle resin to be detected.

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The DSC curves in Figure 3 show the isothermal crystallization results generated on two different PET bottle resins, virgin PET and PET containing recyclate. Standard DSC heating experiments did not make significant distinctions between the two different resins.

The resin containing the recyclate crystallizes at a significantly faster rate compared to the virgin PET polymer. The faster rate of crystallization would have to be factored into subsequent processing or injection molding of the PET resin with recyclate as this would have a major effect on the quality and properties of the end product. As an example, if the resin crystallizes too rapidly, it might not flow properly or completely into the mold during the injection molding process. The isothermal crystallization time can therefore be used as a sensitive quality assurance parameter for applications where the rate of crystallization is critical, such as blow molding of bottles and for injection molding.

One of the most difficult polymers to characterize using the DSC isothermal crystallization test

is high density polyethylene (HDPE). This polymer crystallizes very quickly and a DSC instrument is required which can cool quickly and achieve thermal equilibration rapidly. The low mass furnace associated with the PerkinElmer power compensated DSC provides the necessary quick cooling from the melt and the rapid equilibration at the specific target temperatures. In contrast, the large furnaces associated with heat flux DSC devices are more sluggish and it is very difficult to generate high quality, research grade data on polyethylene materials.

Shown in the Figure 4 are isothermal crystallization results obtained on polyethylene at three different temperatures using the power compensated DSC instrument. It may be seen that the polymer crystallizes very quickly and that even small changes in the isothermal temperature can significantly affect the resulting crystallization behaviors of the polymer.

The results obtained from the power compensated DSC provide a complete exothermic peak even for

the rapid crystallization of polyethylene at 119 C.

Summary

The DSC isothermal crystallization test provides valuable characterization information on the chemistry associated with semi-crystalline polymers, such as nylons, PET, PPS, PEEK. The test frequently shows differences in the make-up of polymers that might not be observed with standard DSC heating studies. This information is useful when processing semi-crystalline polymers for applications such as production of fibers, films, soda bottles and for injection molding. In order to perform this informative test, a DSC instrument is required which provides fast cooling from the melt (e.g., cooling rates of 500 C/min) and the ability to achieve rapid thermal equilibration at the desired isothermal target temperature. The power compensated DSC from PerkinElmer provides the necessary high level of performance required to perform this sensitive isothermal crystallization test.

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