Thermal Analysis Excellence

TMA/SDTA840

TMA/SDTA841^{e}

STAR^{e} System

Innovative Technology

Versatile Modularity

Swiss Quality

Thermomechanical Analysis

for Exacting Requirements

METTLER TOLEDO

Outstanding Performance, Straightforward and Reliable Operation

Thermomechanical analysis (TMA) is used to measure the dimensional changes of a material as a function of temperature. The thermal expansion and the softening temperature determine the application possibilities of the material and provide important information on its composition.

- **Patented mechanical design** – guarantees high quality results
- **Nanometer resolution** – allows very small changes to be measured
- **Dynamic load TMA (DLTMA mode)** – measures weak transitions and elasticity
- **Wide measurement range** – for small and large samples
- **Extremely broad temperature range** – from -150 °C to 1100 °C
- **SDTA** – simultaneous measurement of thermal effects
- **Modular design** – allows future expansion to meet new requirements
- **Gas tight cell** – controlled measurement environment
- **Hyphenated techniques** – evolved gas analysis (MS and FTIR)

The range of applications covers quality control through to research and development. Areas of use include plastics, paints and lacquers, composites, films and fibers, ceramics, glasses, alloys, coatings and adhesives.

TMA/SDTA840
Thermomechanical module
for the high temperature range

Wide measurement range and high resolution

1 000 000 data points are available for the entire measurement range of ±5 mm. This means that both small and large samples (maximum 20 mm) can be measured with 10 nm resolution without the need for range switching.

Defined atmosphere thanks to the gas-tight measuring cell

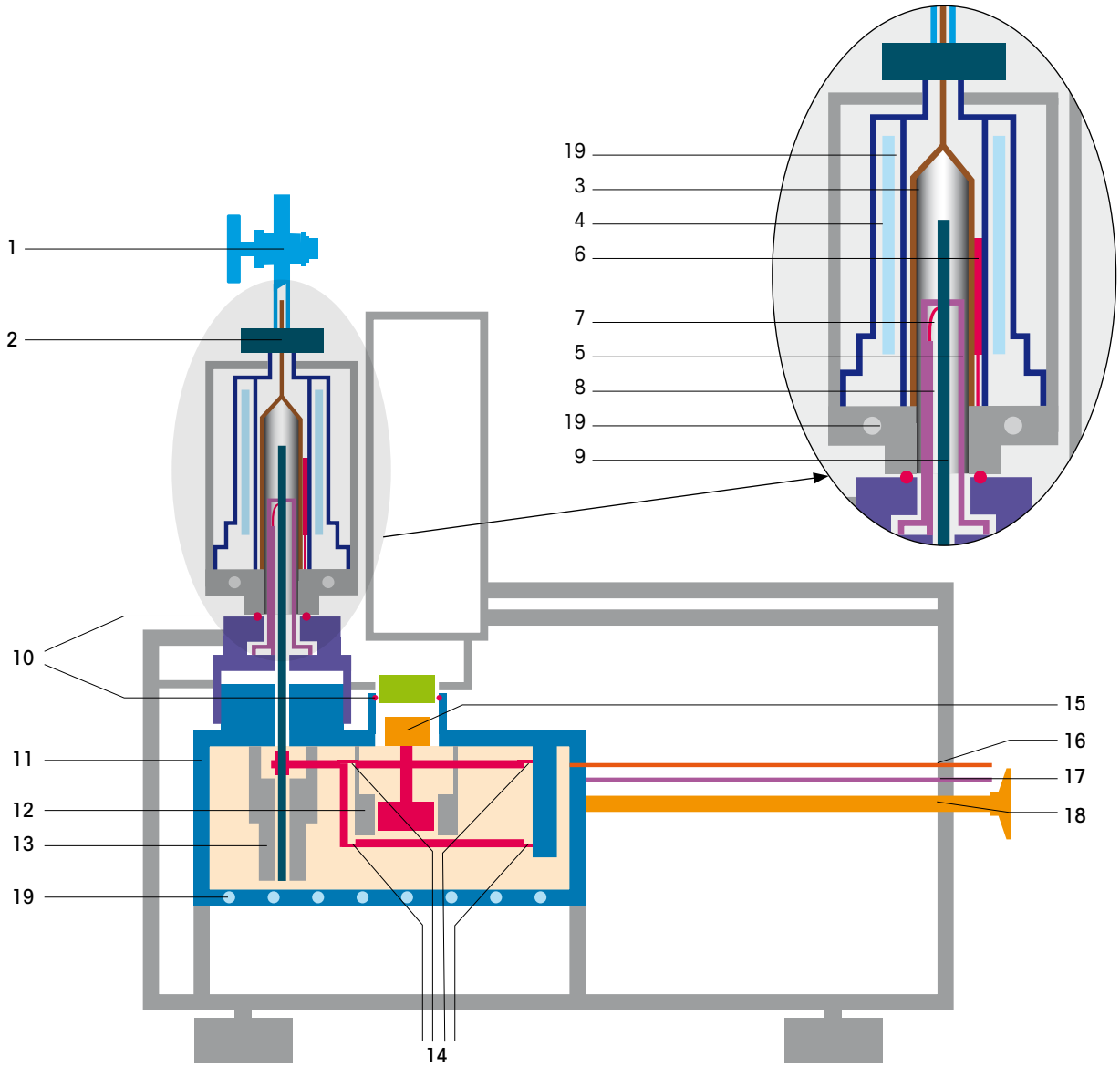
The furnace opens and closes at a stroke of a key, guaranteeing easy and reliable operation. The sample holder and measuring probe are then accessible from three sides. The gas-tight cell can be evacuated and allows you to use a defined atmosphere. Only such a system can provide definitive information on samples sensitive to oxidation.

Wide temperature range with high temperature accuracy

The sample temperature is measured directly below the sample with a sensor protected against contamination by a thin coating of quartz glass. In the calibration, this sensor measures the melting point of pure metals leading to the high temperature accuracy of ±0.25 °C.

Parallel guidance of the mechanical system

A central feature of the TMA cell is the parallel guidance of the measuring sensor. This requires an extremely precise mechanical system based on balance technology. Thanks to this parallel guidance, the probe can move up and down without being affected by frictional forces.



1 Gas outlet stopcock
2 Clamp with screw
3 Furnace windings
4 Water-cooled furnace jacket
5 Sample support
6 Furnace temperature sensor
7 Sample temperature sensor
8 Reactive gas capillary
9 Measuring probe
10 Gaskets
11 Thermostated cell housing
12 Force generator
13 Transducer (LVDT)
14 Bending bearings
15 Adjustment weights
16 Protective gas inlet
17 Reactive gas inlet
18 Vacuum and purge gas inlet
19 Water cooling

The TMA Incorporates
Swiss Precision Mechanics

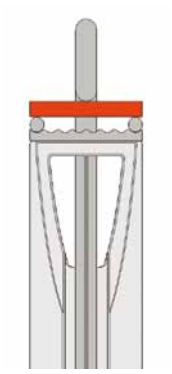
Complementary technique
TMA is an ideal addition to DSC. Besides the measurement of expansion coefficients, TMA is also an excellent method for determining glass transitions that cannot be measured by DSC, for example materials with high filler content. And with penetration measurements, another TMA measurement mode, it is easy to characterize the glass transitions of difficult samples such as very thin coatings.

Cooling
The liquid nitrogen cooling system has been completely automated; manual refilling is not necessary.
This simplifies operation, improves reproducibility and allows measurements to be performed over a long period of time.

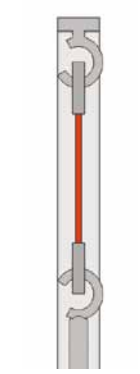
Thermostating
The mechanical part of the measuring cell is incorporated in a thermostated housing. This minimizes drift and guarantees excellent accuracy for the determination of expansion coefficients.

The DLTMA mode (dynamic load TMA) allows you to study the elastic behavior of materials. In DLTMA the force exerted on the probe alternates automatically between two values.

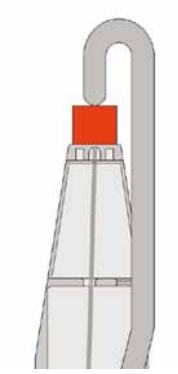
TMA/SDTA841ᵉ
Thermomechanical module
for the low temperature range



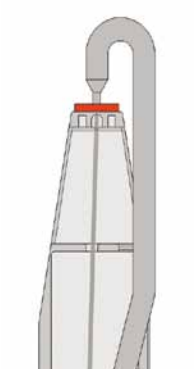
❶ Bending mode



❷ Tension mode



❸ Expansion mode



❹ Penetration mode

Deformation modes

Different accessories enable you to perform measurements on solid samples, foams, films and fibers. The TMA supports the following measurement modes:

❶ Bending, Swelling
❷ Tension
❸ Expansion
❹ Penetration

SDTA signal

The sample temperature is measured very close to the sample by means of a K-type thermocouple. A thin quartz glass coating protects it against direct contact and contamination. This allows temperature adjustment to be performed using the melting points of pure metals and/or the length change of suitable standards. The SDTA signal is the difference between the measured sample temperature and the reference temperature calculated using a model (US Patent 6146013). This means that besides the length change the simultaneously measured DTA signal (SDTA) is also available as a measurement quantity. This can often facilitate the interpretation of a measurement curve.

TMA/SDTA841^{e}
Quartz glass sample support with the K-type thermocouple for sample temperature measurement

Typical areas of application

Industry	Applications
Plastics (elastomers, thermosets, thermoplastics)	Coefficient of thermal expansion, glass transition, creep behavior
Electronics industry	Glass transition, coefficient of thermal expansion, delamination
Paints/lacquers/adhesives/coatings	Softening point
Textile fibers	Expansion and shrinkage behavior
Packaging (films)	Expansion and shrinkage behavior
Chemical (organic and inorganic materials, metals, pharmaceutical products)	Coefficient of thermal expansion and expansion behavior, solid-solid transitions
Universities	Dimensional changes under the most varied experimental conditions

Modular Means
Expandable at any Time

Future-proof investment
You start off with the instrument configuration which covers your immediate needs. Future expansion with an option such as a larger temperature range or automation could not be easier.

Control of external devices
External devices are easily attached to the measuring cells. With the appropriate peripheral option board, startup and shutdown can be controlled by the program.

Computer control
The entire measurement sequence can be developed on a computer with a few commands. Extensions and modifications can easily be entered. At the same time, the STAR^{e} Software checks the entries for correctness. Data are automatically stored in a database and are always available for documentation purposes even years later.
A large number of software options facilitate your work and can even take care of a large part of it.

With a fully automated system, sample changing, measurement, evaluation and result assessment are performed automatically as well as the printing out of the results.

Analysis of the decomposition products with EGA (Evolved Gas Analysis)
The TMA module can be coupled to a mass spectrometer or an FTIR spectrometer. The additional information gained allows a better interpretation of the experimental data.

Save energy
The instrument includes a power management system. To save energy for environmental reasons, the instrument can be programmed to switch off unused external devices. The furnace power can also be switched off. The module then remains in an energy saving mode until a new experiment is started.

Probes and sample holders made of quartz glass

The following measuring probes are available:

- Probe with ball-point (3.0 mm)
- Probe with flat end piece (1.1 and 3.0 mm)

The sample holder used depends on the type of sample and the application:

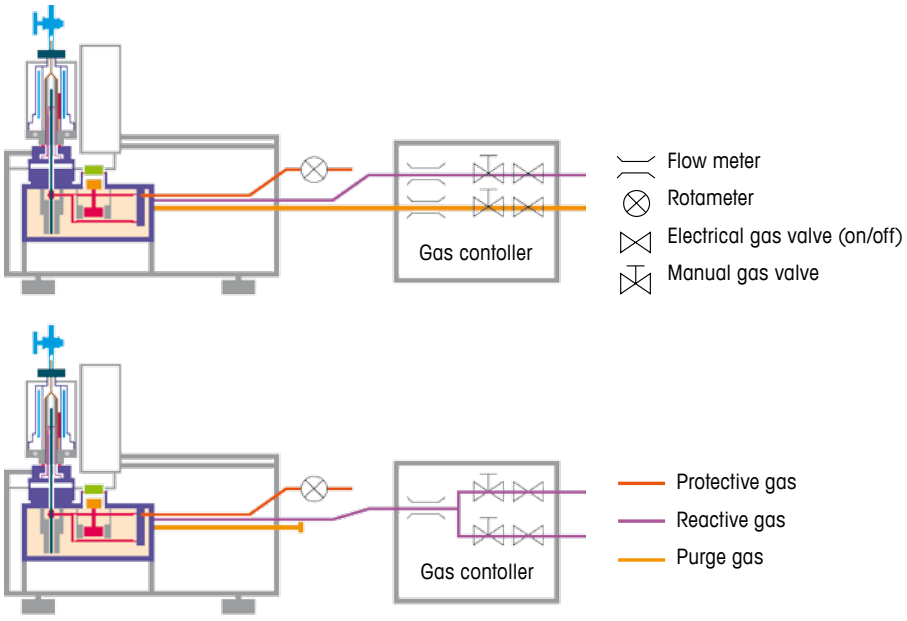
- Standard sample holder
- Film attachement device
- Fiber attachement device
- Bending device

You can change the probes and the sample holders very easily.

Gas controller GC100

Programmable gas switching

The automatic operation can be enhanced with the gas controllers. Depending on the type of controller, one channel or two channels can be turned on and off using the software. The gas controllers measure the flow. Deviations of flow rates from the selected value are recorded and shown on the curve.



Thermomechanical Analysis
for a Wide Range of Applications

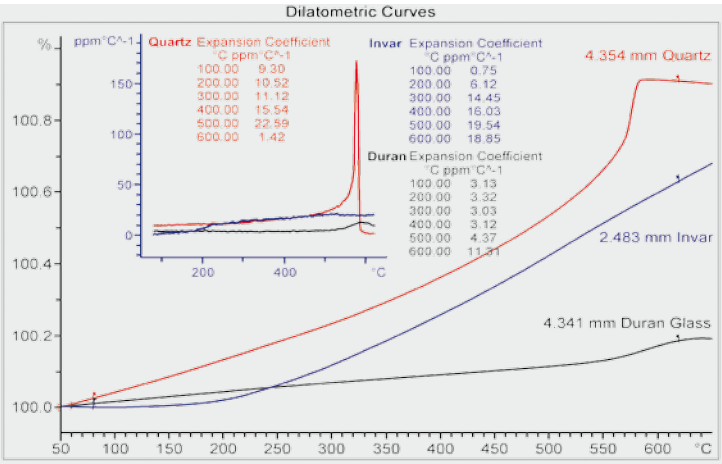
TMA offers a wide range of applications due to easy sample preparation and handling and the choice of a wide range of temperature and stress (force) parameters. TMA quickly provides characteristic information on materials from very thin layers to large samples, on fibers, plates and single crystals.

TMA measures the temperature of effects in which dimensional changes occur, such as glass transitions, softening, solid-solid transitions, fusion and decomposition (foaming, delamination, etc.).

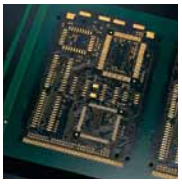
TMA determines the dimensional changes of a sample as a function of temperature. The characteristic values and properties most frequently studied are

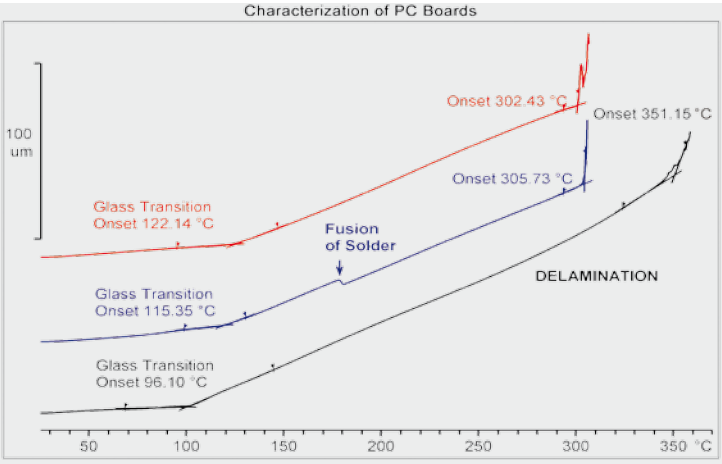
- Expansion coefficients
- Glass transition temperatures
- Softening temperatures
- Solid-solid transitions
- Melting behavior
- Swelling behavior and
- Elastic behavior.

Additionally the effect of changing loads (compression, bending or tension), special gases, and thermal treatment on a material can be studied.

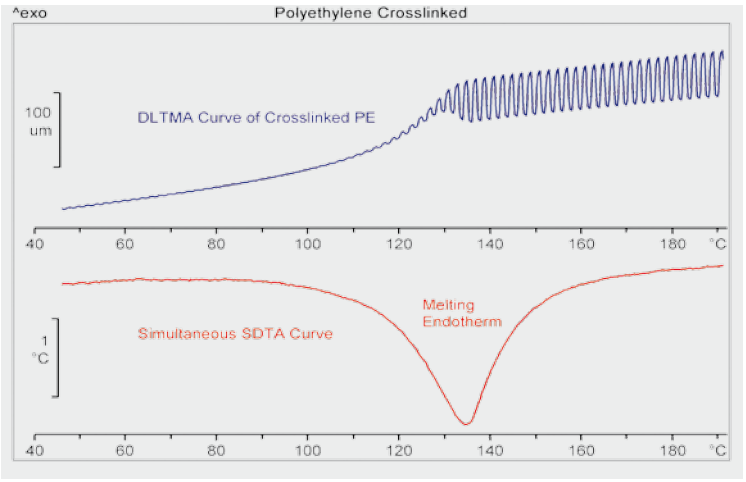


The coefficient of linear thermal expansion expansivity is calculated from the slope of the dilatometric curves. The prerequisites for accurate results are low noise, a low heating rate (< 10 K/min) and blank subtraction. Especially interesting are materials with non-uniform thermal expansion such as the alloy Invar with 36% nickel, which has practically zero thermal expansion at ambient temperature. Duran glass has – like most mineral glasses – very low expansivity below the glass transition. Quartz crystal (which is measured here in a direction parallel to its c-axis) shows a solid-solid transition at about 575 °C. Above the transition, c-axis shrinkage occurs.

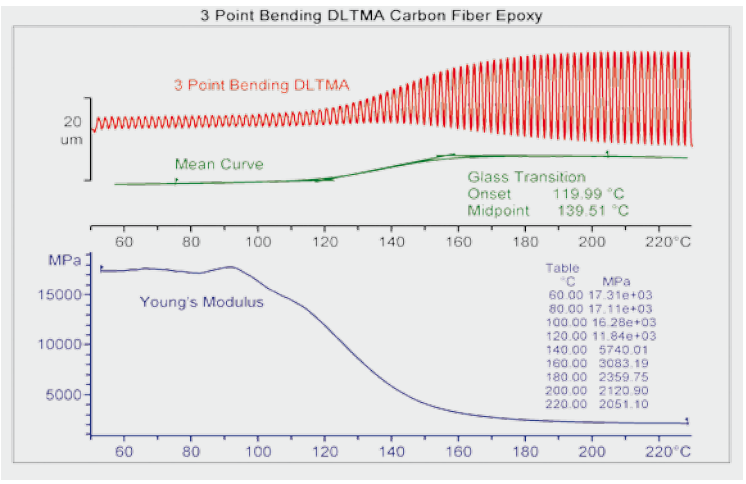




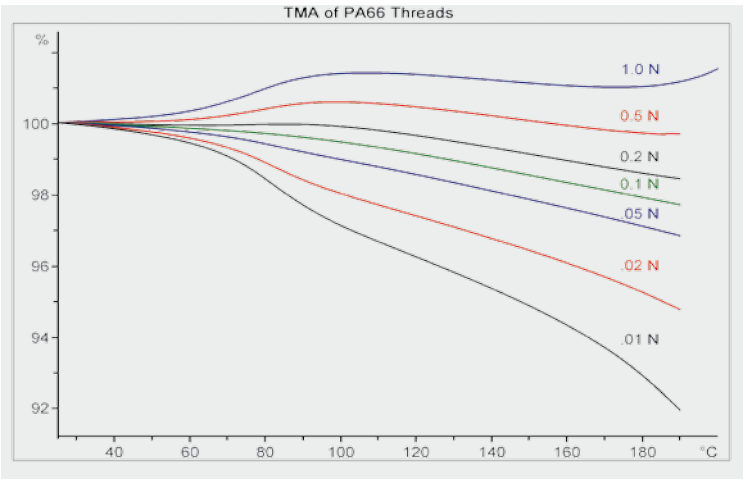
The **dilatometric expansion** behavior of three circuit boards was measured in the z (planar) direction. The sample holder was protected with a small piece of Al foil and the samples covered with a fused silica disk to distribute the force of 0.10 N evenly. The heating rate was 20 K/min. The slope of each TMA curve (expansivity) increases suddenly at the glass transition (96.1, 115.4 and 122.1 °C). The 3-µm step at 180 °C in one of the curves can be attributed to the melting of soldering tin. Delamination of the circuit boards is observed as sharp jumps in the TMA curves above 300 °C caused by the explosive release of internal stress.



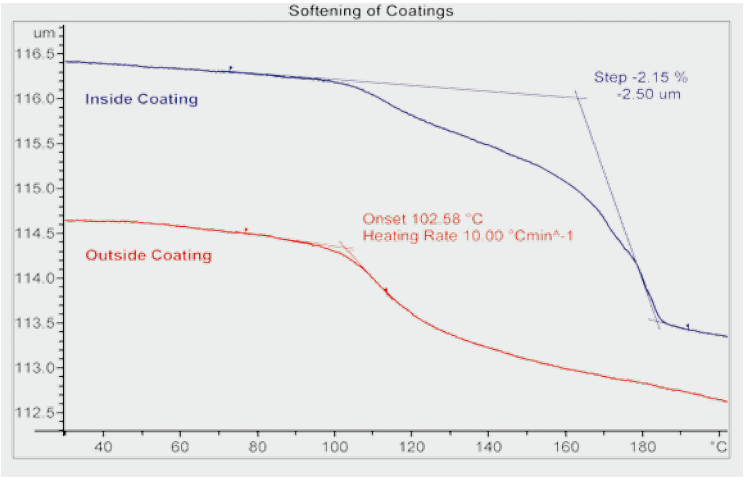
Below the melting point, **crosslinked polyethylene** has many of the properties of standard PE, such as rigidity. However, above the melting point, standard PE flows, where-as crosslinked PE exhibits a rubbery-like behavior. To demonstrate this, a cross-linked PE sample was measured by DLTMA. The sample was placed on the sample holder and covered with a fused silica disk. The load on the sample varied from 0.02 to 0.5 N over a 12-second period. The heating rate was 10 K/min. The simultaneously meas-ured SDTA® curve shows the endothermic melting peak at 135 °C. Above 140 °C there is an elastic deformation of 2.5% due to the changing load.



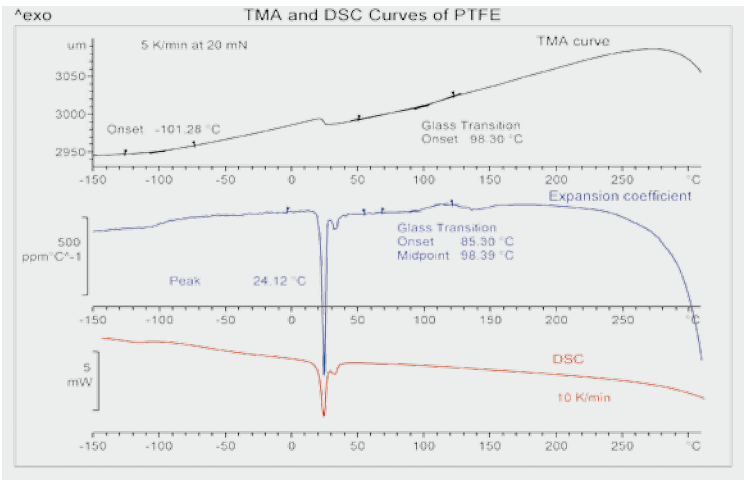
The **8-mm three-point bending** device was used (the active length of three-point bending). A sample of the composite (0.80 mm thick, 2.36 mm wide and 12 mm long) was placed on the device. The 3-mm ball-point probe touching the center of the sample provided the oscillatory load which varied from 0.02 to 0.50 N over a period of 12 s. The sample was heated at 10 K/min. Based on the blank-corrected DLTMA curve, the TMA software calculates the mean (average position) curve as well as the value of Young's modulus. By using 3-point bending, glass transitions of highly filled polymers are much more easily detected than by DSC.



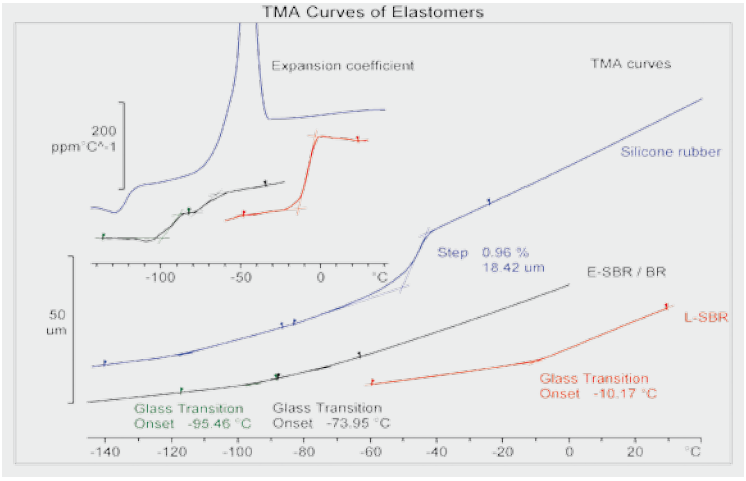
Two bundles of polyamide 66 fibers each with a total linear density of 94 dtex (85 denier) were mounted in parallel in the fiber attachment device with a length of 14 mm. The bundles were heated and cooled at 10 K/min (atmosphere of dry nitrogen 100 mL/min). The tensile force was increased from one measurement to the next as indicated in the diagram. The load during cooling to 25 °C was 0.10 N. The final measurement was performed to 200 °C. With loads below 0.2 N the threads shrink continuously. At higher forces the threads mainly expand. The inflection point at 80 °C indicates the glass transition, while the expansion above 190 °C (at 1 N load only) indicates the onset of softening in the polyamide fibers.



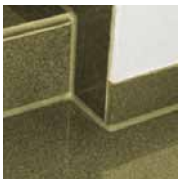
Because of the specific requirements, the inner and outer coatings of **soft drink cans** are very different. TMA penetration tests were performed using the 3-mm ball-point probe with a force of 1.0 N to determine the softening behavior. To make sure that only one coating was measured each time, the other coating was scraped off with a knife. The inner coating softens in the range 100 to 190 °C, the outer coating around 120 °C. The magnitude of the softening (1–3 µm) shows just how thin can coatings can be. TMA penetration is often the most sensitive method for measuring the Tg of thin coatings.

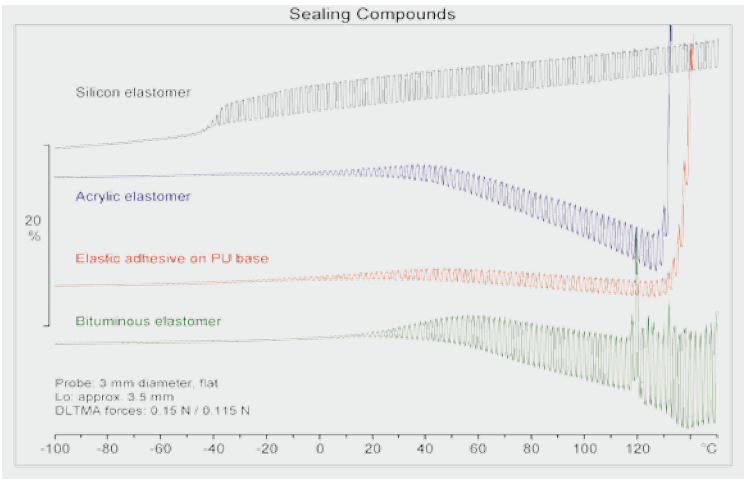


PTFE is a semicrystalline polymer that exhibits several **polymorphic transitions** and a glass transition over a wide temperature range (-150 °C to 300 °C). In the figure, the TMA heating curves are compared with a DSC measurement. The first transition occurs at about -100 °C and shows a stepwise increase in the coefficient of thermal expansion. The transition at 24 °C is accompanied by a marked negative change in volume. In contrast to DSC, the glass transition at 100 °C followed by processing-dependent resintering at 130 °C can be identified in the TMA curve.

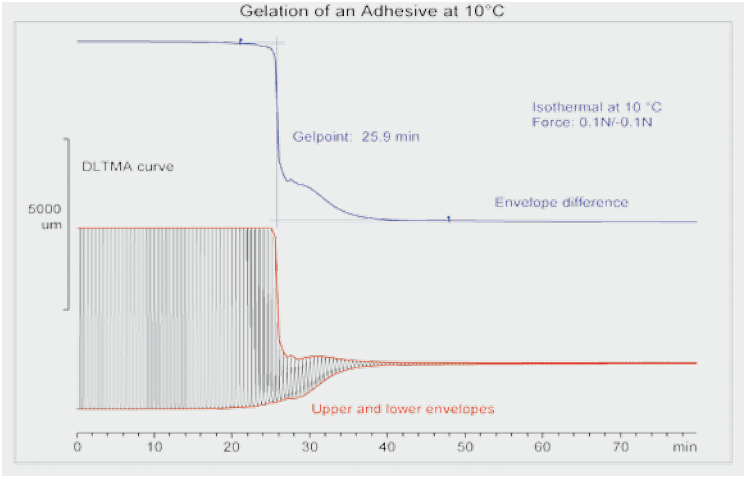


The figure displays **the thermal expansion curves of several different elastomers**, and the inserted diagram the corresponding coefficients of thermal expansion. At the glass transition, the slope of the TMA curve, and hence the coefficient of expansion, show a marked change. In the SBR/BR elastomer blend, two glass transitions are observed because the polymers are present as separate phases. The silicone elastomer has a glass transition at -116 °C. At about -45 °C there is a rapid change in thickness due to volume expansion of the semicrystalline polymer on melting. TMA is a very sensitive method for the analysis of polymer blends.

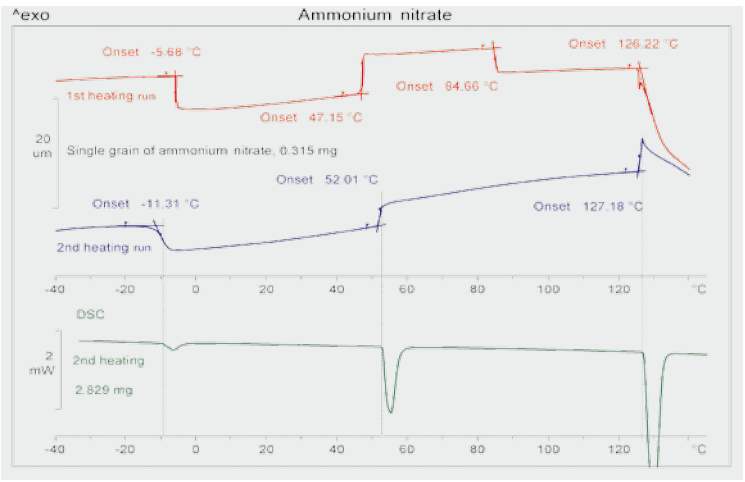




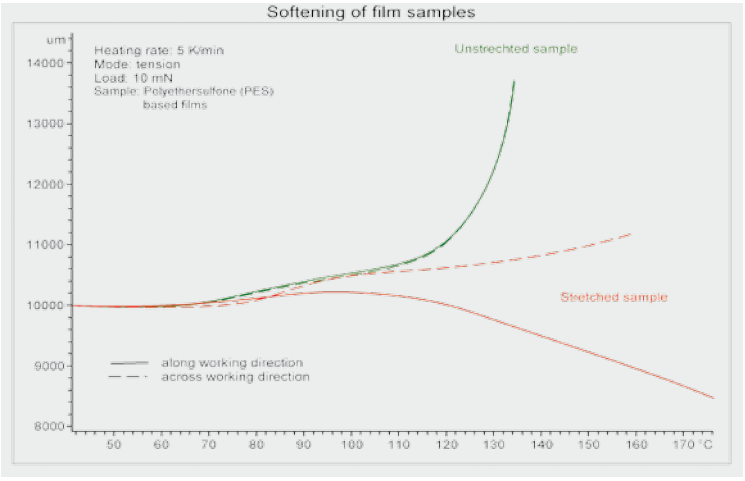
Elastic sealing compounds for joints have different thermal and mechanical properties depending on the requirements for their intended use. DLTMA can be used to measure the dimensional stability and elastic behavior of small samples and to determine the influence of temperature. The DLTMA curves in the figure show the behavior of four different materials on heating in the cured state two weeks after their application. The glass transition is characterized by the increase in amplitude. The silicone elastomer softens at -40 °C with a corresponding increase in volume due to melting. At higher temperatures the sealing compounds begin to flow and foam.



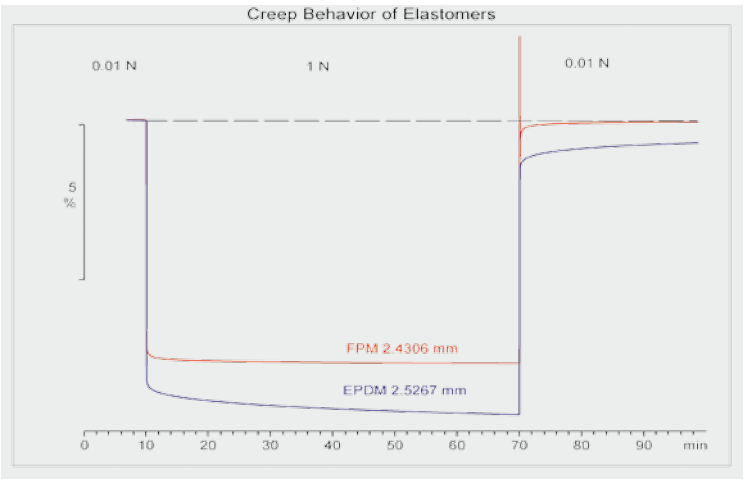
During the isothermal **curing of adhesives**, the viscosity increases with increasing conversion. Initially the material is in the liquid state but then reacts to form a solid. From the technical point of view, the **gel point** is of major interest, i.e. the point at which the adhesive becomes structurally stable. On further reaction, the sample hardens and the amplitude changes to a very small value. Gelation is investigated by periodically inserting the TMA probe into the sample. The reaction time at which the probe can no longer be lifted out of the sample is the gel point. In the measurement shown, the period was 24 s and the force ±0.1 N. The gel point at 10 °C is 26 min. The sample can be inserted into a pre-equilibrated measuring cell.



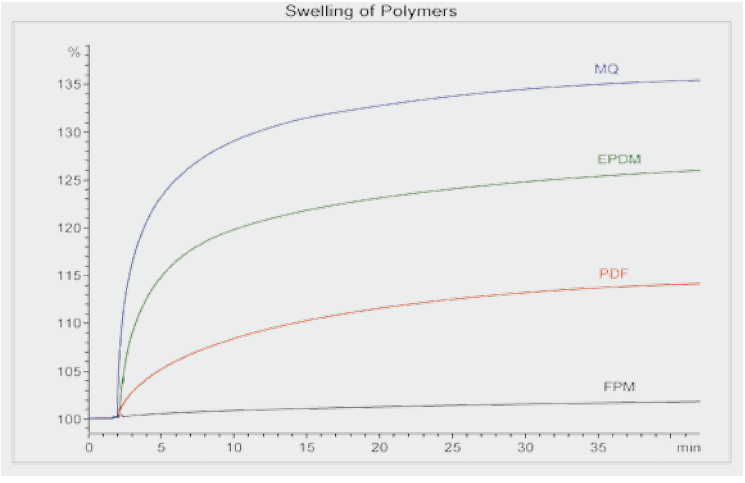
Phase transitions are generally accompanied by volume changes that result from modifications in the crystal lattice. This means that **polymorphism** can be successfully studied by TMA even with just small quantities of sample. This is shown using a single grain (0.315 mg) of ammonium nitrate. Ammonium nitrate is often a main constituent of fertilizers and explosives. Depending on the temperature, ammonium nitrate exists in different modifications. The transitions produce steps in the TMA curve. The curves show that the structural changes occur very rapidly. Some transitions are reproducible while others depend on the thermal history of the sample. For comparison, a DSC curve with the corresponding transitions is displayed.



Streched **films** often have a preferred orientation and hence exhibit **anisotropic mechanical properties**. These properties can be characterized by measuring the expansion behavior with TMA. The figure displays the TMA curves of two different PES-based films: one is stretched, the other unstretched. The unstretched sample is isotropic and shows the same behavior in both measurement directions. The behavior of the stretched sam-ple is very different in the stretched direction compared with at right angles. In the stretch-ed direction, the film shrinks from about 100 °C onward, whereas at right angles to the stretched direction, the length of the film increases with increasing temperature. The stretched sample also exhibits a greater degree of thermal stability.



Creep measurements allow the **recovery behavior** of **sealing rings** to be determined. In the experiment, a force of 1 N was applied to two different sealing rings for a period of 60 min at room temperature and the recovery behavior measured with a force of 0.01 N.
The elastic deformation, the viscoelastic relaxation (gradual change in thickness) and the viscous flow (irreversible change in shape, creep) can be determined from the measurement curve of each sample. The residual deformation of the EPDM sealing ring is greater than that of the FPM ring. In comparison to FPM, the EPDM used exhibits a greater degree of viscous flow and has a smaller modulus of elasticity.



The **swelling behavior** of materials in solu-tion can be measured with the aid of a special accessory. The example shows the swelling behavior of different polymers in toluene at room temperature. While FPM hardly swells at all, the thickness of the silicone rubber (MQ) increases by over 35%.

TMA/SDTA840/841^{e} Specifications

Temperature data	**TMA/SDTA840**	**TMA/SDTA841^{e}**
Temperature range	RT … 1100 °C	-150 °C … 600 °C
Temperature accuracy (room temperature … 600 °C/1100 °C)	±0.25 °C	±0.25 °C
Temperature accuracy (room temperature … -100 °C)	-	±0.35 °C
Temperature accuracy (-100 … -150 °C)	-	±0.5 °C
Temperature reproducibility	±0.15 °C	±0.25 °C
Heating (room temperature … 600 °C/1100 °C)	8 min	< 6 min
Heating (-150 °C … 600 °C)	-	< 8 min
Cooling (600 °C/1000 °C … room temperature)	20 min	< 15 min
Cooling (room temperature … -150 °C)	-	15 min

Length data		
Maximum sample length	20 mm	20 mm
Measurement range	±5 mm	±5 mm
Resolution	10 nm	< 1 nm
Noise (RMS)	5 nm	5 nm

Force data		
Force range	-0.1 … 1.0 N	-0.1 … 1.0 N

DLTMA data		
Frequencies	< 1 Hz	< 1 Hz

SDTA® (Single Differential Thermal Analysis)		
SDTA® resolution	0.005 °C	0.005 °C
SDTA® noise (RMS)	0.01 °C	0.02 °C
SDTA® sensor type	R-type thermocouple	K-type thermocouple
SDTA® signal time constant	33 s	38 s

Data sampling	
Sampling rate	max. 10 data points per second

Approvals	
Safety	IEC/EN61010-1:2001, IEC/EN61010-2-010:2003 CAN/CSA C22.2 No. 61010-1-04 & -2-010 UL Std. No. 61010-1 (2nd Edition)
EMC	IEC61326-1:2005 / EN61326-1:2006 (class B) IEC61326-1:2005 / EN61326-1:2006 (Industrial requirements) AS/NZS CISPR 11, AS/NZS 61000.4.3

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