NETZSCH

Differential Scanning Calorimetry DSC 214 *Polyma*

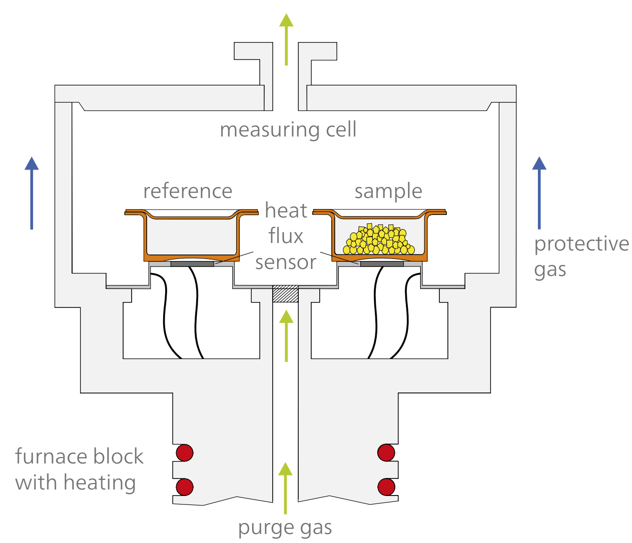
Method, Technique, Applications

Leading Thermal Analysis

Method

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

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*

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 crystal molecular weight (qualitative, via peak shape)

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	Thermal Analysis; Differential Thermal Analysis; Principles
	DIN 53545	Bestimmung des Kälteverhaltens von Elastomeren – Grundlagen und Prüfverfahren
	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
Oxidative Stability (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	Luft- und Raumfahrt: Prüfung von Reaktionsharzsystemen mit und ohne Verstärkung, DSC-Verfahren

DSC 214 *Polyma*

More Than a DSC – A Smart System for Polymers

Low-Mass Furnace for Fast Heating and Cooling Better Replicates Polymer Processing Conditions

The DSC 214 *Polyma* is equipped with the *Arena*® furnace, the fastest furnace available for a heat-flux DSC. It can heat at up to 500 K/min and cool at 200 K/min over a wide measurement range. This even allows for the measurement of isothermal crystallization or isothermal curing for kinetic studies where it is necessary to reach equilibrium conditions as quickly as possible. It is thus possible to replicate real processing conditions very closely in your DSC experiments. Additionally, one can speed up the measurements and thus save working time.

Unique Sensor Concept for Excellent Reproducibility

The *Corona*® sensor and the *Concavus*® pans apply the concept of a ring-shaped contact zone which is always clearly defined. The concave form of the pan bottom prevents it from bulging. Influences to heat transfer are thus negligible, resulting in optimized reproducibility. The high-grade *Concavus*® pans are delivered in 3in1 Trays from which they can be individually withdrawn. This increases their mechanical stability and has an additional positive effect on the reproducibility of the measurement results.

Save Space in Your Lab

Laboratory space is often limited. With its small footprint, the DSC 214 *Polyma* including cooling accessory (e.g., intracooler) is ideally suited for this case. Its flexibility allows for easy setup in a production environment for QA/QC purposes.

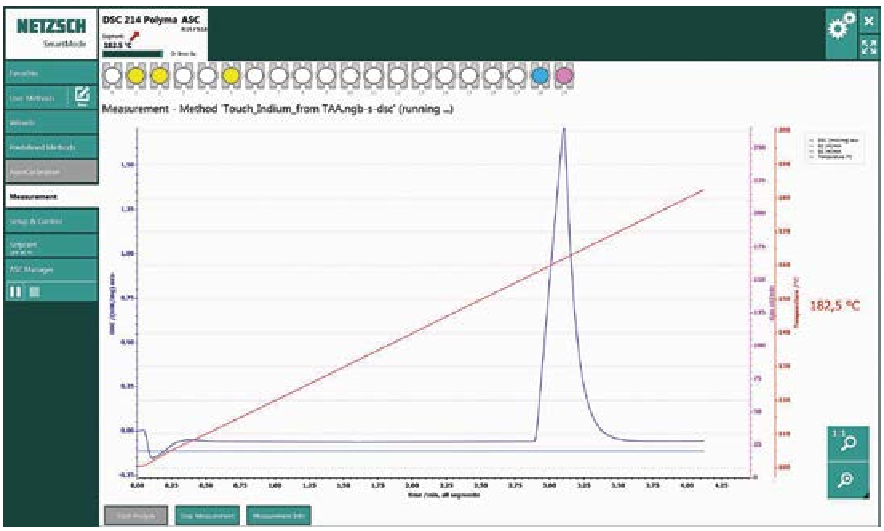
Proteus® Software – Setting the Paradigm in Usability and Intelligence

SmartMode, AutoEvaluation and *Identify* are the keys to making life in a laboratory much easier than ever before. Respectively, these are: A simplified and intuitively designed user interface; autonomous evaluation routines which can serve as a second opinion when assessing unknown samples; and a database system for identifying and verifying materials – all at your side at any time.
AutoCalibration performs calibration runs along the way and keeps your hands free for more important matters. Thanks to its flexibility, the *Proteus*® software can also be used without these little aids in *ExpertMode*, where all software options are accessible.

HIGH SAMPLE THROUGHPUT
SMALL FOOTPRINT
AUTOCALIBRATION
CONCAVUS PANS
FAST FURNACE
EASY SAMPLE PREPARATION
AUTOEVALUATION
SAMPLECUTTER
SMARTMODE
AUTOMATIC SAMPLE CHANGER
HIGH-PERFORMANCE SENSOR
EXPERTMODE
IDENTIFY
EPIC VERSATILITY

Proteus® Software

ALWAYS ONE STEP AHEAD



SmartMode interface during an ASC measurement

The User Comes First

The NETZSCH *Proteus*® software offers far more than ordinary measurement and analysis software for DSC instruments. Its many support features greatly assist operators in their day-to-day work. But users have full control at all times and can decide whether to go the traditional route, the software-aided route or a combination of the two.

SW-Features

- ■ *SmartMode*
- ■ *ExpertMode*
- ■ *AutoCalibration*
- ■ *AutoCooling*
- ■ Advanced DSC-*BeFlat*®
- ■ *AutoEvaluation* (see next pages)
- ■ *Identify* (see next pages)
- □ TM-DSC (temperature-modulated DSC)
- □ ASC (Automatic Sample Changer) support
- □ Specific heat capacity (c_p) determination
- ■ Report Generator
- □ Purity
- □ *Peak Separation*
- □ *Thermokinetics*

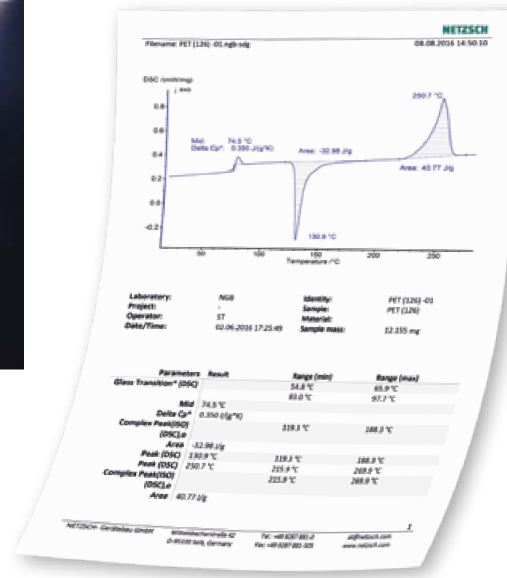
■ included □ optional

SmartMode and *ExpertMode* – Giving You the Flexibility You Need

Due to rapid development in electronics, the timelines of embedded display formats are often quite short. By using *SmartMode*, however, it is possible to have the same intuitive user interface on a tablet, a larger touch monitor or a regular PC – whatever you prefer.

For anyone who favors a more classical user interface or wants access to the entire range of functions afforded by the *Proteus*® software, *ExpertMode* is the solution.

Real-time operation of the software allows for the display of running curves in both modes and – if desired – presents the evaluation immediately when the measurement is finished. In order to start a test run, one may open either wizards (quick-start routines in *SmartMode*), predefined methods (e.g., related to polymer types in *SmartMode*) or user-defined methods (in both *SmartMode* and *ExpertMode*).



Report Generator to Meet Various Needs

Based on a Microsoft Word plug-in each operator can easily create his own report template – including logos, tables, description fields and plots. As an entry several report examples are already delivered together with the *Proteus*® software.

Ideal Flat Baselines Thanks to Advanced *BeFlat*®

Due to material and technical limitations, each DSC sensor has some imbalances which will have an impact on the shape of the corresponding DSC baseline.

Advanced *BeFlat*® is a method to compensate all these influences in a DSC 214 *Polyma* by performing just two measurements (one with a pan only on the reference side and a second one with two empty pans). The result are horizontal DSC baselines with minimal deviations in the µW range.

Temperature-Modulated DSC – TM-DSC

In TM-DSC (optional), the underlying linear heating rate is superimposed by a sinusoidal temperature variation. The benefit of this procedure is the chance to separate overlapped DSC effects by calculating the reversing and the non-reversing signals. The reversing heat flow is related to the changes in specific heat capacity (→ glass transition) while the non-reversing heat flow corresponds to temperature-dependent phenomena such as curing, dehydration or relaxation.

Instrument-Independent Measurement Definitions

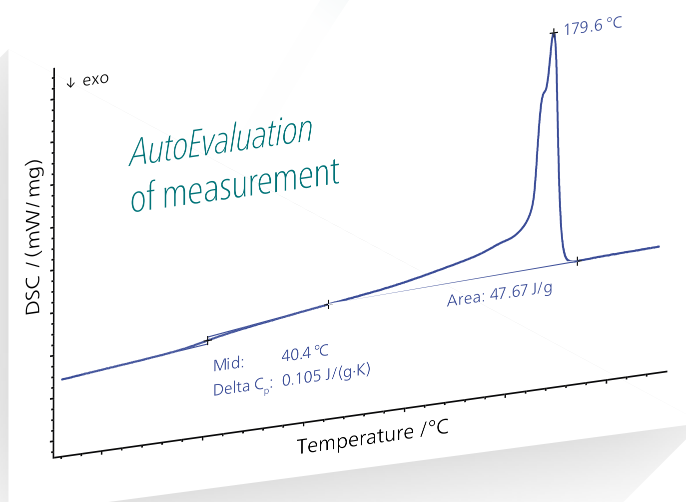
In the ASC mode, each measurement definition can be clearly assigned to the position of the particular sample pan inside the sample tray. Wizards and predefined methods can also be stored on a network drive, accessible from all existing NETZSCH DSCs.

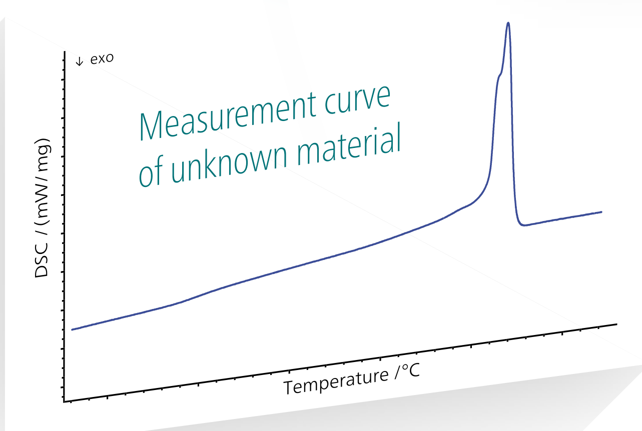
Just like Magic

AutoEvaluation

AutoEvaluation is the first self-acting evaluation routine for DSC curves on the market. Without user-intervention it is able to detect and to evaluate fully automatic glass transition temperatures, melting temperatures or melting enthalpies of unknown polymers or pure metals. Experienced users can take the automatic evaluation result as a second opinion – and, of course, recalculate values if desired.

one CLICK RESULTS



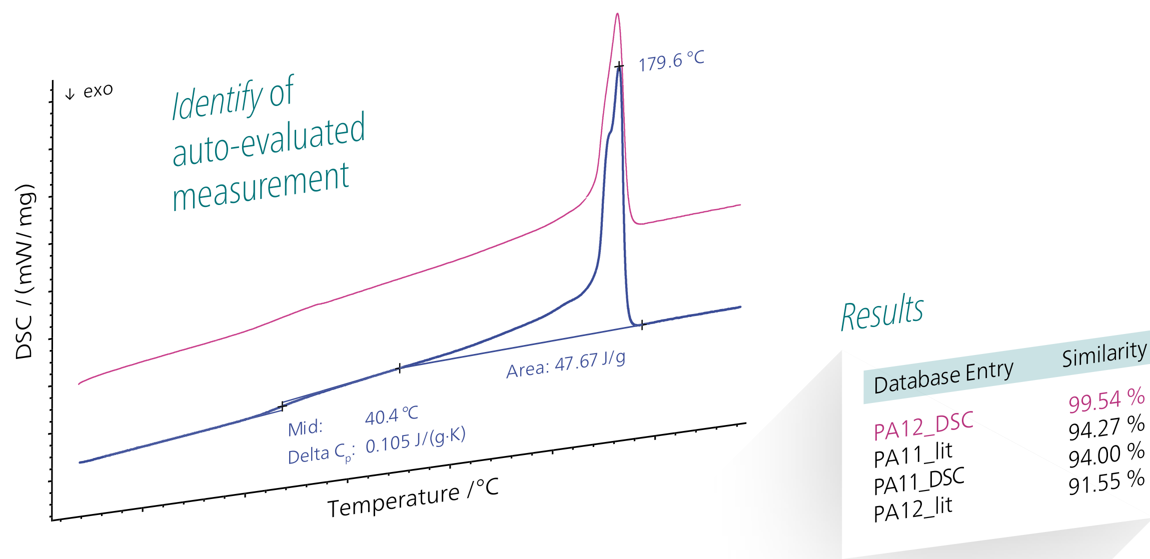


User-independent!

No evaluation macro, no selection of evaluation limits or thresholds!

Identify

- Is a unique curve recognition and interpretation system
- Includes a database with NETZSCH libraries and libraries that can be created by the user
- Manages measurements, literature data and classes



The Curve Comparison Database

Identify

Identify is a unique software package within the thermal analysis field for the identification and classification of materials via database comparison. Besides one-on-one comparisons with individual curves or literature data, it also checks if a particular curve belongs to a certain statistical class are feasible. These classes can consist of curves of the same material type (material identification) but also of reference curves for Pass/Fail testing (quality control).

The provided NETZSCH libraries contain more than 1100 entries related to different application areas such as polymers, organics, inorganics, metals/alloys or ceramics.

The shown similarity hit list is the result of applying *Identify* to the measurement example displayed above. The highest similarity is attributed to PA12 (polyamide 12). The similarity value of 99.5% reflects the excellent conformity with the reference curve (pink).

Accessories

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

Sample Preparation Kit

In addition to the *SampleCutter*, the DSC 214 *Polyma* also comes with a Sample Preparation Kit. This set contains a variety of small tools including a cutting board, scissors, tweezers, spatula, etc. and is designed to make sample preparation as easy and convenient as possible.

The New Benchmark in Sensor Design

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 and accounts for excellent reproducibility.

Automatic Sample Changer – High Sample Throughput

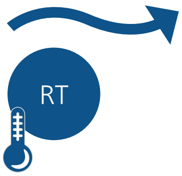
Thanks to the automatic sample changer (ASC), the measurement of up to 20 samples – either belonging to a single series or independent of each other – can be carried out without operator intervention. Different crucible types, different gas atmospheres and individual calibration curves can be handled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

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

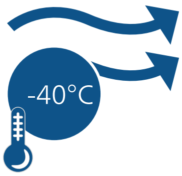
Even the transport and storage of the *Concavus*® pans is consistent with their premium quality, thanks to the 3in1 Tray: 96 pans and lids are packaged in an anti-static box divided into 96 separate compartments. This elaborate packing prevents deformation of the pans while allowing easy access to them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

Broad Temperature Range and Economic Cooling

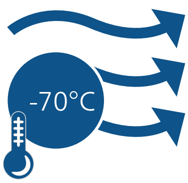
For fast cooling back to room temperature or for tests at sub-ambient temperatures, optimized cooling is required. NETZSCH offers several options for meeting these needs.



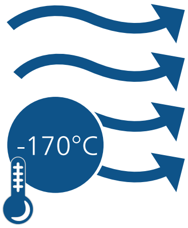
Compressed air cooling (RT to 600°C)



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



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



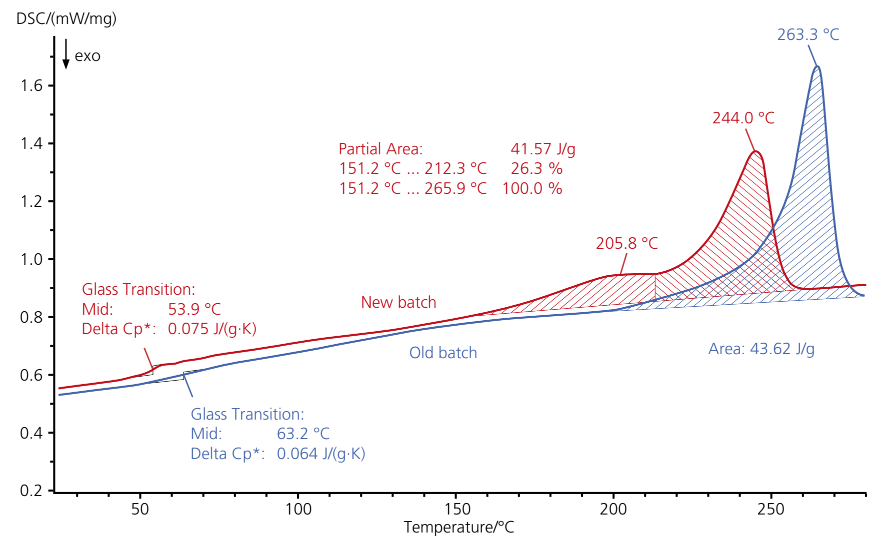
Liquid nitrogen cooling system (-170°C to 600°C)

Applications

THERMOPLASTICS/RECYCLING

Incoming Goods Inspection

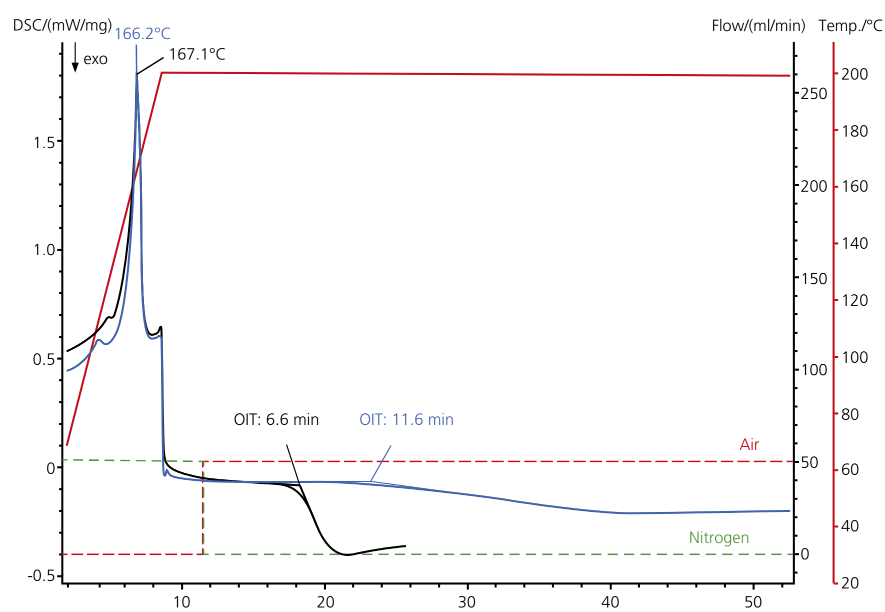
The plot shows the DSC results for two seemingly identical granulate batches, specified as Polyamide 66, which were delivered at different times (2nd heating after controlled cooling at 20 K/min). The blue curve (old batch) shows the glass transition at 63°C (mid-point) and the melting peak at 263°C, 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 N_2 atmosphere.

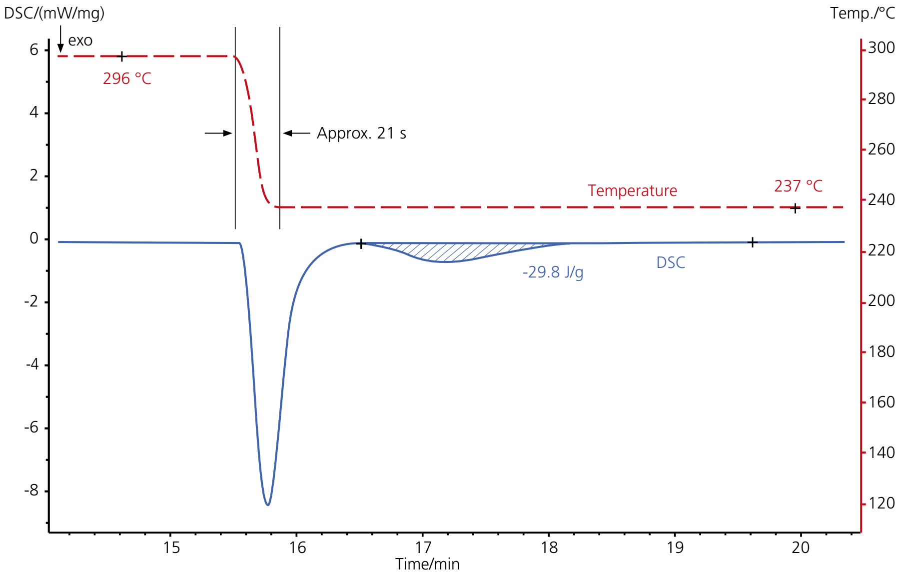
Oxidative Stability

OIT tests (oxidative-induction time) are well-known for evaluating the resistance to oxygen of polymers, in particular polyolefins. In this example, two PP samples were heated to 200°C under a dynamic nitrogen atmosphere. The endothermic peaks detected during heating illustrate the melting of the polypropylene. After 3 minutes at 200°C, the gas was switched to air. The resulting exothermic effects indicate 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 N_2 (50 ml/min), 3 min isothermal under N_2, isothermal under air (50 ml/min) until degradation.

DSC 214 Polyma –
Ideal for Quality Control of Polymers



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. 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. Important for isothermal crystallization experiments is to avoid any temperature-undershoot while changing over from cooling to the isothermal phase.

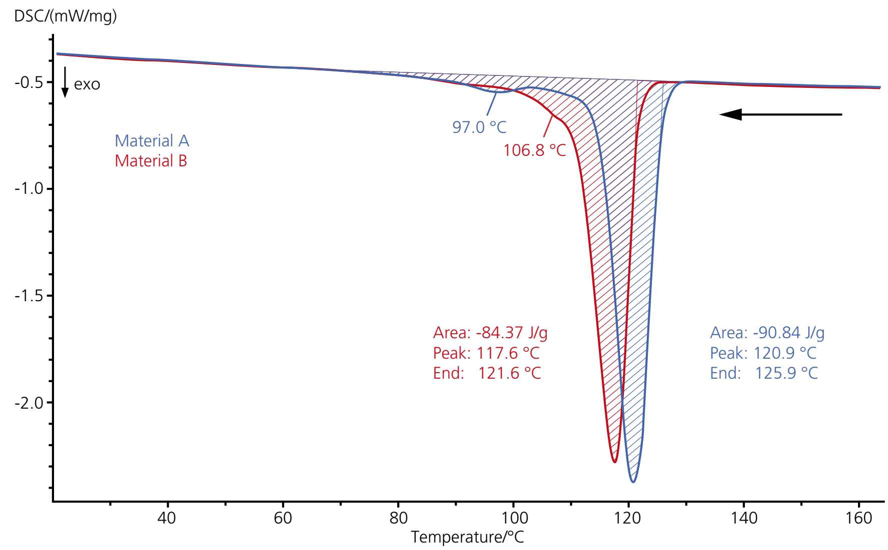
Isothermal Crystallization of a Semi-Crystalline Thermoplastic

Isothermal crystallization tests are often used to simulate the rapid cooling of polymer parts during production (e.g., injection molding). The graph on the left 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. Based on this, it is possible to separate solidification of PA66 from the starting phase of the isothermal segment. This clearly demonstrates the superior cooling performance of the heat-flux DSC 214 *Polyma*.

Failure Analysis – Influence of Recycled Material

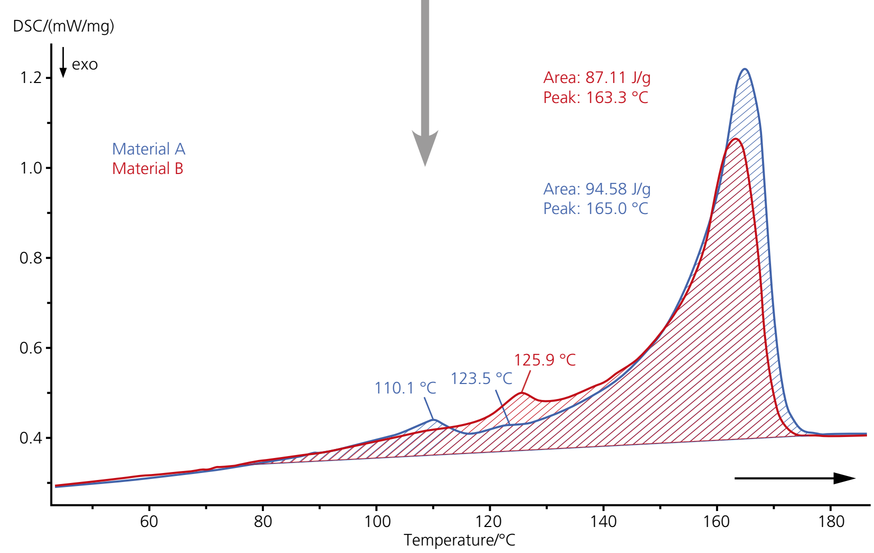
In this example, two recycled polypropylenes were being used for injection molding. Material A was completely crystallized after the molding process whereas material B was still molten. To discover the reason for the differing behavior, DSC measurements were performed.

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 N_2 atmosphere.

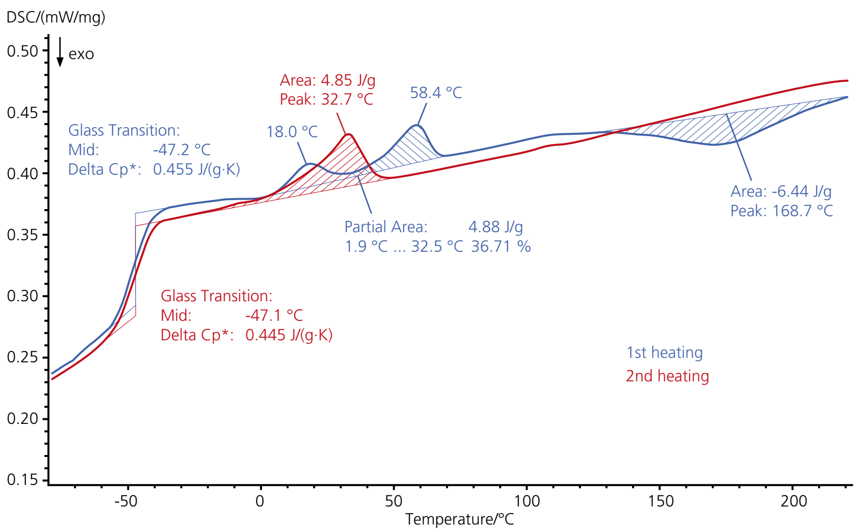
The 2nd heating reveals further information. Besides the peaks at 165°C and 163°C, which are typical for the melting of polypropylene, the blue curve exhibits two additional peaks at 110°C and 124°C, indicating the existence of additional LDPE, LLDPE or HDPE. In contrast with this, material B has only 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 N_2 atmosphere.

An Essential Aid for Process Optimization

RUBBER



Thermal behavior of SBR rubber. Sample mass: 15.41 mg; heating from -100°C to 220°C at 10 K/min, twice; dynamic N_2 atmosphere.

Low-Temperature Performance of Rubber

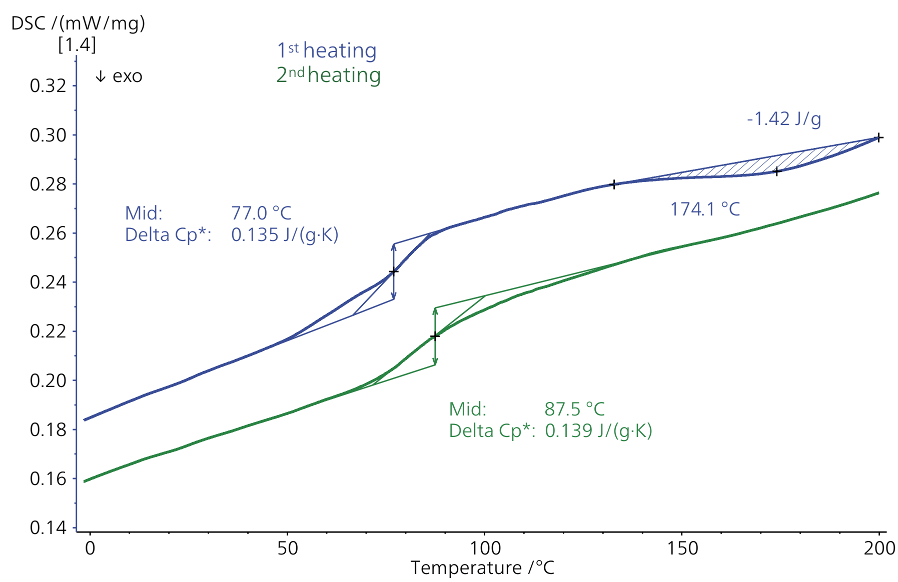
DSC measurements are important for rubbers used in tires because their service temperature range is limited by the glass transition temperature. In this example, an SBR sample was measured twice between -100°C and 220°C. The endothermic step detected at -47°C (mid-point) in both heating sequences is 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 1st heating, is due to post-vulcanization of the elastomer.

THERMOSETS

Epoxy Resin (EP)

As an amorphous polymer, this epoxy resin exhibits a glass transition at 77°C (midpoint) with a specific heat capacity of 0.14 J/(g·K) in the 1st heating (blue) followed by an exothermal effect (peak temperature 174°C), due to post-curing of the resin. As a result of the post-curing, the glass transition temperature in the 2nd heating (green) is shifted to 88°C (midpoint). The step height remains nearly the same. Since no further exothermal effect occurs, it can be assumed that the epoxy resin was entirely cured during the 1st heating.

Both the exothermal effect and the position (and shift) of the glass transition temperature to higher values can be interpreted as an evidence for the degree of curing of the material.



Epoxy resins (EP) undergo a polyaddition cross-linking reaction. The properties of the resin are strongly dependent on the structure, the degree of cross linking, type and amount of the reinforcement material and the processing procedure.

Sophisticated Measurement and Analysis

Key Technical Data

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 (technical)	0.1 µW
Enthalpy precision	▪ ± 0.1% for indium ▪ ± 0.05% to ± 0.2% for most samples
Specific heat determination	Optional
Temperature modulation	Optional
Cooling device options	▪ Compressed air cooling (RT to 600°C) ▪ IC40 (-40°C to 600°C) ▪ IC70 (-70°C to 600°C) ▪ LN_2, automatically controlled (-170°C to 600°C)
Gas atmospheres	Inert, oxidizing, static and dynamic operation
Gas controller	▪ Switches for 3 gases included ▪ MFC for 3 gases, optional
ASC	Up to 20 samples and references, optional
Software	*Proteus*®, including *SmartMode, ExpertMode, AutoCalibration, AutoCooling, AutoEvaluation, Identify, OIT, predefined methods, etc.* The software runs under the operating systems, Windows® 7, Windows® 8.1. and Windows® 10

* 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)


NETZSCH Thermokinetics
Curing of Epoxy Resin
Heat flow rate/(W/g)
0
-0.5
-1.0
-1.5
-2.0
-2.5
20.4 K/min
10.1 K/min
5.0 K/min
150
Temperature/°C

Expertise in Service

Our Expertise – Service

All over the world, the name NETZSCH stands for comprehensive support and reliable service, before and after sale. Our qualified personnel from the technical service and application departments are always available for consultation.

In special training programs tailored for you and your employees, you will learn to tap the full potential of your instrument.

To maintain and protect your investment, you will be accompanied by our experienced service team over the entire life span of your instrument.

Our Expertise – Applications Laboratories

The NETZSCH Thermal Analysis applications laboratories are a proficient partner for nearly any Thermal Analysis issue. Our involvement in your projects begins with proper sample preparation and continues through meticulous examination and interpretation of the measurement results. Our diverse methods and over 30 different state-of-the-art measuring stations will provide ready-made solutions for all your thermal needs.

Within the realm of thermal analysis and the measurement of thermo-physical properties, we offer you a comprehensive line of the most diverse analysis techniques for materials characterization.

Measurements can be carried out on samples of the most varied of geometries and configurations. You will receive high-precision measurement results and valuable interpretations from us in the shortest possible time. This will enable you to precisely characterize new materials and components before actual deployment, minimize risks of failure, and gain decisive advantages over your competitors.

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- Comprehensive Instrument and Method Training

LABORATORY

- Application Service and Contract Testing

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 3,300 employees at 210 sales and production centers in 35 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction) 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.

Leading Thermal Analysis

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