

# Practical aspects of the Flash DSC 1: Sample preparation for measurements of polymers

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**The Flash DSC 1 expands thermal analysis to scanning rates (heating and cooling rates) of several 10 000 K/s (ten thousand Kelvin per second). At such rates, the formation of structure in materials can be investigated in order to gain a better understanding of the behavior of materials in technical processes. A number of practical questions however arise when using the Flash DSC 1.**

## Possible questions

Examples:

- How do you determine the mass of a sample?
- How do you measure the blank curve needed especially for normal and medium scanning rates?
- How do you avoid artifacts that occur at low scanning rates with some materials?
- How do you obtain measurement curves that you can evaluate in the first heating run?

This article proposes various solutions to answer these questions.

## Introduction

Polymers consist of macromolecules with different degrees of branching. The complicated molecular structure influences molecular mobility. As a result, relatively small crystallites form in crystallizable polymers.

The melting point of the crystallites depends on their size. Small crystallites melt at lower temperatures. Furthermore, the materials contain amorphous regions that cannot crystallize.

These polymers are semicrystalline and the structure formed is metastable. This means that structural changes can occur on heating, cooling, or even during isothermal storage.

If a semicrystalline polymer is measured in a conventional DSC instrument, the DSC curves generally exhibit a glass transition whose step height,  $\Delta c_p$ , is proportional to the content of the mobile amorphous regions.

The melting process of the crystallites gives rise to the melting peak. In some materials, an exothermic event known as cold crystallization can occur between the glass transition and the melting peak.

Cold crystallization is a reorganization process in which the degree of crystallinity, that is, the content of crystallites in the material increases.

Reorganization processes often occur in the metastable structures of polymers on heating. The crystallites become more perfect but the degree of crystallinity does not significantly change. Such reorganization processes can hardly be detected by conventional DSC because endothermic processes (destruction of the existing structure) and exothermic processes (the formation of the new structure) take place simultaneously and no significant net exchange of energy occurs.

Processes of this type that occur on heating polymers have been known for a long time. In the 1970s, proposals were made to suppress reorganization processes through the use of sufficiently high heating rates or to study the processes by varying the heating rate [1, 2].

The heating rates of conventional DSC instruments are however not high enough to suppress reorganization processes because the processes that occur in semicrystalline polymers are relatively fast. In references [3, 4], it was shown that heating rates of 400 K/min are too low to prevent reorganization in semicrystalline samples, even for polyethylene

terephthalate (PET), which crystallizes relatively slowly.

A consequence of this is that the melting peak in the DSC curve does not represent the original state of the sample. In reality, it shows the melting process of the crystallites formed through reorganization. The original crystallites frequently melt at appreciably lower temperatures [5].

To measure their melting process, the heating rate has to be increased by several orders of magnitude. The introduction of the Flash DSC 1 has made a commercial DSC available that can be used at heating rates of several tens of thousand Kelvin per second.

The Flash DSC 1 can also perform measurements at relatively low scanning rates. This means that the scanning rates of conventional DSC instruments and the Flash DSC 1 overlap, which makes it possible to directly compare the measurement results.

The Flash DSC 1 is a DSC that uses a chip sensor (UFS 1) based on MEMS technology [6]. The sensor consists of two segments, one for the sample and the other for the reference. Each segment consists of a thin membrane on which the active zone, the actual DSC furnace with the sensors, is located. The active zone of the UHF 1 sensor has a diameter of 0.5 mm.

The Flash DSC 1 is equipped with a microscope to facilitate reliable sample handling. Positioning the sample on the sensor is carried out using a fine brush hair with a naturally grown tip.

Flash DSC 1 measurements allow you to address the following issues:

- Investigation of reorganization and formation of structure on heating.
- Determination of the behavior of the original sample by suppressing reorganization on heating.
- Measurement of crystallization kinetics at a wide range of cooling rates.
- Measurement of isothermal crystallization after cooling from the melt, that is, with a high degree of supercooling.
- Influence of additives on crystallization behavior with a high degree of supercooling.
- Simulation of technical cooling processes at the corresponding cooling rate.

Several questions and problems however arise when using the Flash DSC 1. The topics involved will be discussed in this article:

- What is the optimum sample size for the Flash DSC 1?
- How can you determine the sample mass?
- How can you compare curves measured at very different scanning rates?
- Can you evaluate the first heating run to analyze the original sample?

### Proposal for the classification of DSC scanning rates

The combination of a conventional DSC 1 and a Flash DSC 1 allows scanning rates to be used that cover a range of about seven decades. This range is very helpful for investigating the phase behavior of metastable materials.

Terms such as high heating rates or ultra-high heating rates are often used when classifying particular technical specifications of DSC instruments. Generally, these terms refer to the performance of conventional DSC instrumentation and are used to describe the technical possibilities of an instrument.

We would like to propose a classification of scanning rates here that is based on application-technological and physical factors. The limits given should be regarded as approximate values. The de-

tails on mass refer to the typical size of an organic sample and give a rough idea of the sample mass.

#### Low scanning rates

Less than 0.6 K/min (0.01 K/s). The sample mass is greater than 20 mg.

#### Normal scanning rates

0.6 K/min to 60 K/min (0.01 K/s to 1 K/s). These are heating and cooling rates that can easily be used with a conventional DSC instrument. The typical sample mass is between 20 mg and 1 mg for conventional DSC, and between 1 µg and 200 ng for the Flash DSC 1.

#### Medium scanning rates

60 K/min to 1800 K/min (1 K/s to 30 K/s). At these heating and cooling rates, samples can still be measured in crucibles. The typical sample mass is between 1 and 0.1 mg for conventional DSC, and between 500 ng and 100 ng for the Flash DSC 1.

#### High scanning rates

30 K/s to 1000 K/s: These are scanning rates that occur in many technical processes. Samples can no longer be contained in crucibles because the additional heat transfer makes it impossible to achieve the temperature change defined for the sample. The optimum sample mass in the Flash DSC 1 is between 300 ng and 30 ng.

#### Very high scanning rates

1000 K/s to 50 000 K/s. Up to these scanning rates, samples can be measured in which the thermal behavior is still determined by the volume of the sample. The influence of the surface can often be neglected. The optimum sample size is about 20 ng.

#### Ultra-high scanning rates

Faster than 50 000 K/s. To achieve these scanning rates, the samples used are often so small that their thermal behavior is largely determined by their surface. The sample mass is about 10 ng or less.

If we apply this nomenclature, the Flash DSC 1 with the UFS 1 sensor is a DSC in-

strument for medium to very high scanning rates.

## Sample preparation and curve processing

### Typical sample size

To measure a polymer sample at high and very high scanning rates, the thermal contact between the sample and the sensor must be good and the mass of the sample sufficiently small. The samples used are typically 10 µm thick. They are prepared by cutting thin films from small granules using a simple microtome with razor blades. These films are placed on a glass microscope slide, which is then placed over the sensor.

Samples are cut directly to the required size on the glass slide using a sharp knife and then transferred and positioned on the sensor by means of a hair. This operation is carried out using the microscope mounted on the Flash DSC 1.

The typical sample mass is between 5 ng and several micrograms. Small samples should be used (typically less than 100 ng) at heating and cooling rates above 1000 K/s. In contrast, at relatively low rates (less than 20 K/s) samples of at least several hundred nanograms are advantageous.

The samples are normally first melted on the sensor before the actual measurement in order to obtain good thermal contact with the sensor. The curve from the first heating run cannot be used because the thermal resistance between the sample and the sensor changes markedly.

The procedure used for samples where the first heating run is of interest is described later on.

### Estimating the sample mass

The mass of a sample for the Flash DSC 1 cannot be measured using a laboratory balance. A relatively simple method that is sufficiently accurate to estimate the mass is to use a thermal event, for example melting or the glass transition.

### Estimating the sample mass from the melting peak

A DSC sample of several milligrams is cooled from the melt in a conventional DSC instrument so that the sample crystallizes to a sufficient extent.

In the following heating run, for example at 20 K/min, no peaks due to cold crystallization must occur. The specific enthalpy of melting,  $\Delta h$ , in units of J/g is then determined from the melting peak of the DSC curve.

In the Flash DSC 1, a typical sample is cooled from the melt at the same cooling rate as in the conventional DSC instrument and then heated at a heating rate typical for the instrument (e.g. 100 K/s). The enthalpy of melting,  $\Delta H_{\text{FDSC}}$ , in joules is determined from the melting peak. The sample mass is obtained from the equation

$$m = \frac{\Delta H_{\text{FDSC}}}{\Delta h} \quad (1)$$

If the sample also crystallizes at higher cooling rates, the procedure can be simplified by cooling the sample in the Flash DSC 1 at higher rates (e.g. 100 K/s). The material must however crystallize sufficiently so that it does not undergo further crystallization on subsequent heating.

Heating rates suitable for the Flash DSC 1 (e.g. 100 K/s) are used. The specific enthalpy of melting is then determined from the measurement curve. Subsequent Flash DSC 1 samples then only require a comparison of the enthalpies of melting after corresponding cooling in order to estimate the sample mass.

### Estimating the sample mass from the glass transition

If the material can be transformed to an amorphous state, the step height of the specific heat capacity at the glass transition,  $\Delta c_p$ , can be used to estimate the sample mass. An amorphous sample is first measured in a conventional DSC instrument and  $\Delta c_p$  determined.

In the Flash DSC 1 measurement, a value of 1 ng is entered for the mass of the

amorphous sample obtained after cooling it sufficiently rapidly from the melt.

The evaluation of the glass transition yields an apparent specific heat capacity change of  $\Delta c_{p,a}$ . The sample mass is obtained from the equation

$$m = \frac{\Delta c_{p,a}}{\Delta c_p} 1 \text{ ng} \quad (2)$$

If an amorphous sample cannot be prepared for the conventional DSC measurement, data from the ATHAS data bank [7] can be used for  $\Delta c_p$ .

For many materials, both methods can be used and the results compared.

### Drift correction

To compare DSC curves measured at different heating rates, it is advantageous to normalize the measurement curves with respect to the heating rate. Another possibility is to determine the specific heat capacity.

At scanning rates above about 1000 K/s, one can obtain acceptable specific heat capacity curves directly from the measured heat flow curves. At lower rates, significant errors occur, which increase with decreasing scanning rates. This error is due to instrument drift.

By drift, we mean that part of the measured heat flow that is not caused by the change in enthalpy of the sample. Drift correction is therefore advantageous under the measurement conditions described.

The drift of a conventional DSC instrument is determined mainly by the DSC furnace with lid, the sensor, and the crucible. The influence of the sample can be practically neglected because of its relatively low mass. That is why an empty crucible is measured for correction instead of a sample. The measurement curve obtained is called the blank curve and is subtracted from the sample measurement curve.

In the Flash DSC 1, the heat capacity of the "furnace" on the sensor chip is not

significantly greater than that of the sample. The drift is therefore mainly determined by the sample itself.

This means that the blank curve of an empty calorimeter cannot be used to correct the drift of a sample measurement. Another way must be found to determine the baseline.

The measured heat flow,  $\Phi$ , can be described by the equation

$$\Phi = m \left( c_p + \frac{d\alpha}{dT} \Delta h \right) \beta + \Phi_D \quad (3)$$

where  $m$  is the sample mass,  $c_p$  the specific heat capacity,  $\alpha$  the conversion of a thermal event,  $T$  the temperature,  $\Delta h$  the specific transition enthalpy,  $\beta$  the heating or cooling rate and  $\Phi_D$  the losses in the heat flow. The first summand in equation (3) is due to the change in enthalpy of the sample;  $\Phi_D$  corresponds to the drift.

While the sample component of the heat flow is strongly dependent on the scanning rate, the losses are almost independent of the rate. As a result, at relatively high scanning rates,  $\Phi_D$  has practically no influence on the measurement curve. At lower rates, this influence becomes larger and larger.

At a sufficiently low rate, the losses become significantly larger than the sample component in the measured heat flow. The sample influence on the measurement curve can be neglected. The measured heat flow then corresponds to  $\Phi_D$ .

To perform the corresponding drift correction, a curve is measured in which the influence of the sample can be neglected. That is often the case for scanning rates that are 5 to 10 times lower than the lowest rate at which a measurement curve is to be determined.

The curve measured in this way is heavily smoothed so as not to generate additional noise in the corrected curve and then subtracted from the measurement curves before calculating the heat capacity curves.

A series of measurement curves that have been corrected like this are displayed in Figure 1. The sample was isotactic polypropylene (iPP) that was cooled from the melt at a cooling rate of 4000 K/s before each heating measurement. At this cooling rate, amorphous iPP is obtained.

In the measurements shown in Figure 1, the cold crystallization in particular should be measured at relatively high heating rates. A comparatively small sample mass of 25 ng was therefore chosen.

The heating measurements were performed at heating rates between 5 K/s and 30 000 K/s. This corresponds to a heating rate range of almost four decades. The drift was determined at 0.5 K/s.

At the relatively low heating rates of 5 and 10 K/s (corresponding to 300 and 600 K/min), the signal-to-noise ratio is relatively large. This is due to the sample mass. To reduce the noise and disturbances at this and lower rates requires samples of 10 to 20-times larger mass.

Figure 1 displays the measurement curves of iPP at different heating rates. The glass transition appears as step at about 0 °C followed by the exothermic peak of cold crystallization and finally the endothermic melting peak. The cold crystallization peak is shifted to higher temperatures at increasing heating rates.

Above 2000 K/s, the area of the crystallization peak and thus the enthalpy of crystallization decrease. At 30 000 K/s, crystallization no longer takes place on heating and the sample remains amorphous.

The melting peak is shifted to lower temperatures at higher heating rates. The reason for this is that at higher heating rates the crystallites have less time to grow and are therefore smaller at the melting temperature than at low heating rates. The melting temperature decreases as mentioned earlier with the size of the crystallites.

### Influence of the sample on drift

Samples are usually heated before the actual measurement in order to optimize the contact between sensor and sample. With most semicrystalline polymers, it is normally sufficient to melt them for a short while. Samples with very high viscosity must be left for a few minutes so that the sample can flow.

If the material crystallizes or vitrifies, the mechanical modulus becomes significantly larger and the sample becomes hard. With some materials such as PET, PBT and PA 6, the mechanical contact between sample and sensor is very good. If the sample becomes hard, stresses in the sensor membrane develop. This causes the drift to change during the measurement. Such effects can arise both in heating and cooling measure-

ments. The thermal events in which this occurs are the glass transition, crystallization, and melting.

An example is shown in Figure 2. The curves are heating measurements of amorphous polybutylene terephthalate (PBT). The sample was cooled from the melt at a cooling rate of 1000 K/s before each measurement in order to obtain it in the amorphous state.

The diagram displays the heat flow curves and the blank curve determined from the curve at 1 K/s. The curves show that there are two temperature ranges in which the curvature due to drift behavior is different. The reason for this is the change in the sample stiffness at the glass transition.

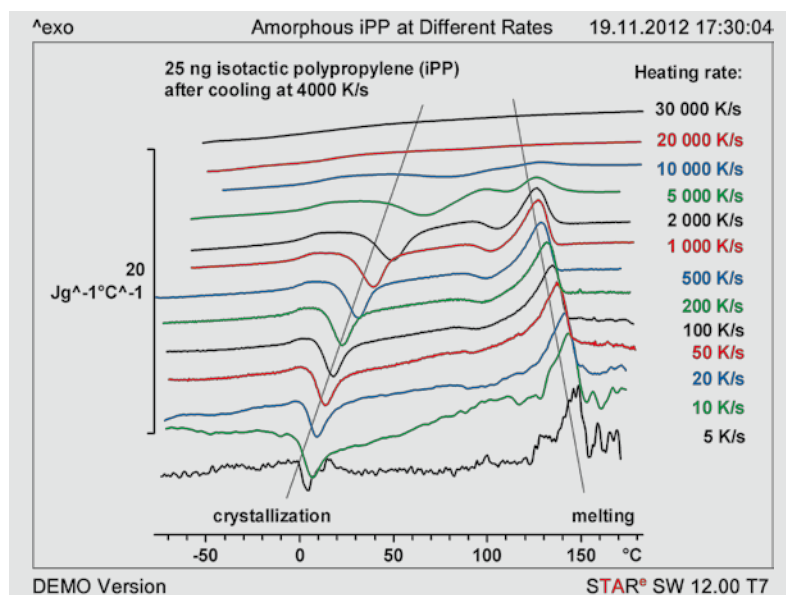
Above the glass transition, the stresses on the sensor decrease because the sample becomes soft. Since this softening process depends on the measurement conditions, the temperature range in which the drift behavior of the measurement curve changes with heating rate also changes.

The measured blank curve cannot therefore completely compensate the drift of the measurement curve in the temperature range in which the sample-induced mechanical stresses in the membrane change strongly. As a result, artifacts occur after subtraction of the blank curve in the corresponding temperature range.

This can be seen in the specific heat capacity curves in Figure 3. Between -20 °C and +20 °C, there is an exothermic peak that is larger at lower heating rates. This peak is an artifact caused by subtraction with the imperfect blank curve. The peak occurs only at heating rates of less than 100 K/s. At 100 K/s, the heat flow induced by the sample is already large enough that the corresponding error in the drift correction can be neglected.

Similar effects are also known from measurements with conventional DSC instruments. If samples are cooled at high cooling rates in DSC crucibles, analogous effects can be observed in the measured

Figure 1. Heating runs of amorphous iPP measured at different heating rates.



DSC curve below the glass transition temperature.

These effects can also be explained by assuming that the sample adheres strongly to the crucible. The stresses due to the different expansion coefficients of the polymer, sample, and crucible then produce artifacts [8].

To avoid the artifacts described above in the Flash DSC 1, the mechanical coupling between sample and sensor must be reduced without the thermal contact becoming significantly poorer. One approach to solving this problem is to use a contact medium, which is applied as thin film to the sensor.

We have experimented with different silicone oils (Wacker Chemie AG). The result of one of these experiments is shown in Figure 4.

In this case, a relatively low viscosity oil (AK 10 000) was used. It was applied only to the sample side using a hair. The quantity of oil was kept to a minimum. Afterward, the sensor was heated to 260 °C several times until the measurement curve no longer changed. In this particular case, this was after the sixth heating cycle.

The sample was then transferred to the sensor and measured. Figure 4 displays the measurement curves with the blank curve and Figure 5 the specific heat capacity curves derived from them.

The exothermic artifact (exothermic peak at temperatures below the glass transition) discussed in Figure 3 has practically disappeared. It is also evident that the cold crystallization peak of PBT is shifted to lower temperatures at lower heating rates.

Further experiments with silicone oils of different viscosity gave the following results:

Low-viscosity oils relatively quickly form a thin film of low heat capacity. This gives rise to just a small additional asymmetry of the measurement system. However,

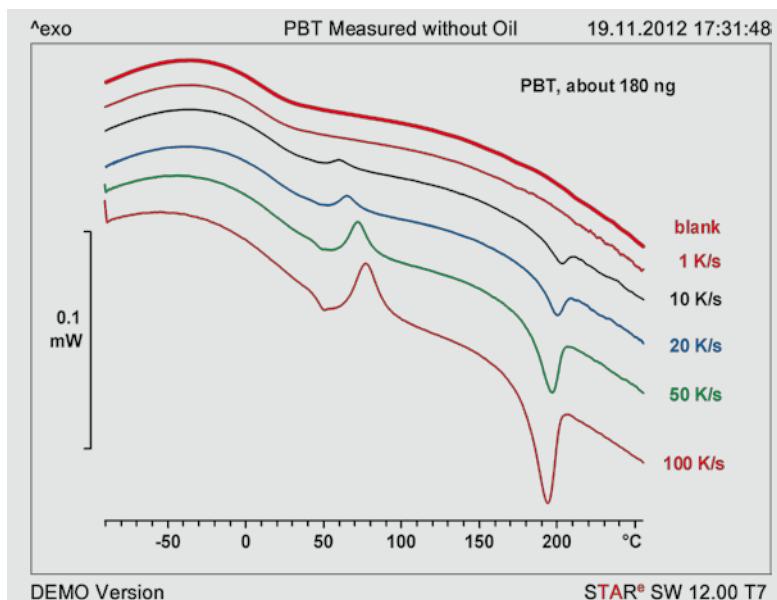


Figure 2. Heating runs of amorphous PBT at different heating rates.

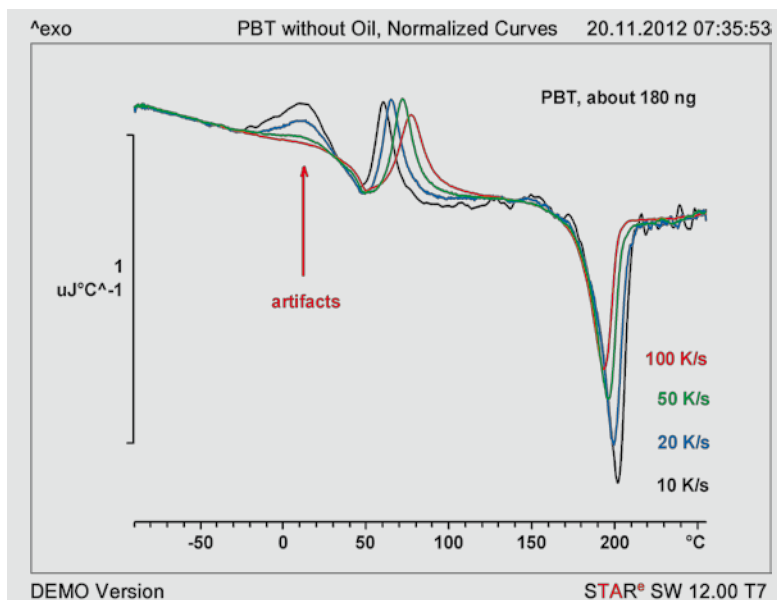


Figure 3. Heating runs of amorphous PBT at different heating rates shown as specific heat capacity curves.

the vaporization of the oil has to be taken into account, especially at relatively low heating rates.

The oil can disappear from the active zone of the sensor after a few heating and cooling cycles. The problems described before due to mechanical contact then occur. A low-viscosity oil is suitable for relatively low temperatures, high scanning rates and small samples. Under these conditions, however, often no oil is needed because the artifacts described in the curves are small and can be neglected.

High-viscosity oils are more stable with respect to the maximum temperature and at lower heating rates. More heating

and cooling cycles are however necessary to achieve stable conditions on the sensor. Furthermore, the additional heat capacity of the applied oil is relatively large because a larger quantity of oil is applied. The greater degree of asymmetry of the measurement system must therefore be compensated by applying oil to the active zone on the reference side of the sensor.

The following working procedure has proven suitable for measuring samples at low heating rates that exhibit drift behavior:

- Apply a very small drop of AK 50 000 to both active zones of the sensor using a suitable hair.

- Heat to 300 °C ten to twenty times at 100 K/s until the measurement curve no longer changes from measurement to measurement.
- Position the sample (if possible larger than 100 ng) on the sensor.
- Perform the measurement after melting the sample.

### Measurement of the first heating run of the sample

If we want to obtain information about the structure and behavior of a material after a production process, we have to evaluate the first heating run. The heating rate should be set sufficiently high so that reorganization processes are largely suppressed.

In the Flash DSC 1, such measurements can only be performed if the thermal contact does not significantly change during the measurement. This is not possible without the use of a contact medium.

We also used AK 50 000 silicone oil for these measurements. The oil was applied to the sensor as described above. The sample was placed on the sensor and the first heating run measured. The sample was then measured again (second heating run) after defined cooling. This second measurement is used to estimate the sample mass.

After the measurement, the sample usually no longer adheres well to the sensor

and can often be removed from the active zone of the sensor using a stiffer hair.

Figure 6 shows the sample side of a sensor with the circular active zone in the middle. The sample that had just been measured is in the active zone. Further away from this are four samples that had already been measured and afterward moved out of the active zone. About five to twenty samples can be measured with one sensor using this procedure.

The drift due to the asymmetry caused by the application of oil to the sample and reference sides is corrected by shifting the sample out of the active zone and performing a measurement without a sample. The blank curve obtained from the blank measurement is subtracted from the measurement curves of the first and all following samples.

The heat capacity curves are determined after the samples have been measured. A blank curve measured at a lower heating rate can also be used for drift correction as previously described.

To illustrate the use of the first heating run, measurements were performed on differently stretched polyethylene terephthalate (PET) films with stretching factors of 1, 3 and 4.5 ( $\lambda = l/l_0$ ,  $l_0$ : length before stretching,  $l$ : length after stretching). The samples were provided by Professor T. Kikutani of Tokyo Institute of Technology.

Figure 7 displays heat capacity curves measured in the temperature range 50 to 320 °C at a heating rate of 6000 K/s. The curves drawn with thick lines are from the first heating run.

The samples were then cooled at 100 K/s and heated again at 6000 K/min (curves drawn with thin lines). In the second heating run, the sample was amorphous. The sample mass was estimated from the step height according to equation (2) and the specific heat capacity curves determined. The mass of the samples was about 100 ng.

Figure 4. Heating runs of amorphous PBT at different heating rates, measured with a film of silicone oil on the sample side.

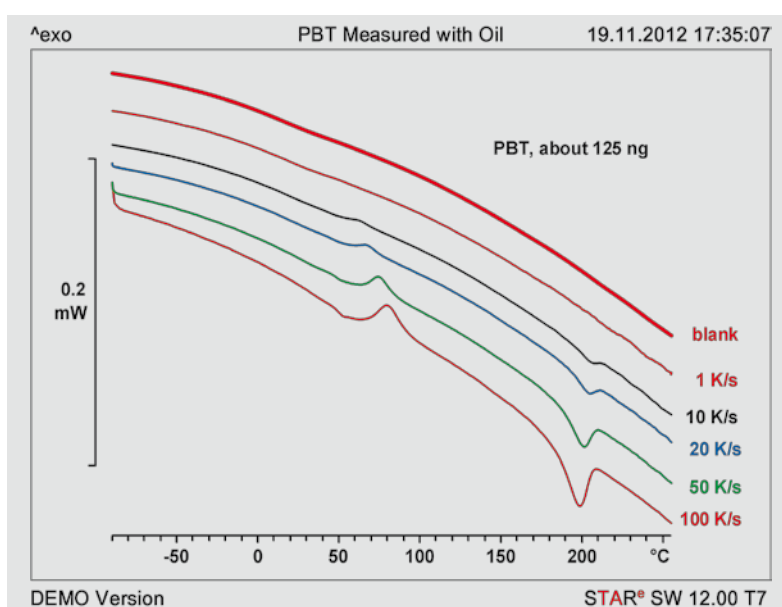
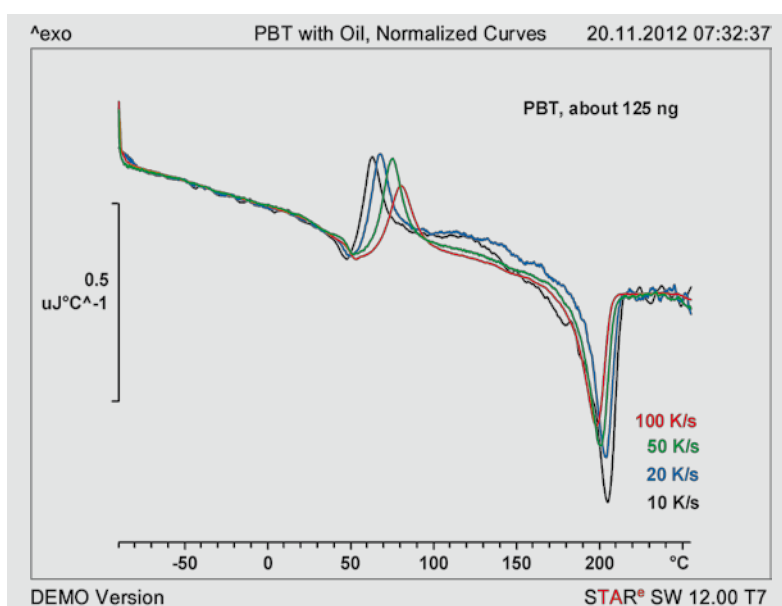


Figure 5. Heating runs of amorphous PBT at different heating rates shown as specific heat capacity curves, measured with a film of silicone oil on the sample side.



The measurement curves of the first heating run show that the glass transition is overlapped by relaxation effects. The unstretched sample is amorphous. The curves of the stretched samples show a small cold crystallization peak followed by a melting peak.

The cold crystallization peak is more pronounced the greater the stretching factor. Even with a material like PET, which crystallizes relatively slowly, the crystallization of a stretched film is so rapid that a heating rate of 6000 K/s is still not high enough to completely suppress reorganization.

Despite this, the curves are much more informative than the conventional DSC measurement curves because only very little reorganization occurs on heating.

If we want to evaluate the first heating run, we must make sure in sample preparation that we have a representative sample. This means that sample preparation must not change the structure of the sample. We can only ensure this by using a sufficiently large sample.

The minimum representative sample size is determined by measuring samples of different size in trial experiments beforehand. Below the size of a representative sample, the measurement curve depends on the sample size. After this, all further measurements then are made with samples that are larger than the minimum representative sample size.

### Limitations in the use of silicone oil as contact medium

As described above, the use of silicone oil as a contact medium opens up new application possibilities for the Flash DSC 1.

There are however certain limitations:

- Due to the additional heat capacity on the sensor, the maximum heating rate is limited to about 6000 K/s. This limit can be higher if low-viscosity oil is used. At the same time, however, the lifetime of the oil layer is reduced.
- The maximum usable temperature of the oil is about 350 °C.

- Silicone oil melts at about  $-40$  °C. Smaller spurious effects in the measurement curve can also occur in this temperature range even after blank curve subtraction.
- Some polymers absorb silicone oil. This can change their structure and properties. This process occurs through diffusion of the silicone oil into the sample and therefore needs time. A change in the sample can usually be avoided because a typical measurement lasts only about 0.5 seconds. Nevertheless, the stability of the sample toward the oil should be checked.

This stability can be investigated in the following way:

A typical measurement program consists of a multitude of segments that define the measurement cycles (e.g. heating – cooling – heating). A test cycle is performed at the beginning of the measurement program in which the sample is cooled from the melt and then heated at rates that cause measurable processes like crystallization and melting to occur.

The test cycle is repeated during the measurement program and at the end. Before the measurement curve is evaluated, the heating and cooling segments of the test cycles are compared with one another. If differences in the measured thermal events are observed after a test cycle, the sample has undergone change beforehand.

In principle, we recommend this procedure for the thermal analysis of samples in complex measurement programs. Unfortunately, in conventional DSC, such measurements are seldom performed because of the additional time they require. With the Flash DSC 1, the additional time can often be neglected.

### Summary and conclusions

The Flash DSC 1 expands thermal analysis to medium to very high scanning rates. Such scanning rates play an important role in technical processes and can be used to study the kinetics of the formation of structures and phase transitions.

Besides the possibility of measuring at high scanning rates, measurements can also be performed at normal and medium rates. This has the advantage that the results can be directly compared with those from conventional DSC measurements.

However, four practical questions arise in the use of the Flash DSC 1:

- How do you determine the mass of the sample?
- How do you determine the blank curve needed especially for normal and medium scanning rates?
- How do you avoid artifacts that occur with some materials at low scanning rates?
- How do you obtain measurement curves that you can evaluate in the first heating run?

This article proposes practical solutions for these four questions:

- The sample mass can be estimated from thermal effects such as transition enthalpy and heat capacity change at the glass transition.
- To achieve an optimum display of measurement curves, a blank curve can be subtracted that is measured at the same scanning rates. At these rates, the contribution of the sample to the heat flow can be neglected.
- Sample-induced changes in drift can occur with polymers that are hard and

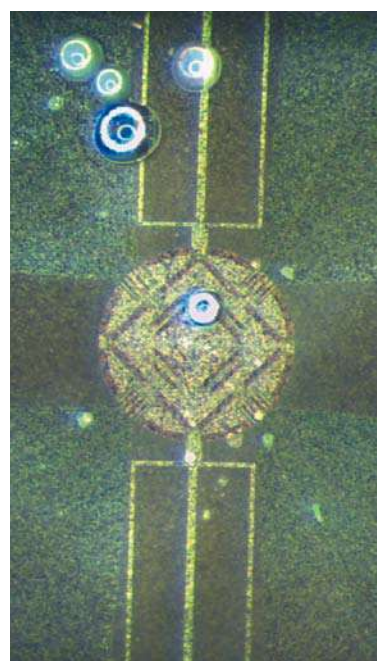


Figure 6. The Flash DSC 1 UFS 1 sensor after measuring the first heating run of the fifth sample using silicone oil. The four previous samples were moved out of the active zone.

in good mechanical contact with the sensor. Changes in drift occur during crystallization or below the glass transition temperature due to mechanical stress. They can be reduced or eliminated by using a contact medium that forms a thin layer with good thermal

conductivity between the sample and sensor. Silicone oil has proven useful for this purpose for measurements of materials such as PA, PBT and PET.

- The first heating run in the Flash DSC 1 can also be measured and evaluated using silicone oil.

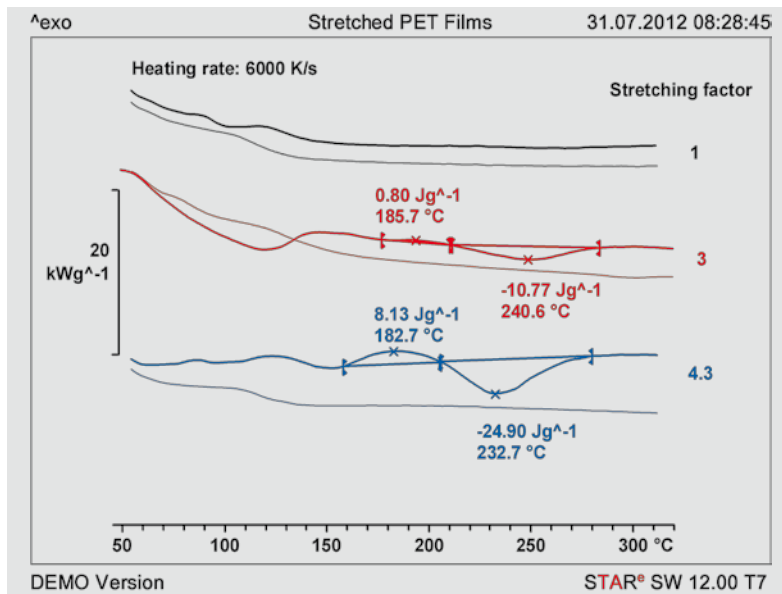


Figure 7. Heat capacity curves of the first (thick lines) and second (thin lines) heating runs of differently stretched PET films.

## References

- [1] K.-H. Illers, *European Polymer Journal*, 10 (1974) 911–916.
- [2] B. Wunderlich, *Macromolecular Physics*, Academic Press, Vol. 1 (1973) and Vol. 3 (1980).
- [3] J.E.K. Schawe, *Thermochimica Acta* 461 (2007) 145–152.
- [4] J. Schawe, Evaluation and interpretation of peak temperatures of DSC curves. Part 2: Examples, *UserCom* 24, 11–15, Figure 2.
- [5] A.A. Minakov, D.A. Mordvintsev, R. Tol, C. Schick, *Thermochimica Acta*, 442 (2006) 25–30.
- [6] J. Schawe, The revolutionary new Flash DSC 1: Optimum performance for metastable materials, *UserCom* 32, 12–16.
- [7] M. Pyda: <http://athas.prz.edu.pl/>
- [8] H. Chen, P. Cebe, *Thermochimica Acta* 476 (2008) 63–65.