U.PORTO
FACULDADE DE CIÊNCIAS
UNIVERSIDADE DO PORTO

MAT 2020

MÉTODOS DE ANÁLISE TÉRMICA

DQB... 2019-2020

DIL: Dilatometry
TMA: Thermomechanical Analysis
DMA: Dynamics Mechanic Analysis

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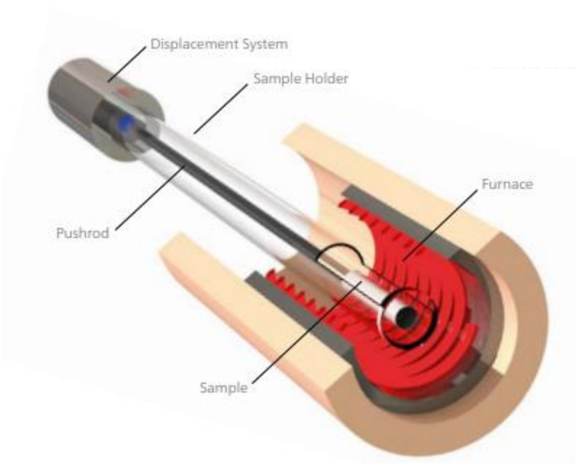
DIL: Dilatometry

Is the method for highly precise **measurement of dimension changes** to solids, melts, powders and pastes at a programmed temperature change and with negligible sample strain



Results obtainable DIL measurements

- Linear thermal expansion
- Coefficient of thermal expansion (CTE)
- Volumetric expansion
- Shrinkage steps
- Softening point
- Glass transition temperature
- Phase transitions
- Sintering temperature and step
- Density change
- Influence of additives and raw materials
- Decomposition temperature of e.g., organic binders
- Anisotropic behavior
- Optimizing of firing process
- Caloric effects by using *c-DTA*®
- Rate-Controlled Sintering (RCS)
- Kinetics Neo

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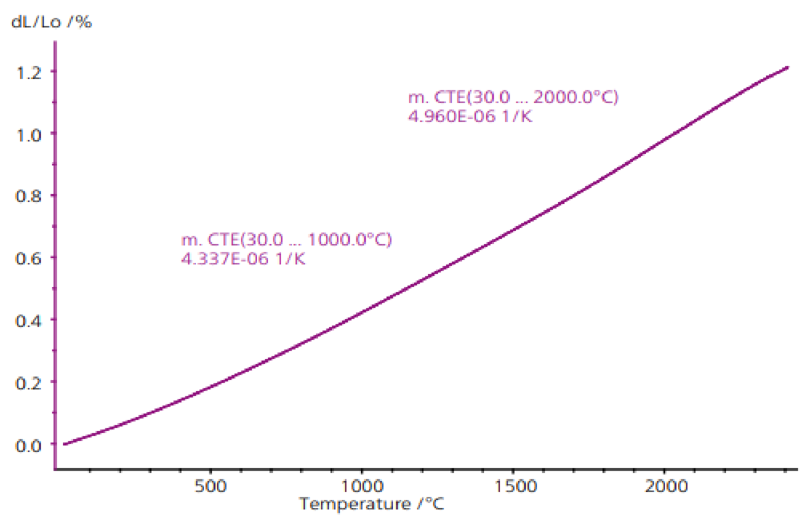

DIL measurement on recrystallized silicon carbide (RSIC), graphite sample holder, graphite protective plates (between the sample and sample holder/pushrod), original sample length: 18.98 mm, He atmosphere (50 ml/min), 10 K/min heating rate

Recrystallized Silicon Carbide up to 2400°C

Recrystallized SiC (RSIC) sintered material is a technical ceramic often manufactured at temperatures around 2400°C. During sintering, a mixture of fine- and coarse-grained powder is transformed nearly shrinkage-free to a compact SiC matrix.

In the present case, the sample shows solely expansion over the entire temperature range from RT to 2400°C with CTE values of 4.337×10^{-6} 1/K (between 30°C and 1000°C) and 4.960×10^{-6} 1/K (between 30°C and 2000°C).

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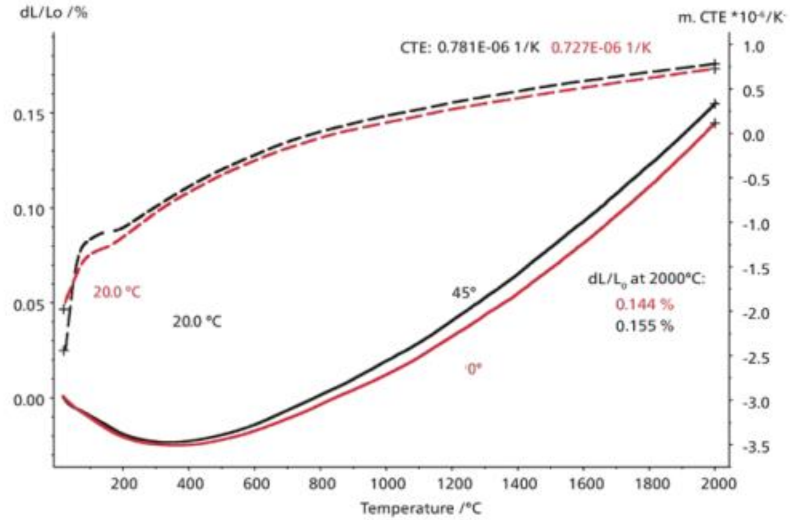
Thermal Behavior of Carbon Fiber-Reinforced Carbon up to 2000°C



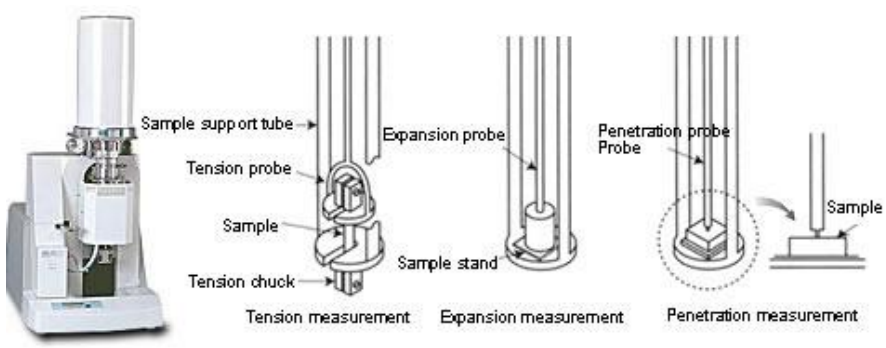
Comparison of two expansion measurements of a C/C material, measured 45° (black) and 0° (red) relative to the fiber direction; heating rate: 5 K/min, He atmosphere, constant contact force: 225 mN, graphite sample holder. Displayed are the relative length changes (solid lines) and the mean coefficients of thermal expansion (m. CTE) based on 20°C (dashed lines).

TMA

THERMOMECHANICAL ANALYSIS

to measure dimensional changes of solid or liquid materials as a function of temperature

expansion, tension, and penetration



https://www.youtube.com/watch?v=lKNOfuW_M3A

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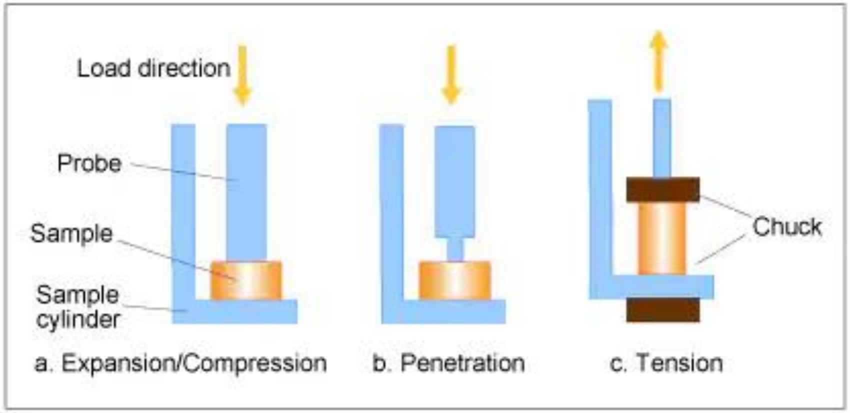

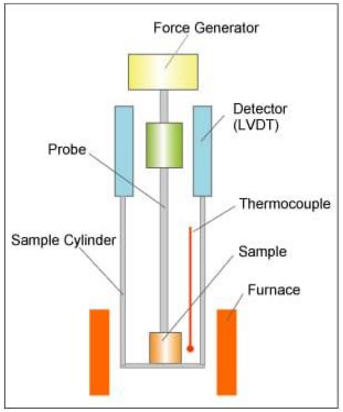

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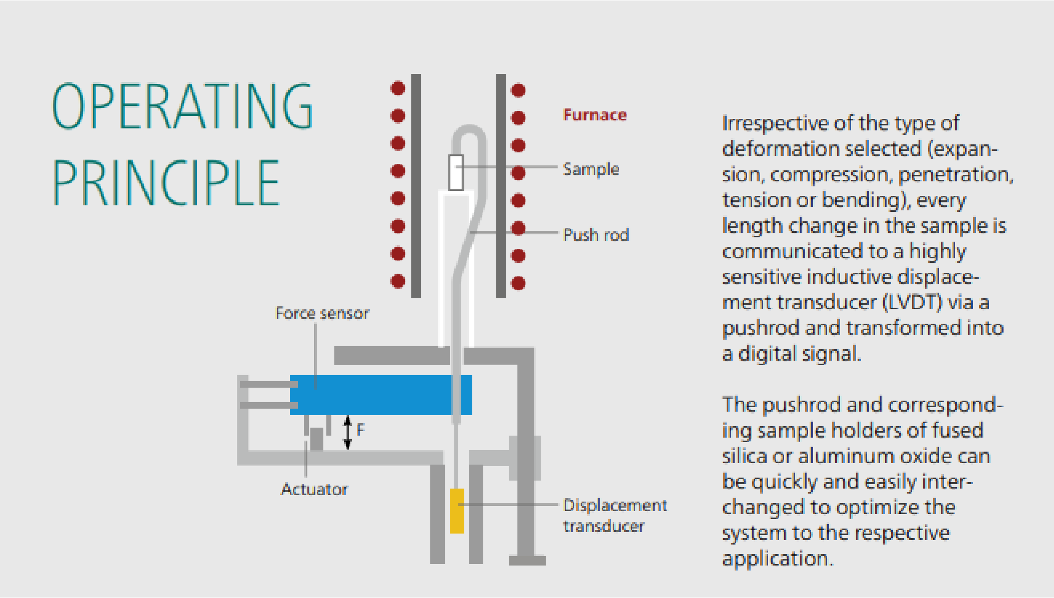

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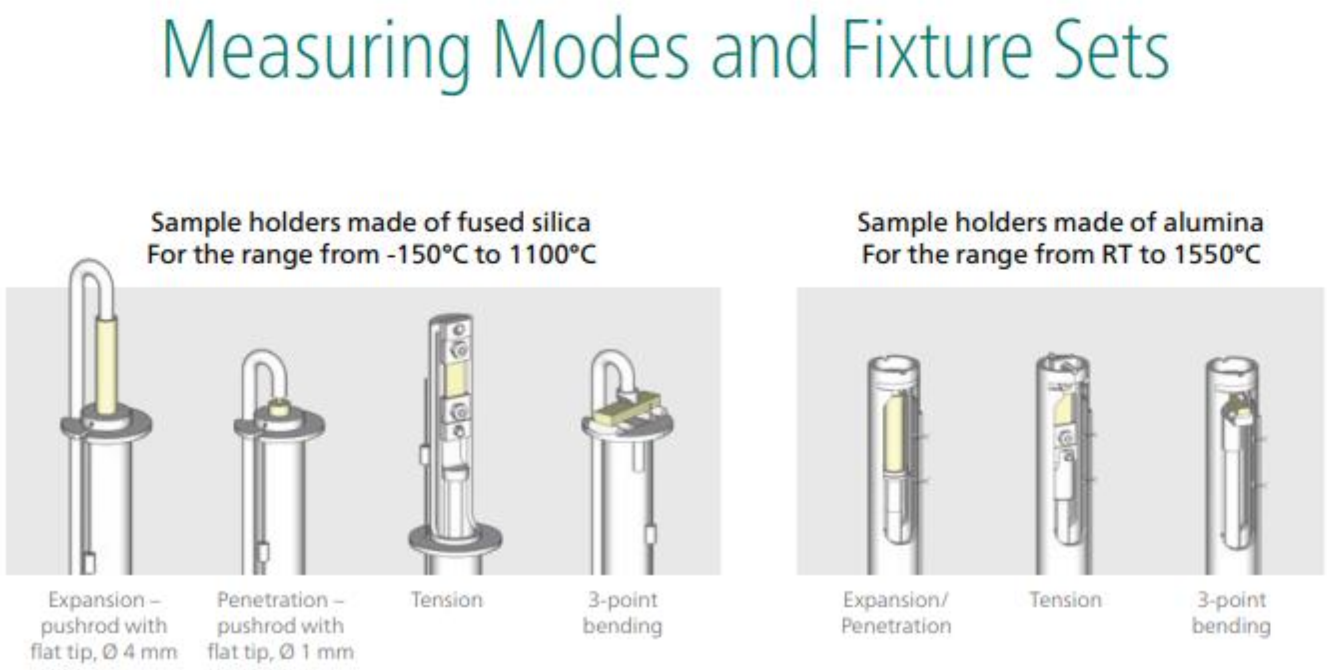

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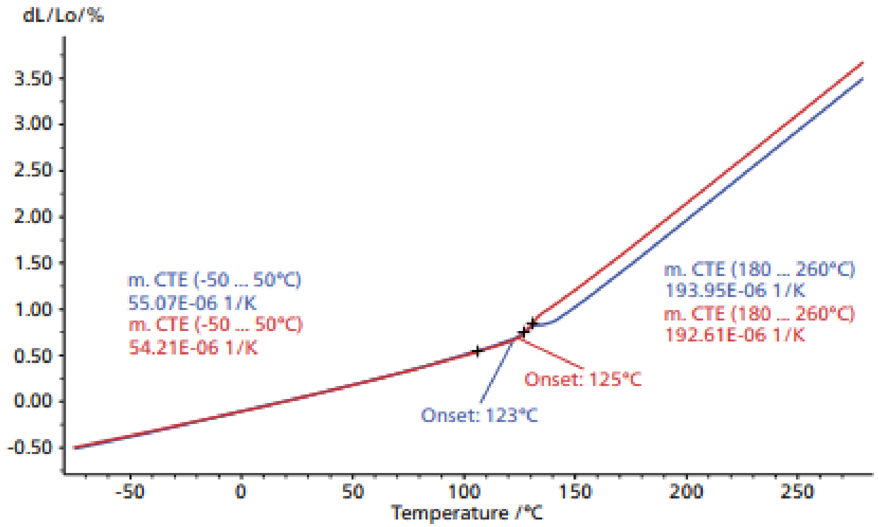

Measurement on an epoxy resin with a sample length of 6 mm in expansion mode (fused silica sample holder); 1st and 2nd heating runs at a rate of 2 K/min

Thermal Expansion

The linear thermal expansion is an important variable for assessing the dimensional behavior of a material in response to a change in temperature.

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 glass transition (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.

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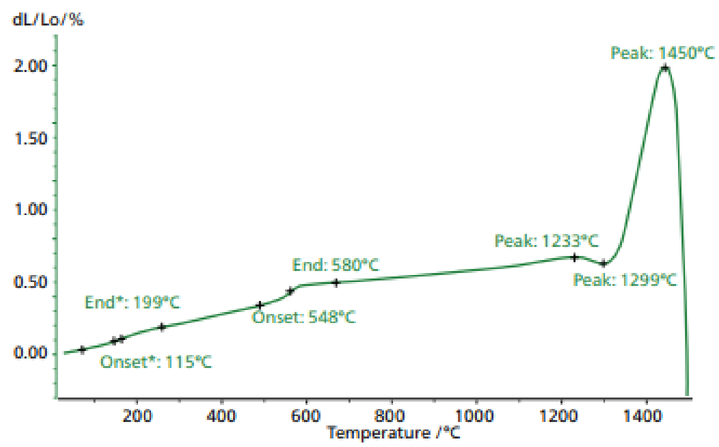
Refractory Materials – Expansion up to High Temperatures

The life span and efficiency of any technical furnace can be greatly improved with appropriate configuration. An important criterion in assessing the materials comprising such furnaces is thermal expansion. Here shown is the thermal behavior of a typical coarse-grained refractory material. At the beginning of the measurement, the α-β transformation of the tridymite is observed, followed by the α-β transformation of the free quartz between 548°C and 580°C. After another transformation between 1233°C and 1299° C, the material begins to soften at 1450°C.



TMA measurement on a refractory material between room temperature and 1550°C.

TMA

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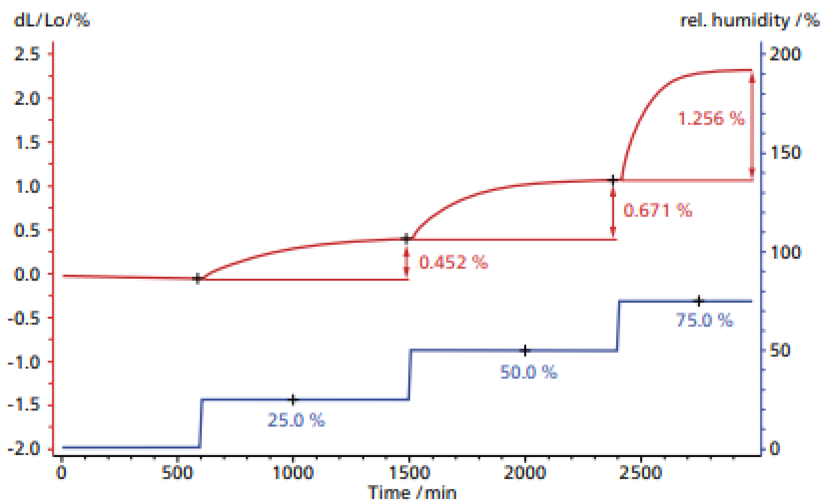

Isothermal measurement at 40°C with copper furnace and humidity generator; sample dimensions: length 15 mm x width 5 mm x thickness 0.25 mm

Hygroscopic Behavior of Polyamide

Depending on the relative humidity, dry PA 6 can absorb moisture from its environment and undergo thermal expansion of up to 10%. Such moisture absorbance can be simulated with TMA.

This plot shows the hygroscopic behavior of PA 6 film at 40°C in tension mode (sample holder made of fused silica). The relative humidity was increased from 0% to 75% in steps of 25% every 15 h. Over the course of 150 h, the total thermal expansion amounted to 2.4%.

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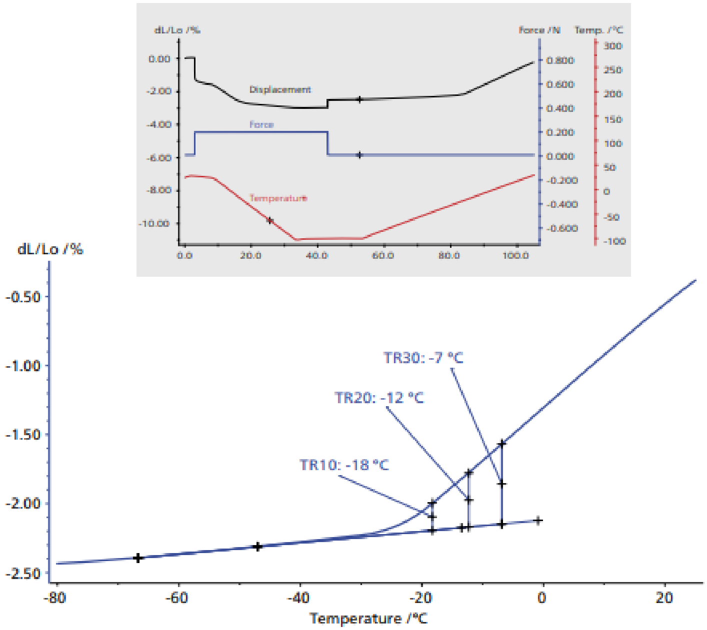

Evaluation of the displacement (main plot) under the force-temperature program (inset); sample holder made of fused silica with edge for penetration

Temperature Retraction (TR) of Small Samples and O-Rings

The TMA *Proteus*® software allows for determination of the temperature retraction (TR). At room temperature, a small load (0.01 N) is applied to the sample to determine its thickness. The load is then increased and the sample is cooled to approx. 50 K below the expected TR10 point (inset). Thereafter, the load is again relieved and the sample is reheated to room temperature at a rate of 2.5 K/min.

For the evaluation of TR, the heating segment is used (main plot). The TR10 value corresponds to a 10% recovery of the sample; the TR20 to a 20% recovery, etc. The TR value is a useful indicator for estimating an elastomer's behavior at low temperatures.

TMA

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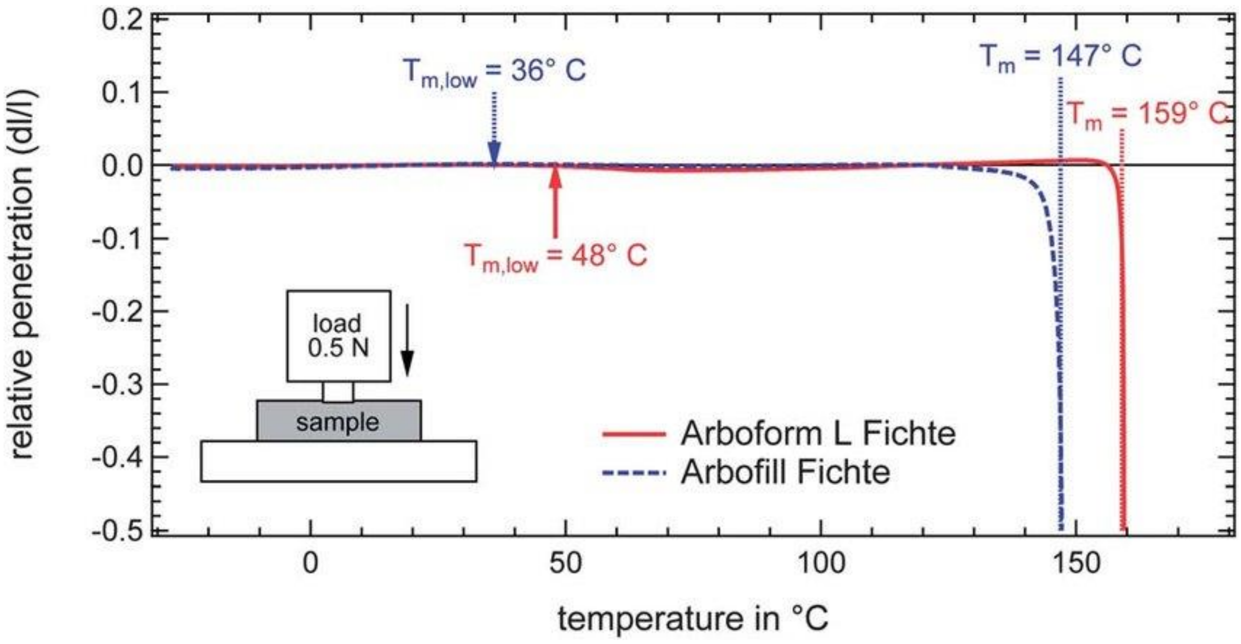
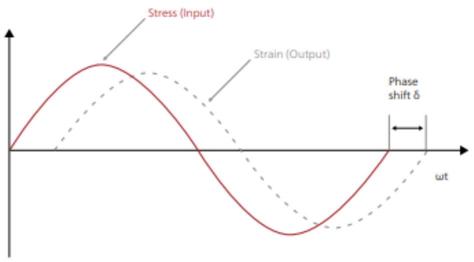
penetration



DMA: Dynamics Mechanic Analysis



DMA – Measurement principle

Used to measure the mechanical and viscoelastic properties of materials
thermoplastics, thermosets, elastomers, ceramics and metals.

In a Dynamic Mechanical Analyzer, the sample is subjected to a **periodic stress** in one of several different modes of deformation.

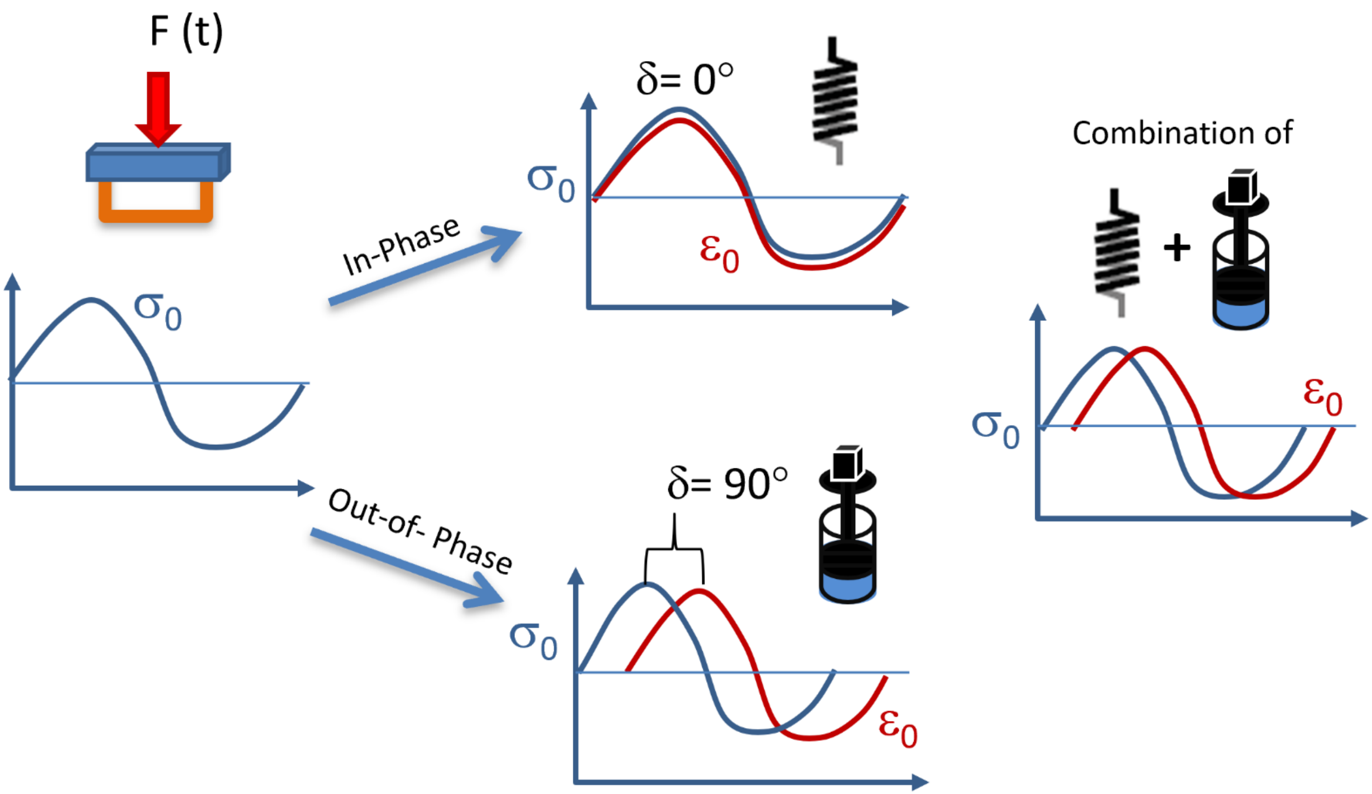
The **force and displacement amplitudes and phase shift** are analyzed as a function of temperature, time and frequency.

DMA provides quantitative and qualitative information that is of great value to process and application engineers, materials research scientists and chemists, such as:

- *Young's modulus and shear modulus*
- *Damping characteristics and viscoelastic behavior*
- *Polymer structure and morphology*
- *Flow and relaxation behavior*

Dynamic Mechanical Analyzer (DMA)

A Dynamic Mechanical Analyzer is used to measure mechanical and viscoelastic properties of materials.



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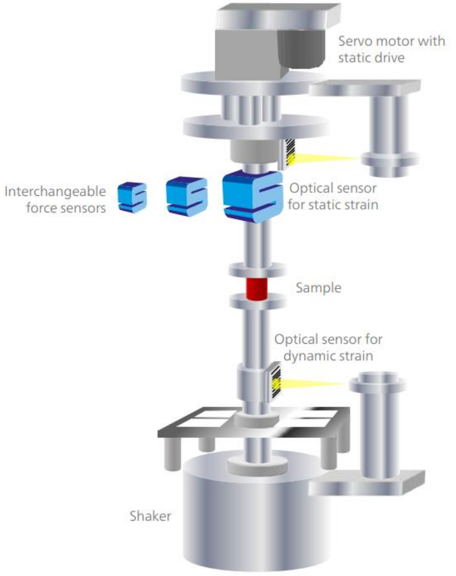


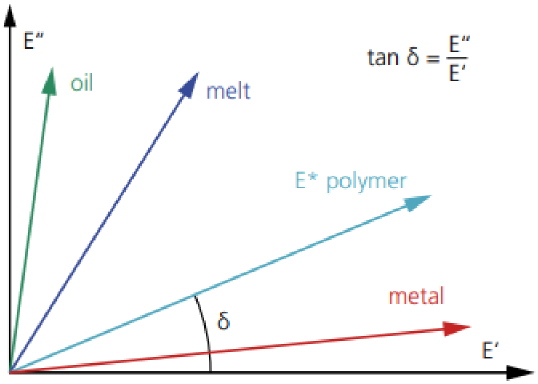


Figure 1: Visco-elastic properties in the complex plane; various material classes exhibit significant differences in phase shifts

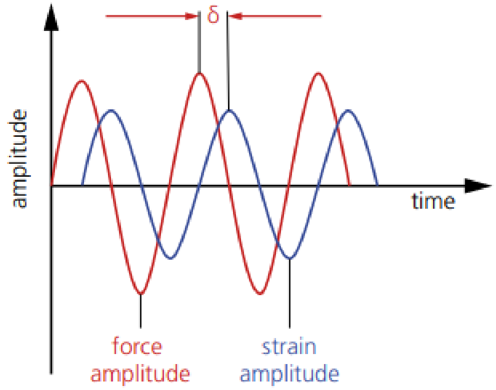
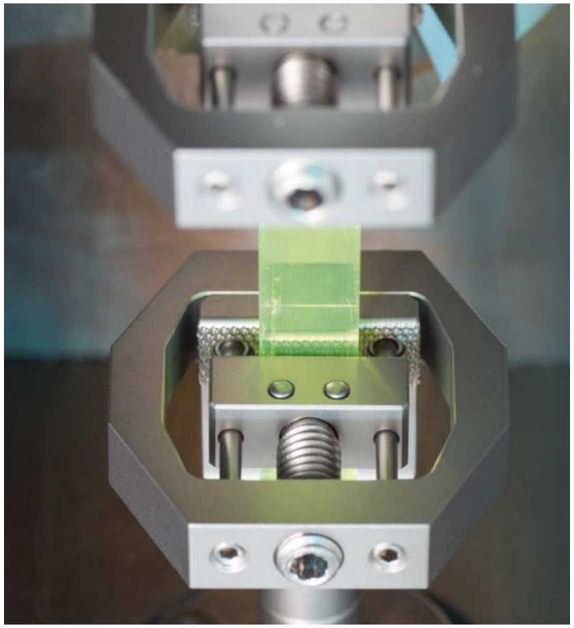
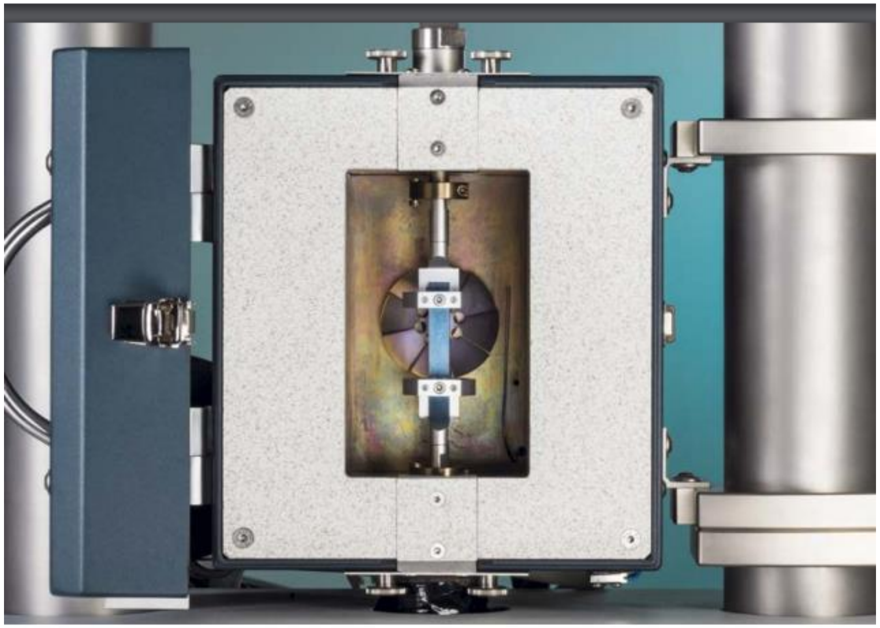


Figure 2: Measured parameters: damping (δ), force and strain amplitudes

DMA: Dynamics Mechanic Analysis

Dynamic Mechanical Testing Systems





DMA: Dynamics Mechanic Analysis

Dynamic Mechanical Testing Systems

Compression

Film tension

Fiber cord tension

3-point bending

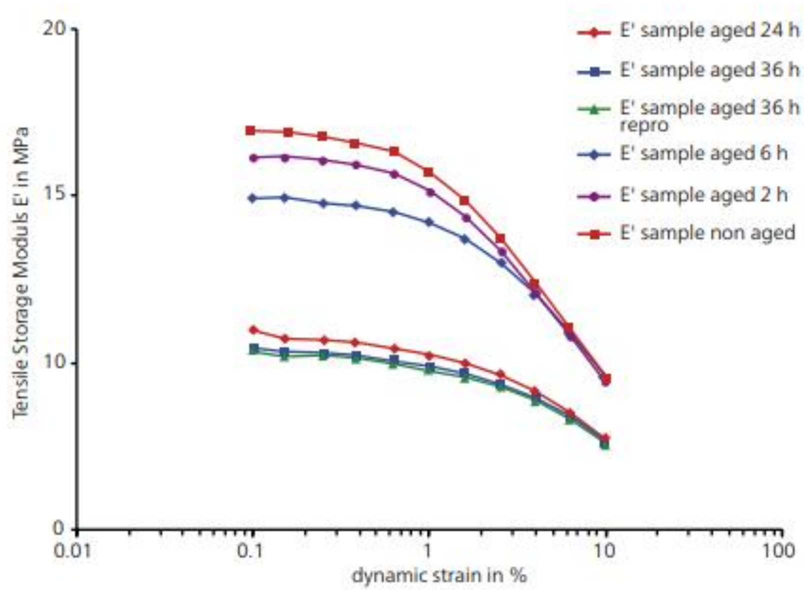
Asymmetric bending

DMA: Dynamics Mechanic Analysis

Immersion for Testing Swelling Behavior and Other Effects

The immersion bath allows for measurements in a liquid such as water or oil in combination with sample holders such as those for 3-point bending tests (picture on the right) or tension tests (picture on the left), in cases where evaporation and decomposition temperature of the solvent or liquid are not an issue.

The plot below shows results of room temperature measurements on rubber carried out at a prestrain of 20% and a frequency of 10 Hz. Amplitude scans were applied after each aging step. It can be clearly seen that E' significantly decreases with immersion time.



Sample holder for tensile tests (left) and bending tests (right) in an immersion bath

DMA: Dynamics Mechanic Analysis

DMA & Dielectric analysis (DEA)