NETZSCH

Proven Excellence.

TMA 402 *F3* *Hyperion® Polymer Edition*

Thermomechanical Analysis – TMA
Tailor-Made for Low-Temperature Applications

Analyzing & Testing

Tailored to Polymer Applications

For research and development, simulation input and quality control

TMA Tests on Polymers

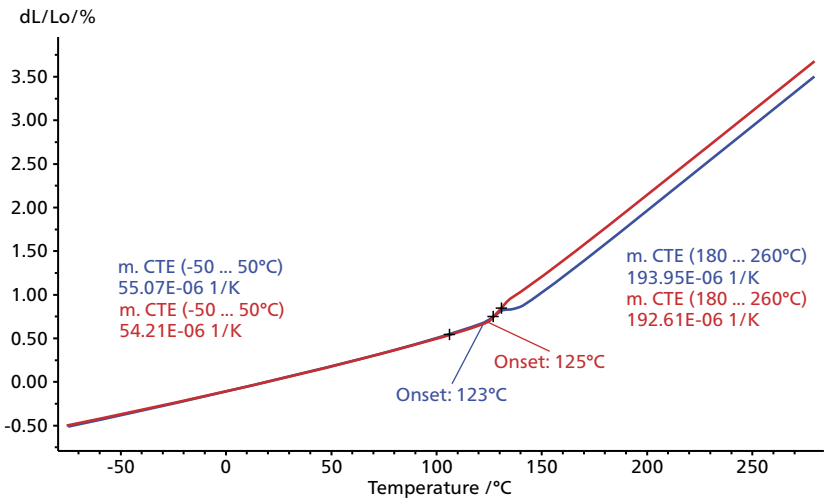
- Coefficient of linear thermal expansion
- Phase transition temperatures
- Glass transition temperatures
- Dilatometric softening point
- Volumetric expansion
- Density changes
- Delamination
- Isostrain
- Creep
- Relaxation
- Stress/strain curve

Thermomechanical analysis (TMA) is a technique for determining the dimensional changes in solids, liquids or pasty materials as a function of temperature and/or time under a defined mechanical force (DIN 51005, ASTM E831, ASTM D696, ASTM D3386, ISO 11359 – Parts 1 to 3). TMA has proven to be the preferred method for measuring the coefficient of linear thermal expansion in plastics, a fundamental material property describing the ability of a polymer to expand when exposed to varying temperatures.

TMA Analysis for Polymers

Polymers undergo changes in their thermomechanical properties during heating and cooling. TMA analyses can give insights into molecular orientation and quenching effects during cooling, thus allowing the design of adhesives and other hybrid joints as well as for quality control of shrink films. Such analyses can provide valuable insight into the composition, structure, production conditions and application possibilities for various materials.

When it comes to the detection of T_g for polymers with fillers or highly crosslinked materials, such as composites or printed circuit boards, TMA offers a higher degree of sensitivity than the DSC method. TMA is therefore a perfect method to be used to detect weak physical transitions that are associated with changes in modulus, post-curing and delamination, which are hard or impossible to measure with other methods.



CTE measurement on an epoxy resin with a sample length of 6 mm in expansion mode (fused silica sample holder); 1st and 2nd heating runs at a rate of 2 K/min

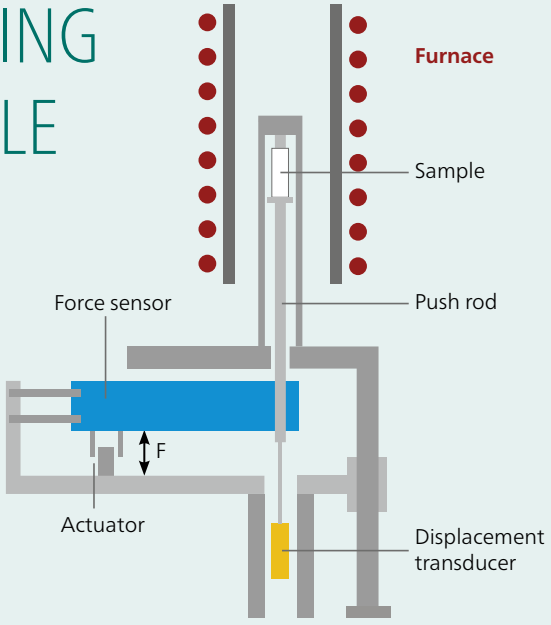
Thermal Expansion

The linear thermal expansion is an important variable for assessing the dimensional change of a material in response to a change in temperature. It shows how much a material will shrink or expand during processing, whether dissimilar materials can be joined, where the phase change occurs and where the CTE changes.

This plot shows the thermal expansion (dL/L_0 in %) of an epoxy resin between -70°C and 270°C. In the first heating (blue curve), the onset of the T_g occurs at 123°C. In the second heating (red curve), the onset of T_g is slightly shifted, to 125°C. This shift could be due to relaxation effects or post-curing.

TMA – THE METHOD PRECISELY DETERMINES DIMENSIONAL CHANGES OF PLASTICS, ELASTOMERS AND COMPOSITE MATERIALS

OPERATING PRINCIPLE



Irrespective of the type of deformation selected (expansion, compression, penetration, tension or bending), every length change in the sample is communicated to a highly sensitive inductive displacement transducer (LVDT) via a pushrod and transformed into a digital signal.

The pushrod and corresponding fused silica sample holders can be quickly and easily changed out, in order to optimize the system for the respective application.

TMA 402 *F3 Hyperion® Polymer Edition*

Gaining Valuable Information about

Detect Even the Slightest Dimensional Changes

The LVDT constitutes the centerpiece of the NETZSCH TMA 402 ***F3*** *Hyperion® Polymer Edition*. The technology behind it is tried-and-true: Even the slightest of length changes, into the nanometer range (digital resolution of 0.125 nm), can be measured and detected.

No-Hassle Cooling to -70°C

The TMA 402 ***F3*** *Hyperion® Polymer Edition* is specifically designed for polymer applications. It comes with a compact, highly reactive furnace capable of covering a temperature range from -70°C to 450°C and uses a mechanical cooling system without the need for LN_2.

Flexible Atmospheres in a Vacuum-Tight TMA System

All joints are designed to be vacuum-tight, allowing for measurements in a highly pure atmosphere or under vacuum. This TMA includes one software-controlled mass flow controller (MFC) and can be upgraded with another independent MFC. This provides optimum flexibility in gas control and in changing the purge and atmospheric gas rate.

Made in Germany by NETZSCH

Product Performance and Processing Behavior

Determination of Visco-Elastic Properties like Relaxation, Creep and Stress/Strain

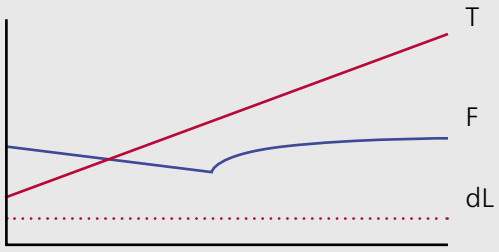
The TMA 402 ***F3*** *Hyperion® Polymer Edition* now offers not only the ability to keep the force constant and to measure the length change, but also to change the dL displacement and measure the corresponding force. This can, for example, be used in a stress relaxation test where a sample is stretched by a specific amount at a defined temperature. During the test, the deformation is kept constant and the progression of the force is recorded. This force continuously decreases as a result of material relaxation. The stress-relaxation strength is ultimately defined by the residual stress measured after a defined exposure period. The data can be depicted graphically in a stress-time diagram. It is then possible to read off both the stress-relaxation behavior and the values for the relaxation rate and time.

Precise Force Control Enables Tests on Sensitive Materials

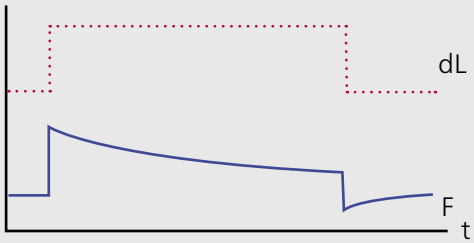
The force operating on the sample is generated electromagnetically. This ensures a quick response time for experiments with a changing load. A highly sensitive force sensor (digital resolution < 0.01 mN, max. force ±3 N) continuously measures the force exerted via the pushrod and readjusts it automatically. This sets the TMA 402 ***F3*** *Hyperion® Polymer Edition* apart from other instruments which only use preset values. The control system allows users to set the force value in the mN-range. This enables testing even on sensitive materials such as thin fibers or films. The force being exerted upon the sample can be altered via the software in a stepwise or linear fashion. This makes it especially simple to carry out tests such as creep.

Displacement control

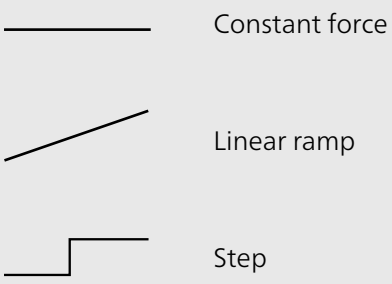
Isostrain



Relaxation



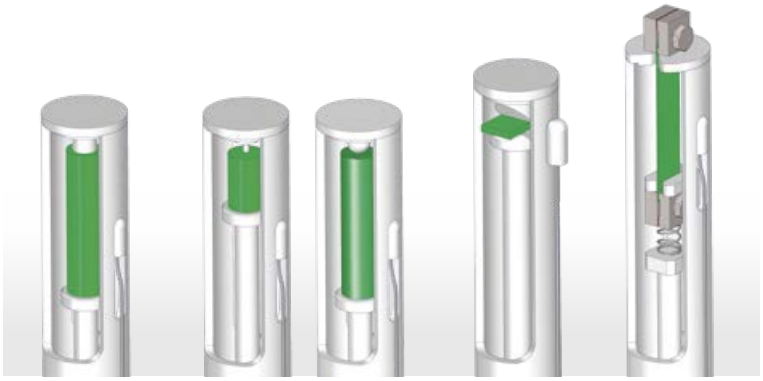
Force control



Accessories for All Application Needs

Easy-to-Change Sample Holders for Various Sample Geometries and Measuring Modes

Fused silica sample holders



Expansion/ Compression – sample holder tube with flat tip, Ø 4 mm

Penetration – sample holder tube with flat tip, Ø 1 mm (left) and Ø 4 mm hemispherical tip (right)

3-Point-Bending, free bending length 5 mm

Tension, max. sample length 30 mm, min. 5 mm

The **expansion/compression** mode is used for samples with different geometries, such as cylindrical or rectangular.

The **penetration** mode determines the softening point of a sample. For this test, sample holders with flat or hemsipherical tips are available.

3-point bending sample holder with a bending length of 5 mm is available.

The **tension** mode is used to measure expansion and shrinkage, creep and relaxation behavior on thin films or fibers.

New tension sample holder with fixed lower clamp for almost force-free tension measurements

Alignment tool for sample preparation for measurements in tension mode

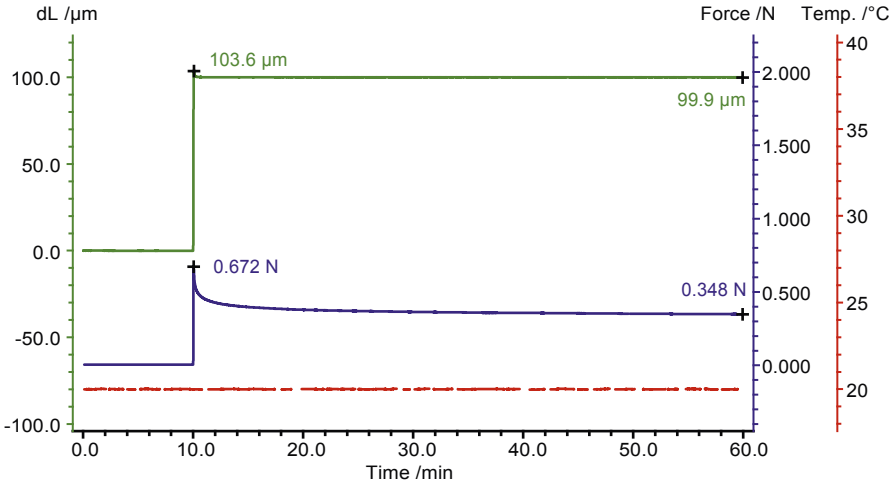
New tension sample holder with sample (green)

Defining Ideal Production and Application Conditions for Polymer Materials

APPLICATIONS

Relaxation – An Important Material Property for Polymer Films

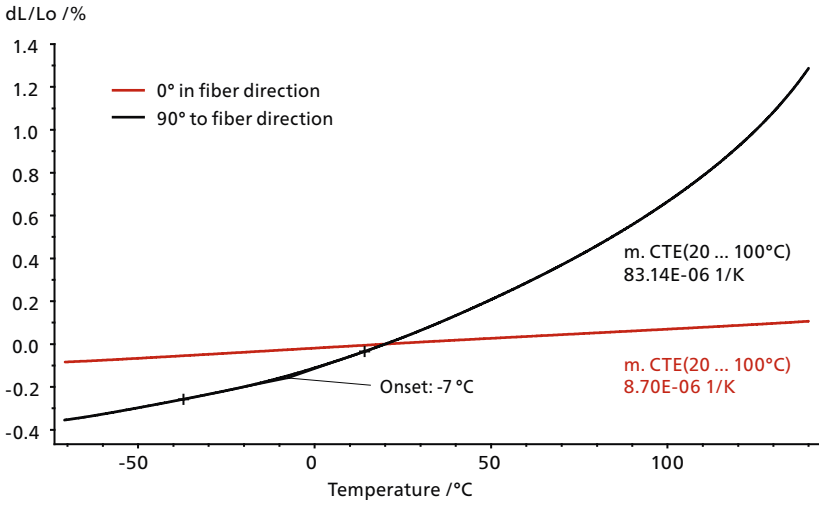
Plastic packaging needs to be flexible, lightweight, strong, sometimes impermeable and, if necessary, easy to sterilize. Both the material used and the process conditions determine the resulting property portfolio. It is important to have knowledge abou ta film material's relaxation properties; this allows for predictions regarding its fatigue and wear resistance during use. Shrink films apply a film's tendency to relax at elevated temperatures after having been pre-stretched during processing. Over time, shrink wrap tends to loosen due to creep and stress relaxation. In the test shown here, the sample was kept under constant strain and the progression of the tensile force was recorded.



Relaxation measurement on an LDPE film, fused silica sample holder. Measured at room temperature under a nitrogen atmosphere; sample length 10 mm; sample width 5 mm.

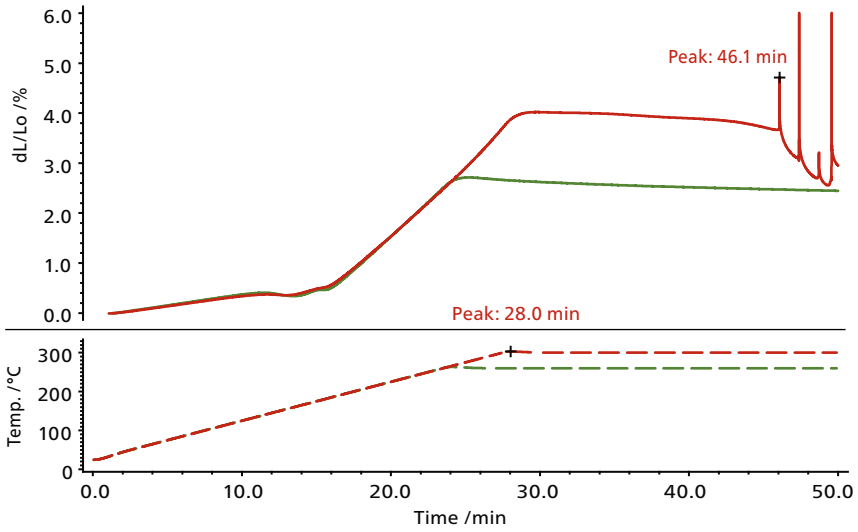
Anisotropic Behavior in Composite Systems

The glass transition temperature (T_g) in a thermoset and thermoplastic matrix composite can be determined by means of TMA. Detection of the onset of the glass transition is therefore a reliable method that determines the upper application limit of a thermoset material. For thermoplastic matrix composites such as PP-GF, the glass transition indicates the area where the material starts to soften. Fibers and other fillers significantly reduce thermal expansion. The degree of anisotropy of the filler and the filler orientation both have a great impact on the linear coefficient of thermal expansion (CTE). For example, uni-directional composites exhibit the CTE of the fibers in the fiber direction. They also exhibit a mixture of the matrix and fiber CTE as a function of fiber volume content perpendicular to the fiber direction. The red curve depicts the measurement in the fiber direction; the CTE is dominated by the low thermal expansion of glass. The sample that is 90° to the fiber direction is dominated by the polypropylene matrix and shows a much higher CTE. Therefore, it is only possible to observe the T_g of PP measured in this direction.



Composite material, measured in two directions; sample length 25 mm, heating rate 5 K/min from -70°C to 140°C, N_2 atmosphere, sample holder made of fused silica for expansion mode.

Specifying the Right Material for Functional Electronics



Determination of time to delamination on an FR4 composite circuit board. Sample size 6.35 mm^2 as defined by IPC, dried for 2 hours pre-measurement at 105°C, heating rate 10 K/min, N_2 atmosphere, sample holder made of fused silica; isothermal segment at 260 and 300°C, respectively.

Industry standards require the measurement of thermal expansion, glass transition and softening point under IPC standards [see IPC-TM-650 2.4.24.1 Time to Delamination (TMA Method)]. After the changeover to lead-free soldering processes in circuit board production, the melting temperature of soldering materials increased. This led to the delamination of printed circuit boards and assemblies due to the higher thermal load. Manufacturers had to react by changing to FR4 substrates with a higher T_g.

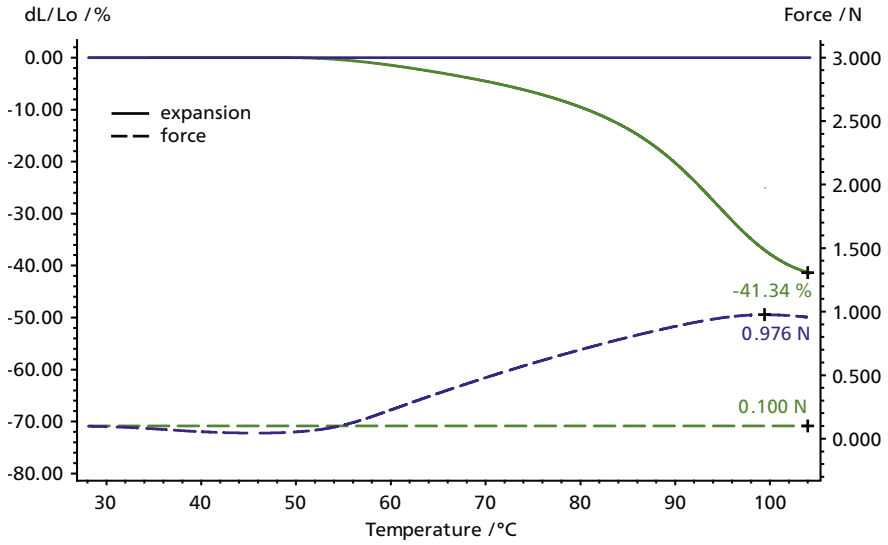
Nevertheless, even today most FR4 substrates are ordered with general material specifications and can vary in their material properties. At the glass transition event, the rate of expansion for the epoxy matrix increases which can lead to delamination between the fibers and matrix and consequently to product failure.

The figure shows a measurement on an FR4 composite in which the time to delamination was recorded. Two measurements were conducted. One with an isothermal temperature of 260°C (green curve) and a second one with an isothermal temperature of 300°C (red curve). In the first measurement, no delamination effect was visible. In the second measurement, the time to delamination was recorded at 18.1 min after being held at anisothermal temperature of 300°C.

Thermal expansion is a major factor in the failure of electronic products.

Typical de-coloration as a sign of beginning degradation: left: before measurement, middle: after being measured at 260°C, right: after being measured at 300°C. Neither of the measured samples shows any visible delamination, although the TMA method is sensitive enough to detect it at 300°C.

Test on Heat-Shrink Tubing

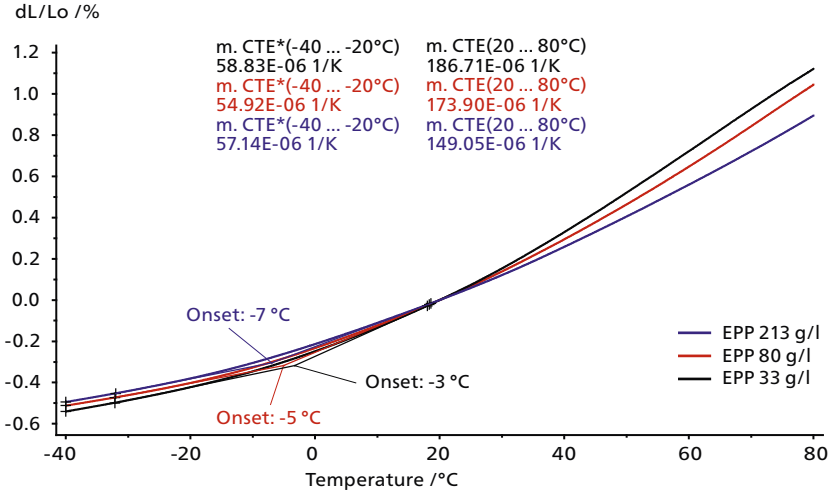


Measurement on a heat-shrink tubing under constant force (green curves) and under constant displacement (blue curves). Heating from RT to 120°C, atmosphere N_2, sample length 25 mm (blue) and 10 mm (green).

Heat-shrink tubing, also known as shrink sleeve, is used to repair and insulate wires and cables. After sliding the tubing onto the cable, a heat source is used to make it shrink and create a tight seal. Heat-shrink tubing, by its very nature, is stretchy and changes its shape. A TMA can help to gather information about the temperature at which the material starts to shrink, how much it shrinks and with how much force. The plot shows the two samples measured. The first sample (green curves) starts to shrink at around 60°C with a shrinkage of 40% by the end of the measurement. In the second sample, the displacement was kept constant and the corresponding force measured. A maximum force of 0.976 N (blue curves) was recorded.

Thermal Expansion of Insulation Material

Polymer foams are used where light weight is required along with an excellent strength-to-weight ratio, superior thermal and acoustical insulation properties, and good energy absorption behavior. Expanded foams such as EPS and EPP are gaining in importance not only in the building, but also in the automotive industry. Therefore, thermal expansion is an important quality criterion when choosing insulation material, since expansion behavior differs significantly among materials with different densities. The foam with the lowest density shows the highest CTE while still having a similar T_g.



Expansion measurements on three different EPP foams with different densities. Sample length 20 mm, heating rate: 5 K/min from -40°C to 80°C under N_2 atmosphere, expansion sample holder made of fused silica and 50 mN sample load.

Proteus® – Only One Click Away From

Input Assistant for a Fast Measurement Start and Method-Based Automatic Evaluation

The *Proteus*® software allows for properties and methods from previously executed measurement files to be applied with a simple mouse click. The evaluation steps for a reference test run can be saved in a method and applied, fully automatically, to a sample measurement after its termination. It is also possible to have the software highlight any results deviating from the selected quality criteria.

AutoEvaluation – The One-Click Evaluation

AutoEvaluation is an intelligent software functionality exclusively offered by NETZSCH. It is a self-acting evaluation of thermoanalytical measurement curves that works without using pre-defined macros. This is an immense support and time saver. *AutoEvaluation* offers special functions for the evaluation of various materials.
When measuring polymers, *AutoEvaluation* will automatically find the onset of the glass transition as well as the peaks of softening points and evaluate these with just one click.

Temperature-Modulated TMA

For temperature-modulated TMA measurements, the modulation amplitude and period can be defined segment by segment. The evaluation software allows for the determination of the

- totel TMA
- reversing and non-reversing TMA
- total CTE
- reversing and non-reversing CTE
- amplitude und phase

with graphic display of the results curve in multi-window technique. *Proteus*® also offers the ability to export graphs and print out or export data as ASCII files.

At a Glance – Highlights of the TMA *Proteus*® Software
TMA 402 ***F3*** *Hyperion*® *Polymer Edition*

Automatic sample length detection	■
Force adjustment/segment	■
Softening point detection	■
c-*DTA*®	□
Force modulation	□
Temperature modulation	□
Strain control	■
Report generator	■
Identify	□
AutoEvaluation	■

■ Included in standard configuration
□ Optional

CLEVER FEATURES FOR INTELLIGENT ANALYSIS

Reliable Results

Identify – Identification and Classification of TMA Curves

The *Identify* database offers a state-of-the-art means of verifying materials; it allows for the comparison of a given curve to other individual curves (e.g., groups of curves in quality control) or to literature data from selected libraries. Any libraries and classes created by the user can be edited or expanded within *Identify*.

Database entries can be filtered by a variety of criteria, and measurement curves – even those of different types – can be overlapped for purposes of comparison.

Software Options for Advanced Evaluation Steps

PeakSeparation for the separation of overlapping effects

Automatic determination of initial sample length in expansion, penetration and tension modes!

TMA 402 ***F3*** *Hyperion® Polymer Edition*	
Furnace	IC-furnace: -70°C to 450°C using mechanical cooling
Heating rates	0.001 K/min to 30 K/min
Measuring ranges/ Δl resolution	▪ 500 µm (± 250 µm) / 0.125 nm ▪ 5000 µm (± 2500 µm) / 1.25 nm
Force and displacement	Simultaneous measurement of force and displacement signal
Force range (load at sample)	0.001 N to 3 N without using additional weights
Force resolution	< 0.01 mN
Sample holder systems	Fused silica
Sample dimensions	▪ Expansion/penetration: Length: 30 mm max.; sample holder Ø 8 mm ▪ Tension: Length: 30 mm max.; width: 6 mm, thickness: 1 mm ▪ 3-point bending: Length: 10 mm max.; width: 5 mm
Atmospheres	1 mass flow controller (MFC, 2nd independent MFC optional), gas flow rate 0 to 250 ml/min (software-controlled), inert, oxidizing, reducing, vacuum (10^{-4} mbar)
Various accessories	Spacers, crucibles and special wax containers


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

Expertise in Service

Our Expertise – Service

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

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

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

Our Expertise – Applications Laboratories

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

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

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

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- Moving Service

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- Comprehensive Instrument and Method Training

LABORATORY

- Application Service and Contract Testing

The NETZSCH Group is an owner-managed, international technology company with headquarters in Germany. The Business Units Analyzing & Testing, Grinding & Dispersing and Pumps & Systems represent customized solutions at the highest level. More than 3,800 employees in 36 countries and a worldwide sales and service network ensure customer proximity and competent service.

Our performance standards are high. We promise our customers Proven Excellence – exceptional performance in everything we do, proven time and again since 1873.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction), the determination of Thermophysical Properties, Rheology and Fire Testing, 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.

Proven Excellence.

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