Importance of DSC Rapid Cooling for the Analysis of Plastic Microwave Food Trays

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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
- Nucleating agents
- 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.

During the manufacture of plastic products, such as bottles, fibers, films, containers, housings, pipes and trays, the thermoplastic is melted, cooled, thermoformed and crystallized. The complete study of the behavior of plastics, which are melt-processed, requires having a DSC instrument that is capable of rapid cooling to simulate and fully explore the properties of these materials.

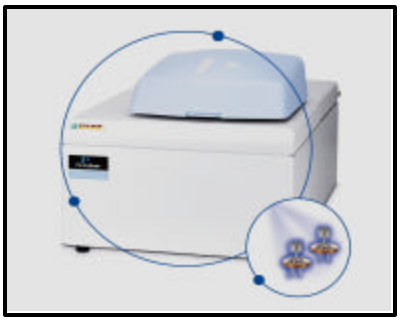
To study the melt-crystallization properties of polymers, several informative DSC tests can be conducted:

- Isothermal crystallization (at a single or multiple temperatures)
- Cooling (at different rates from very fast to normal)
- Reheating after cooling (at different rates)

The successful measurement of these particular tests 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.

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Need for Fast Cooling for Microwave Food Trays

The thermophysical properties of plastic microwave food trays were studied using Power Compensation DSC. The microwave food trays must be capable of withstanding large and rapid extremes in temperatures. The trays are generally thermoformed from polyethylene terephthalate (PET) since this polymer is semi-crystalline and exhibits the desired end use properties such as stability, ease of processing and impact resistance. However, to further enhance the thermal stability of the PET polymer for use as microwave food trays, the crystallinity of the polymer is increased by adding nucleating agents. These agents induce a higher level of crystallization of the PET resin during cooling from the melt. Higher concentrations of a given nucleating agent will result in a higher level of crystallinity of the plastic during processing.

DSC cooling experiments are important for the assessment of the effects of these nucleating agents on the crystallization properties of the PET resin. Standard DSC may not reveal obvious differences between two different nucleated resins, whereas these differences will become evident during DSC cooling experiments. For the highly nucleated and fast crystallizing PET microwave food trays, the PYRIS Power Compensation DSC is necessary for the best in-depth study of the rapid crystallization of the resin.

Experimental

The heat flow properties of two different PET microwave food trays (Tray 1 and Tray 2) were studied, along with the non-nucleated PET precursor resin. The experiment conditions presented in the table were used to study the cooling properties of the PET resins.

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 Conditions

Instrument	PYRIS Power Compensation DSC
Cooling system	Intracooler II
Sample pan	Crimped aluminum standard pan
Sample mass	Approximately 10 mg
Purge gas	Helium
Cooling rate (isothermal crystallization studies)	500 C/min from 300 C
Cooling rates for cool-reheat experiments	400, 300, 100 and 50 C/min between 300 and 0 C
Heating rate for heating experiments	20 C/min

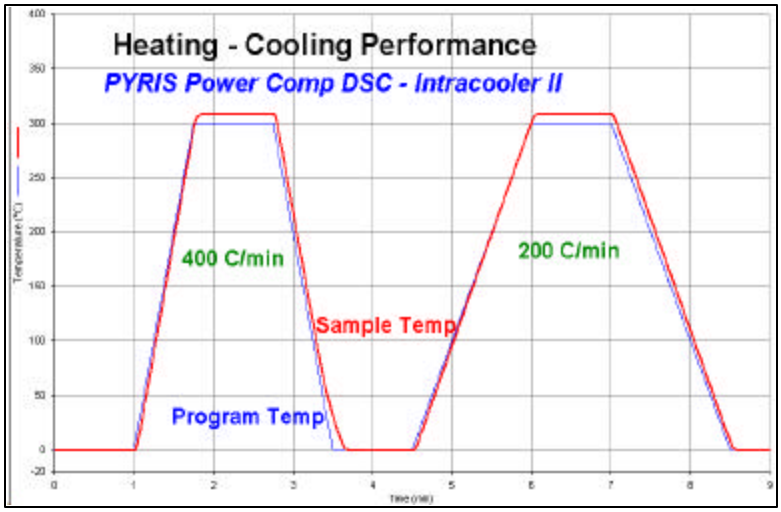

Figure 1. Fast heating and cooling performance of the PYRIS Power Compensation DSC

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Results

Displayed in Figure 2 are the DSC results obtained on the PET precursor polymer before the nucleating agents are added. The plot shows the first and second heating results. The PET resin was rapidly cooled at a rate of 200 C/min between the first and second heats. During the first heating, no crystallization exothermic peak is observed reflecting the fact that the polymer has a high level of crystallinity in its as received state. The resin undergoes melting at 261 C with a heat of melting of 66.7 J/g.

When the PET sample is rapidly cooled down to room temperature and then reheated, a well-defined cold crystallization peak is obtained at 173 C, which is typical for this polymer. The heat of crystallization is found to be 30.1 J/g. During the second heating segment, the PET undergoes melting at 257 C with a heat of melting of 33.0 J/g. The net heat of crystallization (melting – cold crystallization) is 2.9 J/g, which is reflective of a nearly amorphous polymer. This demonstrates the ability of the PYRIS Power Compensation DSC to yield an amorphous polymer directly in the DSC with the application of a fast cooling rate. In comparison, many heat flux DSC instruments require that the sample be physically removed from the hot cell in order to generate an amorphous state by manual quench cooling.

To make the PET resin suitable for the manufacture of the microwave food trays, nucleating agents are added to the polymer. The presence of these nucleating additives drastically changes the morphology of the polymer allowing it to crystallize much more rapidly. Displayed in Figure 3 are the DSC results obtained from the PET sample extracted from a microwave food tray (Tray 1). The sample was heated through its melt temperature and then cooled at a rate of 200 C/min back to room temperature.

When the cooled food tray is reheated, the cold crystallization exothermic peak occurs at a much lower temperature (134 C) and is much smaller than that of the PET chip. These major differences are reflective of the changes caused by the presence of the nucleating agents.

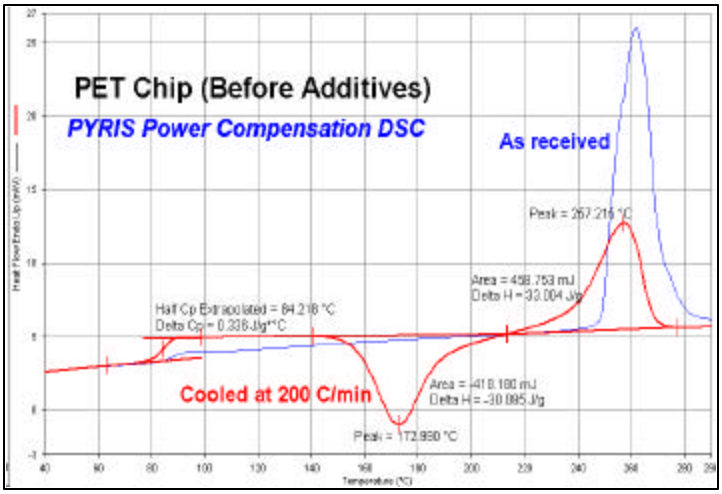

Figure 2. DSC results for PET chip (before additives) showing as received resin and resin after being melted and cooled at 200 C/min

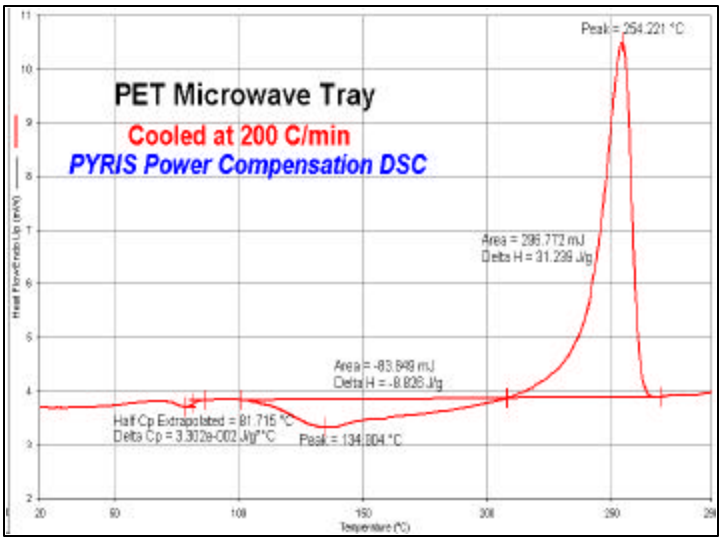

Figure 3. DSC heating results for PET microwave tray resin after cooling from the melt at 200 C/min

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For quality assurance purposes, the manufacturers of the plastic microwave food trays like to induce a more well-defined cold crystallization peak for the nucleating resin. This provides a sensitive indicator as to the effectiveness of the nucleating agents based on the peak shape, magnitude and temperature. However, this requires ballistically cooling the PET resin from the melt to develop an amorphous material. Displayed in Figure 4 are the DSC results obtained on the food tray PET resin when cooled at the very fast rate of 400 C/min. It may be seen that a well-defined cold crystallization peak is observed at 131 C. This is possible only with the cooling capability provided by the PYRIS Power Compensation DSC for such heavily nucleated polymers.

In contrast, most heat flux DSC units can heat at a maximum rate of only 100 C/min. This is not fast enough to avoid crystallization for fast crystallizing polymers such as nylon or nucleated PET. Shown in Figure 5 are the DSC results generated for the PET tray resin when cooled from the melt at a rate of 100 C/min. The cold crystallization peak is just barely observed, as these results demonstrate. Much valuable characterization information on the effects of the nucleating agents is lost when required to use the slower heating rates necessitated with heat flux DSC. The PYRIS Power Compensation DSC provides the ability to cool over an extremely wide range of rates for the most comprehensive characterization information.

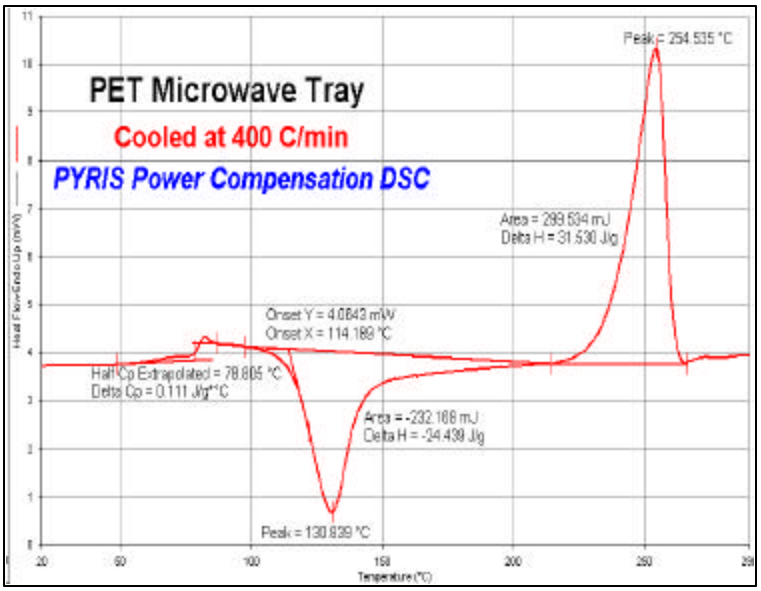

Figure 4. DSC results for PET tray resin after cooling at 400 C/min

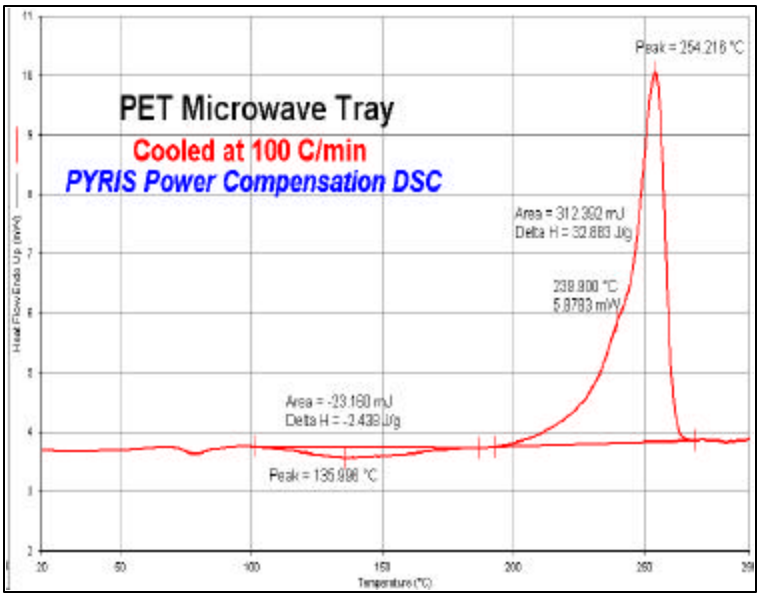

Figure 5. DSC results for PET tray resin after cooling at 100 C/min

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The effects of the applied cooling rate for the PET tray resins may be seen in Figure 6. This shows a direct overlay of the heating curves obtained after cooling from the melt at 400, 200, 100 and 50 C/min. Due to the heavy nucleation of the PET resin, there is a major change in the results when the cooling is slowed from the very fast 400 C/min to 200 C/min. This demonstrates the great importance of the need for the very fast cooling to get a complete picture of the crystallizable nature of this PET resin material.

Additional supplementary characterization information can be obtained by performing isothermal crystallization measurements on the nucleated PET resins. 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

Because of its very fast response time and ability to cool quickly, the PYRIS Power Compensation is ideally suited for the measurement of the isothermal crystallization of polymers.

Displayed in Figure 7 are the isothermal crystallization results generated for Tray 1. The sample was cooled from 300 C to the target isothermal temperatures at a cooling rate of 500 C/min. The crystallization behavior was monitored at temperatures of 230 , 225, 220, 215 and 210 C. At the temperature of 210 C, the resin reached its maximum rate of crystallization in about 30 seconds. This demonstrates the ultra fast responsiveness of the Power Compensation DSC.

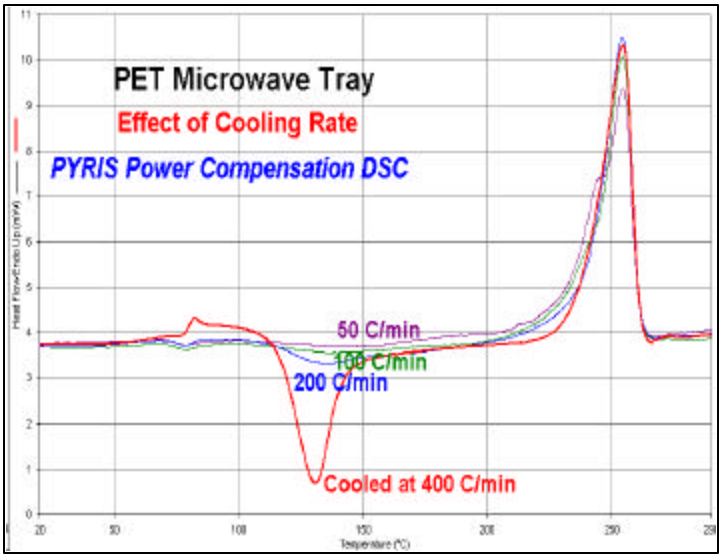

Figure 6. Overlay of DSC results on PET tray after cooling at rates of 400, 200, 100 and 50 C/min

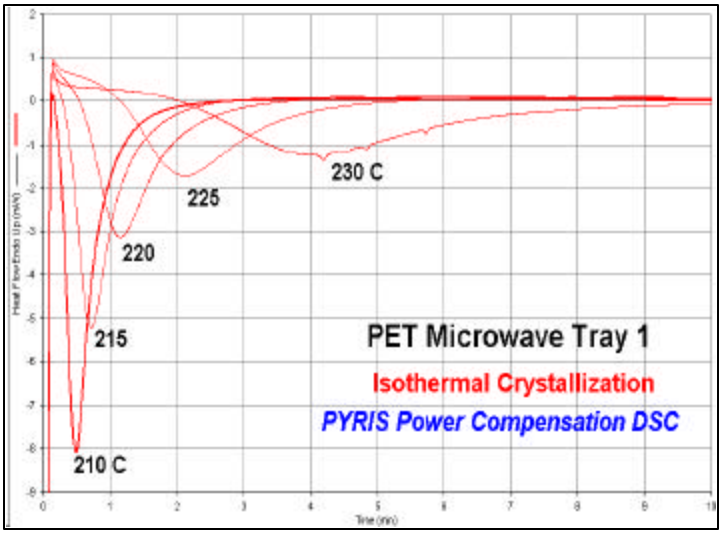

Figure 7. Isothermal crystallization results for PET Tray 1

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Another PET microwave tray (Tray 2) was analyzed using the DSC isothermal crystallization test and these results are displayed in Figure 8. This resin was clearly different in its resulting crystallization behavior as compared to the Tray 1 sample in that it took longer for it to crystallize under identical conditions. This indicates that the Tray 1 resin was more heavily loaded with nucleating agents as compared to Tray 2.

The differences between the crystal-0lization behaviors of the Tray 1 and Tray 2 PET resins is more evident in an overlay (Figure 9) of the isothermal crystal-lization behaviors at 220 C. Tray 1 clearly crystallizes more rapidly as compared to Tray 2. These differences would not be apparent with standard heating DSC, but are very noticeable with the DSC isothermal crystallization measurements. The measurement of the very fast crystallization responses of these nucleated resins requires a DSC with an ultra-fast response time, and this is the PYRIS Power Compensation DSC.

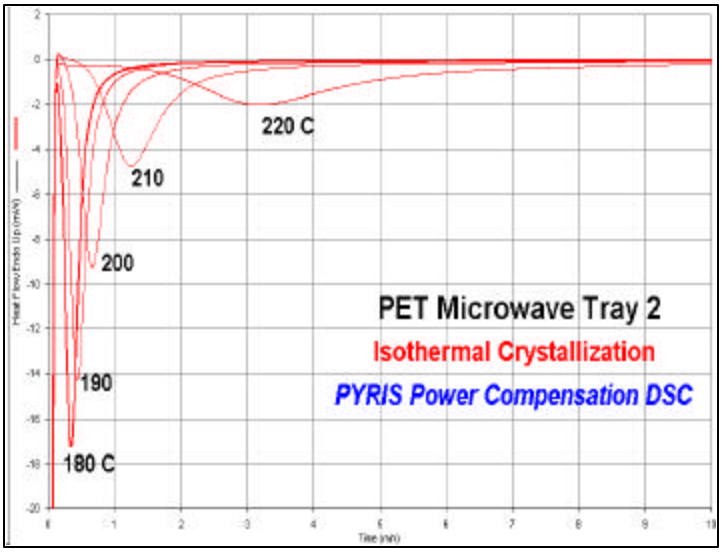

Figure 8. Isothermal crystallization results for PET Tray 2

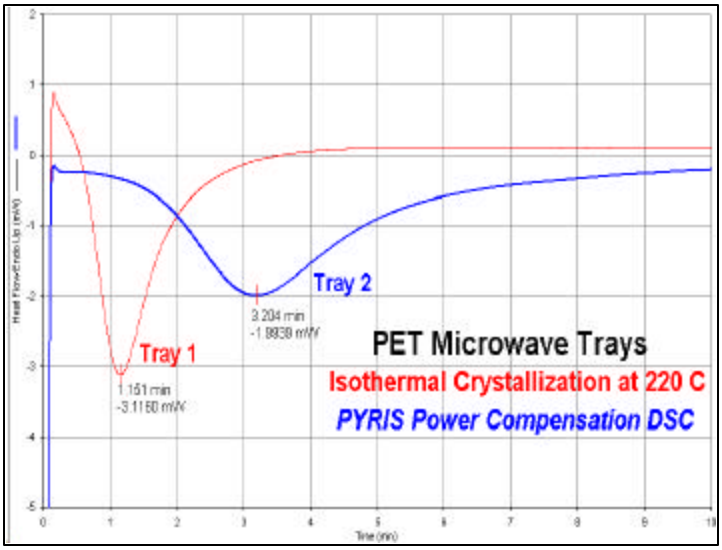

Figure 9. Overlay of DSC isothermal crystallization results at 220 C for PET microwave trays 1 and 2

Summary

Most plastic processes require that the polymer be melted and cooled during the thermoforming stage. The most comprehensive characterization of plastics undergoing melt processing necessitates that the material be studied under both heating and cooling conditions. The cooling analysis allows the effects of nucleating and plasticizing agents to be more fully quantified. Oftentimes thermoplastics may not exhibit any significant differences by standard heating DSC. However, when cooling studies are performed, significant differences, due to the presence of nucleating agents or flow enhancers, may become apparent. Such DSC data is extremely valuable for quality assurance or for process control purposes. The successful performance of cooling studies requires a DSC with a fast response time so that the sample can be analyzed at ballistic cooling rates. The DSC instrument with the fastest response time and the ability to heat and cool ballistically (up to 500 C/min) is the PYRIS Diamond Power Compensation DSC from Perkin-Elmer.

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