

Isothermal crystallization of polypropylene by differential scanning calorimetry

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Isothermal crystallization (IC) is a tool for studying the two-step kinetic processes associated with polymer crystallization from the melt. The first of these processes is the slow formation of nucleation (or seed) sites, and the second is the fast polymer crystallization at those sites. Isothermal crystallization values are sensitive to very minor changes in polymer morphology, additive packages, and process temperatures. For this reason, isothermal crystallization measurements are used in quality control to follow lot-to-lot variations in product and in research to predict product performance or process improvements.

Isothermal crystallization experiments involve conditioning the test specimen, in a differential scanning calorimeter (DSC), at a

ment of test temperature equilibrium (without under- or overshoot), 3) the ability to perform crystallization kinetic calculations, and 4) continuous measurement of sample temperature. Many DSC systems provide only some of the necessary capabilities.

Rapid cooling

Contrary to popular belief, high cooling rates of several hundred Celsius degrees per minute are not required for isothermal crystallization experiments. In the past, DSCs based on the power compensation design were preferred for isothermal crystallization experiments due to their high rate of cooling. However, the high cooling rates promoted by equipment manufacturers are seldom achievable in the temperature



Figure 1 Q1000 DSC.

close coupling may carry the heavy price of large temperature gradients in the sample and drift or curvature in the baseline.

The Q1000 DSC system (*Figure 1*) equipped with an LNCS cooling system (TA Instruments, Inc., New Castle, DE) was used in this study. The system has very high cooling rates of better than 140 °C/min due to the close coupling between the DSC sensor and the cryogenic temperature of the cooling device,¹ making it well suited for isothermal crystallization experiments.

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temperature about 30 °C above the melting temperature, then cooling the specimen to a temperature below the melting temperature. There, the crystallization exotherm is measured under isothermal conditions. Kinetic treatment of a series of such tests, obtained at slightly different temperatures, leads to the desired kinetic results.

There are four characteristics of a successful isothermal crystallization experiment: 1) fast cooling from the annealing to the test temperature, 2) rapid achieve-

range of most isothermal crystallization experiments. Typically, isothermal crystallization experiments are optimally carried out at cooling rates of about 80 °C/min.

To achieve a high rate of cooling, the temperature difference between the DSC cell and the temperature sink must be as large as possible, necessitating the use of liquid nitrogen as the coolant. In addition, this cooling source must be closely coupled to the DSC cell so that energy can flow quickly from the sample to the sink. Such

Rapid temperature equilibrium

Rapid equilibrium at the test temperature is much more important to the quality of the isothermal crystallization data than is rapid cooling. Precise temperature control is achieved in differential scanning calorimeters through the use of proportional band feedback heater control systems. Prop band controllers use a combination of proportion band, integral, and derivative modes to achieve the

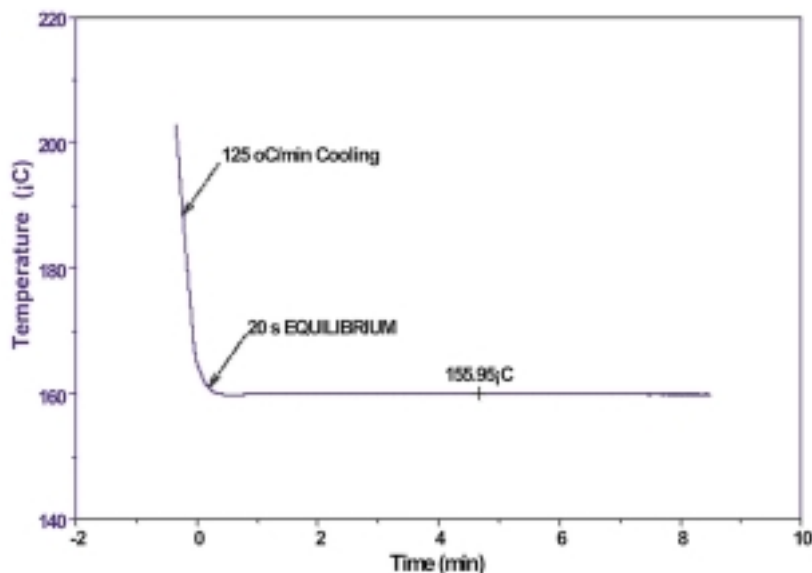


Figure 2 Rapid temperature stability with a tuned controller.

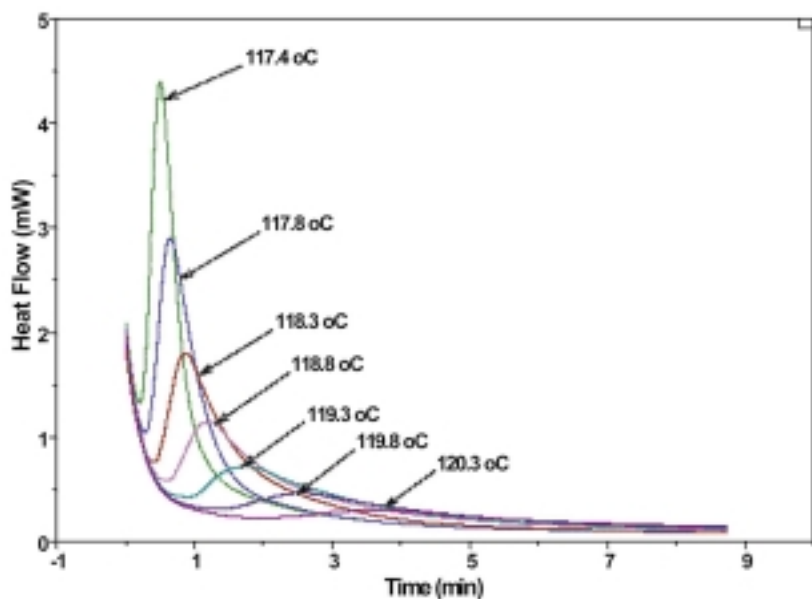


Figure 3 Isothermal crystallization of polypropylene.

desired control. The optimum PID values depend on a wide variety of experimental conditions, including the responsiveness of the system, the presence of any time lags, the load on the system, and the desired rate of change.

Historically, DSCs were designed using a single set of PID conditions optimized for a linear temperature ramp at 10 to 20 °C/min. As it turns

out, the PID settings required for a high cooling rate and those for tightly controlled isothermal temperature conditions are quite different from each other. They are different from those required for a linear ramp and are mutually exclusive. These two extremes of temperature control (rapid cooling and tight temperature control) may not be satisfied with the

same set of PID values. Inappropriate PID values cause the sample temperature to over- or undershoot the programmed test temperature during the transition from rapid cooling to isothermal temperature conditions, a highly undesirable situation.

To overcome this temperature control challenge, modern differential scanning calorimeters, such as the Q series DSCs, have operator-settable PID values as a method segment. The operator is thus able to tune the controller for each method segment, whether it is a linear ramp, ballistic temperature change, or isotherm temperature operation. For example, Figure 2 shows the temperature profile for a system tuned for isothermal crystallization experiments. Here, a ballistic cooling profile with a rate of 125 °C/min achieves the isotherm test temperature within a 20-sec period with no over- or undershoot.

Polypropylene example

There is no more difficult sample upon which to perform isothermal crystallization than polypropylene (PP). Because of its very fast crystallization and very high activation energy, PP may serve as a performance standard to explore isothermal crystallization capabilities. Success achieved with PP ensures success for virtually all other polymers to be tested. Figure 3 shows a family of isothermal crystallization thermal curves for a polypropylene reference material in which the same test specimen is evaluated at a series of closely spaced temperature intervals.

For qualitative IC comparisons, the elapsed time is measured from the establishment of the isothermal test temperature to the peak of the crystallization exotherm. Figure 3 shows that the shape of the crystallization exotherm for PP ranges from a high, narrow peak with an elapsed time of less than 1 min to a low, broad peak of more than 4 min, all within a few

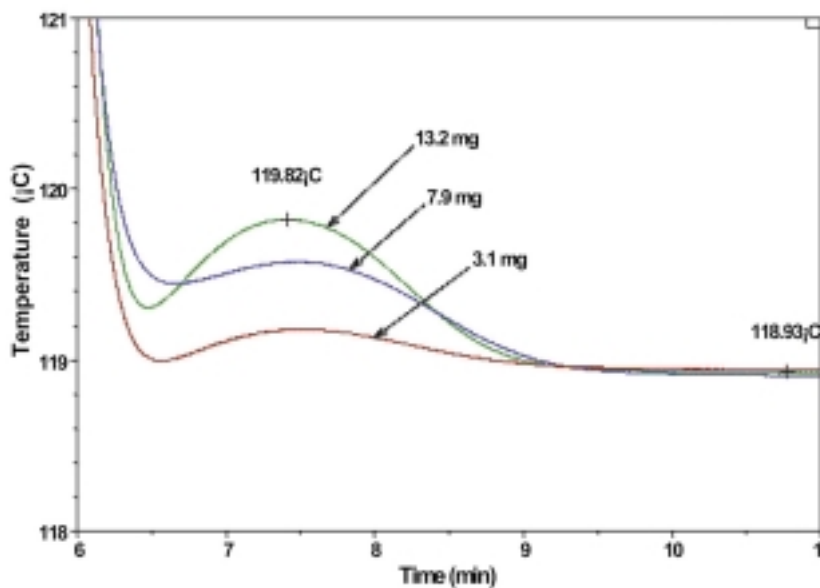


Figure 4 Self-heating of polypropylene.

Celsius degrees. This rapid change of elapsed time with temperature is the reason IC experiments of PP are so difficult.

Kinetics

For a more thorough understanding of the nucleation and crystallization processes, a detailed look at the kinetics of the respective reactions is used. Traditional n th order kinetic models do not apply to two-step processes such as crystallization. For this case, a more robust kinetic model is needed such as that of Sestak and Berggren^{2,3} formalized in ASTM Standard E2070.⁴ The Sestak-Berggren equation is a more general form of the traditional form of the kinetic equation and may be related to the Avrami equation.⁵ The Sestak-Berggren equation has the form:

$$d\alpha/dt = Z \alpha^m (1 - \alpha)^n \exp [E/RT]$$

where E is the activation energy; R is the gas constant ($= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is the absolute temperature; α is the fraction reacted; $d\alpha/dt$ is the rate of the reaction; Z is the Arrhenius preexponential factor; and m and n are the reaction or-

ders, respectively, for the induction and crystallization reactions. In practice, a series of partial area fractions across the isothermal crystallization peak are taken to evaluate the terms of this equation; α is obtained by the ratio of the enthalpy of crystallization up to a particular time, divided by the total enthalpy of reaction.

Using the Sestak-Berggren approach on the PP sample, values were obtained for E of $-1090 \pm 140 \text{ kJ mol}^{-1}$, $\log Z(\text{min}) = -144 \pm 19$, $m = 0.62 \pm 0.15$, and $n = 0.94 \pm 0.29$. As a check on these values, a value of $119.4 \text{ }^\circ\text{C}$ is achieved with a $120 \text{ }^\circ\text{C}/2\text{-min}$ isothermal crystallization reference material.

Measurement of sample temperature

For productivity reasons, one is always interested in obtaining data using conditions that lead to short experiment times. One challenge to short isothermal crystallization periods is the self-heating that takes place within the sample with isothermal crystallization times of less than 2 min. In such experiments, the energy associated with the crystallization process is taken up by the

sample's specific heat, leading to self-heating. This effect can be seen in Figure 4, where the specimen temperature is recorded for a series of polypropylene samples of varying size. As the test specimen size gets bigger, the amount of self-heating increases. To achieve isothermal experimental conditions, the heat flow must remain under 8 mW, which is equivalent to $0.3 \text{ }^\circ\text{C}$.⁶ Figure 4 shows that test specimens of as little as 4 mg exceed this isothermal sample temperature rise requirement. This self-heating issue may be addressed by using smaller sample sizes, by going to higher temperatures, or by using the measured temperature at the peak of the exotherm of the kinetic determinations. Generally speaking, samples with isothermal crystallization times of less than about 1.5 min are particularly vulnerable to this self-heat effect. For larger test specimens and short isothermal crystallization times, this challenge is exacerbated. Clearly, measurement of the specimen's temperature is an important part of any isothermal crystallization experiment.

References

1. Waguespack LE, Blaine RL. Proc 29th Conf N Amer Therm Anal Soc 2001:722-7.
2. Sestak J, Berggren G. Thermochim Acta 1971; 3:1-12.
3. Gorbachev VM. J Therm Anal 1980; 18:193-7.
4. Kinetic parameters by differential scanning calorimetry using isothermal methods. West Conshohocken, PA: American Society for Testing and Materials, 2000.
5. Foreman JA, Blaine RL. Proc Ann Tech Conf Soc Plast Eng 1995; 2:2409-12.
6. E698. Arrhenius kinetic constants for thermally unstable materials. West Conshohocken, PA: American Society for Testing and Materials, 1999.

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