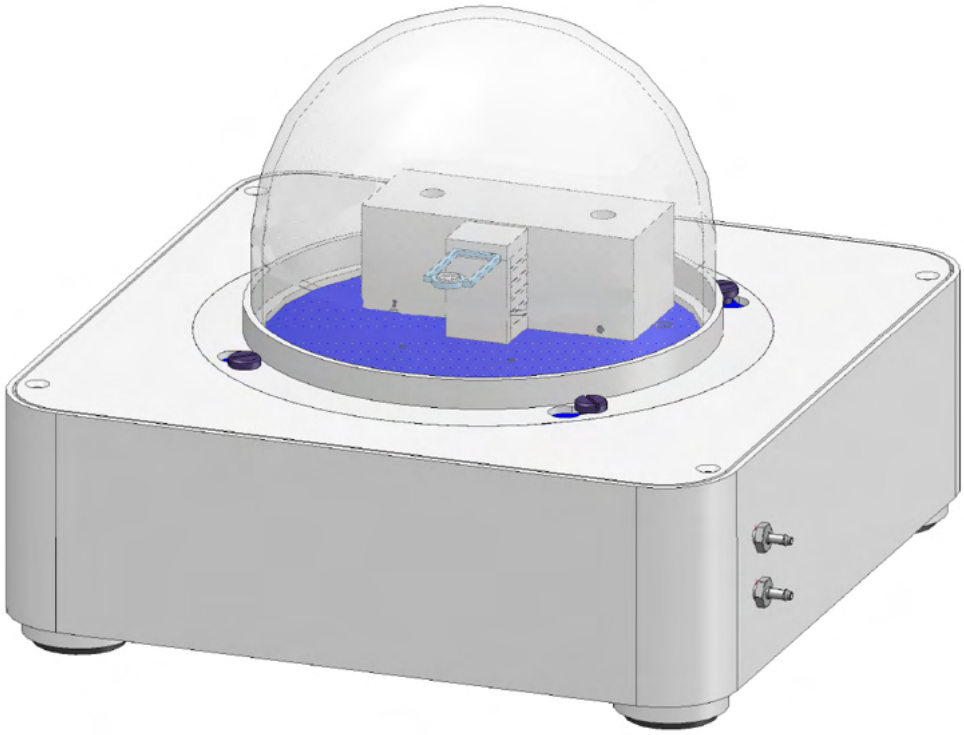
LINSEIS

pushing boundaries

How To Measure Polymers with Chip-DSC



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1. General information

This manual is a short description of how to measure polymer samples with Chip-DSC. The results are highly dependent on the sample preparation and measurement conditions you use for your investigation. So different samples need different properties and this is highly dependent on the physical properties of the sample. Physical properties we have to keep in mind for optimal results are for example heat capacity, thermal conductivity, heat radiation behaviour, temperature range and the transition we want to investigate. Therefore, two examples of standard polymers are compared in this document.

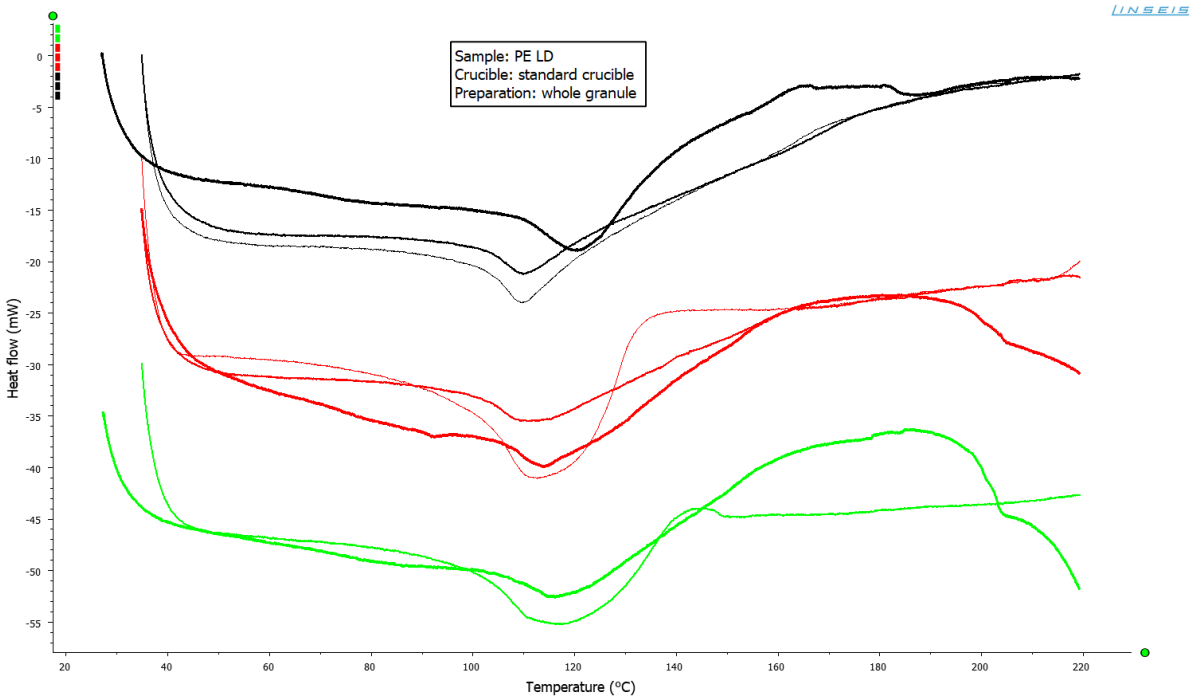
2. LD PE sample

LD PE (Low Density Poly Ethylene) is one of the most common polymers in packaging. For the comparison some of the measurement conditions are similar to make the results comparable.

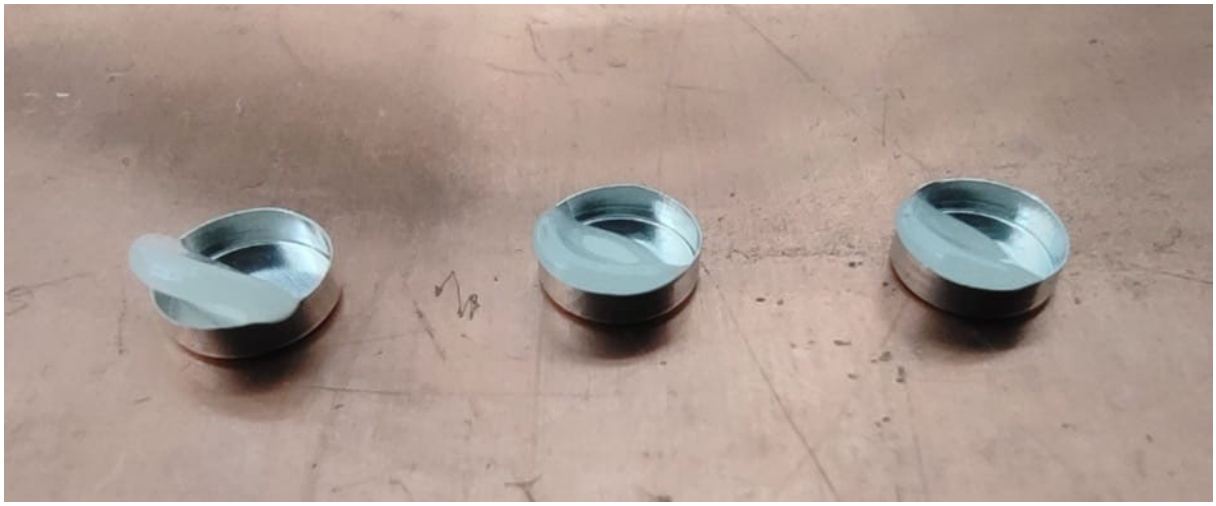
Condition	**Value**
Temperature	RT – 155 °C
Heating rate	20 K/min
Atmosphere	Air
Device	Chip-DSC 10
Sensor	Standard Sensor
Cycles	3
Cooling	ballistic

The temperature range fits to the literature value for the polymer. A heating rate of 20 K/min is common for polymers. Technically higher heating rates are possible but due to kinetics of the sample and a poor thermal conductivity and high specific heat capacity this heating rate was used to avoid temperature gradients on the sample.

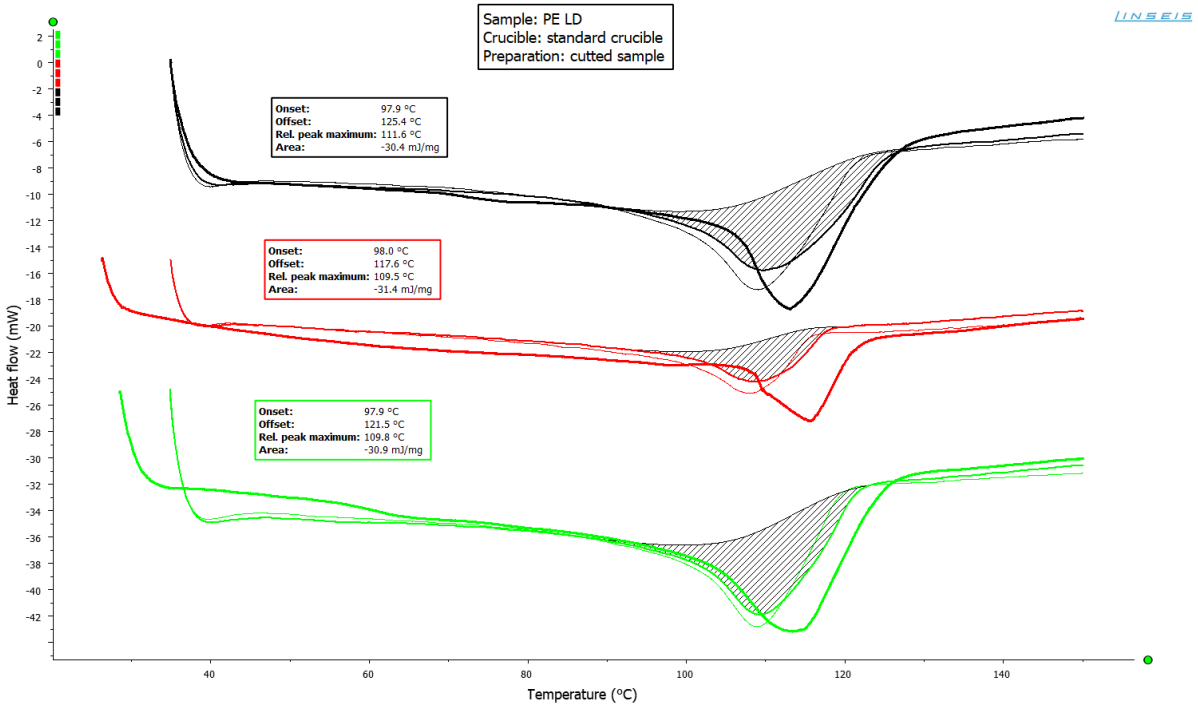
In the first investigation three samples were used and heated up via scheduler. The sample was measured without any sample preparation and in an open standard crucible. So, the whole granule (19 – 25 mg each) was placed in the crucible.



As shown in the diagram, it's almost not possible to receive any reproducible values from these tests. During the first cycle the sample is melting and receive a better contact to the crucible whats visible on the measurement signal. But it last three runs until the sample is complete melted. Furthermore the sample does not melt into the crucible but moves out of the crucible which makes it impossible to receive a reproducible contact.



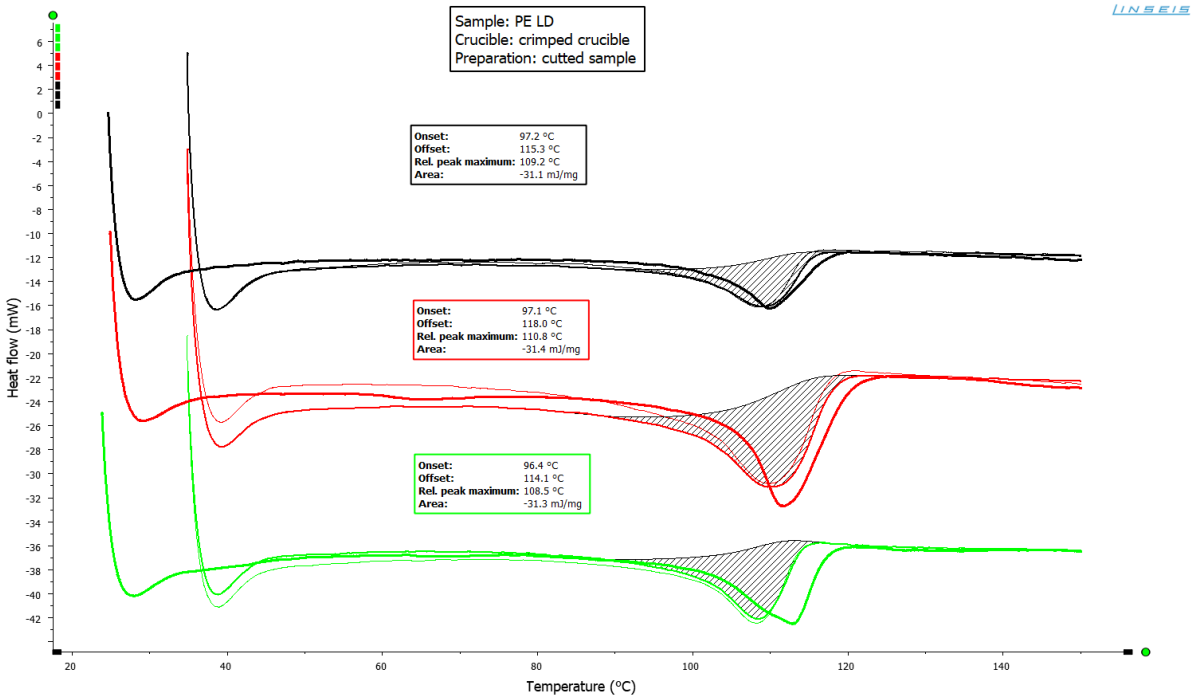
The second diagram shows a cut sample in the standard crucible. So, the height of the sample is lowered and the shape of the sample is improved significantly. Also, the weight is lowered a lot (3 – 8 mg each).



Evaluated is the second peak and it makes clear even with a pity effort on sample preparation the results can be improved a lot. Anyway, the first run of these samples is inconsistent due to different melting behaviour of the different shaped samples.

The third batch of samples were measured with a hermetically sealed crucible (N° 302 93 045 + 302 93 044). Also, these samples are cut previously (3 – 8 mg each) to get a better contact between sample and crucible and a proper heat transfer into the sample.

Due to the perfect reproducibility for heat radiation and convection the measurements show a good



reproducibility. The crimped crucible is working as a susceptor here, causing a homogenous heat around the sample. Furthermore, the good sample contact and lowered heat capacity have a positive effect on the sample and the shape of the peak.

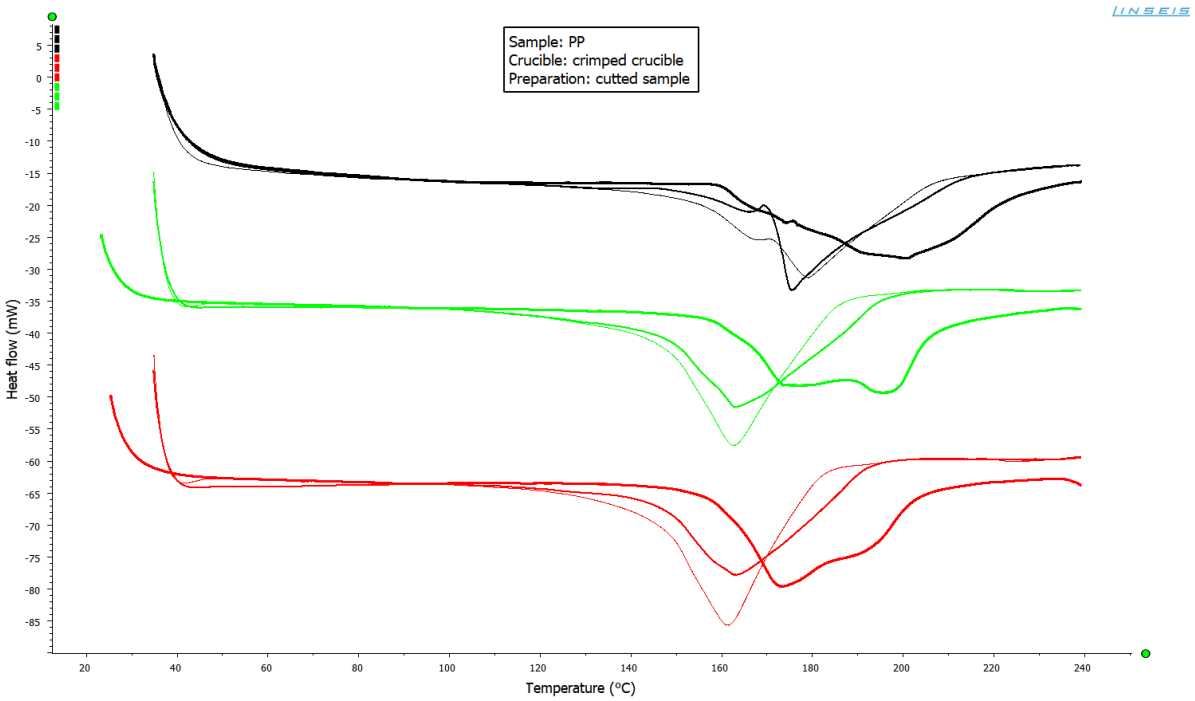
3. PP sample

PP (Poly Propylene) is widely used polymer also. For the comparison some of the measurement conditions are similar to make the results comparable.

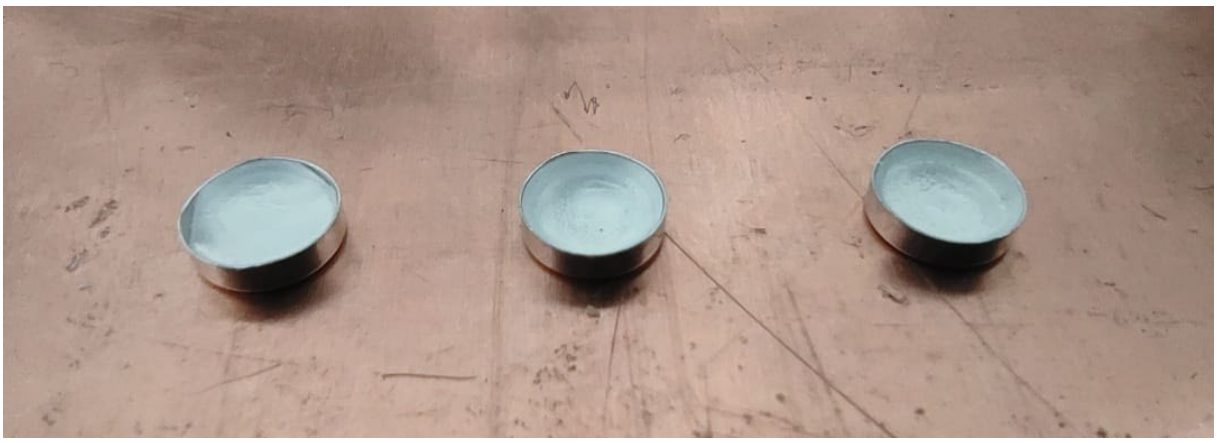
Condition	Value
Temperature	RT – 240 °C
Heating rate	20 K/min
Atmosphere	Air
Device	Chip-DSC 10
Sensor	Standard Sensor
Cycles	3
Cooling	ballistic

The temperature range fits to the literature value for the polymer. A heating rate of 20 K/min is common for polymers. Technically higher heating rates are possible but due to kinetics of the sample and a poor thermal conductivity and high specific heat capacity this heating rate was used to avoid temperature gradients on the sample.

In the first investigation three samples were used and heated up via scheduler. The sample was measured without any sample preparation and in an open standard crucible. So, the whole granule (23 – 28 mg each) was placed in the crucible.

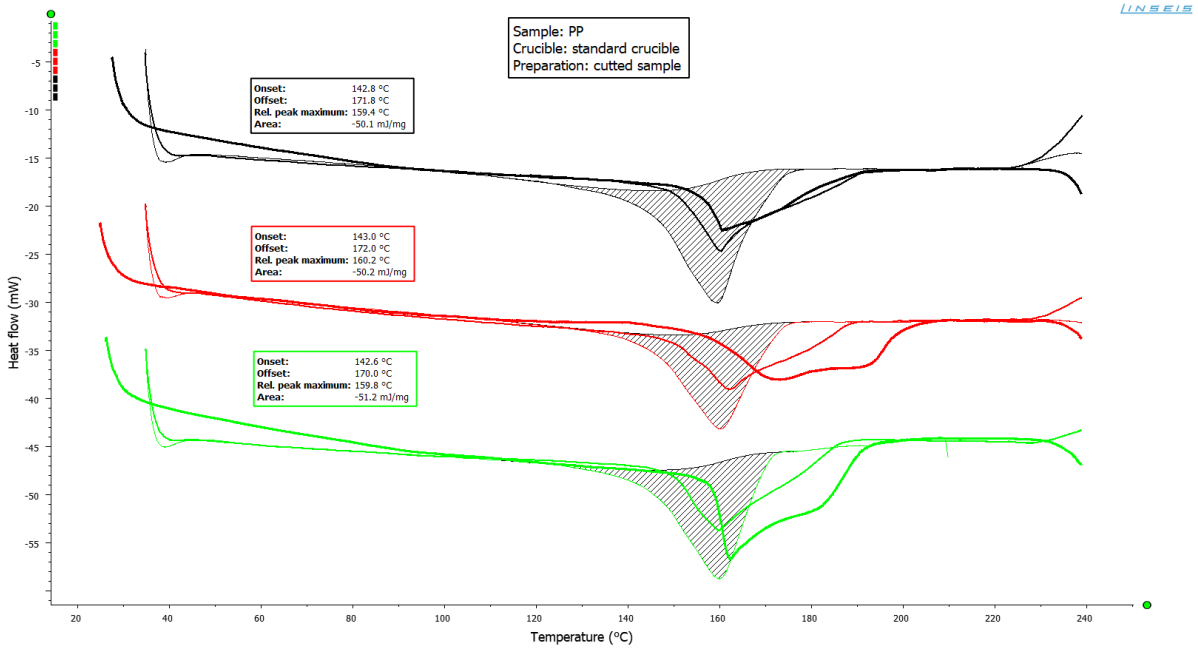


As shown in the diagram, it's almost not possible to receive reproducible values from these tests. During the first cycle the sample is melting and receive a better contact to the crucible what's visible on the measurement signal. But it last three runs until the sample is complete melted. Due to poor sample contact the first batch shows very different results for these tests because a lack of heat transfer (The crucible wasn't placed in the mid of the sensor but on the edge of the sensor). In comparison the PP show a much better melting behaviour for the complete granule because the sample does not move out of the crucible.

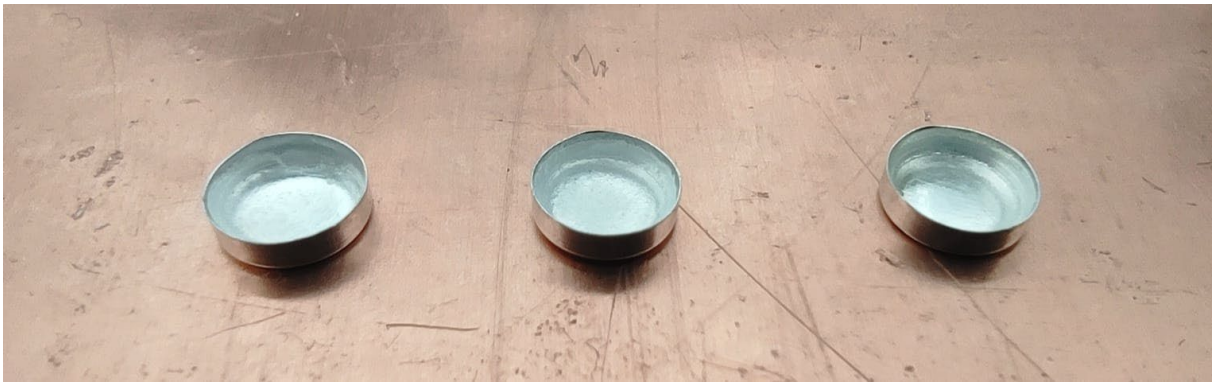


The second diagram shows a cut sample in the standard crucible. So, the height of the sample is lowered and the shape of the sample is improved significantly. Also, the weight is lowered a lot (2 – 10 mg each).

Evaluated is the second peak and it makes clear even with a pity effort on sample preparation the results

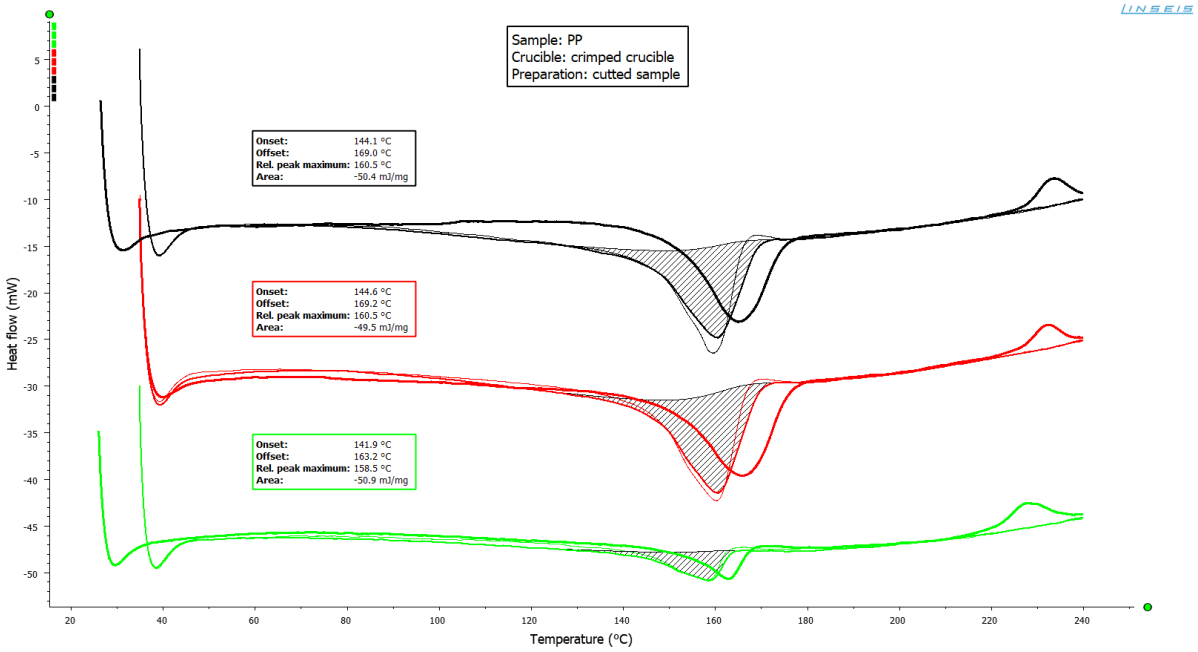


can be improved a lot. Anyway, the first run of these samples is inconsistent due to different melting behaviour of the different shaped samples.



The third batch of samples were measured with a hermetically sealed crucible (N° 302 93 045 + 302 93 044). Also, these samples are cut previously (9 – 12 mg each) to get a better contact between sample and crucible and a proper heat transfer into the sample.

Due to the perfect reproducibility for heat radiation and convection the measurements show a good



reproducibility. The crimped crucible is working as a susceptor here, causing a homogenous heat around the sample. Furthermore, the good sample contact and lowered heat capacity have a positive effect on the sample and the shape of the peak.

4. Measurement Conditions

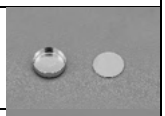
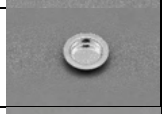
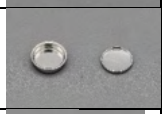
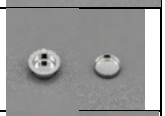
What we can figure out from the above measurements is, the measurement conditions highly influence the results of polymer measurements.

Heating rate: The heating rate has big influence on the peak temperatures and the temperature range a transition appears. Not just because of the time constant of the device but also due to the kinetics of the sample. For this reason, it is highly recommended to use the same heating rate for calibration and measurement. Lower heating rates show better temperature resolution but higher heating rates lead to higher signals due to a bigger temperature difference between sample and reference sensor.

Atmosphere: The atmosphere on the one hand could affect the transitions and on the other hand the heat transfer in the measurement cell. For example, using nitrogen instead of air leads to decomposition instead of an oxidation at higher temperatures. Due to different heat transfer and density of different gases also the peak shape could be affected by using Helium, Argon, Nitrogen or air. Also, the ballistic cooling behaviour is affected by that.

Cycles: Repeating the measurement for polymer investigations could help to figure out the cause of some effects. Due to possible bad shape of the sample and poor heat transfer it is possible the first heating run could differ from following runs even under identical conditions. On the other hand, it is possible the transitions itself differ between the different runs, due to different cooling and crystallization conditions, thermal history and so on. Therefore, it could be helpful to compare several runs of the investigation.

Crucible: Choosing the right crucible is essential for proper results for your investigation. For this reason, we offer different crucibles specialized for different investigations. For example, are there special crucibles for foils and powders as well as closed crucibles for polymer runs, as we figured out in our former tests. A list of most common crucibles is attached.

Name	Best.-Nr.	Description	Picture
Al Standard crucible 6x1,5mm 40µl	30293042	The most lightweight crucible and easy to use	
Al crimpable crucible 100µl	30293043	The biggest crucible for voluminous samples. Crimpable to measure with atmosphere	
Al crimpable crucible 40µl	30293045	The small crimpable crucible to measure with atmosphere	
Al crucible for foils with lid	30293050	Crimpable crucible to measure foils and powders. Special crimping tool is needed.	
Al crucible for small samples with lid	30293051 30293052	Crimpable crucible to measure small samples. Special crimping tool is needed	
Cu crucible	30293049	The copper crucible to measure Oxidation induction time and Oxidation onset temperature	

5. Conclusion

To receive proper results for polymers the sample preparation and measurement conditions are essential. A flat surface of the sample is helpful to make sure there is good thermal contact. Also, a lower mass could be helpful to make sure you receive sharp results. The measurement conditions are sometimes given by norm but should fit to the device's capabilities. To test reproducibility and figure out thermal history it is common practice to run the really same sample multiple times. A closed crucible works like a susceptor which is helpful for samples with bad shape, high specific heat capacity and poor thermal conductivity.