

DSC 214 *Polyma*

Surprisingly Easy – The New All-Inclusive Product Package for DSC



Polyma – More Than a DSC

A Smart System for Polymers

Working with DSC (Differential Scanning Calorimetry) involves not only the handling of a device, but also sample preparation, evaluation and interpretation of the resulting curves. The NETZSCH 360° view for polymer characterization takes this into account, streamlining operational processes while simultaneously simplifying them.

The new DSC 214 *Polyma* is a key part of this concept. It provides everything a user needs in polymer analysis.

Thermal Characteristics Which Can Typically Be Detected by Using DSC

- Melting temperatures and enthalpies (heats of fusion)
- Crystallization temperatures and enthalpies
- Glass transition temperatures
- Oxidative-induction time (OIT) and oxidative onset temperature (OOT)
- Degree of crystallinity
- Reaction temperatures and enthalpies
- Cross-linking reactions (curing)
- Degree of curing
- Specific heat capacity
- Distribution of molecular weight (peak shape), etc.

High Performance DSC 214 *Polyma*

- Powerful sensor-furnace combination for fast heating/cooling
- Outstanding sensitivity and excellent reproducibility

Unique *Concavus* Pans

- High-performance pans for excellent reproducibility
- 3in1 Box for organized storage

Easy Sample Preparation

- Clever and unique *SampleCutter*, especially for brittle materials
- Comprehensive sample preparation set



Smart Measurement

- Simplified user interface
- Automated measurement
- *AutoCalibration*

AutoEvaluation

- Automatic analyses of unknown DSC curves
- User-independent analysis

Innovative Identification

- Data-based test interpretation
- Open for users' own data

DSC 214 *Polyma* – The New Benchmark in Cell Design



1 *Arena Furnace*

Its oval geometry drastically reduces the furnace mass, resulting in faster heating and cooling rates. The double-symmetric design also leads to an even temperature distribution.

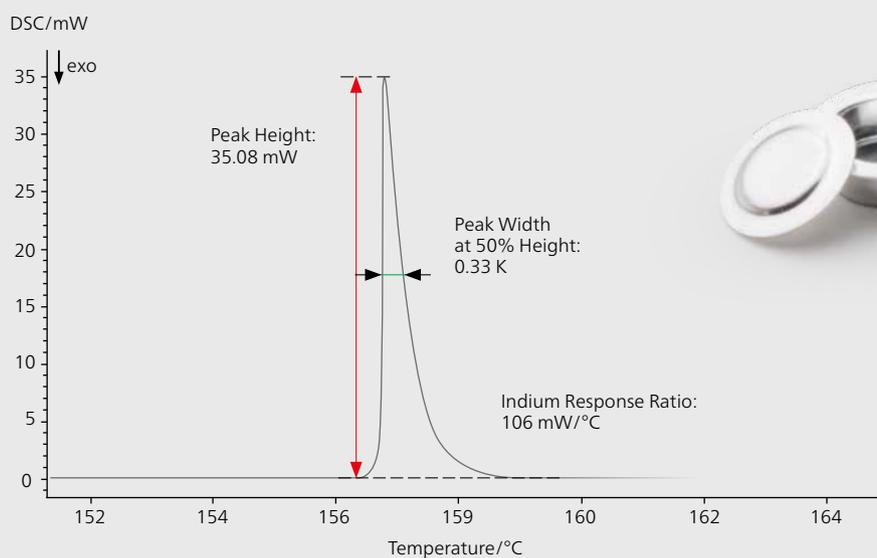
2 *Corona Sensor*

This fast-responding sensor is unmatched in both reproducibility and robustness.

3 *Concavus Pans*

The unique geometry of this sample pan features a concave bottom. In combination with a flat sensor, it provides a ring-shaped contact zone that is always clearly defined.

INSTRUMENT



DSC measurement on indium (7.3 mg)

First-Class Performance Via an Optimum Combination of Furnace, Sensor and Pan

The DSC 214 *Polyma* sets new standards, incorporating the premium *Arena* furnace in combination with a perfectly matched sensor and pan. This unique solution achieves excellent sensitivity and resolution at the same time, which is reflected in the peak height-to-width ratio. Only in this way is it possible to detect weak effects and separate overlapping ones.

The peak height-to-width ratio, called the Indium Response Ratio, is generally used to characterize the separation capability of a DSC. The DSC 214 *Polyma* generates an Indium Response Ratio of more than 100 mW/°C, a unique number for heat-flux DSC systems.

The ideal combination of the low thermal mass *Arena* furnace with the fast-responding *Corona* sensor allows for high heating and cooling rates of up to 500 K/min – values unachievable with common heat-flux DSCs on the market. Its high reproducibility and robustness are the hallmarks of the *Corona* sensor.

The *Concavus* pans – in combination with a flat sensor – always yield a uniform ring-shaped contact zone. These premium pans are specially designed to align to the shape of the *Corona* sensor, resulting in unmatched reproducibility. In addition, the *Concavus* pans are subjected to a careful cleaning process prior to delivery, which eliminates any contamination.

New Furnace, Sensor and Pan Combination

- Fast heating and cooling rates
- Excellent reproducibility
- Unmatched indium response ratio

Technical key data for the instrument can be found on page 23

New Ideas To Get Started

The *SampleCutter* – Perfect for Polymers

One prerequisite for reproducible and reliable DSC results is to have good thermal contact between the sample and pan bottom, which postulates a flat sample area. With the new

SampleCutter, it is easy and comfortable to cut plane sample faces, irrespective of whether the polymer sample is soft, hard or brittle.



3in1 Box – The Clever Solution for Transport, Sampling and Archiving

Even the transport and storage of the *Concavus* pans is consistent with their premium quality, thanks to the 3in1 Box: 96 pans and lids are packaged in an anti-static box divided into 96 separate compartments. This elaborate packing prevents deformation of the pans while allowing easy access to them

and providing a fully functional archiving system. The integrated sample register including name and mass makes it easy to locate retained samples.

The *Concavus* pans are actually also compatible with common heat-flux DSCs.



Tray supports a defined sample position



Sample Preparation

- Clever and unique *SampleCutter*
- New 3in1 Box for easy withdrawal, storage and practical archiving

DSC 214 *Polyma* – Opens the Window for Flexibility



Epic Versatility

With a stand-alone footprint of only 35 cm x 51 cm, the new DSC 214 *Polyma* is extremely compact and leaves room for the set-up of your choice. The instrument can be combined with a variety of computer devices to meet your needs: You can choose to plug it directly into your

classical desktop PC or laptop, or you can use it with an all-in-one touch PC or even a compact tablet PC for small work spaces. A touch interface or mouse and keyboard work equally well. The system runs under Windows XP, Windows 7 or Windows 8.1. It's up to you.

INSTRUMENT

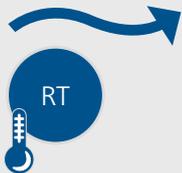
High Sample Throughput

Thanks to the automatic sample changer (ASC), the measurement of up to 20 samples – either belonging to a single series or independent of each other – can be carried out without operator intervention. Different crucible types, different gas atmospheres and individual calibration curves can be handled within the same carousel run.

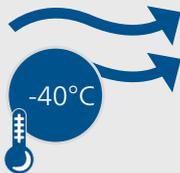


Broad Temperature Range and Economic Cooling

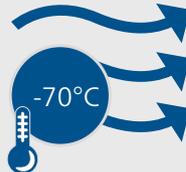
For fast cooling back to room temperature or for tests at sub-ambient temperatures, optimized cooling is required. NETZSCH offers several options for meeting these needs.



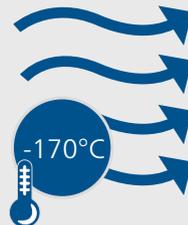
Compressed air cooling
(RT to 600°C)



Closed-loop intracooler IC40
(-40°C to 600°C)



Closed-loop intracooler IC70
(-70°C to 600°C)



Liquid nitrogen cooling system
(-170°C to 600°C)

The *Proteus*® Software Ushers In a New Era

Unmatched Ease of Use – The New *SmartMode* User Interface

The novel, greatly simplified user interface of the *Proteus*® measurement software reflects a true "intuitive design" concept. There's no need to be an expert in thermal analysis to start test runs with the DSC 214 *Polyma*.

SmartMode – Right at Your Fingertips

The user interface boasts a clear structure, a consistent navigation concept and easy-to-access buttons. Thus, even customers unfamiliar with the software immediately know how to proceed. Several instruments can be operated in parallel. Each active instrument is marked by a colored tab. Using *Wizards* (measurement templates), it is possible to start a measurement with just a few inputs. Alternatively, customized methods or predefined methods can be selected to set up an experiment. The predefined methods already contain all required parameters for those materials which are listed in the NETZSCH "Thermal Properties of Polymers" poster.

During the course of a measurement, the curve evolution can be followed – even on a tablet computer. This feature affords the operator a great latitude of action and can significantly improve work efficiency.



New simplified user interface for measurement definition – predefined methods are activated

ExpertMode – Not Just for Professional Users

For those who wish to dive deeper into the software for enhanced option setting or for method definition, switching from *SmartMode* over to *ExpertMode* is the answer. Here, the user has access to the established *Proteus*® software functionality, including dozens of features and all adjustment settings.

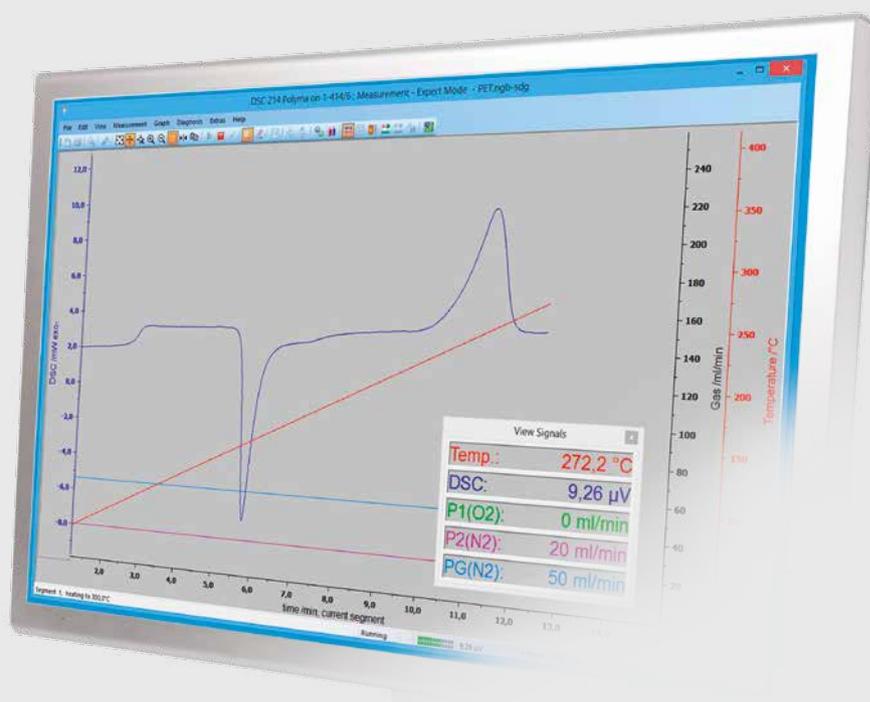
AutoCalibration Allows for Full Concentration on the Measurement Tasks

DSC calibration is essential for ensuring that the instrument is always in a defined state. Calibration procedures, however, should be simple, fast and – ideally – done along the way.

The solution is *AutoCalibration*. This feature provides automatic creation routines for all relevant calibration curves, automatically loading the current calibrations while taking the selected measurement conditions into account and checking their validity periods.

SmartMode and ExpertMode

- *SmartMode* for fast operation
- *ExpertMode* for sophisticated test procedures
- *AutoCalibration*



AutoEvaluation – The First Truly Automatic Evaluation Routine

Autonomous Detection of DSC Effects

AutoEvaluation is something completely new. It is the first and only software feature which automatically analyzes unknown curves of amorphous or semi-crystalline polymer samples such as thermoplastic materials, rubbers, thermoplastic elastomers or cured resins.

Users thus obtain a self-acting software package which evaluates glass transition temperatures, melting enthalpies or peak temperatures. For melting effects, for example, both the peak temperature and the enthalpy are determined; in the case of a glass transition, the software calculates T_g (the glass transition temperature) and the step height, expressed as Δc_p .

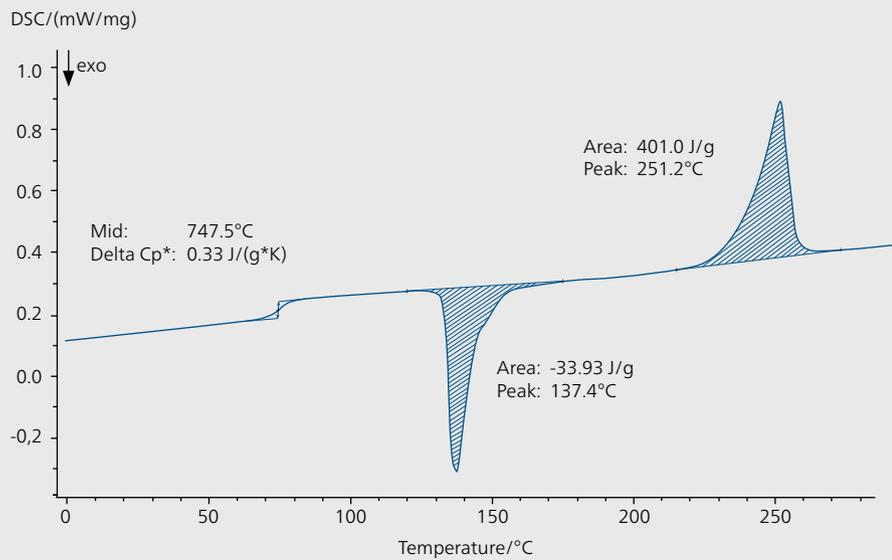
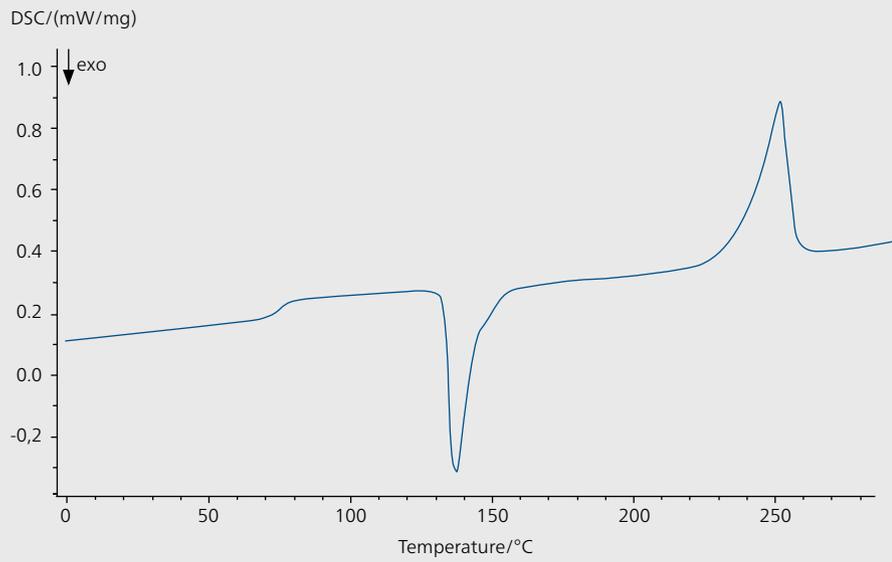
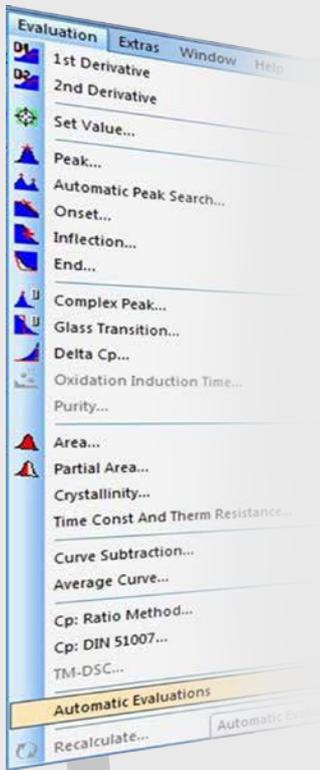
The plot on the right presents a measurement on an unknown polymer. Three effects are visible in

the curve: an endothermic step and two peaks – an exothermic and an endothermic one. Users familiar with the thermal behavior of such semi-crystalline polymers know that the exothermic peak is related to post-crystallization of the material; the endothermic one belongs to the melting range and the step reflects the glass transition of the polymer. For all those who haven't seen such measurements yet, *AutoEvaluation* will handle the curve independently – without any effort on the operator's part.

This ground-breaking technology allows, for the first time in history, test analyses which are fully user-independent and therefore completely objective.

Of course, users can still run manual evaluation, if required.





DSC curve evaluated by means of *AutoEvaluation*

Identify – Makes Every User an Expert

Identify: Unprecedented Database System for Identification and Verification of Polymer Measurements

As far as software-controlled automatic data handling is concerned, *AutoEvaluation* is not even the summit. NETZSCH goes yet a step further and additionally offers software which searches for similar results stored in polymer libraries, providing instantaneous interpretation of the measurement at hand.

With the *Identify* software package, it is possible to carry out one-on-one comparisons with individual curves or

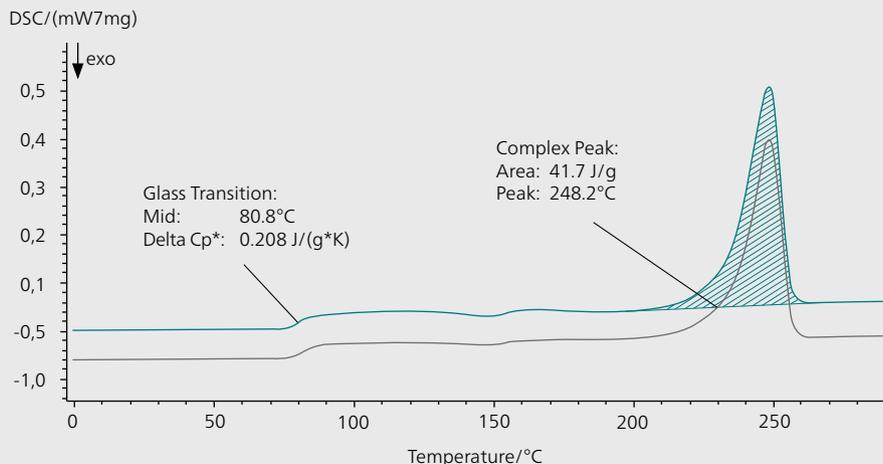
literature data from selected libraries, or to check whether a particular curve belongs to a certain class. These classes may contain sets of data for various types of the same polymer – e.g., several types of PE – but also curves, such as ones which are classified as PASS or FAIL in terms of quality control.

Both the libraries and the classes are boundless and editable; i.e., users can extend them with experiments and knowledge of their own. As standard

libraries, all data and exemplary measurements from the NETZSCH “Thermal Properties of Polymers” poster are provided. The *Identify* results are portrayed as hits sorted by degree of similarity as a percent.

The plot below depicts the results of a search for an unknown sample curve. The DSC curve for the best hit is shown for direct comparison with the unknown sample. The similarities are obvious: The unknown sample is PET.

| Measurement/Literature Data | Similarity [%] | Class | Similarity [%] |
|-----------------------------|----------------|-----------------------|----------------|
| PET 1 | 95.93 ✓ | PET | 86.30 |
| PET | 76.67 | PA | 11.20 |
| PVAL | 64.48 | PA6_GF30_parts_passed | 7.03 |
| PA66 | 58.36 | PVC | 3.38 |
| ETFE | 57.32 | POM | 0.00 |
| ETFE-03_7_7 | 49.98 | PE | 0.00 |
| PA66-GF30-02_7_7 | 39.33 | | |
| PVA-02_7_7 | 26.97 | | |



View of *Identify* results after only one click. The unknown curve is marked in green; the most similar database curve in black.

Identify...

- is a unique DSC curve recognition and interpretation system providing results with a single click!
- is useful for material identification and quality control.
- is both easy to use and sophisticated.
- includes a database with NETZSCH libraries for polymers and libraries that can be created by the user.
- manages measurements, literature data and classes in consideration of the user's knowledge.



PVAL

64.48%

PET 2

76.67%

PET 1

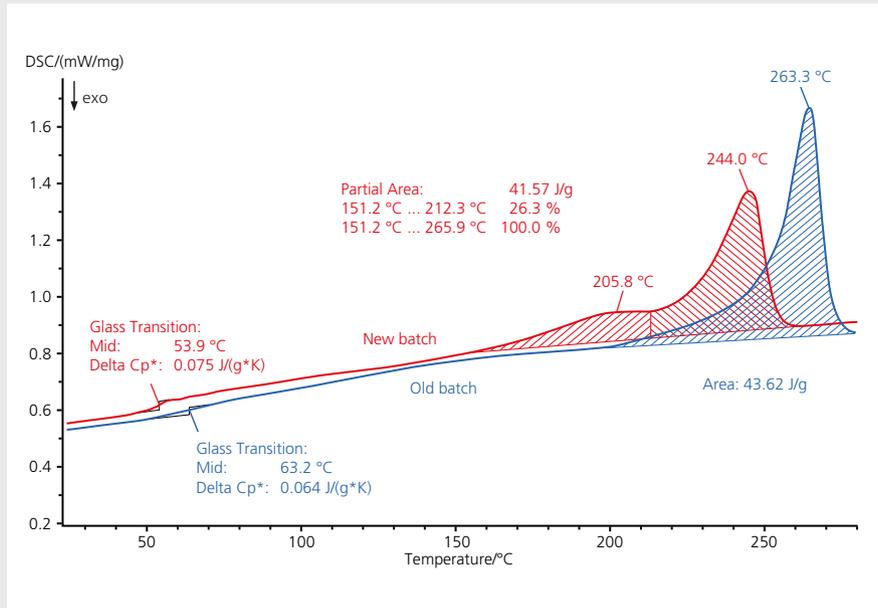
95.93%



DSC 214 *Polyma* – Ideal for Quality Control of Polymers

Incoming Goods Inspection

The plot shows the DSC results for two seemingly identical granulate batches, specified as Polyamide 66, which were delivered at different times (2nd heating after controlled cooling at 20 K/min). The blue curve (old batch) shows the glass transition at 63°C (mid-point) and the melting peak at 263°C, which are both typical for PA66. The new batch (red curve), however, exhibits a double peak with peak temperatures at 206°C and 244°C. This indicates that the new granulate most probably contains a second polymer which blends with PA66.



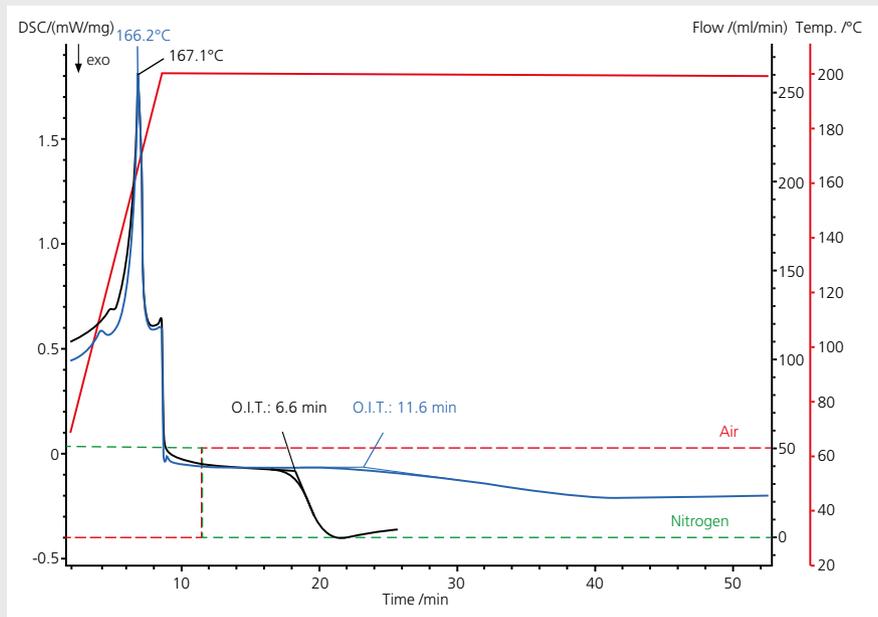
Comparison of two PA66 batches.
 Sample masses: 11.96 mg (blue) and 11.85 mg (red); heating to 330°C at 20 K/min after cooling at 20 K/min, dynamic N₂ atmosphere.

Oxidative Stability

OIT tests (Oxidative-induction time) are well-known for evaluating the oxidative resistance of polymers, in particular polyolefins.

In this example, two PP samples were heated to 200°C under a dynamic nitrogen atmosphere. The endothermic peak detected during heating illustrates the melting of the polypropylene. After 3 minutes at 200°C, the gas was switched to air. The resulting exothermic effect indicates the polymer degradation.

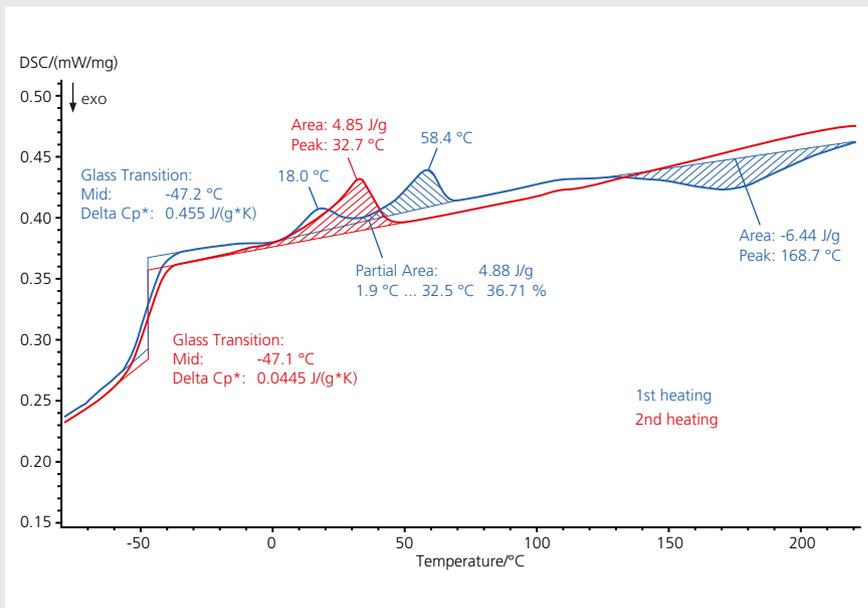
In the present case, oxidation occurs earlier for sample A than for sample B (OIT 6.6 min vs. 11.6 min).



OIT test on PP.
 Sample masses: 9.48 mg (sample A) and 9.55 mg (sample B); heating to 200°C at 20 K/min under N₂ (50 ml/min), 3 min isothermal under N₂, isothermal under air (50 ml/min) until degradation.

Low-Temperature Performance of Rubber

DSC measurements are important for rubbers used in tires because their service temperature range is limited by the glass transition temperature. In this example, an SBR sample was measured twice between -100°C and 220°C. The endothermic step detected at -47°C (mid-point) in both heating sequences is associated with the glass transition of SBR. Between 0°C and 70°C, endothermic effects are detected. They are most probably caused by the melting of additives. The exothermic peak at 169°C (peak temperature), exhibited only in the heating, is due to post-curing of the elastomer.

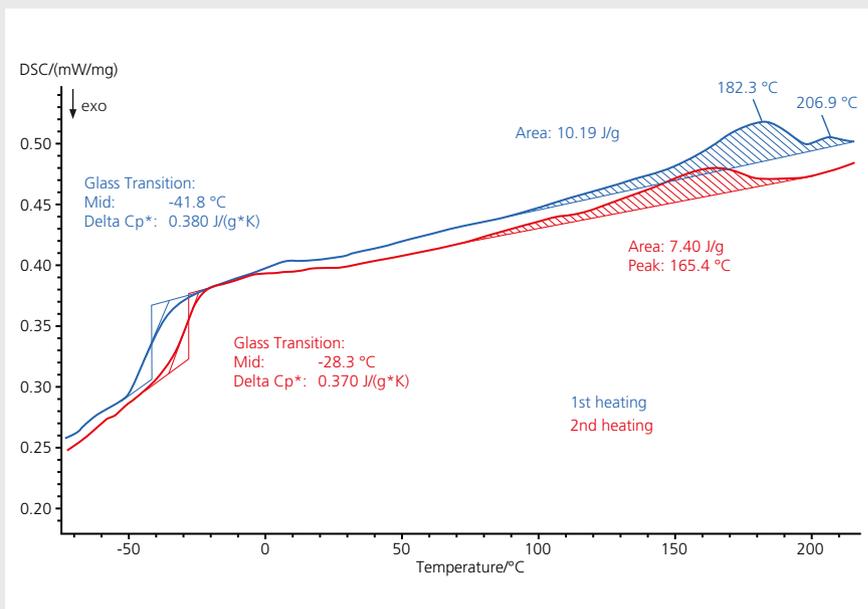


Thermal behavior of SBR rubber.
Sample mass: 15.41 mg; heating from -100°C to 220°C at 10 K/min, twice; dynamic N₂ atmosphere.

Thermal Behavior of Thermoplastic Polyurethane

This plot shows a measurement on TPU. During the 1st heating, the endothermic step at -42°C (mid-point) reflects the glass transition of the soft segments of the sample.

Additionally, the curve exhibits an endothermic double peak between 100°C and 210°C. The reversible part of it, which can be detected again in the 2nd heating (7.40 J/g), is caused by the melting of the hard (thermo-plastic) segments. The irreversible part is probably due to evaporation of volatiles or distribution of additives in the polymer matrix. This process explains the fact that the glass transition was detected at a higher temperature (mid-point at -28°C) in the 2nd heating.



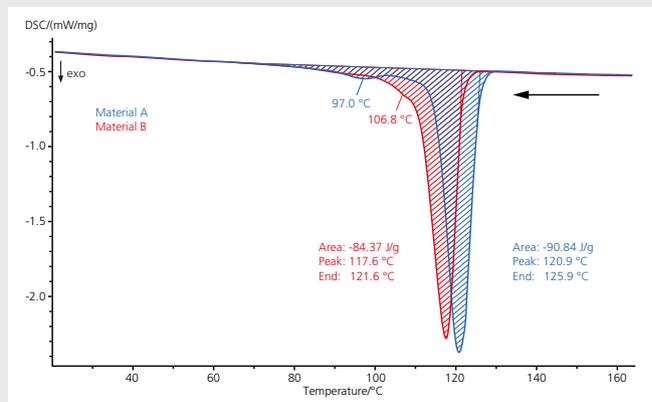
Thermal properties of the soft and hard segments in a thermoplastic polyurethane (TPU).
Sample mass: 10.47 mg; heating from -100°C to 250°C at 10 K/min, twice; dynamic N₂ atmosphere.

DSC 214 *Polyma* – An Essential Aid for Process Optimization

Failure Analysis – Influence of Recycled Material

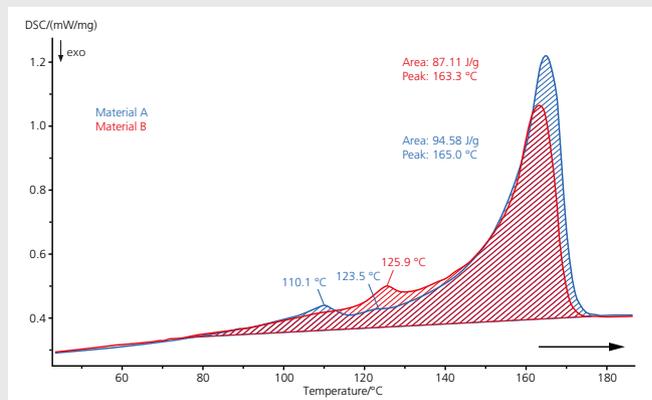
In this example, two recycled polypropylenes were being used for injection molding. Material A was completely crystallized after the molding process whereas material B was still molten. To discover the reason for the differing behavior, DSC measurements were performed.

The exothermic peaks appearing during cooling can be attributed to crystallization of the polymer. Recycled material A starts to crystallize at a higher temperature (endset temperature at 126°C, blue curve) than the second material (endset temperature at only 122°C, red curve). Furthermore, in addition to the peaks at 121°C (blue curve) and 118°C (red curve), a peak at 97°C (blue curve) and a shoulder at 107°C (red curve) occur – clear indications for the presence of a second component. The additional components in material A cause earlier nucleation.



Different solidification of two recycled PP samples. Sample mass: approx. 13 mg; cooling at 10 K/min after heating to 200°C; dynamic N₂ atmosphere.

The 2nd heating reveals further information. Besides the peaks at 165°C and 163°C, which are typical for the melting of polypropylene, the blue curve exhibits two additional peaks at 110°C and 124°C, indicating the existence of additional LDPE, LLDPE or HDPE: The melting temperature increases with increasing density. In contrast with this, material B has only one further peak at 126°C.



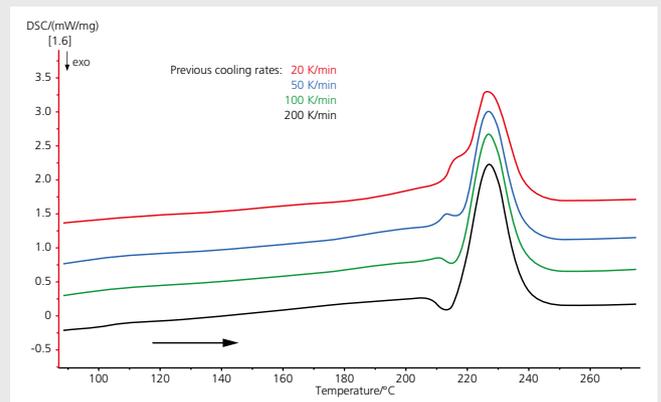
Melting of recycled PP with different PE contamination. Sample mass: approx. 13 mg; heating to 200°C at 10 K/min after cooling at 10 K/min; dynamic N₂ atmosphere.

Development of Process Parameters for Injection Molding

Semi-crystalline polymers such as polybutylene terephthalate (PBT) exhibit a relationship between completion of crystallization and the cooling speed. This factor is important for estimating the temperature at which the mold can be opened in practice to remove a finished solid part.

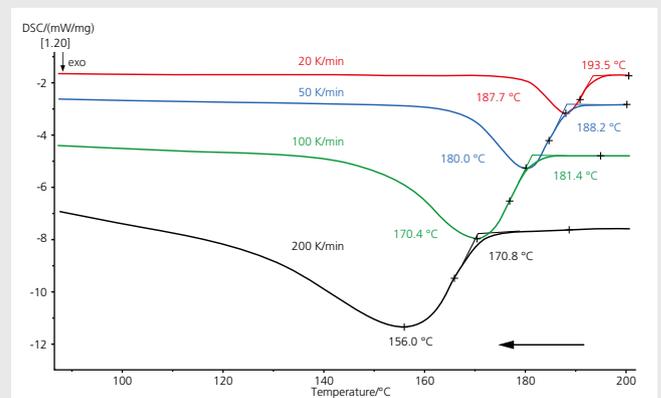
In the example, PBT with 30 wt% glass fibers was subjected to a temperature program consisting of various cooling segments at cooling rates between 20 K/min and 200 K/min.

As to the subsequent heating steps (all performed at 50 K/min), the shoulder of the β -phase, as is typical for PBT, is clearly visible for the sample which had been cooled at 20 K/min (red curve). This effect is shifted to lower temperatures – and therefore better separated from the main peak – for the sample which had been cooled at 50 K/min (blue). Finally, for the curves with a cooling rate of 100 K/min (green) and 200 K/min (black), the endothermic effect completely disappears and gives way to exothermic post-crystallization.



Heating curves of PBT GF30 following different cooling rates. Sample mass: 10.1 mg; heating at 50 K/min.

During cooling at 20 K/min (red), solidification starts at about 194°C and exhibits its maximum at 188°C (peak temperature), whereas during cooling at 200 K/min (black curve), the temperatures are shifted to 171°C and 156°C, respectively. Here, the exothermic crystallization does not end before approx. 120°C, where a small bend is visible in the curve.



Different cooling curves of PBT resulting from different cooling speeds. Sample mass: 10.1 mg; cooling at 20 K/min, 50 K/min, 100 K/min and 200 K/min; dynamic N₂ atmosphere.

DSC 214 *Polyma* – Sophisticated Measurement and Analysis

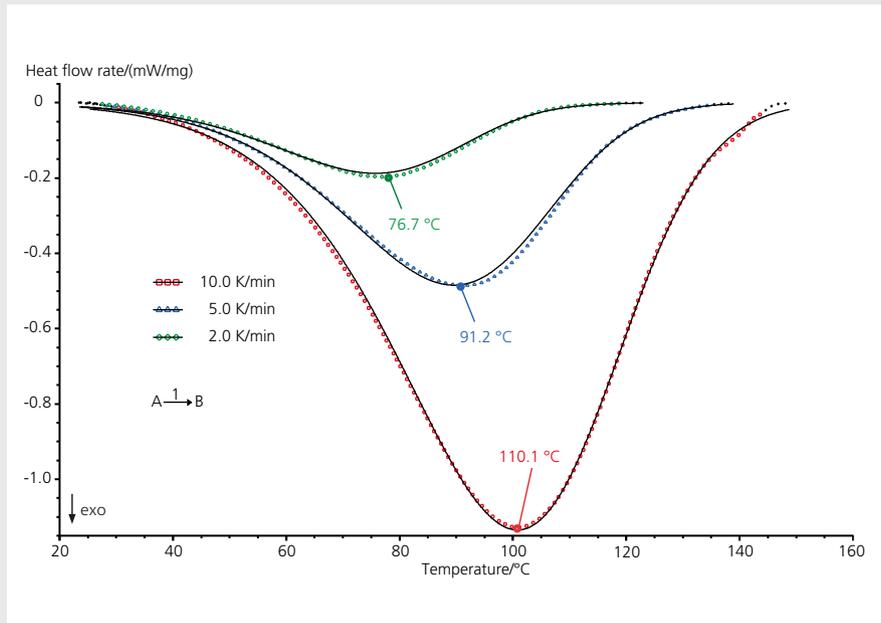
Kinetic Analysis of an Epoxy Adhesive

The NETZSCH *Thermokinetics* software module is used for creating kinetic models of chemical processes. It can also be used to predict the behavior of chemical systems for user-defined temperature conditions and for process optimization.

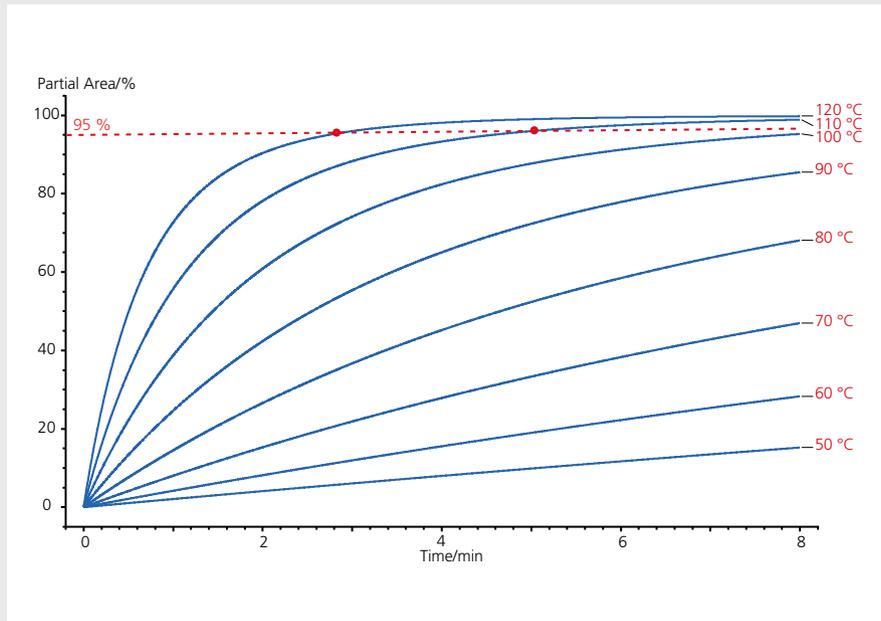
In this example, the curing of a 2-component epoxy adhesive was investigated. Three samples were prepared and heated to 200°C at different heating rates (2 K/min, 5 K/min, 10 K/min). As expected, the peak temperature of the curing effect shifts to higher temperatures as the heating rates increase.

The kinetic model of a one-step reaction is in good agreement with the experimental data, with a correlation coefficient higher than 0.999. Therefore, this model can be used for predictions on isothermal conditions or for a temperature program defined by the user.

The plot shows the degree of curing for different isothermal temperatures. A degree of curing of 95% is reached after nearly 3 minutes at 120°C. Two more minutes are necessary to reach the same degree of curing at a temperature of 110°C.



Comparison of measured curves (dotted lines) and theoretical curves (solid lines) with a one-step reaction.

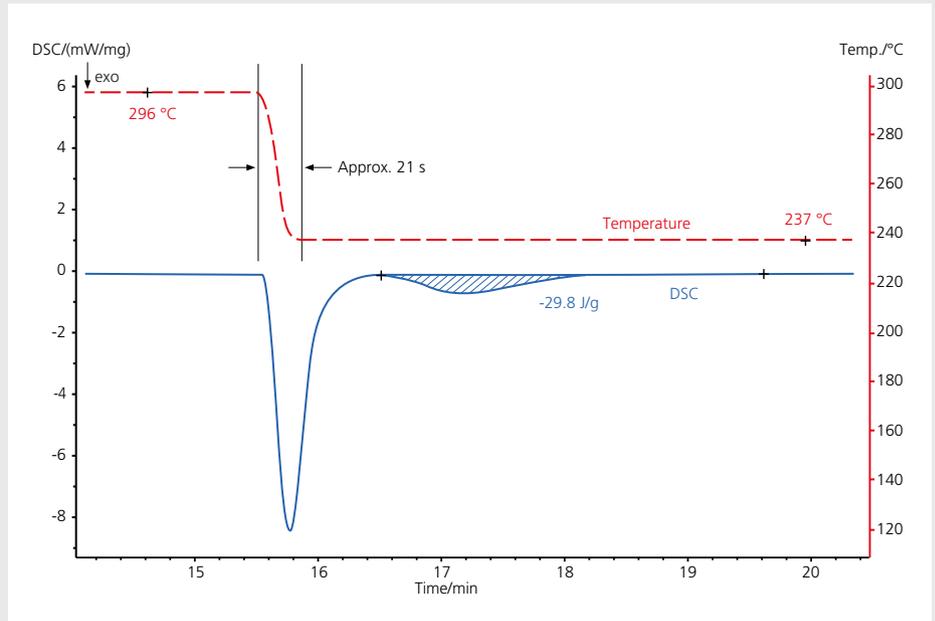


Prediction of the curing reaction for different isothermal temperatures.

Isothermal Crystallization of a Semi-Crystalline Thermoplastic

Isothermal crystallization tests are often used to simulate the rapid cooling of finished polymer parts during production (e.g., injection molding).

The graph on the right depicts an isothermal crystallization experiment on PA66 GF30 (containing 30 wt% glass fiber) using the DSC 214 *Polyma* in combination with the IC70 intracooler. The low thermal mass of the *Arena* furnace allows for a temperature interval of almost 60 K to be bridged within seconds (programmed cooling rate: 300 K/min). Based on this, it is possible to separate solidification of PA66 from the starting phase of the segment. This clearly demonstrates the superior cooling performance of the heat-flux DSC 214 *Polyma*.



Isothermal crystallization of a semi-crystalline thermoplastic. 11.4 mg PA66 GF30 in a dynamic nitrogen atmosphere, intracooler for the temperature range -70°C to 600°C, programmed cooling rate: 300 K/min. The temperature curve is marked in red; the DSC curve in blue. The total crystallization enthalpy at 237°C amounts to approx. 30 J/g.



Appendix

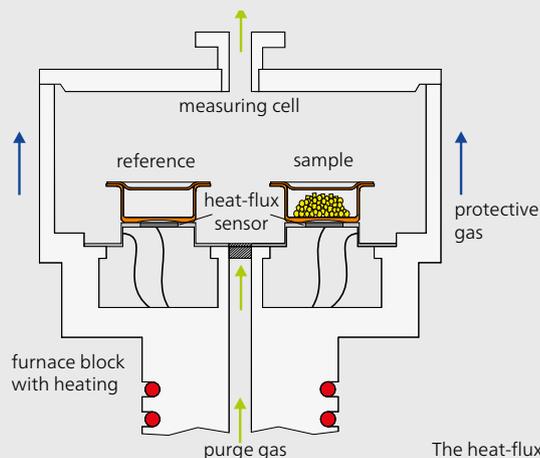
Important Standards for Polymer Testing

There are several relevant standards existing for application, evaluation and interpretation of DSC data in the polymer field. The DSC 214 *Polyma* operates based on all of them. A selection of standards can be found in the following table.

| Category | Standard | Description |
|---------------|------------------------|---|
| General | | |
| | ISO 11357, Part 1 to 7 | Plastics — Differential Scanning Calorimetry (DSC) |
| | ASTM D3417 | Heats of Fusion and Crystallization of Polymers by Thermal Analysis |
| | ASTM D3418 | Transition Temperatures and Enthalpy of Fusion and Crystallization by DSC |
| | ASTM D4591 | Temperatures and Heats of Transitions of Fluoropolymers by DSC |
| | ASTM E793 | Heats of Fusion and Crystallization by DSC |
| | ASTM E794 | Melting and Crystallization Temperatures by Thermal Analysis |
| | ASTM E1356 | Glass Transition Temperatures by DSC |
| | ASTM F2625 | Enthalpy of Fusion, Percent Crystallinity, and Melting Point of Ultra-High Molecular Weight Polyethylene by DSC |
| | DIN 50007 | Differential Thermal Analysis (DTA): Basics (in German) |
| | DIN 53545 | Low-Temperature Performance of Rubbers (in German) |
| | EN 61074 (IEC 1074) | Heats and Temperatures of Melting and Crystallization by DSC of Electrical Insulation Materials |
| | IEC 1006 | Glass Transition Temperature of Electrical Insulation Materials |
| OIT | | |
| | ASTM D3350 | Polyethylene Plastics Pipe and Fittings Materials – Oxidative-Induction Time |
| | ASTM D3895 | Polyolefins by DSC – Oxidative-Induction Time |
| | DS 2131.2 | Pipes, Fittings and Joints of Polyethylene-Type – PEM and PEH for Buried Gas Pipelines |
| | DIN EN 728 | Polyolefins Pipes and Fittings – Oxidative-Induction Time |
| | ISO TR 10837 | Thermal Stability of Polyethylene for Use in Gas Pipes and Fittings |
| Resins/Curing | | |
| | ISO 11409 | Phenolic Resins – Heats and Temperatures of Reaction by DSC |
| | DIN 65467 | Aircraft/Spacecraft: Testing of Thermosetting Resins with and without Reinforcement, DSC Method (in German) |

Method

As per ISO 11357-1 DSC is a technique in which the difference between the heat flow rate into a sample crucible and that into a reference crucible is derived as a function of temperature and/or time. During such measurement, sample and reference are subjected to the same controlled temperature program and a specified atmosphere.



The heat-flux cell of DSC 214 Polyma

Technical Key Data for the DSC 214 Polyma

| | |
|-----------------------------|--|
| Temperature range | -170°C to 600°C |
| Heating/Cooling rate | 0.001 K/min to 500 K/min* |
| Indium Response Ratio | > 100 mW/K ** |
| Resolution (digital) | 0.25 µW |
| Enthalpy accuracy | < 1% |
| Specific heat determination | Optional |
| Temperature modulation | Optional |
| Cooling device options | <ul style="list-style-type: none"> ▪ Compressed air cooling (RT to 600°C) ▪ IC40 (-40°C to 600°C) ▪ IC70 (-70°C to 600°C) ▪ LN₂, automatically controlled (-170°C to 600°C) |
| Gas atmospheres | Inert, oxidizing, static and dynamic operation |
| Gas controller | <ul style="list-style-type: none"> ▪ Switches for 3 gases included ▪ MFC for 3 gases, optional |
| ASC | Up to 20 samples and references, optional |
| Software | <p><i>Proteus</i>[®]</p> <p>The software runs under the operating systems Windows XP, Windows 7 and Windows 8.1.</p> |

* Maximum rates depend upon the temperature

** Related to indium as standard material under measurement conditions typically used for polymer investigation (10 mg sample mass, 10 K/min heating rate, nitrogen atmosphere)

The NETZSCH Group is a mid-sized, family-owned German company engaging in the manufacture of machinery and instrumentation with worldwide production, sales, and service branches.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 3,000 employees at 163 sales and production centers in 28 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Adiabatic Reaction Calorimetry and the determination of Thermophysical Properties, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

www.netzsch.com/n21467



NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42
95100 Selb
Germany
Tel.: +49 9287 881-0
Fax: +49 9287 881 505
at@netzsch.com

www.netzsch.com