APPLICATION NOTE

Thermal Analysis

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Isothermal Crystallization Study for Quality Assurance

Introduction

The crystallization behavior of polymer resin is important to know. For polymer processors, it helps to optimize the processing conditions like mold temperature and holding time. DSC is traditionally used to study the thermophysical properties of polymers. The isothermal crystallization experiment is very useful to determine the crystallization kinetic parameters. In an isothermal crystallization experiment, the polymer sample is first heated to above its melting temperature and held for some time to fully melt out any existing crystals. Next, the sample is quench-cooled quickly to the desired isothermal temperature which is usually between its melting temperature and its glass transition temperature. The sample is left crystallized under this temperature and the heat generated during this crystallization process is recorded by the DSC instrument. The experiment may stop when the crystallization finishes and heat flow signal reaches the baseline. The isothermal crystallization experiment can be conducted at a series of temperatures and the result curves can be processed by the software to get kinetic parameters like reaction order and activation energy.

The isothermal crystallization result is very sensitive to the sample properties. It can be influenced by many factors, including average molecular weight, molecular weight distribution, type and concentration of nucleating agent, and its concentration, presence of plasticizers or presence of regrind. Therefore, it is a sensitive test and can be used to show the difference between various batches of material, which may show little difference under a conventional heating experiment. Batches with different crystallization behavior will lead to variation in the quality of the final processed product. For polymer resin manufacture, it can be used for quality assurance purposes, the optimization of resin formula or the evaluation of a competitor's resin.

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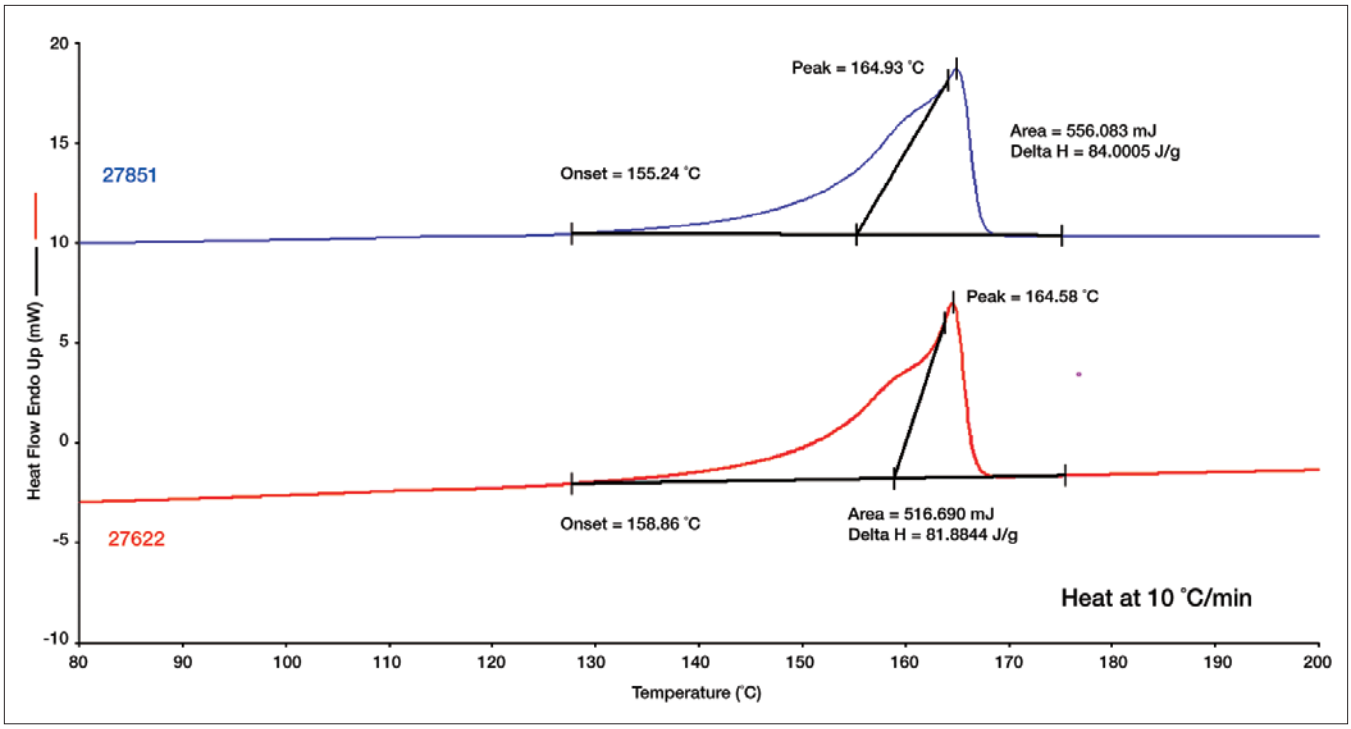

Figure 1. Conventional heating scan on batch A and B.

Power compensation DSC has been preferred for this application. A true isothermal crystallization experiment can only be performed on power compensation DSC due to its null principle and power compensation scheme. In heat flux DSC, the sample temperature can actually increase during the isothermal crystallization experiment because of the exothermal reaction of crystallization. Fast cooling is also very critical for the accurate determination of kinetic data. Fast cooling is critical for the accurate determination of kinetic data and in this case, a high rate of cooling is needed to prevent the resin from crystallization before it reaches the isothermal temperature. This is especially true for some polymers with high rates of crystallization. Conventional heat flux DSC has a big furnace and cannot achieve the fast cooling rate needed for an isothermal crystallization experiment. On the contrary, power compensation DSC has a much smaller furnace and can achieve a controlled cooling rate up to 500 °C/min. So, improved isothermal crystallization data can be obtained from power compensation DSC.

The Challenge

In this case, a polypropylene resin manufacturer had made two batches of product resin. They were suspected to be of different quality. Conventional heating experiments were conducted, but failed to show any difference. The isothermal crystallization test was tried and was able to show the difference clearly between the two batches.

The Result

The variation of crystallization behavior of resin will affect the final product's crystallinity after injection molding, and thus the physical properties of the molded part. It is important to make sure the polymer crystallizes reproducible and that any variations in the crystallization are detected. Conventional heating and cooling experiments were first performed on these two batches and the results are shown in Figures 1 and 2.

The heating was done at typical 10 °C/min and cooling at 20 °C/min. The melting profiles upon heating look similar with some difference in melting enthalpy. The crystallization peaks during cooling are almost the same. The heating and cooling method was not effective at detecting the difference between batch A and B.

Since the isothermal crystallization test is very sensitive to resin property, it was tried on these two batches. The resin was first heated above its melting temperature to 220 °C, and held for 2 minutes to melt any crystalline structure. Next, it was rapidly cooled to the isothermal crystallization temperature, which was 140 °C in this case. The sample was left to sit at 140 °C for 5 minutes to complete the crystallization process.

The successful isothermal crystallization experiment depends on the quick cooling to the isothermal temperature so that no significant crystallization will happen before it reaches the isothermal temperature. Power compensation DSC is

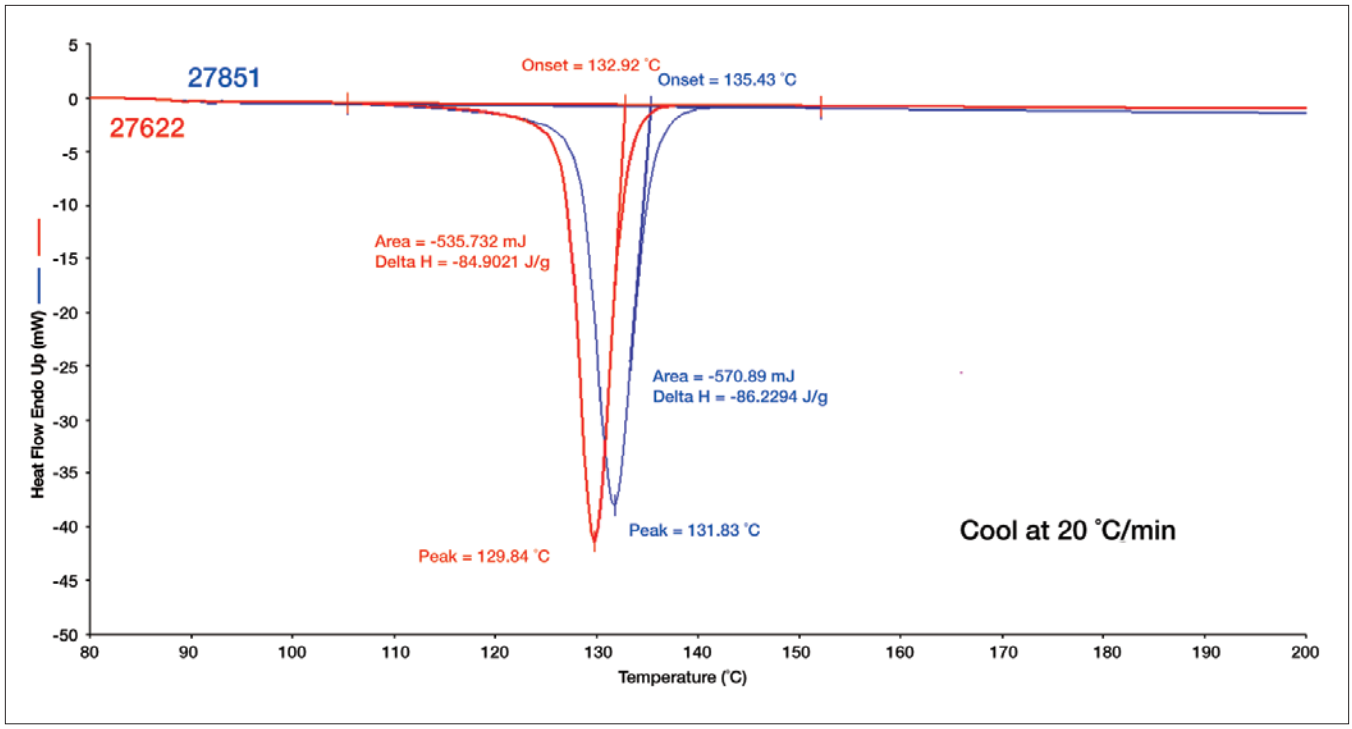

Figure 2. Conventional cooling scan on batch A and B.

known for the fastest cooling rate in DSC. In this case, 200 °C/min cooling rate was used and the sample temperature vs. time was plotted in Figure 3. As shown in Figure 3, the controlled cooling was realized over this temperature range. Note, in this experiment setup, only a water circulator was used as a cooling accessory with helium purge. Intracooler or liquid nitrogen cooling accessory will allow even faster cooling rate. The PerkinElmer® DSC 8000 can achieve a cooling rate up to 500 °C/min.

The isothermal crystallization experiment results for batches A and B are shown in Figure 4. For batch A resin, the crystallization at 140 °C finished at around 3 minutes and the peak position is at 1.333 minutes. However, for batch B, the crystallization completed within 2 minutes and crystallization peak appeared at 0.867 minute. The difference is clearly demonstrated. Batch B crystallizes more quickly than batch A at this temperature. For resin quality assurance, the source of variance needs to be identified.

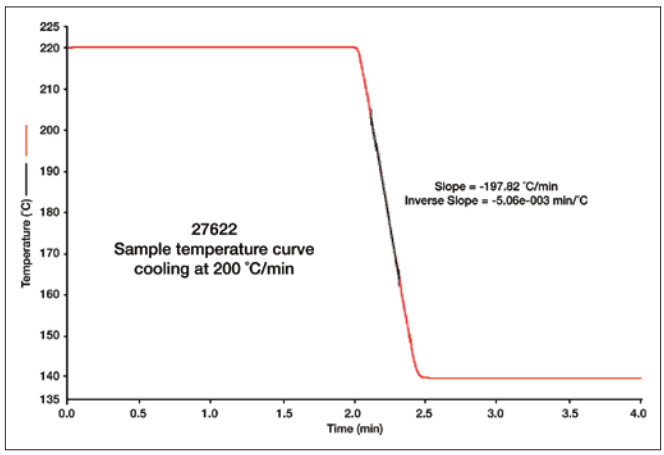

Figure 3. Sample temperature vs. time profile of the isothermal crystallization experiment.

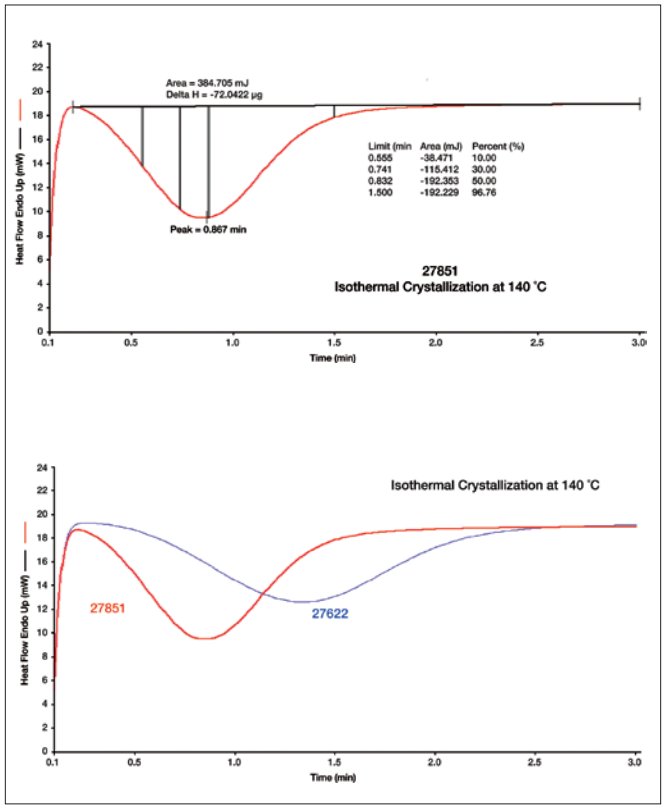

Figure 4. Overlay of the isothermal crystallization results of batch A and B.

Summary

The isothermal crystallization test has been shown to be able to detect the difference between two batches of polypropylene resin, which is otherwise not seen by conventional heating and cooling experiment. This information is useful to resin manufacturers for quality assurance purposes. The DSC 8000 with power compensation is the ideal tool for isothermal crystallization experiment. The fast cooling rate and true isothermal operation give superior results.

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