NETZSCH
Proven Excellence.

Thermal Characterization of Polymers

Thermoplastics, Thermoplastic Elastomers, Elastomers and Thermosets

Analyzing & Testing

The World of Polymers

Polymer materials have greatly changed the world we live in – without them, the world would not be as we know it today. There is something innately fascinating about them, yet we've become accustomed to their integral presence in our everyday lives. And today, the possibility of recycling them makes them even more interesting from an ecological and economical point of view.

Henri Braconnot's work in the 1830s is perhaps the first modern example of polymer science. He, along with others, developed derivatives of the natural polymer cellulose, producing new, semi-synthetic materials, such as celluloid and cellulose acetate. Since that time, eight Nobel Prizes have been dedicated to polymer science.

Just 50 years ago, materials we now take for granted were non-existent. With further advances in the understanding of polymers, and with new applications being researched all the time, there is no reason to believe that this revolution will stop any time soon.

The importance of polymers in our daily lives has not come about arbitrarily, but rather as a result of the distinct advantages that they offer. These advantages include:

- Low density
- Light weight
- Good thermal and electrical insulation capacity
- Resistance to corrosion effects
- Chemical inertness
- High strength and dimensional stability
- Absorption of mechanical shocks
- Resistance to abrasion effects
- Good coloring
- Potential for decorative surface effects
- Low production costs
- Easy processability
- Great flexibility of form

Films
Adhesives
Fibers
Resins/Paints
Thermoplastics
Thermosets
Biopolymers
POLYMERS
Foams
Composites
Rubber
Thermoplastic Elastomers
Elastomers
Coatings
Additives

Thermal Analysis

During their production, processing and application, polymers are subjected to temperature-dependent structural changes. Therefore, thermal analysis for characterization of polymers is widely practiced today in research and industry. More and more applications are being backed up by national and international standards (ISO, EN, ASTM, DIN, etc.).

Thermal analysis techniques give insight into the thermal properties of polymer materials and products and gain information regarding the condition or processing history of specific samples relative to reference samples.

This makes thermal analysis very well-suited for quality control and quality assurance. Incoming materials inspection as well as materials selection can be carried out safely and easily. Also for the research and development of new materials, thermal analysis is an indispensable tool for investigating a broad range of materials properties.

With our broad product line of thermoanalytical instruments and applications knowledge acquired over several decades, NETZSCH Analyzing & Testing ranks among the best as far as meeting the high demands associated with the manufacture of reliable products and state-of-the-art technologies.

This brochure gives an overview of our various methods and corresponding application examples from thermoplastics to composites.

The variety of thermoanalytical test methods opens a broad application range for polymer testing, e.g.:	
Specific heat capacity	DSC
Thermal transitions	DSC, DIL, TMA, LFA
Melting, crystallization and reaction enthalpies	DSC
Glass transition temperatures	DSC, TMA, DMA, DEA, LFA
Degree of crystallinity	DSC
Thermal stability	TGA, STA
Oxidation Induction Time/ Oxidation Onset Temperature (OIT, OOT)	DSC
Viscoelastic behavior	DMA, TMA
Young's modulus	DMA, TMA
Kinetics of reactions	DSC, TGA, DIL, TMA, DEA
Compositional analysis	DSC, TGA, EGA
Thermal expansion coefficient	DIL, TMA, DMA
Filler content	TGA, STA
Thermal conductivity/diffusivity	LFA, HFM
and many more	

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is the most frequently employed thermal analysis method. It can be used to analyze nearly any energetic effect occurring in a solid or liquid during thermal treatment. DSC analysis in accordance with ISO 11357 provides the following valuable information for the development and quality control of polymers:

Product Identification and Characterization

- Melting/crystallization temperatures
- Melting/crystallization enthalpies
- Cross-linking temperatures
- Cross-linking enthalpies
- Degree of crystallinity
- Glass transition temperatures
- Specific heat capacity

Advanced Materials Analysis

- Decomposition effects
- Oxidative stability (OIT, OOT)
- Reaction behavior and kinetics
- Predictions
- Degree of curing
- Purity determination for additives
- Curing by UV irradiation
- Stability under pressure
- *Peak Separation*

Product/Process Information

- Incoming goods inspection
- Thermomechanical history
- Failure analysis
- Competitor product analysis
- Process optimization

DSC 300 *Caliris® Select/Supreme* with touch display and ASC for up to 192 samples

DSC 214 *Polyma*

DSC Systems Made for Polymer Applications

The DSC 214 *Polyma* features high heating and cooling rates, making it useful for both research and quality assurance in production.

In complement to this, the DSC 300 *Caliris*® *Select/Supreme* features exchangeable sensor-furnace modules, a large automatic sample changer and the ability to be coupled. The P-Module is specially designed for the examination of polymers.

Thermally activated reactions can be studied by conventional DSC, but cationic polyadditions and radical polymerizations can also be started by UV irradiation with sufficiently high energy. For this purpose, NETZSCH offers the Photo-DSC 204 ***F1*** *Phoenix*®. The DSC 3500 *Sirius* is the economic entry-level model.

DSC 3500 *Sirius*

High-Pressure DSC

Numerous physical processes and chemical reactions are influenced by the surrounding gas pressure. In practice, it is therefore often necessary to define a higher pressure under which to conduct DSC measurements. With the high-pressure DSC 204 HP *Phoenix*®, thermal effects in a sample can be analyzed in the pressure range from vacuum to 15 MPa (150 bar) and at temperatures from -150°C to 600°C, depending on the type of gas.

DSC 204 HP *Phoenix*®

Thermogravimetric Analysis (TGA)

Thermogravimetry (TG), or Thermogravimetric Analysis (TGA), is a well proven thermal analysis method for measuring mass changes as a function of temperature or time. TGA is used in the research & development of various substances and engineering materials – both solids and liquids – in order to obtain knowledge about their thermal stability and composition.

In recent decades, TGA has been used increasingly in quality control and assurance for raw materials and incoming goods, as well as in the failure analysis of finished parts, especially in the polymer-processing industry.

TGA provides complementary and supplementary characterization information to DSC.

Various international standards describe the general principles of thermogravimetry for polymers (ISO 11358) or other specific applications, such as the TGA method for the compositional analysis of rubber (ASTM D6370).

Our vertical, top-loading design not only provides for easy operation and sample loading, but also allows gases to flow naturally in an upward direction. Evolved gas analyzers such as mass spectrometers, FT-IR (Fourier Transform Infrared) spectrometers and/or GC-MS (gas chromatograph-mass spectrometers) can be coupled directly to the gas outlet on the top of the furnace.

The Automatic Sample Changer (ASC) can also be used to conduct routine measurements around the clock.

TG 209 ***F3*** *Tarsus*® entry-level model with ASC

TG 209 ***F1*** *Libra*® premium model with ceramic furnace and ASC for up to 192 samples

Simultaneous Thermal Analysis (STA)

STA 449 ***F1*** *Jupiter®*

Simultaneous Thermal Analysis (STA) generally refers to the simultaneous application of thermogravimetry (TG) and DSC to one and the same sample in a single instrument. Main advantages are the identical test conditions for the TGA and DSC signals (same atmosphere, gas flow rate, vapor pressure of the sample, heating rate, thermal contact to the sample crucible and sensor, radiation effect, etc.). In addition, sample throughput is improved as more information is simultaneously gathered from each test run.

The DSC, TGA and STA systems all meet the majority of the respective instrument and application standards, including: ISO 11357, ISO 11358, ASTM E967, ASTM E968, ASTM E793, ASTM D3895, DIN 51004, DIN 51006, DIN 51007.

TGA Measurement Information

- Mass changes
- Temperature stability
- Estimation of product lifetime
- Oxidation/reduction behavior
- Filler content
- Moisture and volatiles content
- Decomposition
- Compositional analysis of multi-component materials/blends
- Data for kinetic evaluation using Kinetics Neo

DSC Measurement Information

- Specific heat capacity
- Melting/crystallization behavior
- Solid-solid transitions
- Polymorphism
- Degree of crystallinity
- Glass transition temperatures
- Cross-linking reactions
- Oxidative stability
- Purity determination for additives
- Data for kinetic evaluation using Kinetics Neo

Thermal Analysis Coupled to Evolved Gas Analysis (EGA)

Top-level polymer research and characterization can be achieved by coupling the thermoanalytical methods of TGA, DSC, STA, TMA and DIL to a mass spectrometer (MS), gas chromatograph/mass spectrometer (GC-MS) or Fourier Transform Infrared (FT-IR) spectrometer. These hyphenated techniques may also include simultaneous coupling of the MS and FT-IR or GC-MS and FT-IR to the thermal analyzer. In addition, the unique adapter allows for coupling even when used in combination with an Automatic Sample Changer (ASC).

TGA-FT-IR coupling via an external FT-IR gas cell

Coupling Possibilities

- TGA-, DSC-, or STA-MS via capillary coupling
- STA-MS via *SKIMMER* coupling
- TGA-, or STA-GC-MS
- TGA-, DSC-, or STA-FT-IR
- TMA-MS
- DIL-MS

Evolved gases are directed straight to the gas analyzer via a heated capillary or transfer line. In addition to decomposition, such systems can also be used for investigating composition, evaporation and solid-gas reactions.

Measurement Information by Means of Evolved Gas Analysis Coupled to Thermal Analysis

Compositional analysis

- Polymers
- Plasticizers
- Solvents
- Additives
- Propellents

Evaporation

- Vapor pressure
- Sublimation

Decomposition

- Dehydration
- Stability
- Residual solvent
- Pyrolysis

Solid-gas reactions

- Combustion
- Oxidation
- Adsorption/desorption

PERSEUS STA 449 ***F1*** *Jupiter*®
and GC-MS coupling

Thermomechanical Analysis (TMA)/ Dilatometry (DIL)

Thermomechanical analysis (TMA) and dilatometry (DIL) are two of the most important characterization techniques in the field of thermal analysis. DIL determines the length change of samples under a negligible load (DIN 51045). The closely related TMA method also determines the dimensional changes of solids, liquids or pasty materials as a function of temperature and/or time under a defined static load (ISO 11359, DIN 51 005, ASTM E831, ASTM D696, ASTM D3386).

With the TMA 402 ***F3*** *Hyperion® Polymer Edition*, measurements can be carried out in expansion, penetration, tension and bending mode. Investigations can be realized on plastics and elastomers, paints and dyes, composite materials, adhesives, films and fibers. The NETZSCH dilatometers (DIL 402 *Expedis*) and TMA 402 ***F3*** *Hyperion® Polymer Edition* are based on the instrument and application standards for polymers and composites.

TMA/DIL Measurement Information

- Thermal expansion
- Coefficient of linear thermal expansion
- Volumetric expansion
- Density change
- Delamination
- Glass transition temperatures
- Softening points
- Penetration behavior
- Phase transitions
- Creep/relaxation behavior
- Stress/strain curve
- Anisotropic behavior
- Young's modulus
- Data for kinetic evaluation using Kinetics Neo

Variety of TMA 402 sample holders

TMA 402 ***F3*** *Hyperion®*

DIL 402 *Expedis Supreme*

Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) allows for the quantitative determination of the mechanical properties of a sample under an oscillating force and as a function of temperature, time, frequency and strain (DIN 53513, DIN EN ISO 6721, DIN 53440, DIN-IEC 1006, ASTM D4065, ASTM D4092, ASTM D4473, ASTM D5023, ASTM D5024, ASTM D5026, ASTM D5418). The results portray the linear viscoelastic properties, typically depicting them as a graphical plot of E′ (storage modulus), E″ (loss modulus), and tanδ (loss factor) versus temperature.

The DMA 303 *Eplexor*® and the high-force DMA GABO EPLEXOR® systems identify transition regions, such as glass transitions in plastics and resins, and may be used for quality control or product development in the temperature range from -170°C to 1500°C.

Dynamic Mechanical Testing Supports Research and Quality Control of Polymers

R&D

The DMA method is a very sensitive tool for generating data that can help define the mechanical properties of polymers and composites in order to support product development in industries such as automotives.

Quality Control

α and β transitions can be used to compare production with standards and competitors' products.

Our DMA experts support you by finding the right approach for specific applications and areas of interest.

High-force DMA GABO EPLEXOR® 500

DMA Measurement Information

- Design data concerning stiffness and damping properties (modulus values and damping factor under a variety of conditions)
- Data on the composition and structure of polymer blends (miscibility)
- Glass transition of highly cross-linked, amorphous or semi-crystalline polymers and composites
- Curing/post-curing
- Aging
- Creep and relaxation
- Stress and strain sweeps
- Multi-frequency tests
- Prediction of the material behavior using Time-Temperature-Superposition (TTS) experiments
- Immersion tests
- Durability test
- Fatique test
- Hysteresis

DMA 303 *Eplexor*®

Dielectric Analysis (DEA)

A variety of questions may arise during the curing process of reactive resins.

- At which temperature, or after how much time, does the resin begin to cure?
- How high is the reactivity?
- When is curing completed?
- Is the curing profile identical for every position in the mold?
- How can the curing cycle be optimized in order to save energy and costs?
- Is there any potential for post-curing?

For investigation of the curing behavior of thermosetting resin systems, composite materials, adhesives, paints and coatings, dielectric analysis (DEA) in accordance with ASTM E2038 or E2039 has stood the test of time.

Measurement Principle

DEA allows for the measurement of changes in the dielectric properties during curing. The liquid or pasty resin must be placed in direct contact with two electrodes comprising the dielectric sensor. A sinusoidal voltage (excitation) is applied and the resulting current (response) is measured, along with the phase shift between voltage and current. These values are then used to determine the ion mobility (ion conductivity) and the alignment of dipoles. In turn, the dielectric properties of permittivity ε' and loss factor ε"are calculated from these effects. Of primary interest with regard to curing is the ion viscosity. This is the reciprocal value of the ion conductivity, which is proportional to the loss factor.

Use of the DEA technique is not limited to the lab environment; it can also be applied to monitor in-situ curing in the mold under processing conditions. For production monitoring and process control, a specific ion viscosity value can be programmed to trigger demolding when the part being produced is sufficiently cured. This reduces cycle times and increases throughput.

Portable Version

With up to seven channels, this DEA is the flexible version for your day-to-day work. It can be easily transported between different measurement locations.

Rack Version for Integration into an Industrial Process

The 19” Rack version is designed for an electrical cabinet. It supports 8 simultaneous measuring channels which can be extended up to 16 modules.

DEA Measurement Information

- Ion viscosity
- Reactivity
- Cure monitoring
- Degree of cure
- Glass transition temperature
- Process control and optimization
- Diffusion properties
- Aging and decomposition effects

DEA 288 *Ionic*

Laser Flash Technique (LFA)

Thermal conductivity and thermal diffusivity are the most important thermophysical material parameters for describing the heat transport properties of a material or component.

During development and quality control, the extent to which materials fulfill their performance expectations is continuously scrutinized. Some of the questions which arise include:

- How is a particular insulation material performing?
- What is the ideal coating material?
- How can the heat transfer from an electronic component be improved?
- How must a heat exchanger be designed in order to achieve the required efficiency level, and what is the best material to use?

For issues such as these, the Laser Flash technique (LFA) has become a fast and reliable tool; it is an absolute method for determining thermophysical properties, including the specific heat capacity. This data can then be used for:

- Prediction of the heat transfer and temperature profile for description of the processing behavior
- Thermal diffusivity and thermal conductivity as input data for numerical simulation

For polymer applications in the temperature range from -100°C to 500°C, the compact LFA 467 *HyperFlash* is available. The integrated Automatic Sample Changer can test up to 16 samples in one run. The LFA 467 *HyperFlash* is able to test thin and high-conductivity materials as well as 2- and 3-layer structures – a capability which allows for such analyses as the influence of coatings on heat transfer under real conditions.

The LFA 467 *HyperFlash* operates in accordance with national and international standards (e.g., ASTM E1461, DIN EN 821).

LFA 467 *HyperFlash*

Broad variety of LFA sample holders for liquids, powders, fibers, for studies of anisotropic behavior

Insulation Testing by Means of the Heat Flow Meter (HFM)

Materials with low thermal conductivities can be tested in HFM or GHP.

All NETZSCH HFM and GHP instruments are based on all respective application and industry standards:

- ASTM C177, ASTM C335-05Ae1, ASTM C1363-05, ASTM D5470-06, ASTM E1530-06, ASTM F433-02(2009), ASTM C1363-05
- DIN EN 12667/12939, DIN EN 13163
- ISO 8301, ISO 8302, ISO 8894-1 (EN 993-14), ISO 8894-2 (EN 993-15)
- JIS A 1412

Heat Flow Meters

Heat Flow Meters are precise, fast and easy-to-operate instruments for measuring the thermal conductivity of insulations (e.g., polystyrene or polyurethane foams). The HFM 446 *Lambda* series owes its speed of measurement and precision to patented temperature control and heat flux measurement technology. High stability over the course of several days provides excellent repeatability. This is valuable for conducting aging studies or examining the long-term consistency of a product.

The HFM 446 *Lambda* allows the operator to apply a precise load on the specimen, enabling control over the thickness, and thus density of compressible materials – requirements for obtaining reproducible thermal conductivity results.

The HFM 446 series consists of three instrument versions which cover the plate temperature range from -20°C to 90°C.

HFM 446 *Lambda Small*
Specimen size: 203 x 203 mm

HFM 446 *Lambda Medium*
Specimen size: 305 x 305 mm

HFM 446 *Lambda Large*
Specimen size: 611 x 611 mm

Advanced Software Module

Kinetics Neo

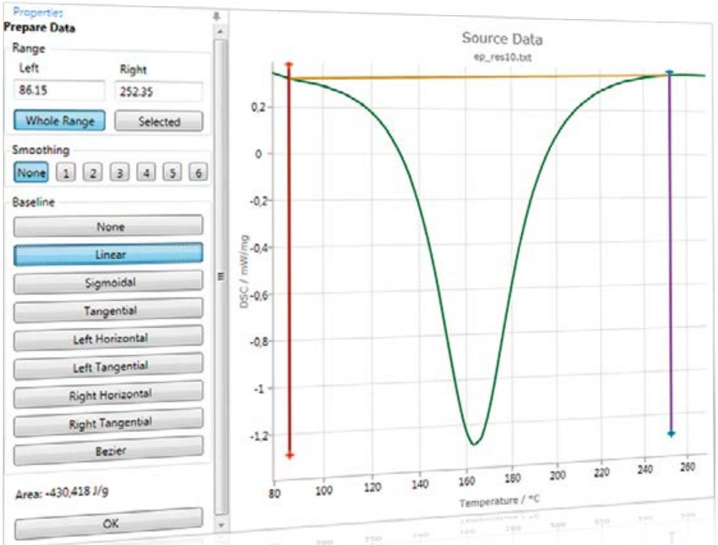
can analyze any process for which the rate depends on temperature

NETZSCH Kinetics Neo software is used to analyze kinetics of temperature-dependent chemical processes. The result of such analysis is a kinetics model or method correctly describing experimental data under different temperature conditions. Use of the method/model allows for predictions of a chemical system's behavior under user-defined temperature conditions. Alternatively, such models can be used for process optimization.

The software can analyze different types of thermal curves that depict the changes in a given material property measured during a process. Potential data sources include studies using thermogravimetry, dilatometry, differential scanning calorimetry, Fourier-Transform infrared spectroscopy, mass spectrometry and rheometry, as well as temperature analysis during adiabatic measurements.

The unique model-based kinetic analysis is capable of determining **the number of reaction steps**, and for each step the following values:

- Enthalpy (exo/endothermal DSC effects) or mass loss (TGA)
- Reaction type
- Activation energy
- Pre-exponential factor
- Order of reaction
- Order of autocatalysis
- Additional kinetic parameters



Range: Left 86.15, Right 252.35

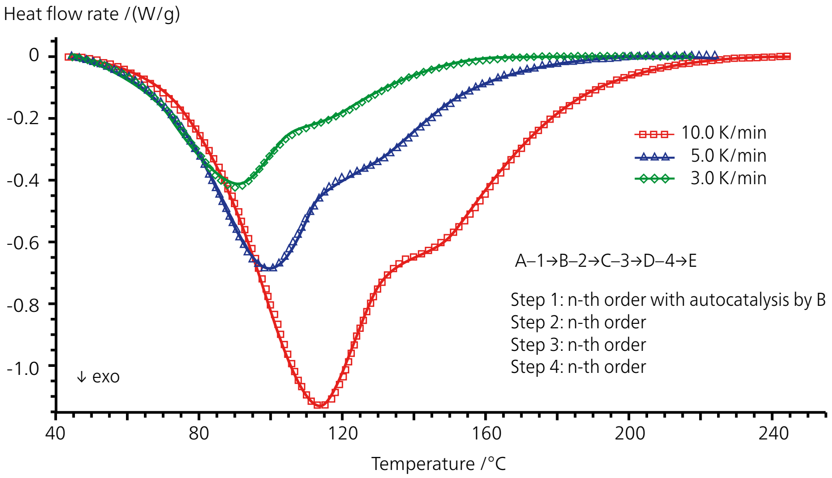
Area: -430,418 J/g

All Kinds of Advantages

The primary advantage of Kinetics Neo is its ability to analyze both heterogeneous and phase-boundary reactions – and to analyze such reactions with diffusion and nucleation. Furthermore, reactions with partial diffusion control can be studied; for example, processes which change the state of a substance from the glassy to the non-glassy state.

Kinetic Analysis

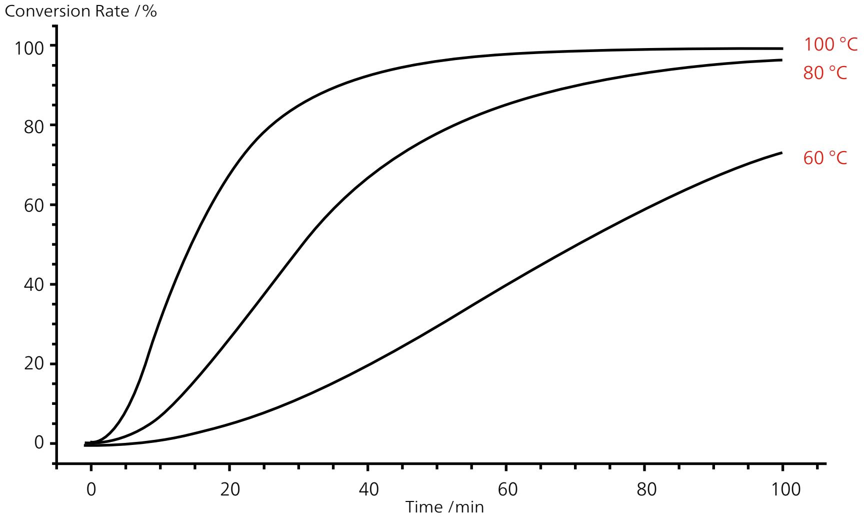
Kinetic analysis allows a set of kinetic parameters to be found – e.g., the number of reaction steps, the contribution of each step to the total effect of the process, the reaction type, the activation energy, or the reaction order for each step. This information is then used to solve prediction problems for new temperature/time programs or to optimize behavior for a given system.



Curing of an epoxy resin at different heating rates

Curing Behavior of an Epoxy Resin

In this example, an uncured epoxy resin was heated at rates of 3, 5 and 10 K/min with the DSC 204 ***F1*** *Phoenix*®. In the Kinetics Neo software program, exothermal curing was simulated. The almost perfect fit was achieved as a formal nth-order 4-step reaction. The start of the actual curing was described well by a first-order reaction with autocatalysis.



Prediction of the curing behavior at different isothermal temperatures

In this plot, the curing behavior is predicted based on the simulations shown above. For different isothermal temperatures, the conversion rate is plotted against time. For example, at 100°C, the material investigated here was totally cured after 65 min (degree of curing of 100%).

APPLICATIONS

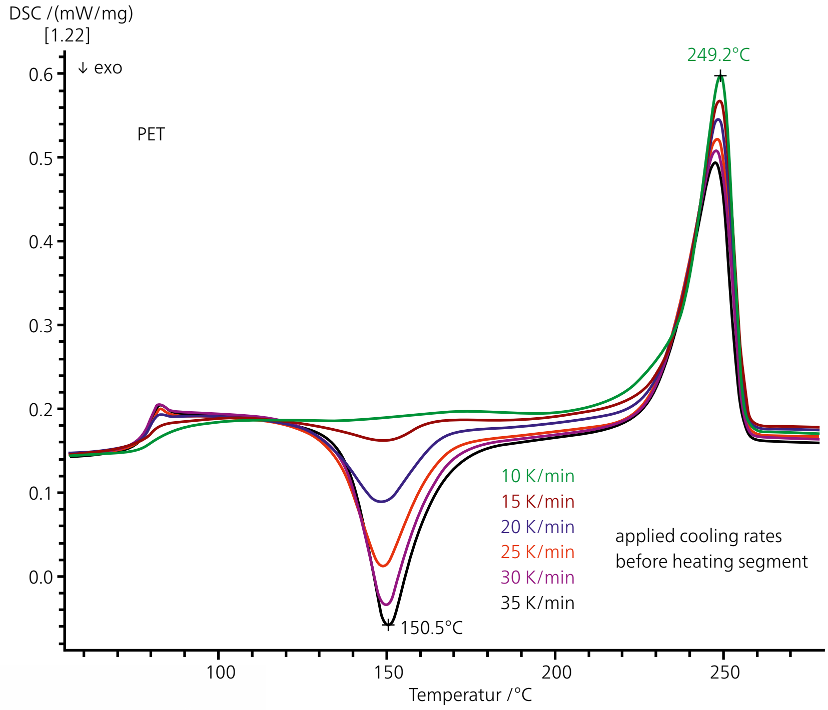
Thermoplastics

Differential Scanning Calorimetry

Crystallization Behavior of Semicrystalline PET

Polyethylene terephthalate (PET) is a semi-crystalline thermoplastic polymer with a relatively slow crystallization rate. High cooling rates lead to a high amorphous content, high glass transition steps (T_g) and post-crystallization during heating.

Low cooling rates allow more crystalline parts to crystallize during cooling, leading to a smaller glass transition step and no post-crystallization. The material then has an increased crystallinity and therefore loses its transparency.

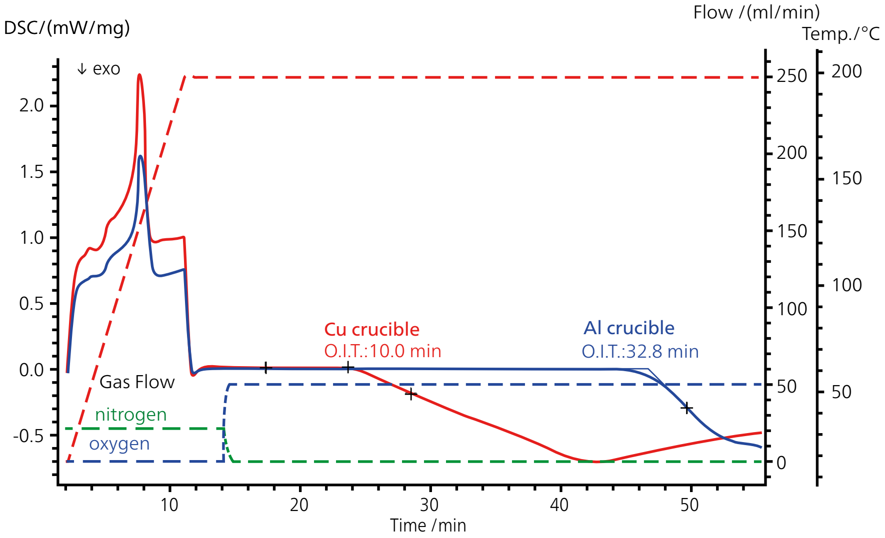


PET: glass transition, cold crystallization and melting measured at a heating rate of 10 K/min after different cooling rates – change in the crystallinity degree by means of DSC

Oxidative Induction Time (OIT)

Factors that influence OIT include test temperature, sample preparation, sample geometry, sample mass, particle size, crucible material, etc. The Oxidative Induction Time (OIT) can be determined in standard aluminum or in open copper crucibles in accordance with ASTM D3895.

This plot represents OIT measurements on high-density polyethylene (HDPE) carried out in a copper and in an Al crucible (red and blue curves, respectively). It can clearly be seen that, under isothermal conditions at 250°C under an oxygen atmosphere, oxidation of HDPE begins approximately 23 min earlier in the copper crucible than in the Al crucible. Copper works here as a catalyst for the oxidation.

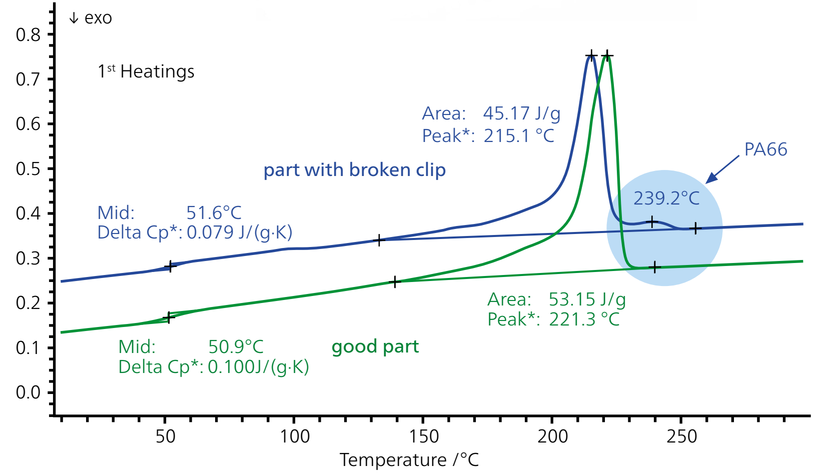


Influence of the crucible material on the Oxidative Induction Time (OIT) of HDPE by DSC; sample masses 12.21 mg and 12.11 mg

Failure Analysis of a PA6 Clip

Failures might be due to a variety of causes, including selection of the wrong material for the application, manufacturing defects in the plastic raw material, production defects in the plastic part, or degradation of the plastic by exposure to aggressive chemicals, contaminants, UV radiation, etc. DSC is a convenient method for comparing good parts with poor ones.

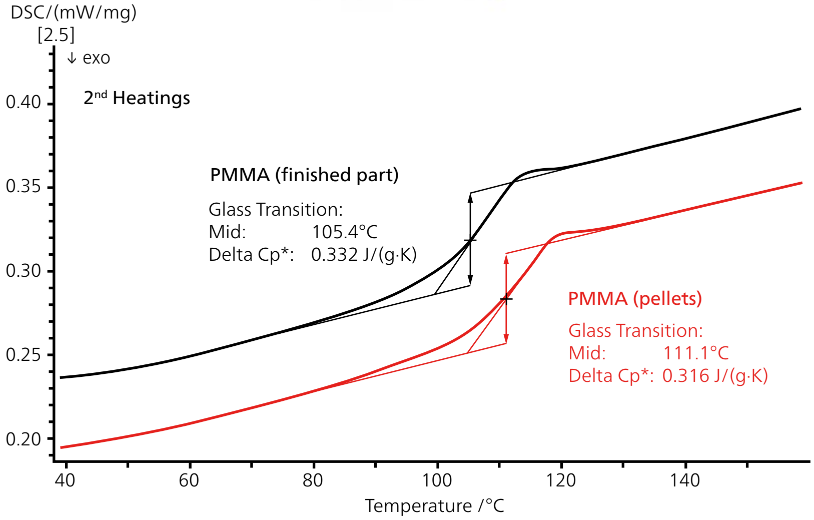
In this example, the first heating runs on two PA6 clips already show that the poor clip (blue curve) has an additional melting peak at 239°C. This indicates the presence of PA66, which is often blended with PA6. The presence of a second component is confirmed in the 2nd heating.



DSC comparison of the 1st heating runs of two clips made of PA6 reinforced with glass fiber; sample masses 12.98 mg and 13.13 mg; heating rate 10 K/min

Influence of the Thermo-mechanical History on Amorphous PMMA

The thermal and mechanical properties of polymer materials may vary greatly as a result of the thermal history associated with the sample. This DSC plot depicts the second heating runs of polymethyl methacrylate (PMMA) pellets and a finished PMMA part. It can clearly be seen that the glass transition temperature observed for the pellets (midpoint 111°C, red curve) is shifted to a lower temperature in the finished part (midpoint 105°C, black curve). Each additional unit of thermomechanical treatment of the polymer during thermoplastic processing may result in degradation of the molecular mass, in turn leading to a reduction of the glass transition temperature.

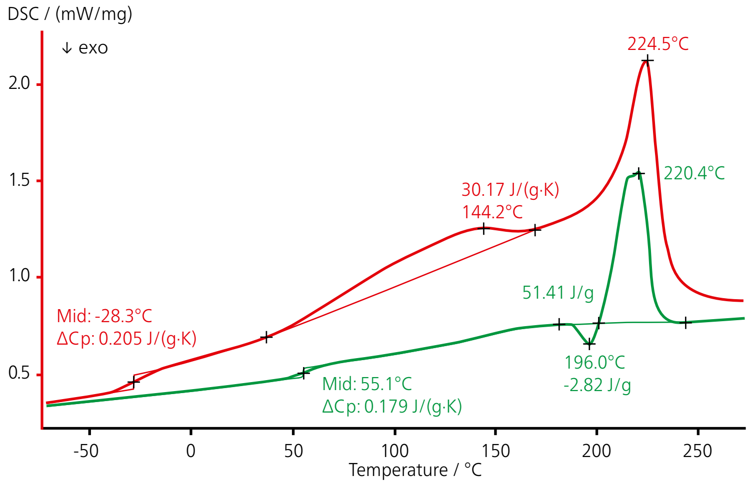


DSC measurement: shift of the glass transition to lower temperatures with increasing production steps; sample masses 11.54 mg and 12.5 mg; heating rate 10 K/min

Influence of Atmospheric Moisture

Polyamides absorb atmospheric moisture, which affects their mechanical properties.

The endothermic step at -28°C of the 1st heating (red curve) indicates the glass transition of the moist PA6. The endothermic effect between 20°C and 180°C is due to the evaporation of water contained in the sample. In the 2nd heating, the sample is dry and the glass transition temperature is shifted to 55°C. Water acts as a plasticizer and lowers the glass transition temperature. The peaks at 225°C (1st heating) and 220°C (2nd heating) are related to melting. The 2nd heating additionally shows a cold crystallization at 196°C.



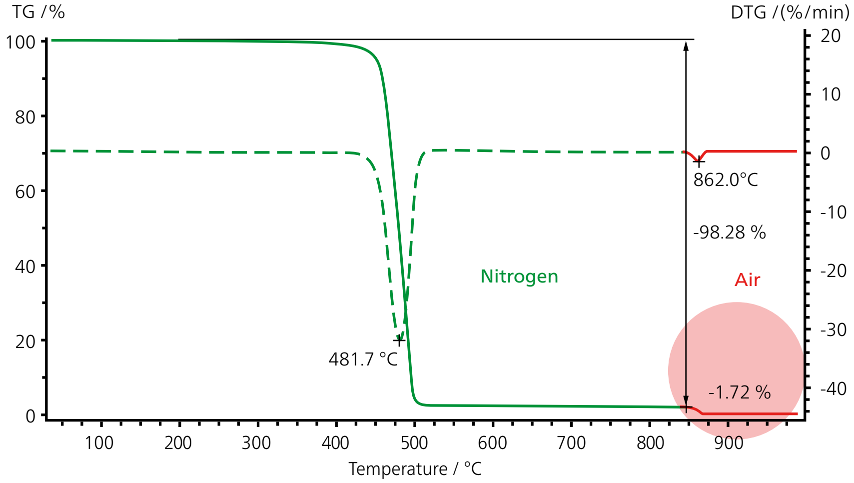
1st and 2nd heating of moist PA6 by means of DSC; sample mass 9.4 mg; heating rate 20 K/min

Thermogravimetric Analysis

Detection of Added Carbon Black

Static electricity may build up in polyethylene materials unless anti-static additives are used. PE macro-molecules are also broken down by UV light and burns readily unless flame retardants are applied. Carbon black is one of the best and most economic stabilizers.

The level of added carbon black content in PE can be easily determined by means of a vacuum-tight TGA system. After the total decomposition of PE in a highly pure nitrogen atmosphere, combustion of even the smallest amounts of added carbon black can be observed in an oxidizing air atmosphere.

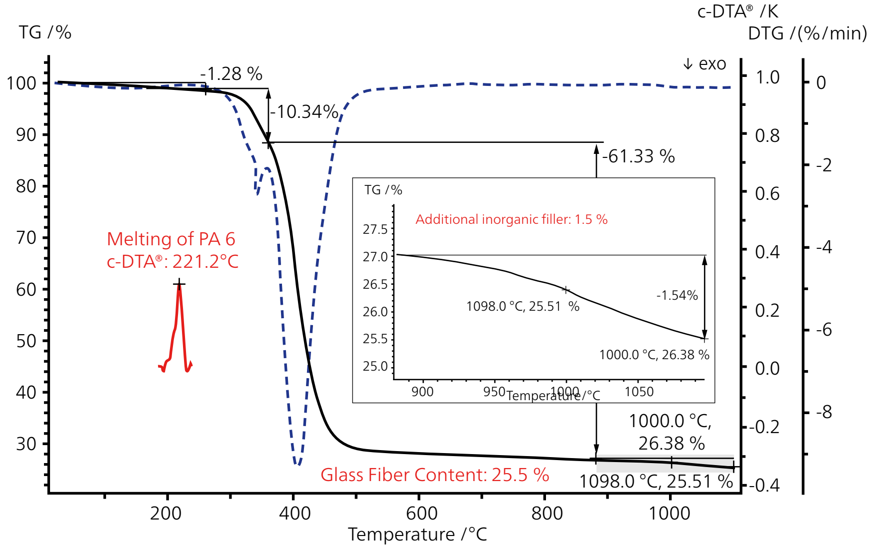


TGA measurement on polyethylene with added carbon black; sample mass 17.39 mg; Al_2O_3 crucible; heating rate 10 K/min

Determination of Different Filler

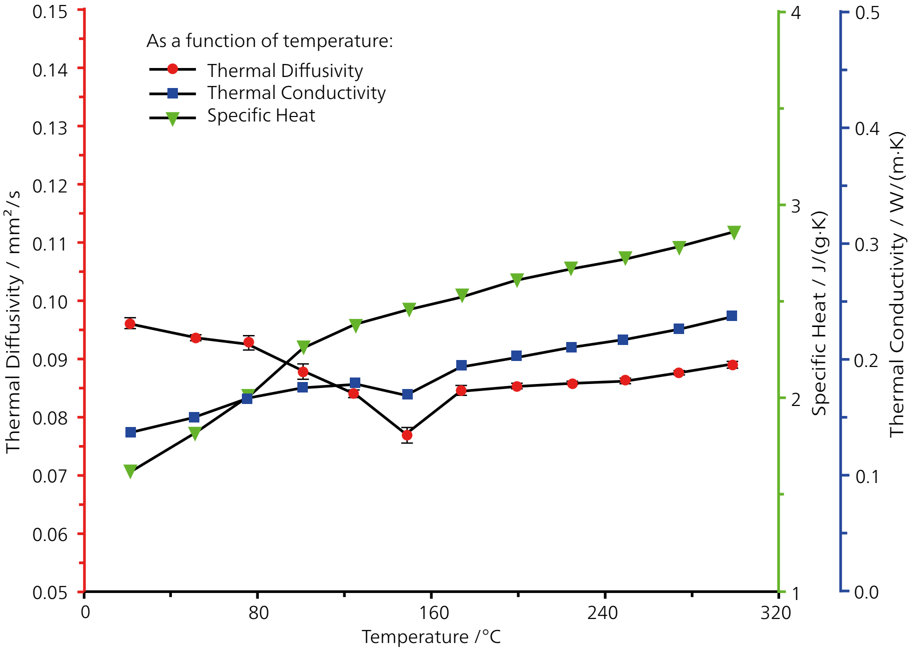
Fillers were previously used mostly to lower the price of finished products. Today they are primarily used to improve the technical characteristics of polymer products.

In this example, the determination of the inorganic filler (here glassfiber) in a PA6 sample is carried out by means of TGA. The sample was filled with 25.5% glass fiber. Decomposition of an additional inorganic filler can be observed between 900°C and 1100°C (see inset). Furthermore, by applying the c-*DTA*® feature of the TG 209 ***F1*** *Libra*® before polymer decomposition starts, an endothermic peak at 221°C can be detected. This effect represents the melting peak of PA6.



Determination of the melting temperature (identification) and filler content by TGA with c-*DTA*®; sample mass 12.45 mg; Al_2O_3 crucible; heating rate 10 K/min

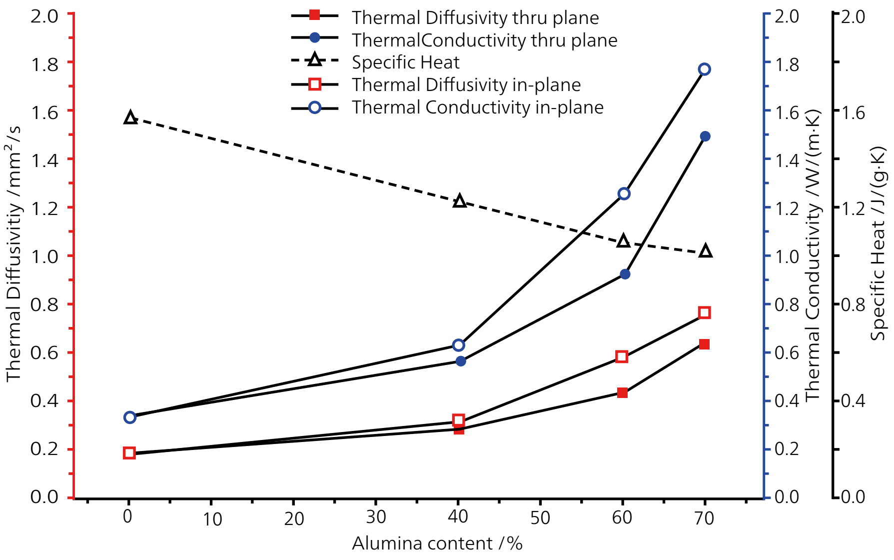
Determination of the Thermophysical Behavior Even in the Molten State



LFA measurement on PP between 20°C and 300°C; sample thickness 1.05 mm, Ø 11.0 mm

This measurement plot shows that the thermal diffusivity of a PP sample decreases significantly from 0.098 to 0.075 mm²/s from room temperature to the onset of melting at 150°C (extrapolated onset of the melting peak from a DSC run). After melting, it reaches an almost constant value of 0.085 mm²/s at 250°C. As expected, the specific heat capacity increases during heating: from 1.5 J/(g·K) at RT to 2.2 J/(g·K) at 90°C and, during softening and melting, from 2.3 J/(g·K) to 2.8 J/(g·K) at 250°C. Below and above melting, the resulting thermal conductivity shows an increase from 0.14 W/(m·K) to 0.2 W/(m·K) (250°C).

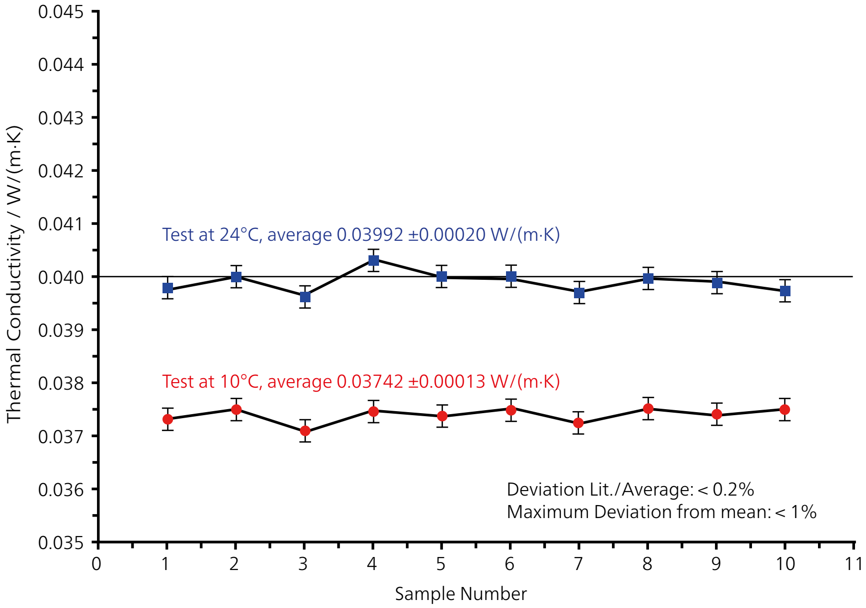
Thermal Diffusivity and Thermal Conductivity of PA46 Filled with Al_2O_3 by Means of LFA



Thermophysical properties of filled PA46 depending on the alumina content at room temperature

The use of glass fiber and other reinforcements such as Al_2O_3 in highly crystalline PA types improve the mechanical properties (modulus, strength). These fillers also influence the thermophysical properties (TPP, thermal diffusivity/conductivity and specific heat capacity), which can be tested by means of LFA. Tests can be carried out in the thru-plane and the in-plane directions. For the in-plane tests, a special sample holder for laminates is available. In the case of nylons, only PA46 has a very low thermal conductivity. With an increasing filler content (here Al_2O_3), the specific heat capacity decreases while the thermal diffusivity and thermal conductivity increase.

Thermal Conductivity by Heat Flow Meter



Quality control of 10 EPS samples from the same batch between 10°C and 24°C; thickness 50 mm, HFM *Lambda* measurements, NIST 1450c callibration standard

Thermal Conductivity of Expanded Polystyrene Foam (EPS)

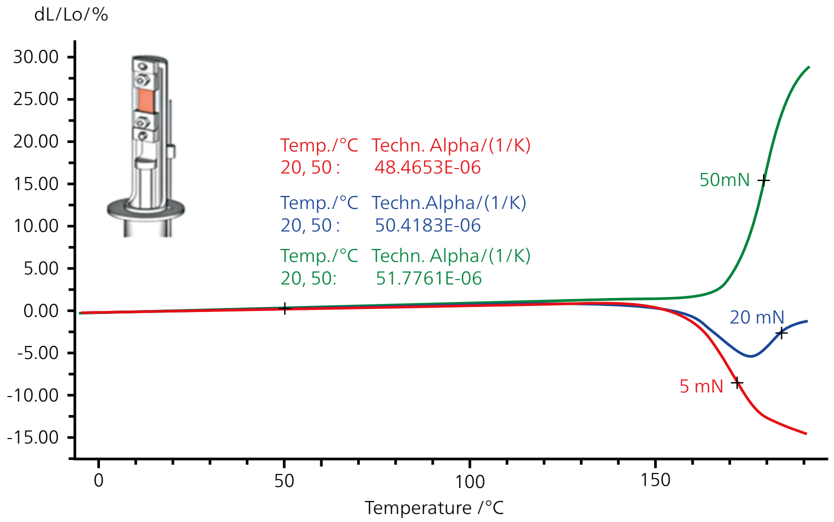
The tests shown here were of the typical quality control purpose types conducted on ten EPS samples from the same batch, to determine the thermal conductivity in accordance with DIN EN12667.

It can be seen that the thermal conductivity does not vary significantly from sample to sample. The values measured are around 0.04 W/(m·K), which is exactly the value specified for insulating materials in the datasheet.

The high test speed of the HFM allows for a large throughput to be tested. This becomes important if an insulating foam needs to be analyzed in accordance with DIN EN13163. In that procedure, the number of samples influences the $\lambda_{90/90}$ value which is determined from the test results.

Thermomechanical and Dynamic Mechanical Analysis

Tension Test on a Shrink Film of PC



Orientation effects of a PC shrink film measured with the TMA 402 ***F1** Hyperion*®; sample thickness 40 µm; length ≈ 5 mm; heating rate 5 K/min

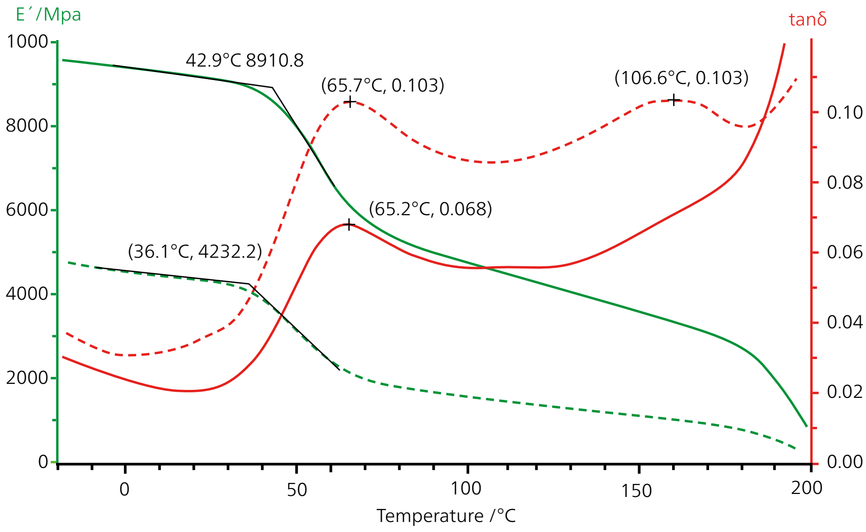
Orientation effects, stretch condition and shrinkage are measured under load for films with the TMA 402 ***F1** Hyperion*®. In these examples, the expansion and contraction of a 40-µm-thick film of polycarbonate (PC) were tested under tensile load.
The results vary significantly depending on the applied load. Under low amounts of force (5 mN), the film contracts at higher temperatures; however, it expands if a higher force (50 mN) is applied.

Anisotropic Behavior of a Glass Fiber-Reinforced (PBT) by Means of DMA

High mechanical stiffness due to glass fiber reinforcement

The DMA measurements of a finished part made of glass fiber-reinforced PBT were carried out on samples taken parallel or perpendicular to the cavity filling direction in order to investigate the anisotropic behavior.

The viscoelastic properties parallel to the fiber orientation (solid lines) indicate a significantly higher stiffness (E') and a lower damping (tanδ level). In the perpendicularly-oriented fiber direction (dotted lines), on the other hand, damping is higher and stiffness is correspondingly lower.



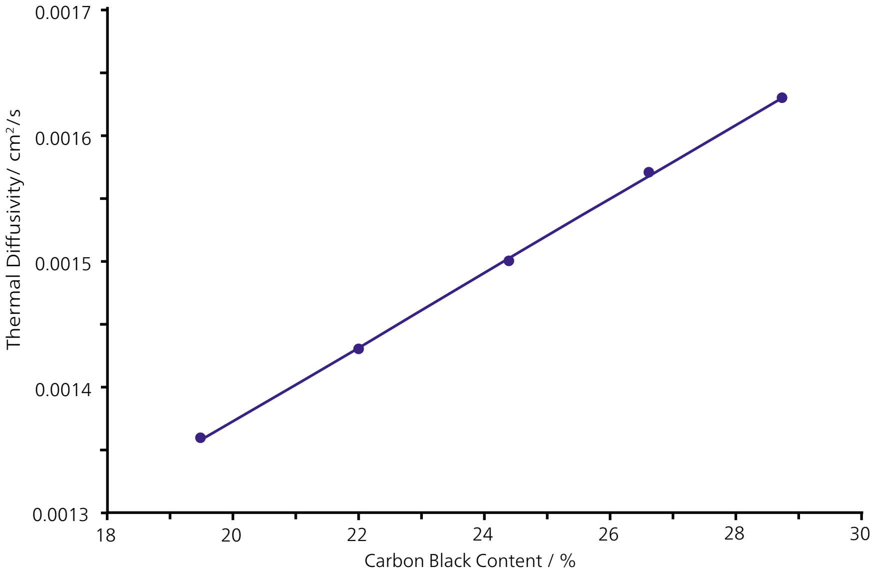
Polybutylene Terephthalate: DMA measurements on PBT/30%GF parallel to the fiber direction (solid curves) and perpendicular to it (dotted curves); 3-point bending; heating rate 2 K/min; frequency 1 Hz

Elastomers

Laser Flash Analysis

Influence of Carbon Black on Thermal Diffusivity in a Rubber Compound

The flash method also offers a fast solution for determination of the effect of the filler content on the thermal conductivity of a polymer. This example on NR shows the linear correlation of the thermal diffusivity, measured at room temperature, and the carbon black content of a rubber mixture.
With an increasing carbon black content, the thermal diffusivity rises.

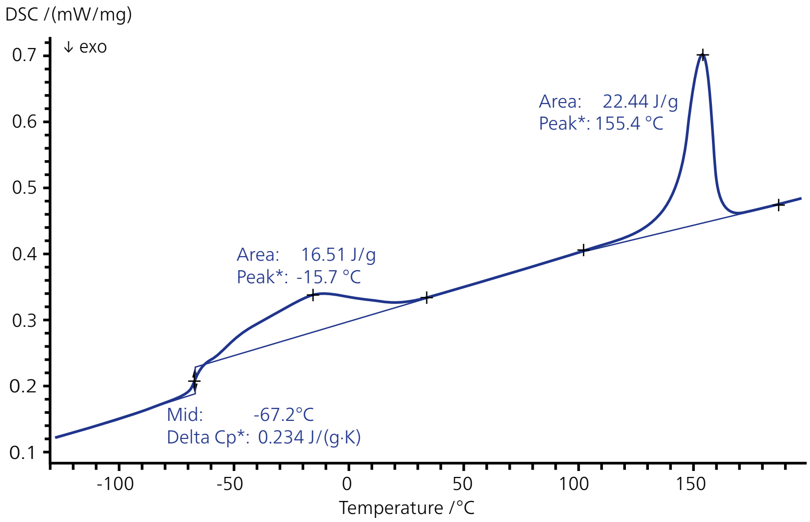


LFA measurement: thermal diffusivity of rubber mixtures filled with different quantities of carbon black at room temperature

Differential Scanning Calorimetry

Brittleness Point

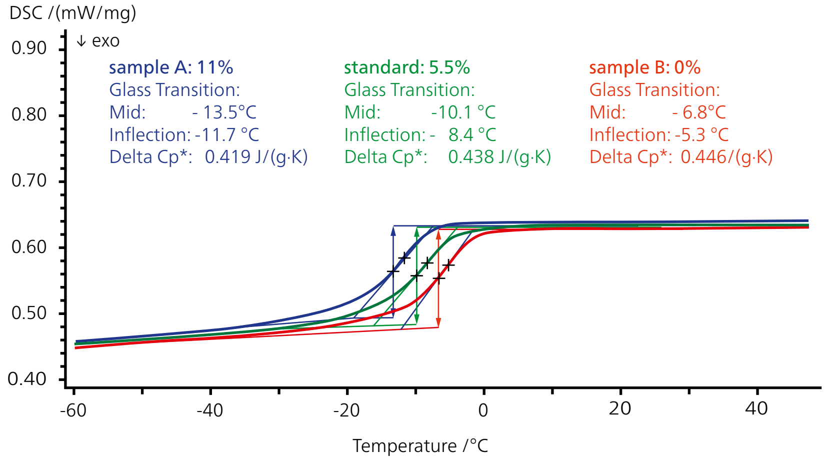
This DSC measurement was carried out on an SEBS+PP blend at a heating rate of 10 K/min. The SEBS component shows the glass transition temperature of the soft segments at -67°C. Melting of the hard segments occurs at -16°C. These effects are followed by melting of the PP component at 155°C. The glass transition temperature correlates with the brittleness point (DIN EN ISO 11357). This is a material property that is required by the automotive industry.



DSC measurement of the thermoplastic elastomer SEBS+PP

Differential Scanning Calorimetry, Thermogravimetry and Gas Analysis

Plasticizer Influence on the Cold Flexibility



DSC measurements on NBR. With increasing plasticizer contents, the glass temperature is shifted to lower values; sample masses ≈ 10 mg; heating rate 20 K/min

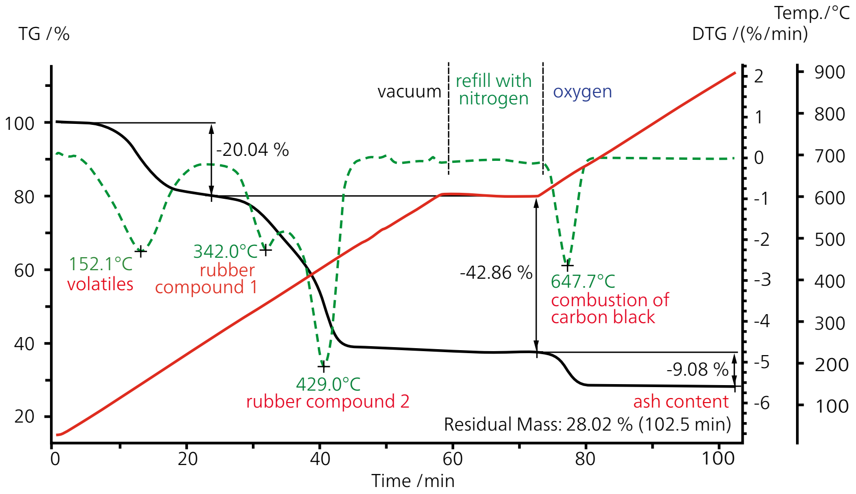
Plasticizers or dispersants are additives which increase the plasticity or fluidity of a material. When cooled below the glass transition temperature, the viscous chain segments "freeze" into fixed geometries and the rubber abruptly loses its high elasticity, although the process is reversible. The DSC method offers fast and reliable tests for investigating the influence of the plasticizer content in rubbers.

These measurements were carried out on three NBR samples differing in their plasticizer content. It can be observed that modification of the NBR plasticizer content yields different glass transition temperatures. The cold flexibility can be improved by increasing the plasticizer content.

Comprehensive Rubber Characterization

Clear separation and precise identification of rubber compounds can be achieved by using the vacuum capability of the TG 209 ***F1*** *Libra®*. Under vacuum, the boiling point of the volatiles is reduced, which leads to their release at lower temperatures while the decomposition of the rubber components is shifted by an insignificant amount.

In the first measurement segment of the plasticizer release (152°C, DTG peak) is clearly separated from the decomposition of the two rubber components at 342°C and 429°C (DTG peaks). After decomposition of the rubber components at 600°C, the TGA system is refilled with nitrogen under isothermal conditions. In the following step, the atmosphere is changed to oxygen, which leads to the immediate combustion of carbon black (9%) under increasing temperatures (remaining ash content 28%).

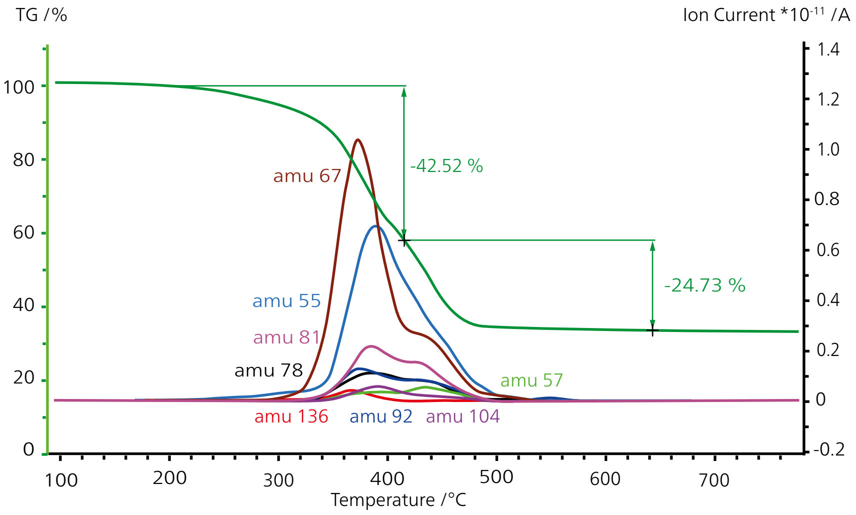


TGA measurement on a rubber mixture under vacuum and back-filling with nitrogen followed by combustion of carbon black in oxygen; sample mass 10.05 mg; heating rate 10 K/min; Al_2O_3 crucible

Classification of the Gases Evolved During Rubber Decomposition: Plasticizer and PAHs by Means of Gas Analysis Coupled to TGA

Coupling of gas analyzers such as mass spectrometers to TA methods allows for the chemical identification of the evolved gases. An example of a question here would be whether the rubber releases potentially carcinogenic polycyclic highly aromatic hydrocarbons (PAHs).

During heating of the rubber sample to 800°C, two mass-loss steps of 42.5% and 24.7% were observed. From the MS signals (only a few exemplary mass numbers are shown), conclusions can be drawn as to which organic molecules evolved at which temperature. For example, at 350°C, mass number 67 (most probably due to C_5H_7) indicates the release of the plasticizer.



STA-MS measurement detects evolved gases during decomposition of a tire sample

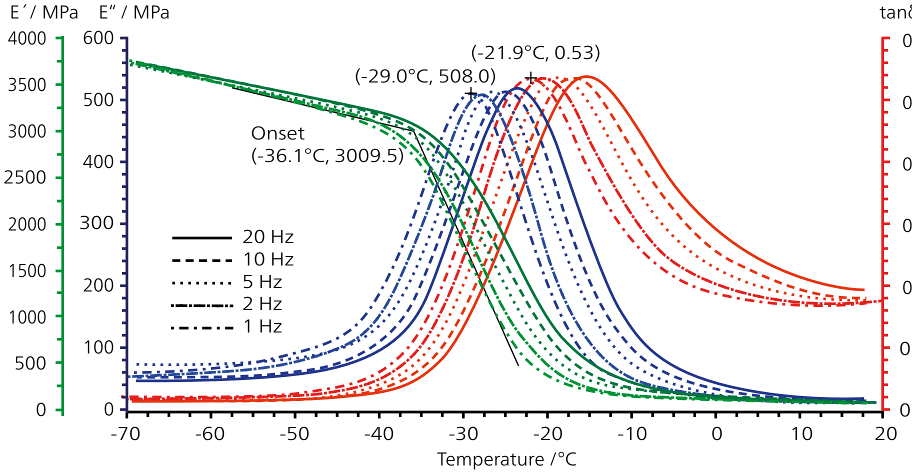
Dynamic Mechanical Analysis

Influence of the Frequency on the Glass Transition Temperature of an SBR Rubber Mixture by Means of DMA

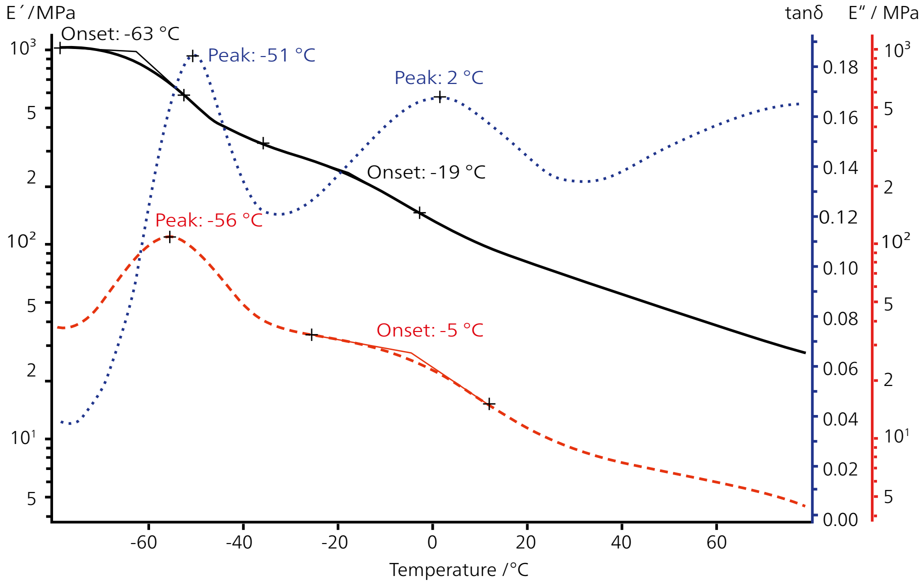
The modulus and damping factor are the main viscoelastic properties of polymers measured by DMA. The storage modulus, E′, is a measure of the stiffness and is temperature-dependent. The mechanical damping (tanδ, internal friction) of filled rubbers is highly relevant for such functions as the wet grip behavior of a tire or the seal behavior of an O-ring.

This example of an SBR (styrene butadiene rubber) mixture shows that at low temperatures (-70°C to -45°C), the loss factor tanδ is also very low, because there is so little free volume in the polymer that polymer segments are not able to move at all. This results in a low energy dissipation and the polymer transitions into the glassy state with a high storage modulus (high elasticity and high stiffness).

As temperature increases, the polymer segments also exhibit increased movement, thus yielding high values for loss modulus (E″) and tanδ with a maximum at the glass transition. Increasing frequencies shift these peak temperatures for the glass transition to higher temperatures. Additionally, higher E′ values are obtained with increasing frequencies.



DMA measurement of the viscoelastic properties of an SBR rubber mixture: storage modulus (E′, green), loss modulus (E″, blue) and damping factor (tanδ, red) as a function of frequency; heating rate 2 K/min



DMA measurement of the thermoplastic elastomer EPDM+PP

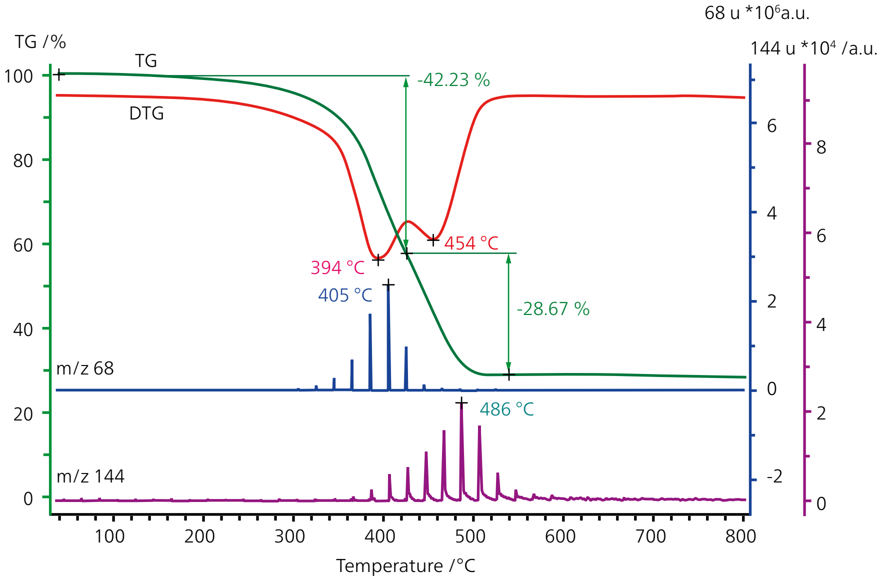
Viscoelastic Properties of a TPE

DMA is a valuable tool for determining the viscoelastic properties of TPE materials. The plot exhibits a DMA measurement on Santoprene®.

This TPE is a blend of EPDM rubber and the semi-crystalline poly-propylene (PP) thermoplastic. The DMA measurement was carried out between -80°C and 80°C at a frequency of 1 Hz. Depicted in the plot are the storage modulus (E’), loss modulus (E”) and loss factor (tanδ). The glass transition of the EPDM component can be observed in E' at -63°C (E’, onset), again in E” at -56°C (peak) and finally in tanδ at -51°C (peak). Subsequently, the glass transition of the PP component can be also observed in E' at -19°C (onset), again in E" at -5°C (also onset), and finally in tanδ at 2°C (peak).

Evolved Gas Analysis

TGA-GC-MS Measurement for Significantly Improved Interpretation of Organic Vapors



Identification of the gases evolving during decomposition of a rubber mixture; sample mass 5.28 mg; heating rate 20 K/min; 1 min injection intervals

The very high-sensitivity TGA-GC-MS coupling yields information on the composition of evolved gases. Separation of the volatiles is made possible by use of the GC column.

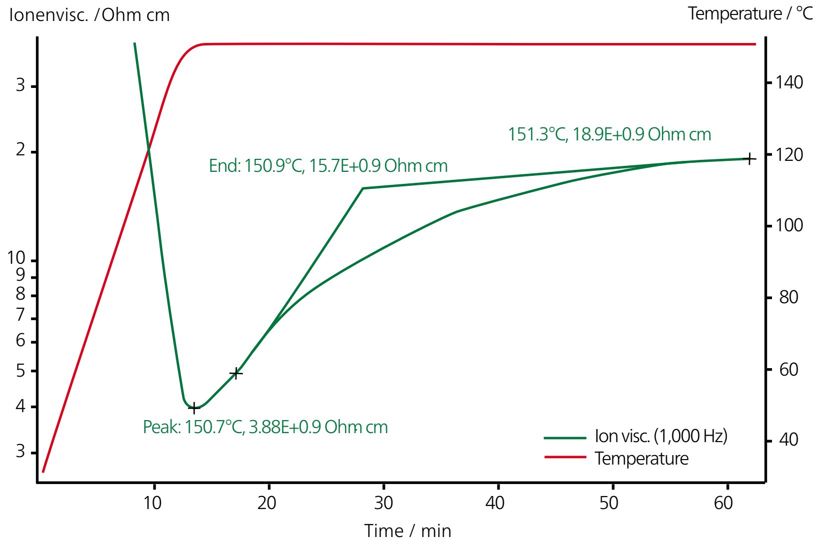
The plot depicts a measurement on NR/SBR rubber. The GC-MS was operated with a fixed column temperature (250°C) and short injection intervals of 1 min. The TGA and DTG curves indicate an overlapping decomposition of the individual rubber components. However, the evolved gases can be identified in good temperature and time correlation with he TGA and DTG results. The DTG peak at 394°C is due to the release of isoprene (1,3-butadiene, 2-methyl, m/z 68) which is typical for NR. The DTG peak at 454°C corresponds to the release of $C_{11}H_{12}$ (1-cyclopentene-1-1yl-benzene, m/z 144) which is representative of the SBR component.

Dielectric Analysis

Cure Monitoring of EVA

The EVA copolymer is used for encapsulation of electric devices. As the polymerization reaction is irreversible, the thermal treatment is crucial in the encapsulation process.

The plot presents the sample behavior of the ion viscosity at 1 Hz. The cross-linking reaction from using peroxide was observed under isothermal conditions at 150°C. The subsequent increase in ion viscosity correlates with the increase in the degree of cure. After 60 min, the ion viscosity remains nearly constant, which indicates that the cross-linking reaction has practically terminated.

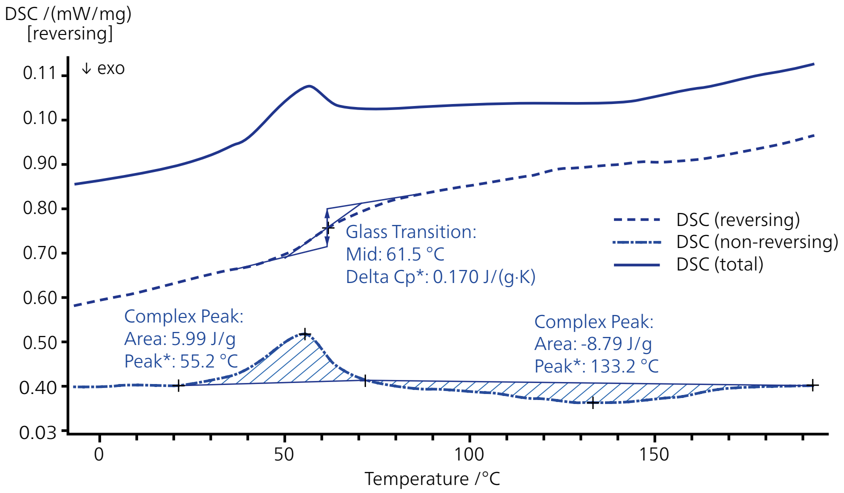


Multi-frequency test on EVA was carried out at frequencies between 1 Hz and 10000 Hz while monitoring the ion viscosity (Ωcm). The plot shows the measurement at 1 Hz at 150°C.

Thermosets and Composites

Differential Scanning Calorimetry

Glass Transition and Curing of a PUR Resin

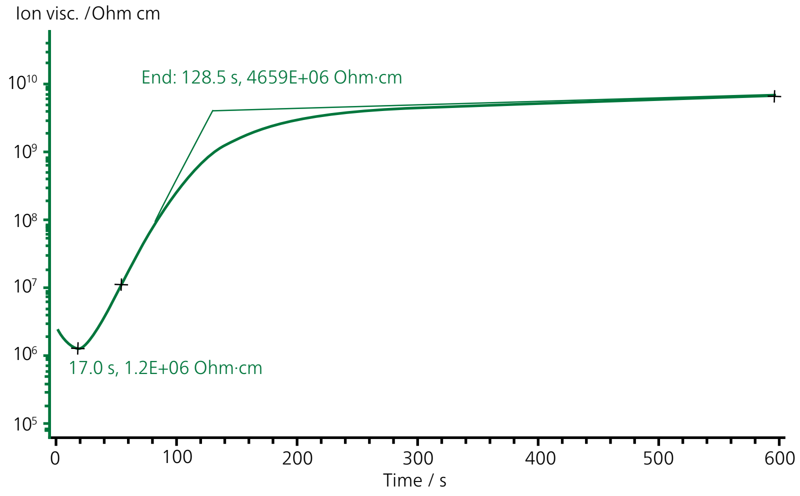


TM-DSC measurement of a polyurethane resin

Temperature-Modulated Differential Scanning Calorimetry (TM-DSC) is a DSC technique in which the sample is subjected to a superposition of a linear and a periodic temperature program. With TM-DSC, it is possible to separate overlapping DSC signals by calculating the reversing and the non-reversing part. Glass transitions can therefore be well separated from other effects such as relaxation, curing, decomposition, evaporation or cold-crystallization processes.

The overlapping relaxation in the total DSC curve can be clearly separated from the endothermic glass transition (reversing) and exothermic curing (non-reversing) in a single run.

Fast UV Curing of an Epoxy Resin



UV curing of a cationic epoxy resin at room temperature with the DEA at 1000 Hz

The fast curing of this epoxy adhesive can be observed with the DEA by using an IDEX sensor and applying a frequency of 1000 Hz. The UV light exposure (intensity 55 mW/cm^2 to 60 mW/cm^2) was applied for 60 s on the sample layer, which was approx. 200 µm thick, at room temperature. After 17 s of light exposure, curing began. This was evidenced by the increase in ion viscosity. The adhesive was completely cured after approx. 350 s.

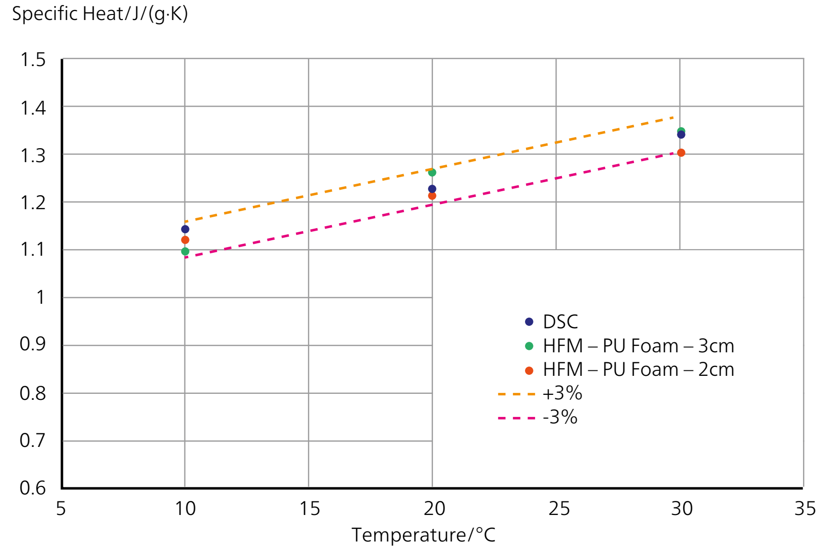
Heat Flow Meter

Specific Heat Capacity of a PU Foam

The plot compares the specific heat results of a PU foam between 10°C and 30°C (10 K steps) measured by DSC and HFM. The sample mass for the DSC test amounted to 10 mg; for the HFM tests, the sample masses were 38 g and 51 g, respectively.

The differences between the DSC and HFM results are less than 3%, which is within the stated uncertainty for the instruments and homogeneity of the material.

These tests show that the HFM 446 *Lambda* is capable of determining the specific heat capacity of large-volume and inhomogeneous materials typical for applications in the building and insulation industries.



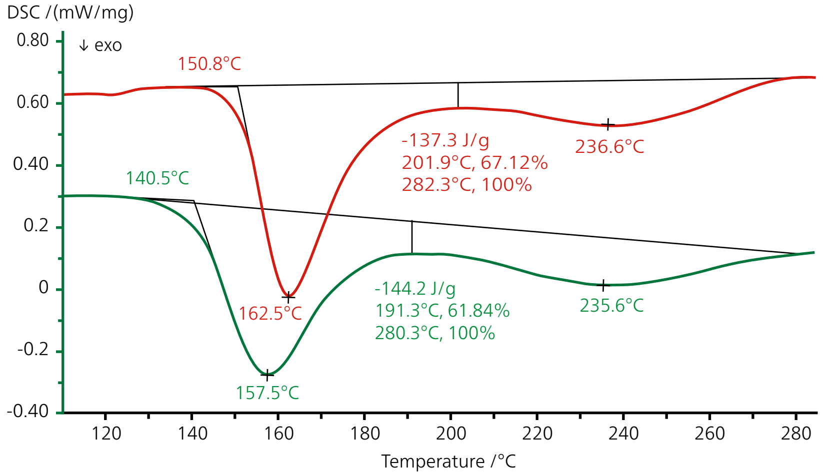
Comparison of the c_p test results on a PU foam obtained by the DSC 204 ***F1*** *Phoenix*® and HFM 446 *Lambda*. Sample thicknesses for the HFM tests were 2 cm and 3 cm, respectively.

High-Pressure DSC

Polycondensation of Phenolic Resin

The curing reaction of phenolic resins is caused by polycondensation. The endothermal release of the polycondensation products overlaps the exothermal curing. In such cases, curing can only be investigated with standard DSC measurements using autoclaves, or with high-pressure DSC measurements.

This test example shows two phenolic resins measured with the DSC 204 HP *Phoenix*® under a practical pressure of 9 MPa (90 bar). The differences between these resins can be seen in the fact that curing begins at 141°C and 151°C (extrapolated onsets), respectively, as well as in the different results of the partial area evaluation.



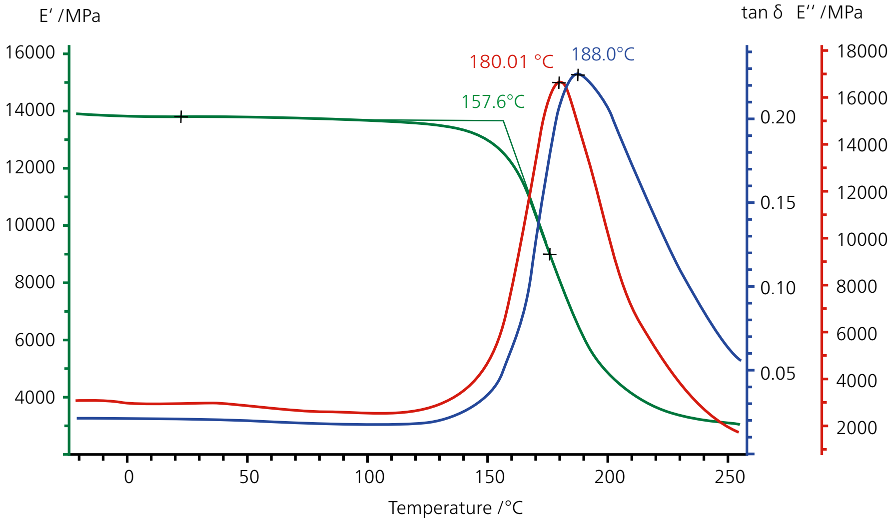
DSC 204 HP: exothermal curing behavior of two phenolic resins under high pressure; sample mass 10.5 mg; heating rate 10 K/min; pressure 9 MPa; atmosphere inert

Dynamic Mechanical Analysis

Stiffness Determination

This example depicts the storage modulus E′ (green), loss modulus E″ (red) and loss factor tanδ (blue) of a carbon fiber-reinforced epoxy resin. The sample was measured in the bending mode at a frequency of 10 Hz and a heating rate of 3 K/min using the DMA. Prior to reaching 120°C, the material is even stiffer than titanium, at a value of 140,000 MPa.

At 158°C (extrapolated onset temperature of E′), the modulus drops due to the glass transition of the epoxy matrix. The corresponding peaks for E″ and tanδ are at 180°C and 188°C, respectively.



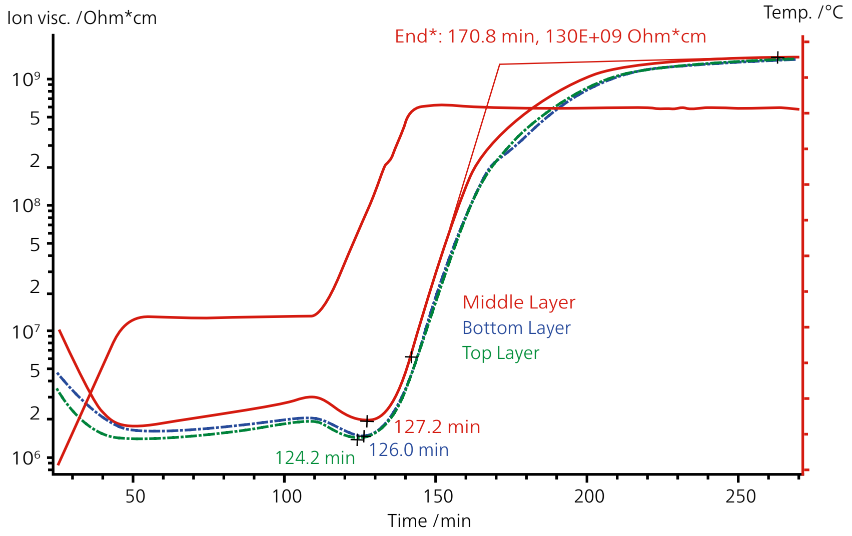
DMA measurement on a high-modulus carbon fiber-reinforced epoxy resin

Dielectric Analysis

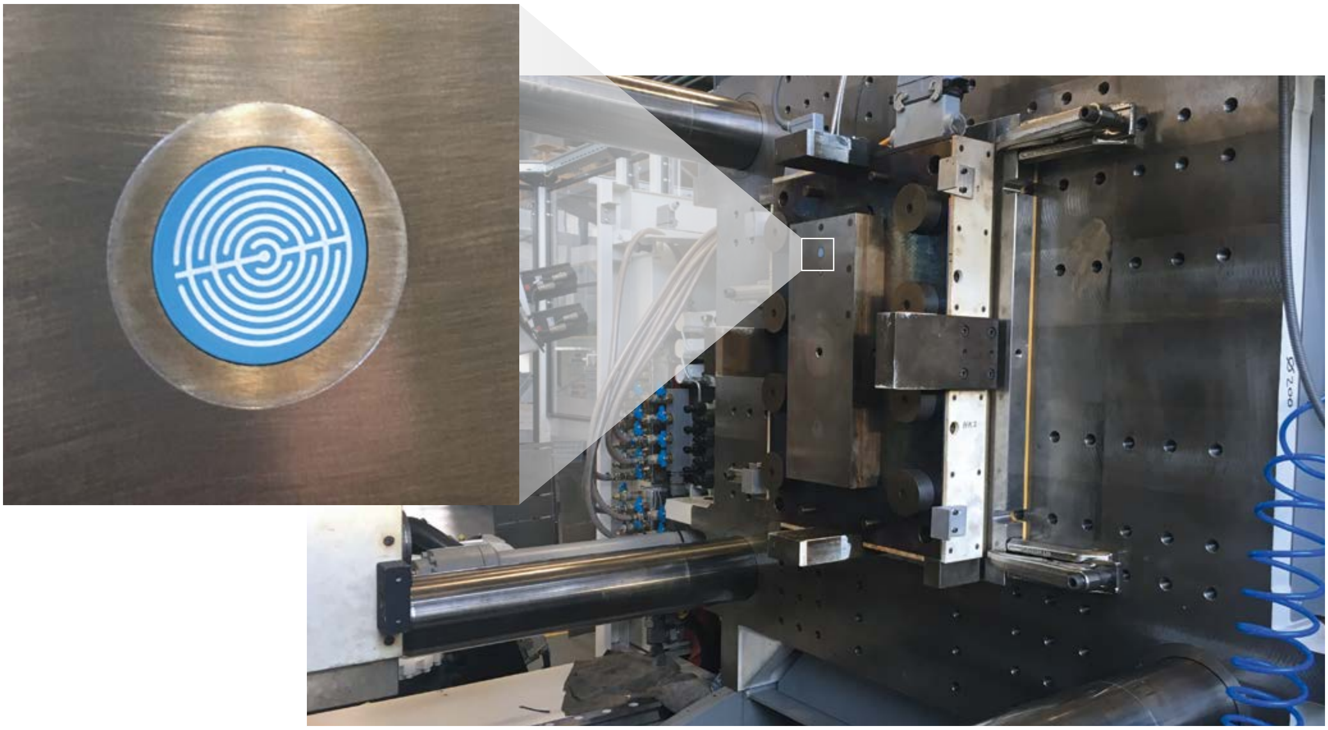
Cure Monitoring of a CF-Reinforced Epoxy Resin

After what amount of time or at what temperature does a curing reaction start? Is the thermosetting resin already fully cured? Such or similar questions are those that resin producers and thermoset processors would like to answer comprehensively.

The plot depicts the curing of a carbon fiber-reinforced epoxy resin (DEA measurement) during Resin Transfer Molding (RTM) for aircraft applications. During a two-step temperature curing program, the ion viscosity initially decreased due to the temperature increase. It then increased during the first isothermal segment, due to the start of curing. While heating to 180°C, the temperature increase counteracted with the curing so that the ion viscosity first decreased before curing began to dominate. Thereafter, the ion viscosity was recorded with a rising degree of cure. As soon as the curing was completed, the ion viscosity reached a constant value (here evaluated as extrapolated onset at 1.3 x 10^9 Ωcm).



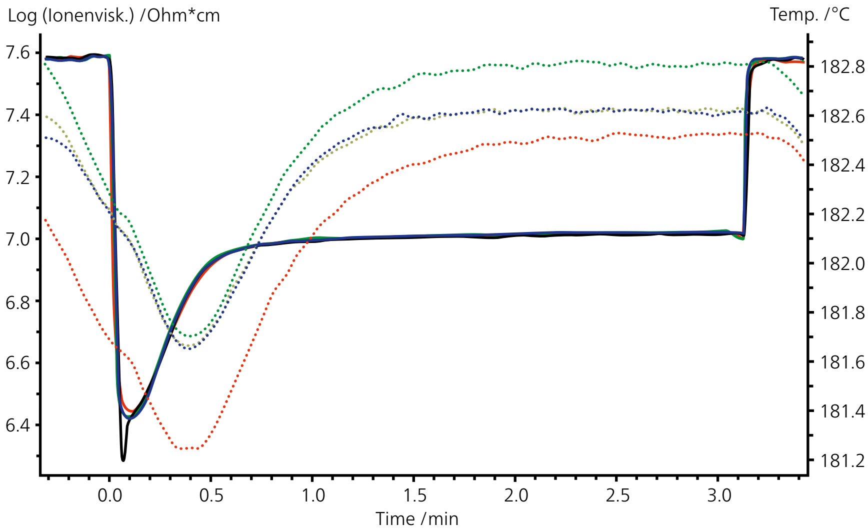
Dielectric analysis (DEA) with different IDEX sensor positions



In-Process Cure Monitoring

The NETZSCH DEA 288 *Ionic* can be applied as a sensor for online cure monitoring during thermoset injection molding.
The upper pictures show the DEA sensor (blue area) integrated in a test mold applied at a injection molding machine.

The lower picture shows the ion viscosity signals for the four subsequent shots as a function of time. All shots show excellent agreement thus depicting perfect reproducibility of the process conditions used.



Curing Behavior of a thermoset during molding process; mold temperatures are represented in solid lines, ion viscosity in dotted curves


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

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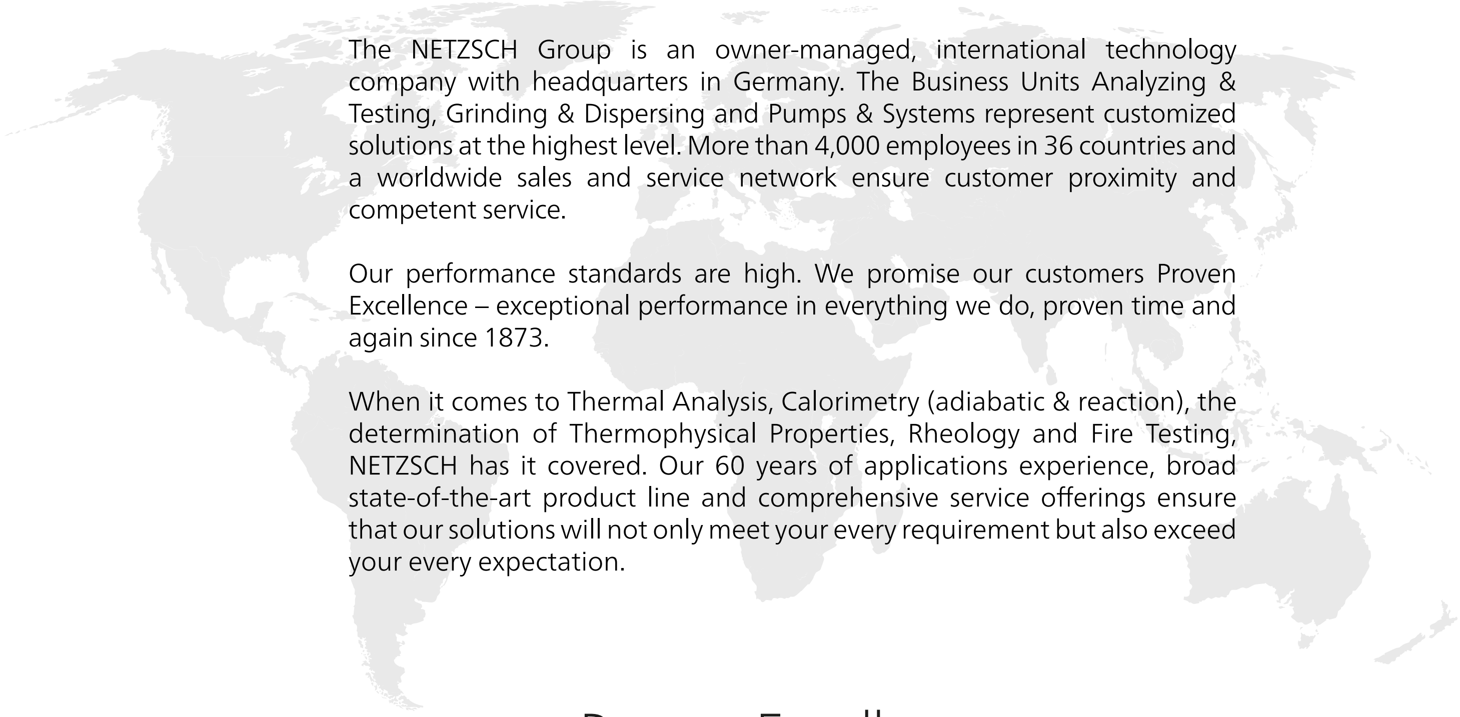
Consult with the experts in our applications laboratories to choose the best-suited measuring method for your specific needs.

You will be working with scientists (physicists, chemists, materials scientists) possessing consolidated knowledge about the most varied of methods and materials spectra.



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