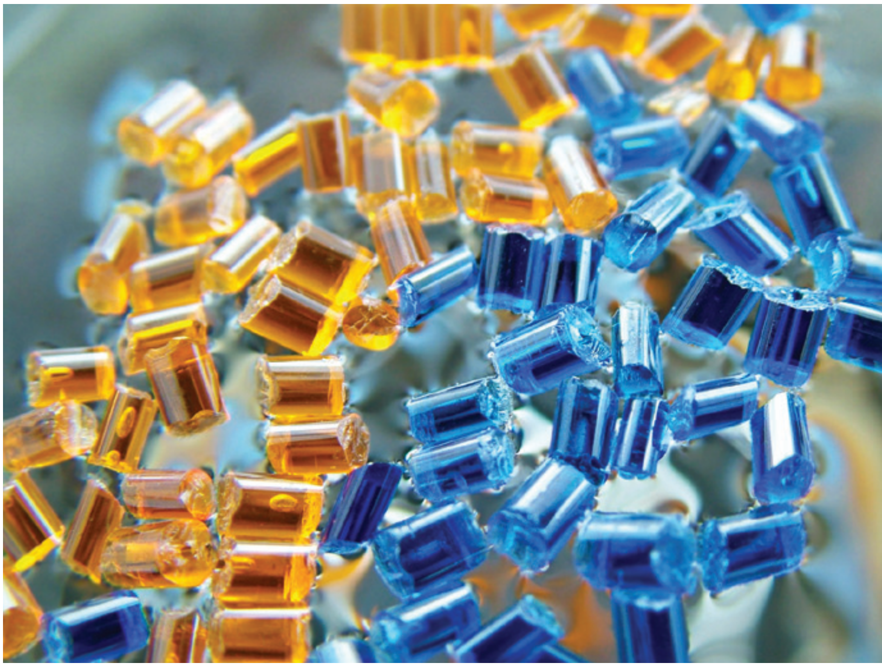

APPLICATION NOTE

Thermal Analysis

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Detecting Weak Glass Transition (Tg) in Polymers by HyperDSC

Introduction

Many polymers are semi-crystalline material. The percentage of crystallinity depends on many factors including chemical structure, interaction between polymer chains and processing conditions. When polymers get heated, the amorphous part will change from the glassy state to the rubbery state at the glass transition temperature (Tg). Since only the amorphous part contributes to the glass transition, for highly crystalline polymers, the glass transition (Tg) can be very weak. One typical example is High Density Polyethylene (HDPE), a highly crystalline engineering thermoplastic. It is typically used in applications demanding a material that is chemically inert, does not absorb moisture, can be utilized over a wide range of temperature, and exhibits a high tensile modulus.

The amorphous region in HDPE is generally accepted to account for about 5% or less of the sample. Historically, the glass transition for a highly crystalline material like HDPE could not be determined by DSC since the step change in the heat flow signal as the material is heated through its glass transition cannot be observed at traditional scanning rates.

For the Better

The advance of fast scanning DSC technology offers the opportunity to detect weak Tg in such cases. The step change in heat flow signal during glass transition is proportional to the heating rate. The sensitivity is increased by a fast scanning rate. HyperDSC® can be performed on a double-furnace DSC, such as the PerkinElmer® DSC 8500. In contrast to most single-furnace DSCs, the double-furnace DSC uses ultra lightweight furnaces with very low thermal inertia and can achieve the fastest possible DSC response time. It allows very fast controlled linear heating and cooling scanning (up to 750 ˚C/min). In this study, an HDPE sample is used to demonstrate the increased sensitivity and ability to detect weak glass transitions with HyperDSC.

Result

The DSC 8500 with liquid nitrogen cooling was used for this study. While the data generated for this work was performed utilizing HyperDSC, the DSC 8000 with scanning rates up to 300 ˚C/min can also be used for traditional as well as StepScan DSC studies, which is one of the modulated temperature DSC technologies.

The data in Figure 1 indicates the Tg of the HDPE sample to be approximately -111 ˚C. For comparison, the same sample was run under conventional DSC conditions at 10 ˚C/min. As indicated in Figure 1, there is no detectable transition in this temperature range even when zooming into the curve with conventional 10 ˚C/min scanning rate. This result clearly demonstrates the increased detection sensitivity with HyperDSC.

Also worth noting is that the experiment started at -150 ˚C, just 40 ˚C below the expected glass transition at 100 ˚C/min. This is only possible with a double-furnace DSC because the ultra light double-furnace enables very fast response times. It takes less than 10 seconds for the DSC curve to stabilize and a valid measurement to be made. Therefore

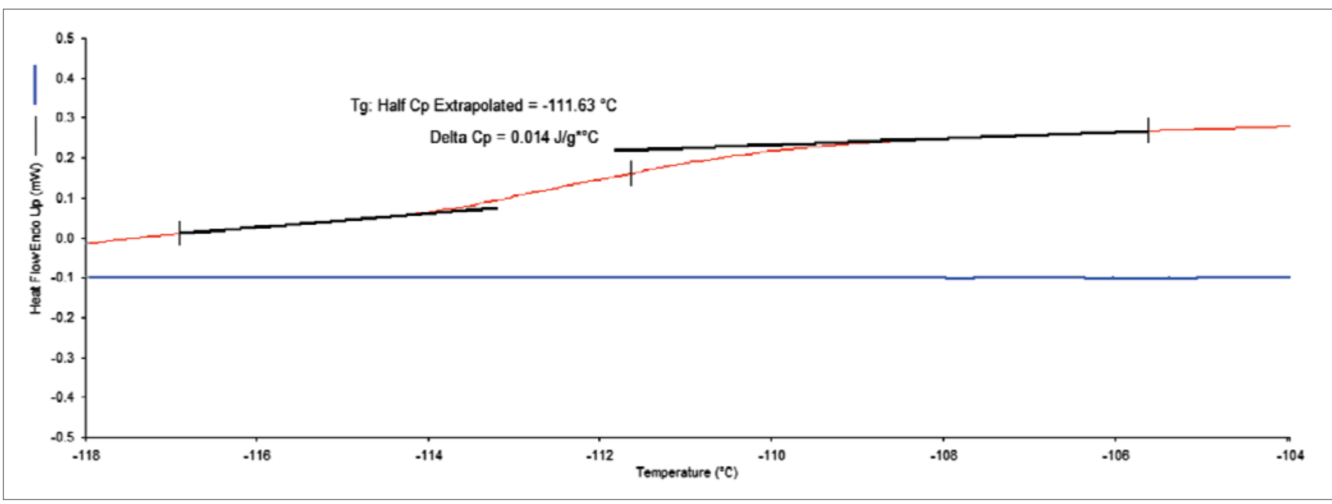

Figure 1. HDPE heating at 100 ˚C/min (red) and 10 ˚C/min (blue).

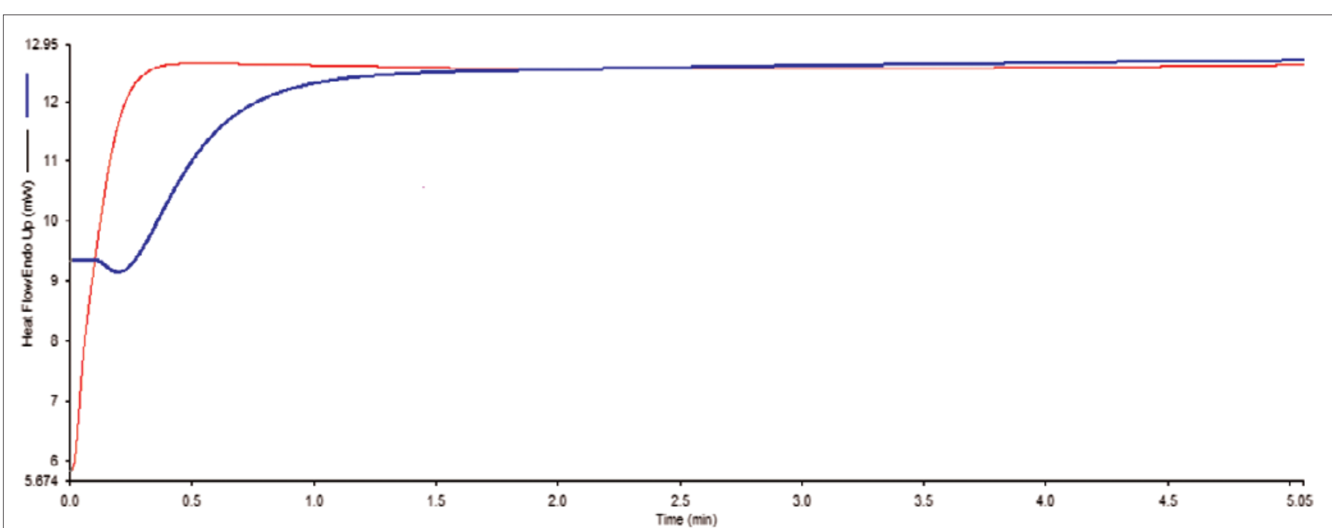

Figure 2. Example of startup transition of double-furnace DSC (red) and single-furnace heat flux DSC (blue) with the same experimental condition.

the startup transition is just 15 ˚C. So the 40 ˚C temperature range below the expected transition is already enough for this experiment. This fast response is not achievable with a heat flux DSC because of its bigger, heavier furnace. As illustrated in Figure 2, the single-furnace heat flux DSC has a much longer startup transition than the double-furnace power compensation DSC. In the case of HDPE experiment, if the startup transition for heat flux DSC takes 1 min, then the experiment will have to start at least 100 ˚C below the expected glass transition at a heating rate of 100 ˚C/min. That means that the experiment needs to be started at as low as -211 ˚C which is not achievable on liquid nitrogen cooling accessory.

Summary

Since the ordinate axis in DSC data is expressed in units of power, or energy per unit time, the fast scanning rate increases the signal and sensitivity of a DSC measurement. HyperDSC, which employs heating rates of approximately an order of magnitude faster than traditional DSC, makes it possible to detect some challenging weak glass transitions, such as that of HDPE. The very quick response of the double-furnace power compensation DSC also makes the measurement feasible with the liquid nitrogen cooling accessory.

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