NETZSCH

Analyzing & Testing

Thermal Characterization of Polymers

Thermoplastics, Thermoplastic Elastomers, Elastomers and Thermosets

Leading Thermal Analysis

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. Polymers are used not only to create plastic and rubber parts, but also to produce fibers, films, adhesives and glues, and varnishes and paints. 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 sciences.

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 his 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:

- Light weight
- Good thermal and electrical insulation capacity
- Resistance to corrosion effects
- Chemically inert
- High strength and dimensional stability
- Absorption of mechanical shocks
- Resistance to abrasion effects
- Good dyeability
- Potential for decorative surface effects
- Low production costs

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

Thermal Analysis

During their production, processing and application, polymers are often subjected to temperature-dependent structural changes. 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 measure the thermal transitions (DSC, DMA, DIL, LFA), chemical reactions and decompositions (TGA, DSC, DEA, rheology), viscoelastic properties (DMA, rheology), and thermal conductivity/ diffusivity (HFM, GHP, LFA) as a function of temperature, heating rate, deformation, and atmosphere. These techniques give insight into the specific thermal properties of polymer materials and products, but more importantly, they can be used to determine the composition of plastic and rubbers compounds, and to gain information regarding the condition or processing history of specific samples relative to reference samples.

Thermal Analysis Measurement Tasks

The variety of thermoanalytical test methods opens a broad application range for polymer testing, e.g.:

- Specific heat
- Thermal transitions
- Melting, crystallization and reaction enthalpies
- Glass transition temperatures
- Degree of crystallinity
- Thermal stability
- Oxidation Induction Time / Oxidation Onset Temperature (O.I.T., O.O.T.)
- Viscoelastic behavior
- Young’s modulus
- Kinetics of reactions
- Compositional analysis
- Thermal expansion coefficient
- Filler content
- Thermal conductivity/diffusivity, etc.

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.

NETZSCH Analyzing & Testing has a product portfolio and applications in thermal analysis and thermophysical properties testing that rank among the best in the market as far as meeting the high demands associated with reliable manufacturing and state-of-the-art technologies.

Our solutions consist of well-proven test methods in R&D and quality control for studying nearly any kinds of material used in the various branches of the polymer industry.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry

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

- Thermophysical properties
  Specific heat
- Product Identification and Characterization
  Melting/crystallization temperatures
  Melting/crystallization enthalpies
  Cross-linking temperatures
  Cross-linking enthalpies
  Degree of crystallinity
  Glass transition temperatures
- Advanced Materials Analysis
  Decomposition effects
  Oxidative stability (O.I.T., O.O.T.)
  Reaction kinetics
  Degree of curing
  Purity determination of additives
  Curing by UV irradation
  Stability under pressure
  Peak separation
- Product/Process Information
  Incoming goods inspection
  Thermomechanical history
  Failure analysis
  Competitor product analysis
  Process optimization
- Thermokinetics
  Reaction behavior
  Predictions
  Process optimization

For standard applications, the DSC 204 ***F1*** *Phoenix*® and DSC ***F3*** *Maia*® can be used. The systems are easy to handle and can be operated from -180°C to 700°C.

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*®.

DSC 200 ***F3*** *Maia*®

DSC 204 ***F1*** *Phoenix*®

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. The sample chamber atmosphere can be static or dynamic. The electronic pressure monitor and control, along with precise regulation of the purge gas flow, provide for excellent accuracy and reproducibility of the measurement results.

DSC 204 HP *Phoenix*®

Photo-DSC 204 ***F1*** *Phoenix*®

Additional Information

www.netzsch.com/dsc

Thermogravimetric Analysis (TGA) and Simultaneous Thermal Analysis (STA)

Thermogravimetry

Thermogravimetry (TG), or Thermogravimetric Analysis (TGA), is a well proven thermal analysis method for measurements of mass changes versus 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 the most commonly used methods of thermal analysis.

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 D 6370).

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 then be coupled directly to the top of the unit. The Automatic Sample Changer (ASC) can also be used to conduct routine measurements around the clock.

TG 209 ***F3*** *Tarsus*®

TG 209 ***F1*** *Libra*®

NETZSCH

Simultaneous Thermal Analysis

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. The main advantage of this is that test conditions are perfectly identical 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.


STA 449 **F1** *Jupiter*®

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
- Thermokinetic analysis

DSC Measurement Information

- Specific heat
- Melting/crystallization behavior
- Solid-solid transitions
- Polymorphism
- Degree of crystallinity
- Glass transition temperatures
- Cross-linking reactions
- Oxidative stability
- Purity determination of additives
- Thermokinetic analysis


Variety of STA sample holders

Additional Information

www.netzsch.com/dsc
www.netzsch.com/sta_tg

Thermal Analysis Coupled to Evolved Gas Analysis (EGA) and Thermomechanical Analysis (TMA)/Dilatometry (DIL)

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 systems 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).

Instrument Coupling Possibilities

- TGA-, DSC-, or STA-MS via capillary coupling
- STA-MS via *Skimmer*® coupling
- TGA-, or STA-GC-MS
- TGA-, DSC-, or STA-FTIR
- 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.

Coupling Measurement Information

- **Compositional analysis**
  Polymers
  Plasticizers
  Solvents
  Additives
- **Evaporation**
  Vapor pressure
  Sublimation
- **Decomposition**
  Dehydration
  Stability
  Residual solvent
  Pyrolysis
- **Solid-gas reactions**
  Combustion
  Oxidation
  Adsorption/desorption

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

STA-GC-MS coupling

Additional Information

www.netzsch.com/coupling

Thermomechanical Analysis and Dilatometry

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).

In addition, measurements under bending, tension and penetration under modulated forces can be carried out with the TMA 402 ***F1*** *Hyperion*®.

Investigations can be carried out on plastics and elastomers, paints and dyes, composite materials, adhesives, films, fibers and composite materials.

NETZSCH offers a broad range of dilatometers and TMA systems for polymers and composites. All instruments fulfill the respective instrument and applications standards for dilatometry and thermomechanical analysis.

TMA/DIL Measurement Information

- Thermal expansion
- Coefficient of thermal expansion
- Volumetric expansion
- Density change
- Shrinkage steps
- Glass transition temperatures
- Softening points
- Penetration behavior
- Phase transitions
- Creep behavior
- Anisotropic behavior
- Young’s modulus
- *Thermokinetics*

TMA 402 ***F1*** *Hyperion*®

Variety of TMA 402 sample holders

DIL 402 C

Additional Information

www.netzsch.com/dil
www.netzsch.com/tma402

Dynamic Mechanical Analysis (DMA) and Dielectric Analysis (DEA)

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA or DMTA) 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 viscoelastic properties, typically provided as a graphical plot of E', E", and tanδ versus temperature.

DMA identifies 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 -180°C to 600°C.

DMA 242 D

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.

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 (compatibility)
- Glass transition temperature 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

Special sample holder with ball-shaped pushrod for curing of low-viscosity liquids

Additional Information

www.netzsch.com/dma

Dielectric Analysis

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 and paints, dielectric analysis (DEA) in accordance with ASTM E2038 or E2039 has stood the test of time.

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.

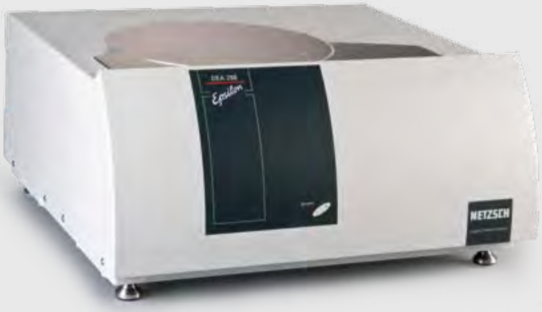
Use of the DEA technique is not limited to the lab environment; it can also be applied to in-situ curing in the mold under processing conditions. For production monitoring and process control, a specific ion viscosity value can be programmed to trigger demolding when the part being produced is sufficiently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

The modular concept of the DEA 288 *Epsilon* allows for the study of the curing behavior of thermosetting resins, adhesives, paints and coatings in nearly every application. The lab version with up to 8 channels can be used in conjunction with a newly designed furnace with cooling options for research & development. The industrial versions are intended for production monitoring and process control, and are designed with up to 16 channels.

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 *Epsilon* – Slim Version



DEA 288 Epsilon – Lab Version

Additional Information

www.netzsch.com/dea

Thermokinetics – Laser Flash Technique (LFA)

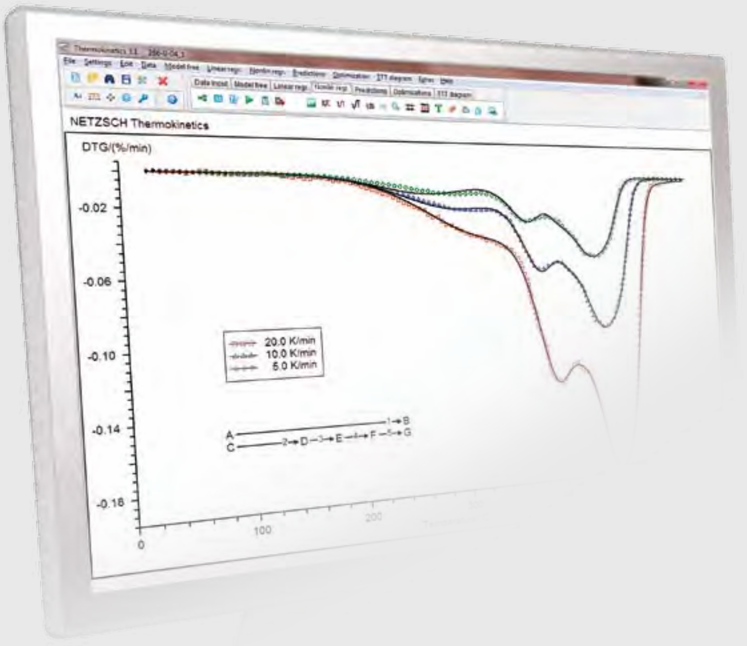
The *Thermokinetics* Advanced Software Module

Having an understanding of the behavior of various polymers under different temperature and pressure conditions is crucial when producing polymer materials which must have specific final properties, in order to ensure that material failure does not occur when used in its intended application.

Today, many different polymer types are appearing on the market which might be considered to exhibit improved behavior over former materials or to meet new application requirements. However, their thermal behavior might prove critical during the production process or later as a finished part. Time- and temperature-dependent curing reactions play an important role. Fluctuations in the curing agent may occur and require special attention.

The NETZSCH *Thermokinetics* Advanced Software module is capable of creating kinetic models of any chemical processes for which the reaction (e.g., cross-linking, curing, decomposition) is a function of temperature and time. It can also be used to predict the behavior of chemical systems for user-defined temperature conditions and to achieve process optimization.

The software can analyze different types of thermal curves which show changes in various measured material properties during the reaction process, including data from DSC, TGA, DIL, DMA, DEA, rheology, FT-IR and mass spectrometry analyses.



Two Main Tasks of *Thermokinetics*:

- Prediction → to predict the polymer for a new temperature program
- Optimization → to find the optimum temperature program in order to achieve a given polymer reaction

The software allows for the analysis of heterogeneous reactions, including phase-boundary reactions, reactions with diffusion and nucleation, and reactions with partial diffusion control, such as processes which change from the glassy to the non-glassy state.

Analysis in *Thermokinetics* allows for the determination of a number of reaction steps, and for each step, the following values:

- Reaction type
- Activation energy
- Order of reaction
- Other kinetic parameters

Various Methods of Kinetic Analysis and Predictions are Integrated into the Program:

- Model-free kinetic analysis (Friedman, Ozawa-Flynn-Wall, and ASTM E698)
- Model-fit using multivariate non-linear regression (model definition, multiple step reactions, 18 different reaction types, F-test with regard to fit quality and significance of an additional step, graphic presentation)
- Multiple-step reactions (up to 6 steps)
- Isothermal prediction and prediction on the basis of a user-defined temperature program

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. These data can then be used for:

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

LFA sample holder variety for standard and special applications

NETZSCH offers three LFA models covering the entire spectrum of medium- to high-conductivity materials and temperatures. The LFA systems operate in accordance with national and international standards (e.g., ASTM E1461, DIN EN 821).

The LFA 447 *NanoFlash*® und LFA 457 *MicroFlash*® are employed for polymer applications. Especially for composites, multi-layer systems, or fiber-reinforced polymers, the flash technique is an ideal choice. Easy sample preparation, fast testing times, and high accuracy are only some of the many advantages of this non-contact test method.

In addition to the already broad variety of measurement possibilities, the LFA systems also accommodate special sample holders for:

- Liquids
- Powders
- Pastes
- Laminates
- Fibers
- Study of anisotropic behavior
- Studies of compressible and layer systems

LFA – Insulation Testing

LFA

For standard polymer applications in the temperature range from RT to 300°C, the compact, xenon flash-based LFA 447 *NanoFlash*® is available. The integrated automatic sample changer can test up to four samples in one run. The LFA 447 *NanoFlash*® is able to test 2- and 3-layer structures – a capability which allows for such analyses as the influence of coatings on heat transfer under real conditions.

The production/molding process can be optimized in various ways, one of which is by using finite element simulations. In order to apply these, the thermophysical properties must be known – not only for the solid region, but also at temperatures above and below the glass transition.

For demands such as these, it is the LFA 457 *MicroFlash*® with low-temperature furnace (-125°C to 500°C) which fulfills the measurement requirements. This instrument is additionally vacuum-tight and allows for a determination of the thermal diffusivity under well-defined atmospheres or vacuum.

LFA 447 *NanoFlash*®

LFA 457 *MicroFlash*®

Additional Information

www.netzsch.com/lfa

Materials with low thermal conductivities, such as insulators, can be tested in a Heat Flow Meter (HFM) or Guarded Hot Plate (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 accurate, fast and easy-to-operate instruments for measuring the thermal conductivity of insulations (e.g., polystyrene or polyurethane foams). The HFM 436 *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 436 series consists of four instrument versions which cover the plate temperature range from -30°C to 100°C. The maximum specimen size ranges from 300 mm x 300 mm x 100 mm to 600 mm x 600 mm x 200 mm.


HFM 436 *Lambda*

Guarded Hot Plate

The GHP 456/476 *Titan*® is the ideal tool for researchers and scientists in the field of insulation testing. The GHP principle is based on the absolute measurement method and therefore requires no calibration standards.

There are two vacuum-tight instrument versions available, depending on the plate materials in use. For polymer foams and insulations, for example, the system covers the temperature range from -150°C to 250°C.


GHP 456 *Titan*®

Additional Information

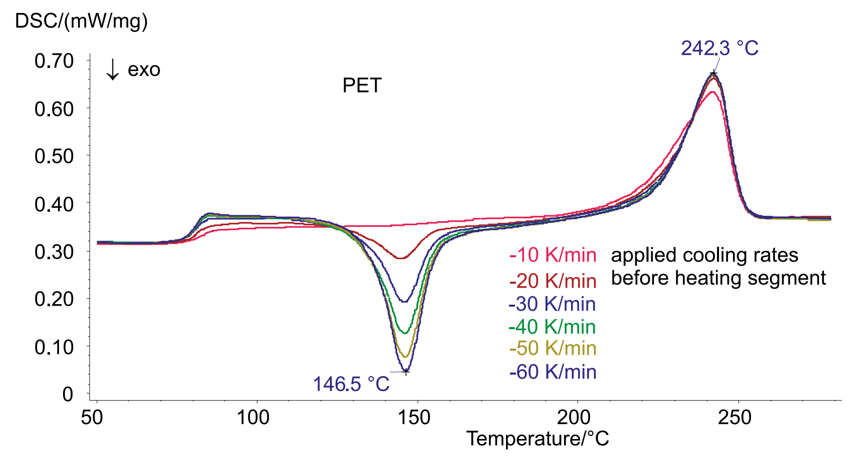
www.netzsch.com/hfm436
www.netzsch.com/ghp456

Thermoplastics

Thermal Behavior of Semi-Crystalline 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 (Tg) 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.



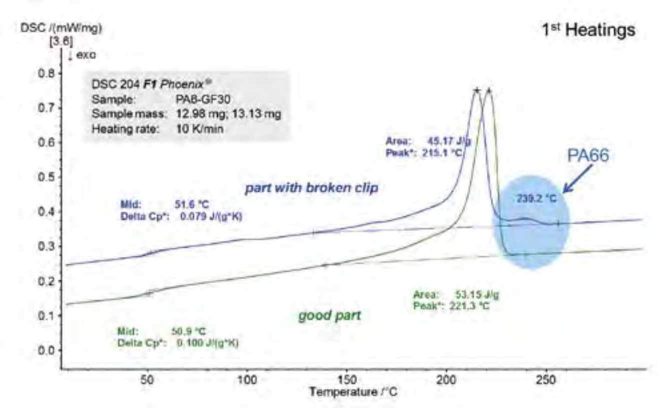
Glass transition, cold crystallization and melting as a function of different cooling rates – change in the crystallinity degree by means of DSC

In the DSC experiments, the various levels of amorphousness (Tg 75°C to 85°C), cold crystallization (146°C) and melting (242°C) are apparent. The samples were cooled from the melt by means of the DSC 204 ***F1*** *Phoenix*® with intracooler at different cooling rates prior to the heating runs shown.

Failure Analysis of a PA6 Clip

Occasionally, failures occur in thermoplastic parts which can result in significant property damage or injury. The failure 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.

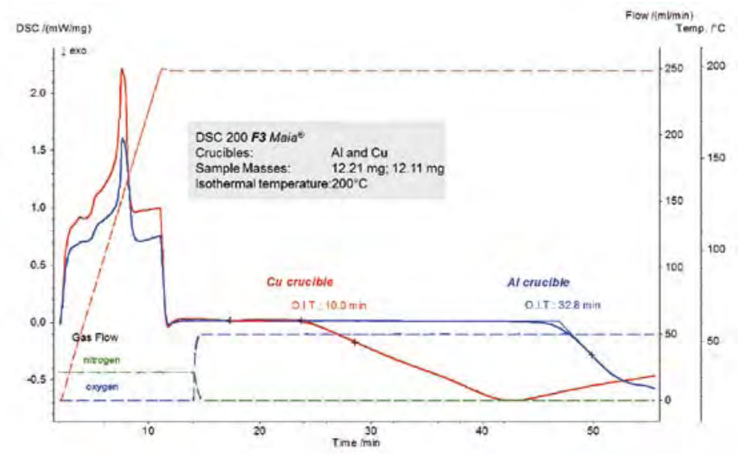
DSC is a convenient method for comparing good parts with poor ones. In this example, the first heating runs on two PA6 clips already show that the poor clip (blue curve) has an additional melting peak at 239°C. This indicates the presence of a second phase. The peak temperature correlates with the melting temperature of PA66, which is often blended with PA6. This is confirmed in the second heating.



DSC comparison of the 1st heating runs of two clips made from PA6 reinforced with glass fiber

Oxidation Induction Time (O.I.T.)

The Oxidation Induction Time (O.I.T.) has been proven to be a useful diagnostic tool in assessing the extent of degradation in polymers under an oxygen gas flow. Factors that influence O.I.T. include test temperature, sample preparation, sample geometry, sample mass, particle size, crucible material, etc. The Oxidation Induction Time (O.I.T.) can be determined in standard aluminum or in open copper crucibles in accordance with ASTM D3895.

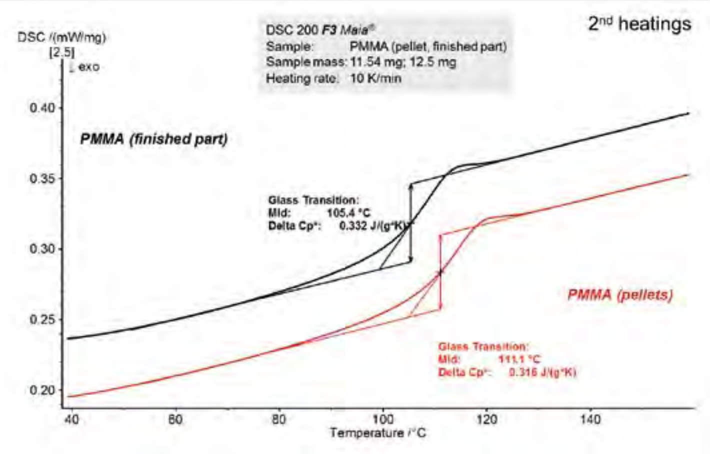


Influence of the crucible material on the Oxidation Induction Time (O.I.T.) of HDPE by DSC

This plot represents an O.I.T. measurement 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 Thermal 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 step in the production process from the pellet to the finished part influences the material's properties.



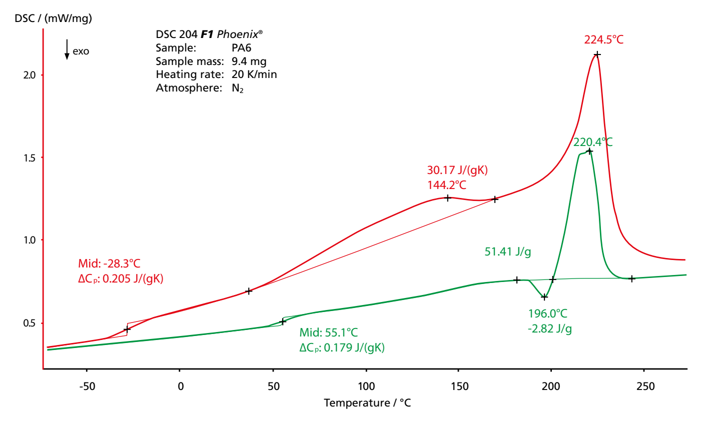
DSC measurement: shift of the glass transition to lower temperatures with increasing production steps

Thermoplastics

Influence of Atmospheric Moisture in PA6

Among the most important polyamides, PA6 is a major fiber-forming polymer and useful in engineering plastics. Polyamides can adsorb atmospheric moisture, which affects their mechanical properties.

The endothermic step at -28°C of the first 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 second heating, the sample is dry and the glass transition temperature is shifted to the real value of 55°C.



1st and 2nd heating of moist PA6 by means of DSC

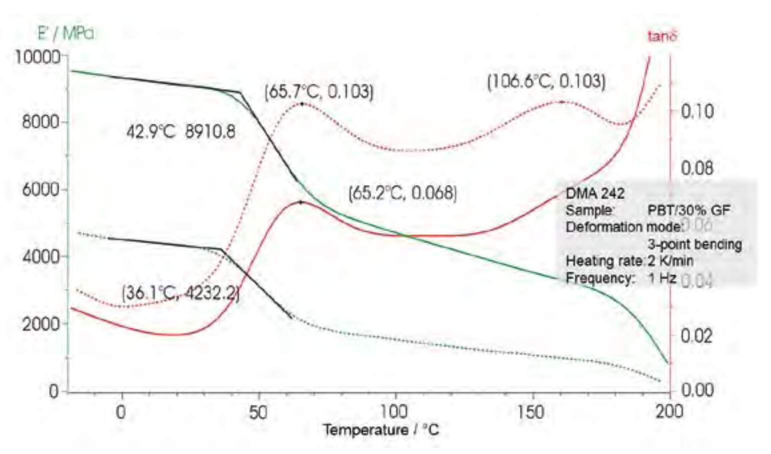
Water acts as a plasticizer and lowers the glass transition temperature. The peaks at 225°C (1st heating) and 220°C (2nd heating) are related to melting. The 2nd heating additionally shows a cold crystallization at 196°C.

Anisotropic Behavior of a Part of Glass Fiber-Reinforced Polybutylene Terephthalate (PBT)

A glass fiber-reinforcement to PBT gives the polymer a high mechanical stiffness and thermal stability.

In this example, the viscoelastic properties of a finished part made of glass fiber-reinforced PBT were determined using the DMA 242 D. The measurements were carried out in the direction of the fiber and perpendicular to it 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 lower, respectively.

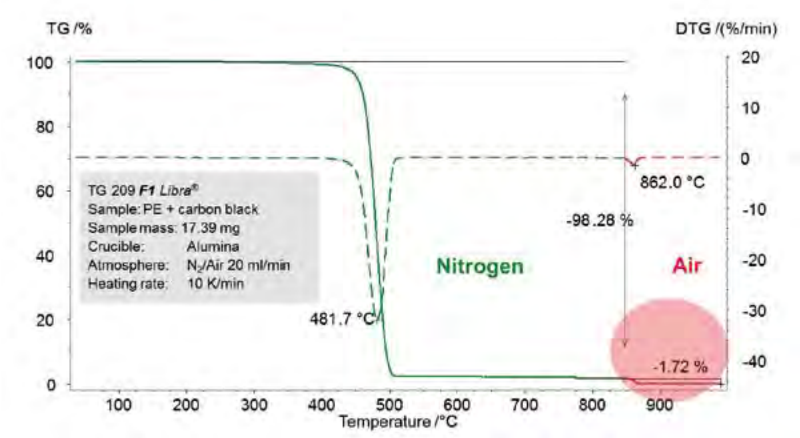


DMA measurements parallel to the fiber direction (solid curves) and perpendicular to it (dotted curves)

Detection of Added Carbon Black in PE by TGA

Polyethylene (PE) is one of the most common materials in day-to-day life. However, static electricity may build up in polyethylene materials unless additives are used. PE is 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. When homogeneously distributed in components made of PE, such as pipes, it can prevent UV degradation for serveral years even if stored in open sunlight.

The level of added carbon black content in PE can be easily determined by TGA measurements. The prerequisite is 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.

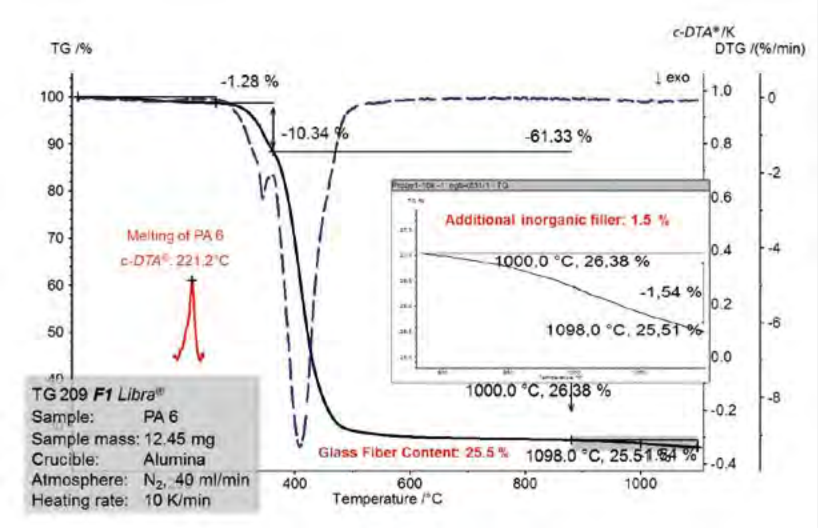


TGA measurement on polyethylene with added carbon black

Determination of Different Filler Contents in PA6 by TGA

Fillers are very important raw materials contained in many articles we use in our day-to-day life. Whereas fillers were previously used mostly to lower the price of finished products, they are nowadays primarily used to improve the technical characteristics of finished products.

The determination of inorganic fillers can be carried out in a nitrogen atmosphere by TGA. This PA6 sample was filled with 25.5% glass fiber. Decomposition of an additional inorganic filler can be observed between 900°C and 1100°C (see insert). 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.



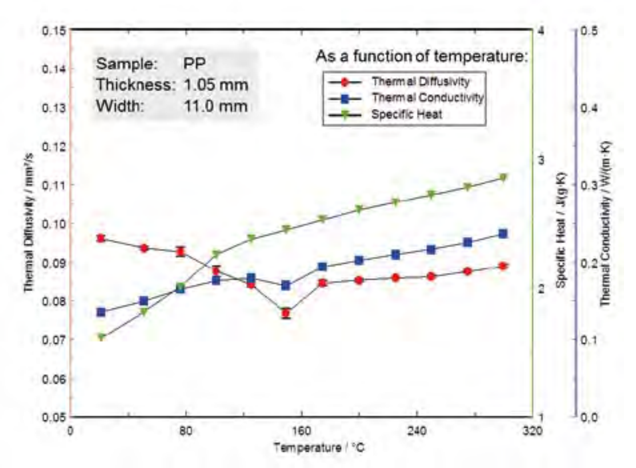
Determination of the melting temperature (identification) and filler content by TGA with c-*DTA*®

Thermoplastics

Thermophysical Behavior of PP – Even in the Molten State

Thermophysical properties measurement refers to the process of directly measuring a material's physical properties as it is subjected to changes in temperature. In this example, the thermophysical properties of polypropylene (PP) were determined between 20°C and 300°C with the LFA 447 *Nanoflash*®.

From room temperature to the onset of melting at 150°C (extrapolated onset of the melting peak from a DSC run), the thermal diffusivity decreases significantly from 0.098 to 0.075 mm²/s. After melting, it reaches an almost constant value of 0.085 mm²/s at 250°C. As expected, the specific heat 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.

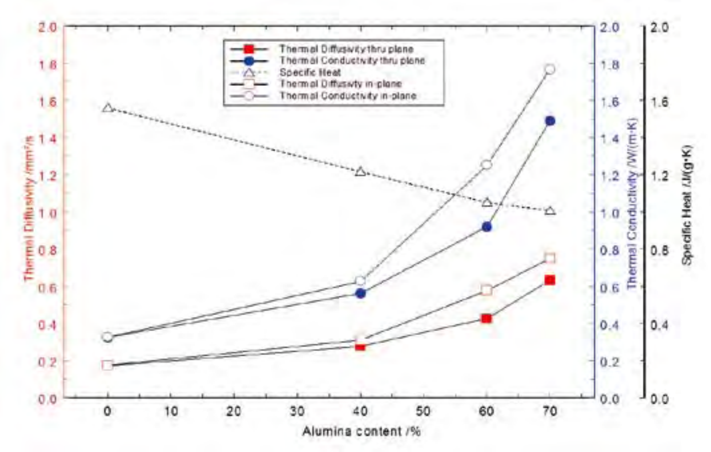


Thermophysical behavior of PP between 20°C and 300°C, measured with the LFA 447 *NanoFlash*®

Prior to and after 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

The crystalline nature of polyamide (PA) significantly affects its physical and mechanical properties. Highly crystalline types can be stiff and hard. The use of glass fiber and other reinforcements such as Al_2O_3 can improve the mechanical properties (modulus, strength). These fillers also influence the thermophysical properties (thermal diffusivity/conductivity and specific heat).



Thermophysical properties of filled PA46 at room temperature, measured with the LFA 447 *NanoFlash*®

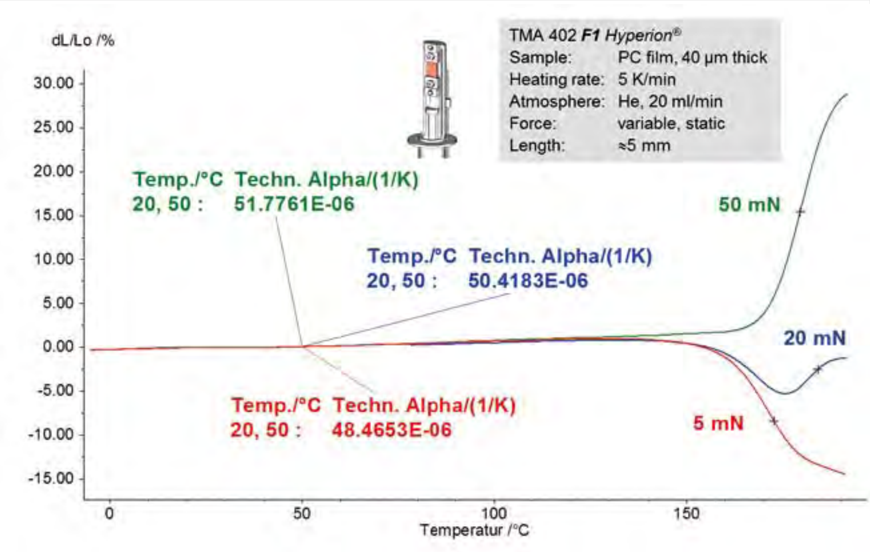
The influence of fillers in the thermophysical properties can be tested with the LFA 447 *NanoFlash*®. Tests can be carried out in the thru-plane and the in-plane directions. For the in-plane tests, a special sample holder for laminates is available.

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 decreases while the thermal diffusivity and thermal conductivity increase.

Tension Test on a Shrink Film of PC

At the glass transition, many physical properties of an amorphous plastic or of the amorphous domains of semicrystalline thermoplastics undergo stepwise changes. The same applies to their coefficient of linear thermal expansion (CTE).

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.



Orientation effects of a PC shrink film measured with the TMA 402 ***F1*** *Hyperion*®

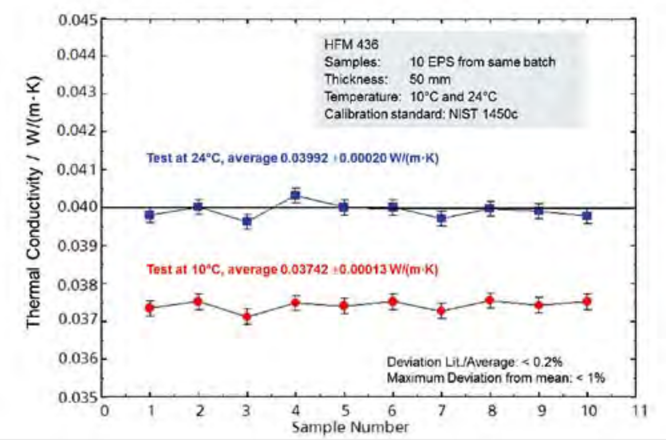
Thermoplastics – Thermoplastic Elastomers

Expanded Polystyrene (EPS)

EPS has many useful properties. It can be used as an insulator against heat or cold. It is excellent at absorbing shocks and protecting fragile items.

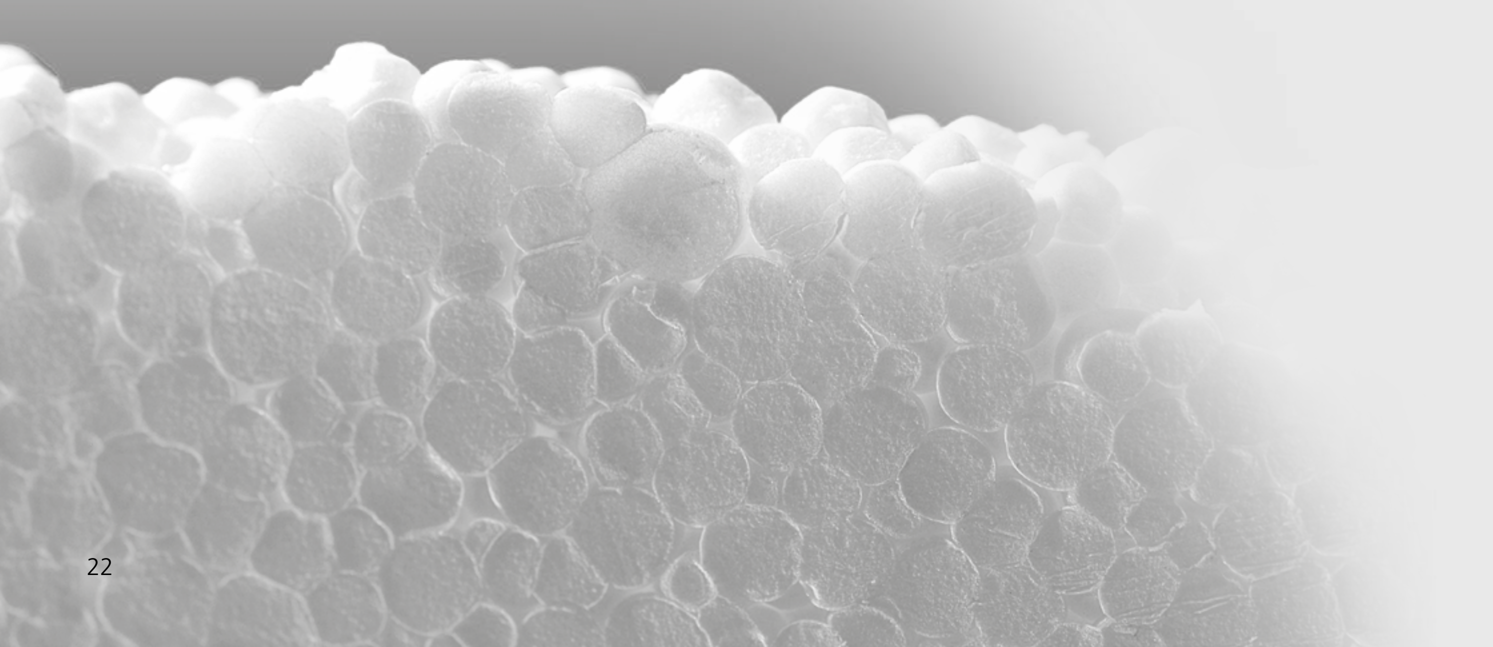
The tests shown here were of the typical quality control purpose types conducted on ten EPS samples from the same batch at 10°C and 24°C, to determine the thermal conductivity in accordance with DIN EN12667.

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 this insulating material.



Quality control of EPS with the HFM 436

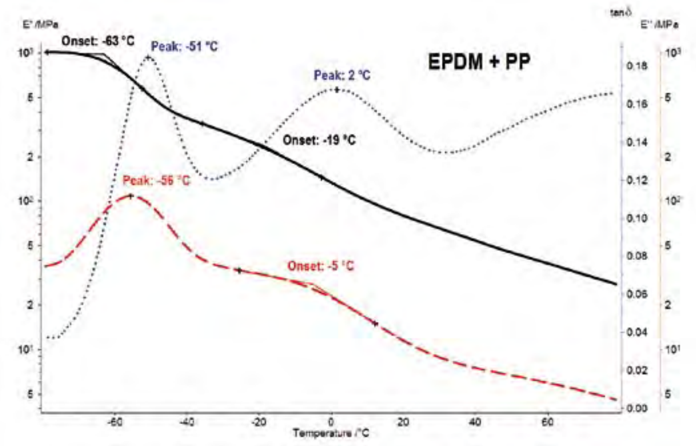
The high test speed of the HFM 436 allows for a large throughput to be tested. This becomes important if an insulating foam needs to be analyzed in accordance with DIN EN13163. In that procedure, the number of sample tests influences the λ90/90 value which is determined from the test results.



Viscoelastic Properties of a TPE

Thermoplastic elastomers (TPEs) possess the qualities both of rubber-like mechanical response and of ease of application in thermoplastic manufacturing. Dynamic mechanical analysis (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 polypropylene (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). Melting of the PP component is not measured by DMA but can easily be evaluated at approx. 160°C by the DSC method.



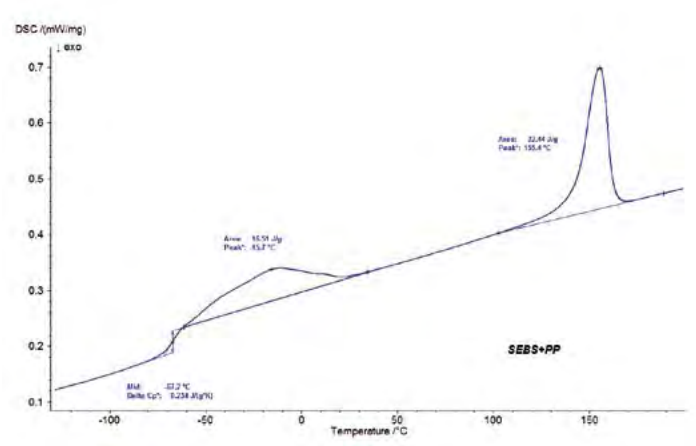
DMA measurement of the thermoplastic elastomer EPDM+PP

Phase Transitions of a TPE Blend

Styrene-ethylene-butylene-styrene block copolymer (SEBS) belongs to the group of thermoplastic elastomers exhibiting a better high-temperature strength retention and resistance to solvents than SBS. In addition, it is paintable, recyclable and can be upgraded with stabilizers for a higher UV resistance and improved aging behavior as required in automotive interior and exterior applications.

This DSC measurement was carried out on a SEBS+PP sample at a heating rate of 10 K/min with the DSC 200 ***F3*** *Maia*®. 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.



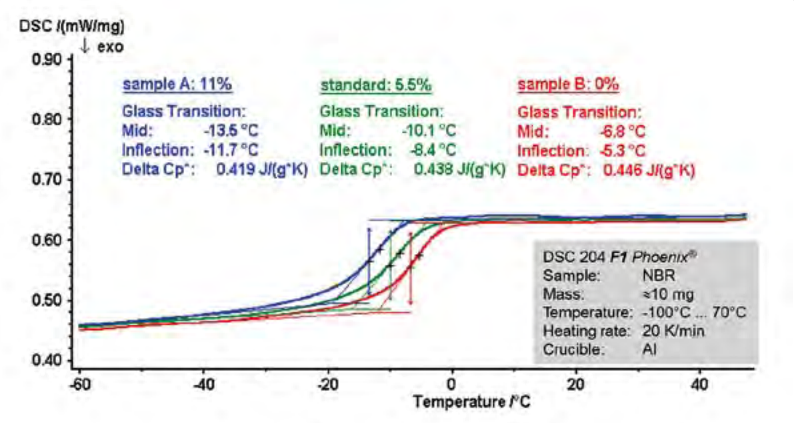
DSC measurement of the thermoplastic elastomer SEBS+PP

Elastomers

Plasticizer Influence on the Glass Transition of Rubber

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

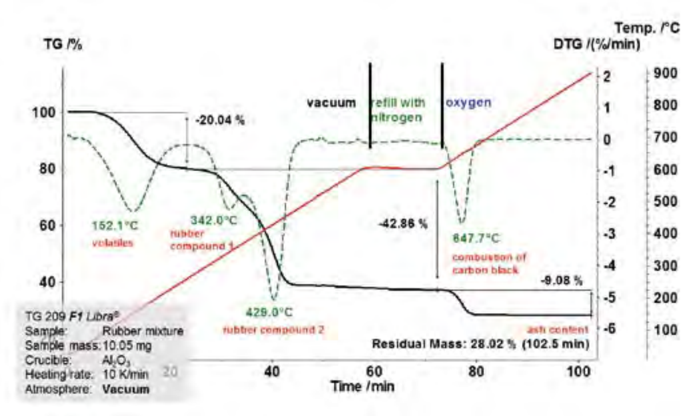
These measurements were carried out on three NBR samples differing in their plasticizer content. It can be observed that modification of the NBR plasticizer content yields different glass transition temperatures. Pure NBR has its glass transition temperature at -6.8°C (midpoint). With an increasing plasticizer content of 5.5% from 11%, the glass transition temperature shifts to -10°C and -14°C, respectively. The cold flexibility can thus be improved by increasing the plasticizer content.



DSC measurements on NBR with different plasticizer contents

Comprehensive Rubber Analysis

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.

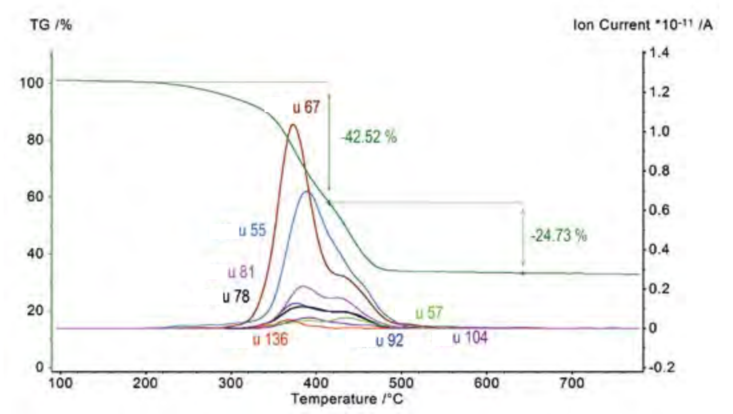


TGA measurement under vacuum and back-filling with nitrogen followed by combustion of carbon black in oxygen

In the first segment of this TGA measurement under vacuum, 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 peak temperatures). 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. The ash content amounts to 28% and remains in the crucible.

Classification of the Gases Evolved During Rubber Decomposition: Plasticizer and PAHs

Thermal analysis (TA) is typically used for the study of the temperature stability and decomposition of rubber. One important question to answer would be how much plasticizer of which type is realeased at which temperature. Coupling of TA methods to gas analyzers such as mass spectrometers allows for the chemical identification of the evolved gases. An example of a question here would be whether the rubber releases potentially carcinogeric polycyclic highly aromatic hydrocarbons (PAHs).



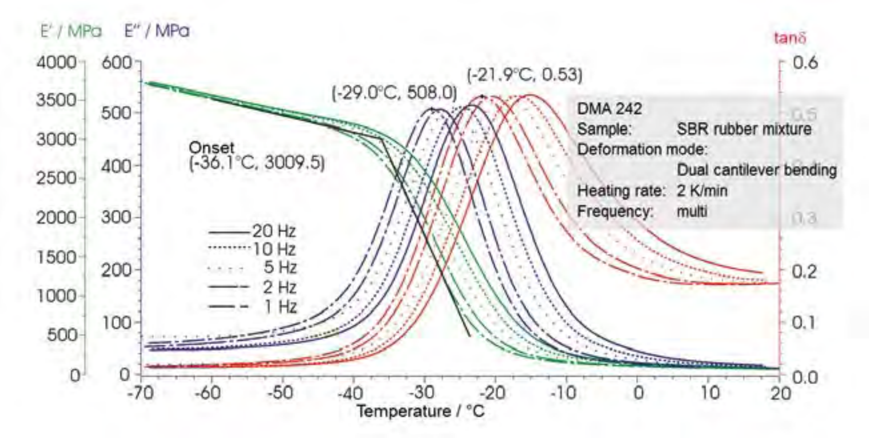
STA-MS measurement detects evolved gases during decomposition of a tire sample

By means of simultaneous TGA and mass spectroscopy (MS), the pyrolytic decomposition of a rubber sample was investigated in this example. During heating of the 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. No PAHs were detected.

Elastomers

Influence of the Frequency on the Glass Transition Temperatures of an SBR Rubber Mixture

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.

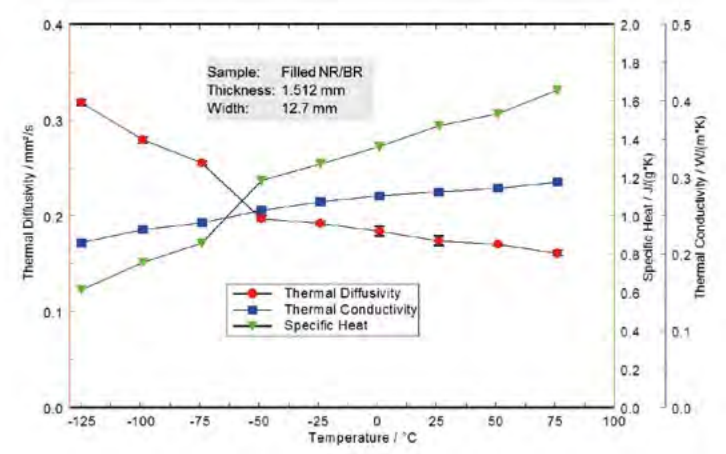


DMA measurement of the viscoelastic properties of an SBR rubber mixture: storage modulus (E’, green), loss modulus (E”, blue) and damping factor (tanδ, red) as a function of frequency

This example of an SBR (styrene butadiene rubber) mixture shows that at low temperatures (-70°C to -45°C), the tanδ values are 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 higher. Additionally, higher E’ values are obtained with increasing frequencies.

Thermophysical Properties of an NR/NBR Rubber at Lowest Temperatures

The LFA 457 *MicroFlash*® laser flash system offers determination of the thermophysical properties (TPP) of rubber mixtures even at temperatures below the glass transition.



LFA measurement: thermophysical properties of an NR/NBR rubber mixture before, during and after the glass transitions

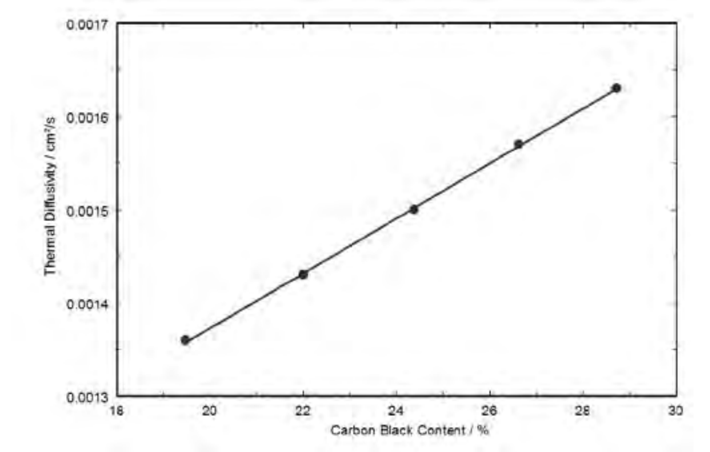
In this example, a thin filled NR/NBR rubber material (thickness of 1.512 mm, width of 12.7 mm) was measured in the temperature range between -125°C and 80°C. Increasing temperature leads to increasing thermal conductivity while the specific heat is rapidly increasing and the thermal diffusivity is decreasing. These drastic changes in specific heat and thermal diffusivity occur around the glass transition of the two components at temperatures between -70°C and -45°C. This decrease in thermal diffusivity and increase in specific heat cancel each other out so that no significant change in thermal conductivity occurs.

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 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.



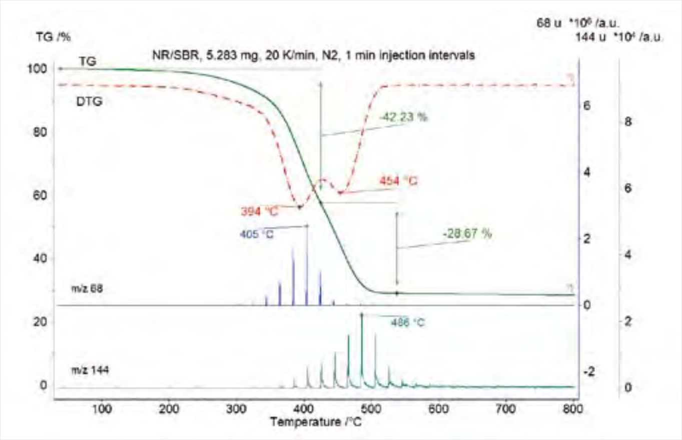
LFA measurement: thermal diffusivity of rubber mixtures filled with different quantities of carbon black at room temperature

Elastomers – Thermosets

TG-GC-MS Measurement of an NR/SBR Rubber

The very high-sensitivity TG-GC-MS coupling yields information on the composition (mass numbers of elements and molecules) of evolved gases. Separation of the volatiles is made possible by use of the GC column. This allows for a significantly improved interpretation of organic vapors.

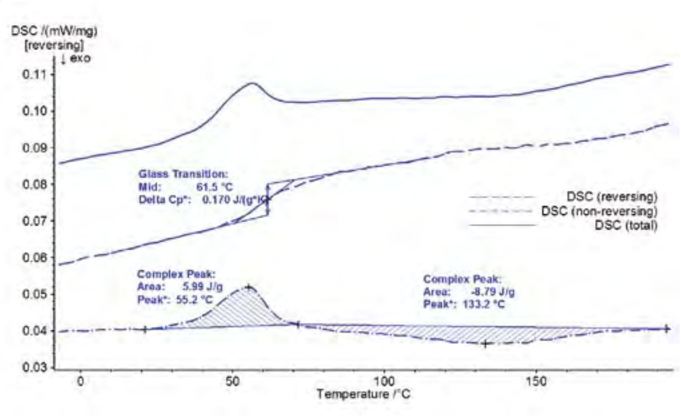
This example shows the TG-GC-MS run on an NR/SBR rubber. The GC-MS was operated with a fixed column temperature (250°C) and short injection intervals of 1 min. The TG and DTG curves indicate an overlapping decomposition of the individual rubber components. However, the evolved gases can be identified in good temperature and time correlation with the TG and DTG results. The first 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 second DTA 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.



Identification of the gases evolving during decomposition of a rubber mixture

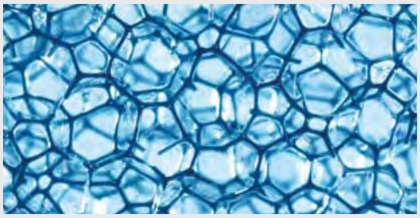
Glass Transition and Curing of a PUR Resin

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. This TM-DSC measurement shows the glass transition, relaxation and curing of a polyurethane (PUR) sample. 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 TM-DSC test.



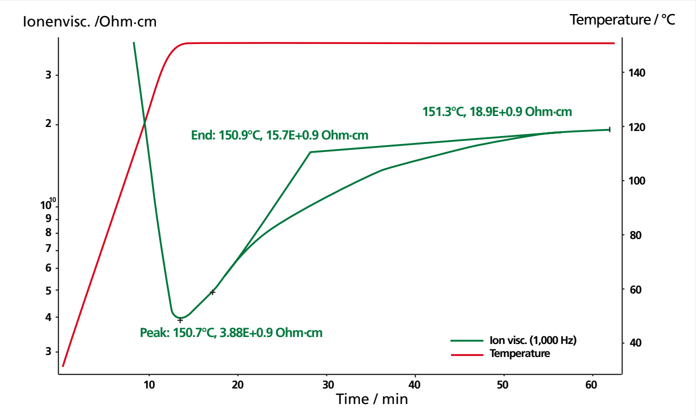
TM-DSC measurement of a polyurethane resin

* The TM-DSC software extension is not available in Japan



Cure Monitoring of EVA

The EVA copolymer (ethylene vinyl acetate copolymer) is one of the most commonly used encapsulant materials. As the polymerization reaction is irreversible, the thermal treatment is crucial in the encapsulation process. The quality and lifetime of encapsulated materials are determined by this production process.

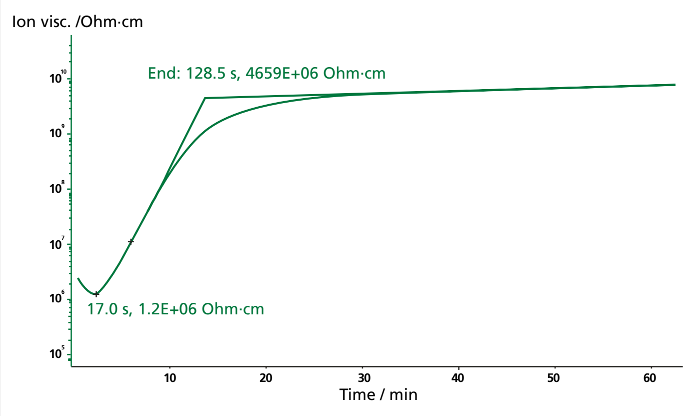


DEA test results of EVA curing at 150°C at 1 Hz

The multi-frequency test in this sample was carried out at frequencies between 1 Hz and 10000 Hz while monitoring the ion viscosity (Ωcm). Presented here is the behavior of the ion viscosity at 1 Hz. The cross-linking reaction from using peroxide was observed under isothermal conditions at 150°C. The 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.

Fast UV Curing of an Epoxy Resin

In addition to exhibiting excellent adhesion, special UV-curing sealants with a high water barrier effect are developed to guarantee a long lifetime. The epoxy adhesive here investigated (DELO Katiobond LP655) stands out for its low water vapor permeation and short curing time.



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

The fast curing can be observed with the DEA 288 Epsilon 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.

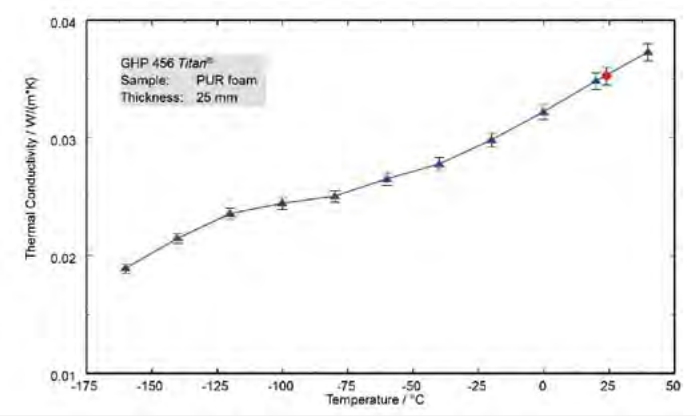
After 17 s of light exposure, curing began. This was evidenced by the increase in ion viscosity. The adhesive was completely cured after approx. 350 s.

Thermosets – Composites

Thermal Conductivity of PUR Foam

Polyurethane (PUR) foams constitute the largest category of cellular polymeric materials. They are produced, for the most part, either in flexible or in rigid form. Within these major groups, the density and other properties vary depending on the end use. PUR foams offer an attractive balance of performance characteristics (aging properties, mechanical strength, elastic properties, chemical resistance, insulating properties) versus costs.

Presented here is a comparison of an HFM test at room temperature and a GHP test down to -160°C. The two sets of results are in perfect agreement. Additionally, the GHP results show the impact of cell-gas condensation between -125°C and -50°C.



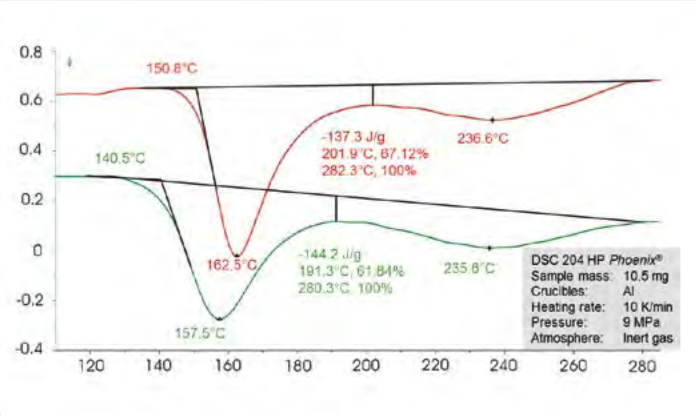
Low-temperature GHP measurement of a PUR foam and comparison of an HFM test result at 25°C

High-Pressure DSC Measurements on Phenolic Resins

Phenolic resins are found in many industrial products. Phenolic laminates are made by impregnating one or more layers of a base material – such as paper, fiberglass or cotton – with phenolic resin, and then laminating the resin-saturated base material under heat and pressure. The resin fully cures during this process.

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

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.

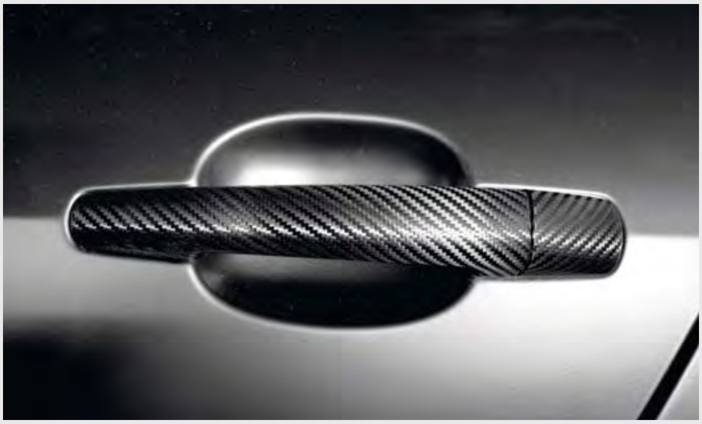


DSC 204 HP: exothermal curing behavior of two phenolic resins under high pressure

Characterization of High-Modulus Composites

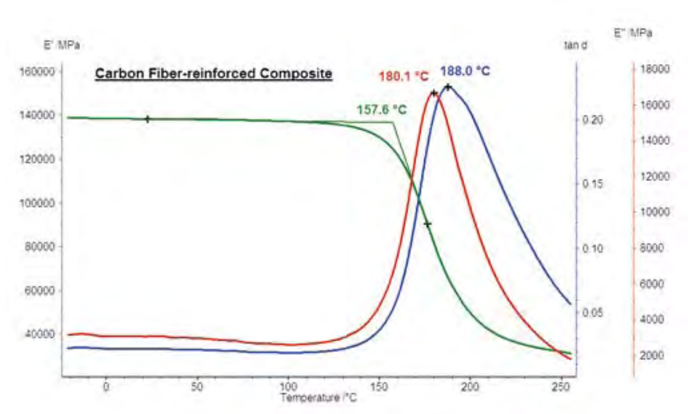
Today's research trends – especially in the automotive industry – focus on lighter materials, but without sacrificing the required stiffness over a broad temperature range. The key to reducing vehicular weight has been found in the use of fiber-reinforced polymers.

These high-modulus composites have already proven their performance in the aircraft and aerospace industries. However, cycle times for the production of car parts are much shorter and the thermosetting resin must therefore cure in only a few minutes, not a few hours.



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 lamellar 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

Composites – Thermokinetics

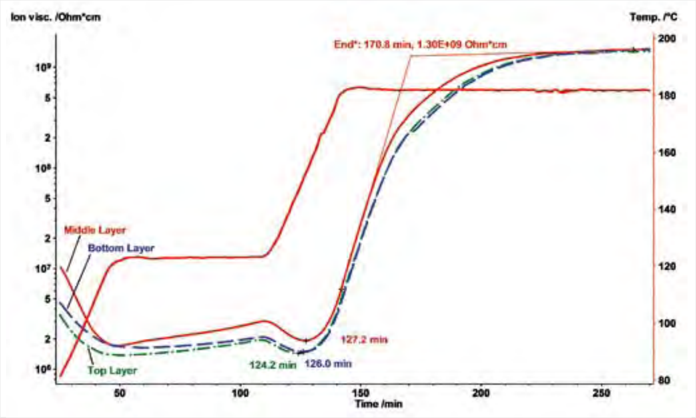
Cure Monitoring of a CF-Reinforced Epoxy Resin

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.

Thermal analysis (TA) methods are capable of providing such answers. However, conventional TA can only be used in a restricted way since curing and solvent release might be overlapped or the curing reaction takes places faster than mixing and weighing of the sample, etc.
Such problems can be solved, however, by using dielectric analysis (DEA). This method can even be applied in-situ, i.e. during the actual process in the plant.

The plot depicts the curing of a carbon-fiber-reinforced epoxy resin 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; it increased by approx. three orders of magnitude. 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).

With a multi-channel DEA, the progress of curing can be monitored at different locations in the mold. Here, three IDEX sensors were placed between different carbon fiber layers comprising the part thickness. The ion viscosity curve for the middle layer position (red) provided the fastest curing (highest reactivity) in the shortest curing time.



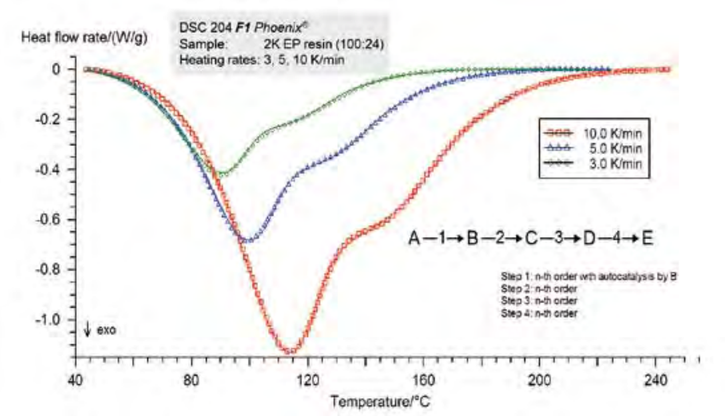
Dielectric analysis (DEA) with different IDEX sensor positions

Thermokinetics: Evaluation of the Curing Behavior of an Epoxy Resin

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.

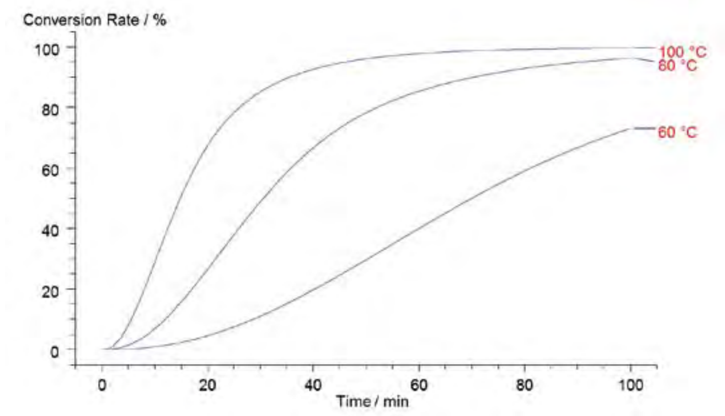
Epoxy resins are a group of polymer materials that are widely used in industrial applications. Questions about the duration of curing, or the conditions under which a defined level of cure is achieved, are issues for which kinetics provides answers. Model-free analysis cannot be used in such cases because there are strong limitations to this method, caused by issues at its core.

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 *Thermokinetics* software program, exothermal curing was simulated. The almost perfect fit was achieved as a formal n^th^-order 4-step reaction. The start of the actual curing was described well by a first-order reaction with autocatalysis.



Curing of an epoxy resin at different heating rates

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%).



Prediction of the curing behavior at different isothermal temperatures

Expertise in Service

Our Expertise – Service

All over the world, the name NETZSCH stands for comprehensive support and expert, 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.

Summary of Our Services

- Installation and commissioning
- Hotline service
- Preventive maintenance
- Calibration service
- IQ /OQ/PQ
- On-site repairs with emergency service for NETZSCH components
- Moving/exchange service
- Technical information service
- Spare parts assistance

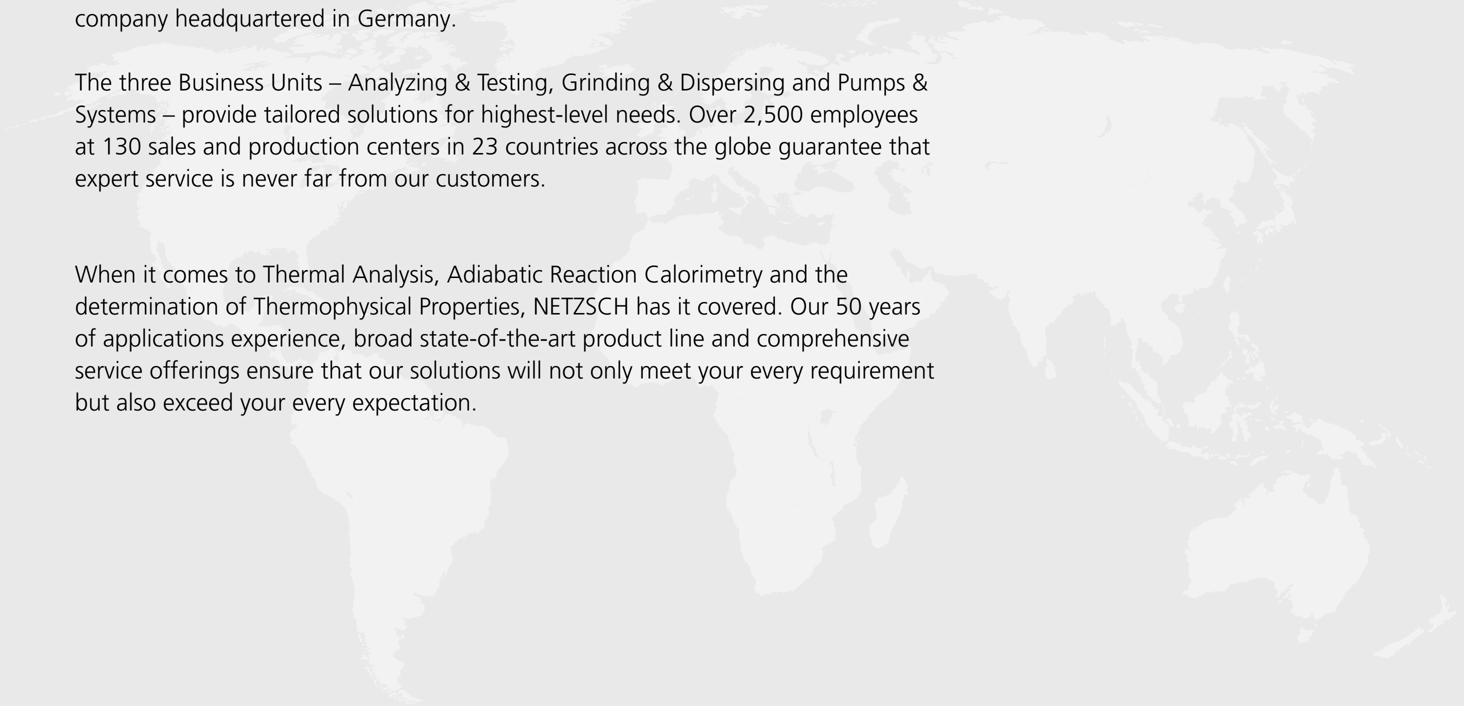
Our Expertise – Applications Laboratories

The NETZSCH Analyzing & Testing applications laboratories are proficient partners for nearly any Thermal Analysis issue. Our diverse measuring methods and over 30 different state-of-the-art test stations will provide ready solutions for all your thermal needs.

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 our expert team. This will enable you to precisely define new materials and components before actual deployment, minimize risks of failure, and gain decisive advantages over your competitors.

For production problems, we can work with you to analyze causal issues and work out solution concepts. The option of commercial testing is a relatively low investment which generally pays itself off in a few days or weeks and provides fast and reliable support for research on new materials or resolving any kinds of production issues.

NETZSCH



The NETZSCH Group is an owner-managed, internationally operating technology company headquartered in Germany.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 2,500 employees at 130 sales and production centers in 23 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.

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