SII NanoTechnology Inc.

DSC AS PROBLEM-SOLVING TOOL: ISOTHERMAL CRYSTALLIZATION OF POLYETHYLENE

Problem

A manager of an analytical laboratory has a need to perform accurate and reproducible isothermal crystallization measurements of the company's high density polyethylene resin and also to perform evaluations of competitive resins. The isothermal crystallization data is important as it will be utilized for quality assurance purposes and to optimize the formulation of the polyethylene resins. The technique and the instrument must be easy to use as numerous operators will be assigned to characterize the resins.

Solution

Differential scanning calorimetry (DSC) provides an easy means of determining the crystallization behaviors of polymers, including polyethylene. This is done by melting the polymer and holding it under isothermal conditions to fully melt out the existing crystalline structure. The molten polymer is then rapidly cooled to an isothermal temperature which is between the sample's glass transition event (Tg) and its melting point (Tm). The crystallization of the polymer is monitored as a function of time under isothermal conditions. An exothermic peak will be obtained and the peak maximum represents the resin's maximum rate of crystallization. The time to reach the maximum is a very sensitive characterization parameter.

The time to reach the DSC peak maximum is strongly dependent upon the isothermal test temperature. There are two competing factors which influence the crystallization time:

- resin viscosity
- increasing time to form nucleating sites as temperature increases

As the temperature decreases, the molten resin viscosity increases which makes it increasingly more difficult for the resin to undergo crystallization. On the other hand, as the isothermal temperature increases and approaches the melting temperature, it becomes more difficult for nucleating sites to be established and this lengthens the time for the resin to crystallize. At some temperature below the melting temperature, the polymer will achieve its maximum possible rate of crystallization based on the two competing factors of resin viscosity and the establishment of nucleating sites. It is best to conduct the DSC isothermal crystallization test at a temperature significantly higher than this temperature so that the polymer does not crystallize too rapidly.

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The isothermal crystallization test provides information on the following properties of polymers:

- type of nucleating agent(s)
- concentration of nucleating agent(s)
- average molecular weight
- molecular weight distribution
- presence of plasticizers

The Seiko Instruments EXSTAR DSC6200 and DSC6200R (robotic) combine both ease of use and a high level of performance, in terms of sensitivity and reproducibility, which makes them suitable for quality assurance purposes as well as for competitive product evaluations and research purposes.

In this study, the isothermal crystallization behavior of a high density polyethylene resin was characterized. Approximately 7 mg of sample was placed into a crimped aluminum pan. The Seiko DSC was operated with the following PID furnace settings to permit rapid thermal equilibration of the DSC cell: P = 40, I = 20 and D = 0.50.

The following thermal program was utilized to melt the polyethylene sample directly in the DSC and the quickly cool to the desired isothermal target temperature:

- heat from 25 to 160°C at 20°C/min
- hold at 160°C for 5 minutes
- cool from 160°C to target temperature at 50°C/min
- hold at isothermal temperature for 60 minutes

The high density polyethylene sample was held at isothermal crystallization temperatures of 124.5, 125.0, 125.5, 126.0, 126.5, and 127.0°C. These temperatures were chosen since well-defined crystallization exotherms can be obtained.

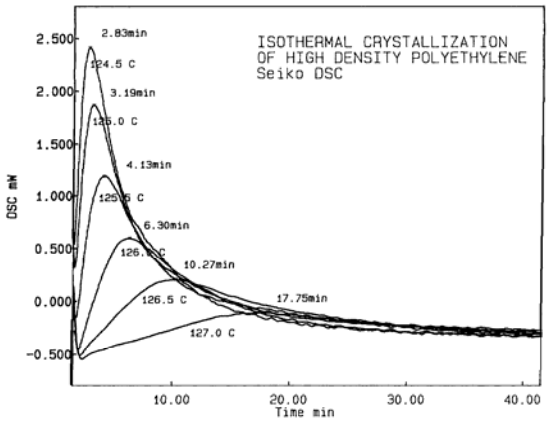

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Figure 1

Displayed in Figure 1 are the isothermal crystallization results obtained on the 7.8 mg sample of high density polyethylene at the various temperatures. At the lower test temperature of 124.5°C, the resin reaches its peak maximum in the shortest amount of time (2.83 minutes), while at the highest test temperature of 127.0°C, it takes 17.8 minutes for the resin to achieve the maximum rate of crystallization. These curves reflect the effects of temperature upon the time required to establish nucleating sites.

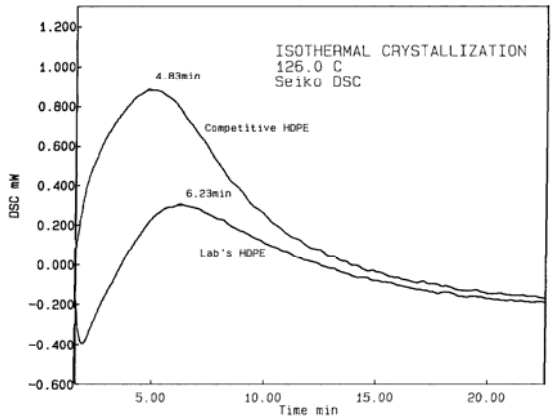

Figure 2

A competitive high density polyethylene sample was characterized using the isothermal crystallization test at a temperature of 126.0°C. The DSC results obtained on the two polyethylene resins are displayed in Figure 2. The data reveals that the competitive sample has a greater propensity to undergo crystallization since its time to peak maximum (4.83 minutes) is significantly shorter than the laboratory's polyethylene material (6.23 minutes). The data indicates that the two end products produced from these two HDPE resins could be different in terms of their end-use characteristics since the type of level of crystallinity that develops during processing will be affected.

Summary

The DSC isothermal crystallization test provides a sensitive means of characterizing the properties of semi-crystalline polymers, such as polyethylene, PET, nylon, polypropylene, etc. The Seiko EXSTAR DSC6200 provides a highly stable isothermal temperature test environment which yields accurate and reproducible data on the crystallization behaviors of the resins. The isothermal crystallization results can furnish valuable information on

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the end-use performance of resins such as optical clarity, barrier resistance, stiffness, long term stability, and propensity to undergo creep.

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