Improving and Speeding up the Characterization of Substances, Materials, and Products: Benefits and Potentials of High-Speed DSC

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High-speed calorimetry, and specifically high-speed differential scanning calorimetry (DSC), has received a great deal of attention in recent years. Commercially, most calorimeters are able to perform controlled, constant heating experiments at rates higher than a standard rate, typically 10 °C/min. Currently only one type of calorimeter is available that is capable of measuring at controlled, constant, and appreciable high heating and cooling rates: the power-compensation DSC (PerkinElmer, Shelton, CT, U.S.A.). Due to its small furnace, strictly controlled cooling at, e.g., 300 °C/min and heating up to 500 °C/min are possible, depending on the temperature range of the measurements and the cooling accessory used.

The reason high-speed calorimetry is becoming increasingly popular is that 1) in practice, some processes occur at much higher rates than realizable using standard DSC; and 2) most materials and substances, including polymers and pharmaceuticals, are in metastable states. Thermal history—specifically cooling and heating rates—and sample/product treatment can change their behavior drastically, including end properties. Such phenomena, as related to metastability, are well known to thermal analysts; daily they encounter supercooling, amorphization, cold crystallization, recrystallization, annealing, etc.

Researchers need the capability to change the measurement conditions in order to influence and study the metastability present. This article demonstrates examples of metastability and the use of high-speed DSC employing its commercial versions: the Pyris 1 and Diamond DSCs with the HyperDSC™ technique (PerkinElmer).

Results and discussion

Because it is important in industry to be able to drastically vary cooling and heating rates, a project was initiated in the late 1990s at DSM Research (Geleen, The Netherlands) to address this issue. It was realized that increasing rates demand decreasing sizes of relevant components of the measuring equipment—especially the measuring cell—in order to decrease the thermal conductivity paths. Decreasing the sample mass to values between 1 µg and 1 mg is necessary also. Therefore, a commercially available DSC was chosen that offered the advantage of the power compensation design, providing direct heat flow rate measurements for optimum results (see Figure 1). Of particular significance are the influences of the heating and cooling rate and sample mass on temperature calibration for high-speed DSC and specifically calibration in cooling. This approach was called High Performance DSC (HPer DSC) and was later commercialized by PerkinElmer and trademarked with HyperDSC.

Figure 1 also depicts the ultrafast chip calorimeters, which achieve extremely high temperature rates (e.g., rates of 600,000 °C/min are possible), especially in heating. However, they are not commercially available, are not user-friendly, and are time consuming to use. They are well suited for scientific research purposes but are not usable for daily practice in industry.
Linking experiment with practice and processing

As an example of an industry-relevant experiment, in Figure 2 the drastic reduction in the crystallization temperature at increasing cooling rates is shown for polypropylene. In addition, the areas of the peaks are decreasing, meaning that the crystallinity is lowered as well.

Using the various cooling rates available, some rates that occur during processing can be mimicked (see Figure 3 for polyamide 6). The cooling rate at the skin of a mold is too high to mimic using HyperDSC; therefore, a chip calorimeter must be used. However, the exact information on the actual cooling rates as a function of the depth (from skin to core) of a part processed is still missing, because calculation by modeling requires the right experiments, like the ones shown here and in Refs. 1, 2, and 6.

In industry, this type of information is critical because of the high expense of the processing equipment used. Thus, in processing, as in the case of injection molding, optimization of the process—and specifically shortening of cycle time—is of major importance. Realistic information is also vital to realizing fast iteration within the “cycle of knowledge” in order to speed up the materials development of new grades and to optimize existing grades.

A striking example was presented in Refs. 1 and 7. At 10 °C/min cooling—as in the case of standard DSC—two peaks were observed for crystallization of a low-density polyethylene/linear low-density polyethylene (LDPE/LLDPE) blend. This would lead to the risk of segregation by crystallization during film blowing, resulting in numerous problems in the film (i.e., optical and mechanical). HyperDSC measurements at 150 °C/min cooling show that it is possible that no problem will occur at all: Only one crystallization peak has been observed. This must still be verified for the even higher cooling rates in the case of film blowing. Most likely, extensive co-crystallization of molecules of different origin takes place at this (controlled) cooling rate. Obviously, without the appropriate equipment, the researcher/thermal analyst could easily steer important and costly developments in the wrong direction.

During heating at 10 °C/min (as in the case of standard DSC) after cooling at high rates, one often faces the problem of extensive reorganization (Figure 4). Two melting peaks are seen instead of one following high cooling rates. Measurements at varying heating rates prove unequivocally that this reorganization originates from recrystallization. Heating at a higher rate of 300 °C/min (Figure 5) totally suppresses recrystallization; in heating at this rate, just one (the low-temperature) melting peak results. Thus, recrystallization is effectively eliminated.

In many instances, the relationship between cooling (such as during injection molding) and heating, and between crystallization and melting, is obscured by reorganization phenomena, especially in the case of polymers and pharmaceuticals. If this happens, the relationship between the melting peak temperatures and morphology information obtained from measurements by, e.g., X-ray transmission electron
microscopy (TEM), and atomic force microscopy (AFM) performed at room temperature is lost. Then, as a consequence, important relationships reported in the literature (such as the Gibbs-Thomson relationship) no longer apply. Therefore, many of the reported studies would need to be redone by applying much higher heating rates to avoid such reorganization.

Quantitative measurements

Fast measurement takes minimal time, and instrumental drift can be negligible. Thus, it is possible to work quantitatively, even at high rates, hence the name High Performance DSC. HPer DSC provides more than high speed. Ref. 1 gives examples in which heat capacity measurements at rates such as 100 °C/min are shown. Recently, an extreme heating experiment was presented on a 0.39-mg high-density polyethylene (HDPE) sample from −175 °C to 200 °C in one run at 150 °C/min: a continuous heat capacity measurement across a tremendously wide temperature range in just a few minutes.

Higher sensitivity; working on minute amounts of material

High rates increase sensitivity but require small samples in order to keep thermal lag acceptable. The ability to obtain quantitative data on small samples is an advantage also, because it facilitates research on minute amounts, which was previously impossible.

How low can a sample mass be? The authors learned that measurements on samples down to 400 ng (see Ref. 2) can be done. One might ask: Is working with a few micrograms still representative of my product? If the material is homogeneous (modern materials are produced more and more pure while contamination during processing continues to decrease), there is no problem. If not, the contaminants, gels, discolored matter, irregular surface parts, etc., can be studied using HyperDSC.

A good example of the use of the low-sample mass capability of HyperDSC is outlined in Figure 6. Removal by evaporation of the eluent used by a size exclusion chromatograph (SEC) provides a way to deposit and spread the remaining polymer sample on a germanium disk as a function of molar mass: It is fractionated according to molar mass. It can then be measured by FTIR to determine the short chain branching content (if present) as a function of molar mass. Removal of fractions from the disk enables measurement by HyperDSC. Since the amount of starting material for SEC (typically 800 µg of polymer) has decreased over the years (20 years ago it was typically 5 mg), HyperDSC is the only technique capable of measuring (de)vitrification, crystallization, melting, etc., in detail on such minute amounts. The technique provides information on the distribution of the short chain branches (SCB) as a function of molar mass on the basis of the crystallization and melting
behavior, which then can be combined with the average content from FTIR.

Recently, the authors were able to apply this method to a heterogeneous, metallocene-based ethylene-1-pentene copolymer. This new type of copolymer crystallizes and melts across extremely wide temperature ranges due to its broad ethylene sequence length distribution; still it can be measured effectively, as is seen for the 10-µg fraction shown in Figure 6. Obviously this can be very useful, for instance, if only a small amount of material is available from polymerization.

Interesting and useful areas of research are possible when only minute amounts of material are available: (sub)microscale synthesis, fractions, explosives, nanostructures, electronics, additives, contaminants, multilayers, coatings, thin films, skin-core problems in areas such as chemicals, materials, products, and forensic studies.

Degradation can be hindered or even avoided by fast heating, in the same way chemical changes during heating can be prevented by simply spending much less time in a critical temperature range. The fast operation of HyperDSC has been proven to enable high-throughput experimentation.

**Conclusion**

Researchers who are willing to explore high-speed calorimetry instrumentation will become accustomed to measuring at different rates. As such, the intention of this paper is not to promote the use of high rates only, but rather to present the option of choosing an optimal rate or spectrum of rates, depending on the sample and on the question posed. This enables mimicking real-life processes; and studying the kinetics of processes of, e.g., polymers and pharmaceuticals, including (hot, cold, re-) crystallization, melting, reorganization, annealing, de(vitrification), and measuring on minute amounts of substances, materials, and products with high sensitivity in a short time. As HPer DSC, commercially available as HyperDSC, is increasingly applied, more and more researchers will learn how to benefit from this exciting development.

**References**

7. www.hyperdsc.com; see also webcast by V. Mathot through this Web site; www.scite.nl.

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