Thermal Analysis
Information for Users

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**Dear Customer,**

The lead articles in UserCom21 and UserCom22 focused on method development in thermal analysis. This time we would like to concentrate specifically on method development in dynamic mechanical analysis (DMA). In this technique, a larger number of parameters need to be defined than in the more familiar DSC, TGA and TMA methods.

In addition, several interesting application articles are included that could well give you new ideas for your own work.

# How to determine the optimum experimental parameters for DMA measurements

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## Introduction

For successful DMA measurements, it is extremely important to choose the "right" experimental parameters, probably more so than in most other thermoanalytical techniques. In practice, the difficulty is that the deformation mode, sample geometry and mechanical measurement parameters (force and displacement amplitude) are interdependent. This article discusses important factors that need to be considered when planning a DMA experiment.

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## Choosing the deformation mode

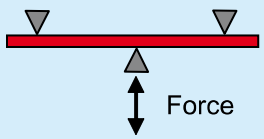
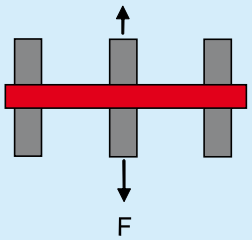
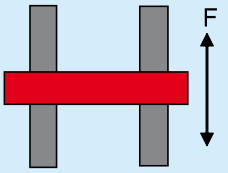
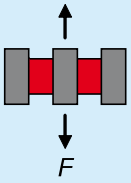
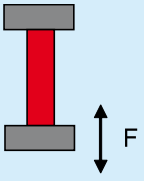
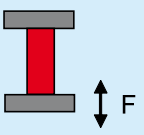
Samples can be mechanically stressed in a number of different ways in DMA. The mode you finally decide to use depends on the information required and the sample itself. For example, if you want to determine the shear modulus, you have to use the shear mode; and if you want to measure thin films, you cannot do this in the 3-point bending mode. Table 1 presents an overview of the different deformation modes and characterizes them with respect to their mechanical advantages and disadvantages as well as their most important applications.

Besides the mechanical properties of the sample holders, it is also important to consider their thermal properties and the frequency ranges accessible with the deformation modes.

## Choosing the heating rate

DMA samples are usually large compared with those measured in other thermoanalytical techniques (e.g. DSC or TGA). As a result of this, the furnace is relatively large and has a corresponding large thermal mass and inertia. The sample clamping assemblies are also large and react slowly to temperature changes. DMA experiments are therefore generally performed at heating rates of less than 3 K/min.

Table 1.
Overview of the different modes of deformation and their main areas of application.

| Mode | Advantages | Comments | Applications |
|---|---|---|---|
| 3-point bending<br>  | • Very accurate modulus values with hard samples (Young's modulus)<br>• Large range of sample dimensions possible<br>• No effects due to sample clamping | • Requires an offset force.<br>• Changes in geometry have a large effect on the modulus value.<br>• High demands on sample preparation (parallel surfaces) | • Samples that exhibit modulus changes of less than about 2 decades:<br>- Composites<br>- Ceramics<br>- Metals<br>• All materials in a glassy state |
| Dual cantilever<br>  <br>Single cantilever<br>  | • Large range of sample dimensions possible | • Bending does not begin where the sample is physically clamped but projects into the clamping assembly → The clamping length is not accurately known; it changes with the stiffness of the sample and with the clamping force.<br>• Thermal expansion of the sample leads to horizontal stresses in the sample holder. This results in artifacts in the measurement curves (the so-called "frog effect")<br>• Changes in geometry have a marked effect on the modulus values. | • Samples that soften (e.g. after a glass transition):<br>• Thermoplastics |
| Shear<br>  | • Is the only mode that yields the shear modulus<br>• A modulus range of 8 decades can be measured in one experiment<br>• Frequencies up to 1000 Hz | • Modulus values above about 1 GPa cannot be accurately measured<br>• Sample is held in place only by friction | • All polymers<br>• Powders (as pressed tablets)<br>• Pastes<br>• Viscous materials (bitumen, waxes) |
| Tension<br>  | • Yields the most accurate modulus values (Young's modulus)<br>• Easy to calculate the geometry factor | • Requires pretension<br>• With suitable sample geometry, high modulus values can also be determined (up to 100 GPa) | • Films and fibers<br>• Thermoplastics<br>• Elastomers also possible |
| Compression (uniaxial)<br>  | • Is the only way to determine the Young's modulus of foams<br>• Easy to calculate the geometry factor | • Requires precompression<br>• Unsuitable for stiff samples | • Foams made from polymeric materials<br>• Elastomers also possible |

With isothermal experiments, the temperature should be allowed to stabilize for at least 30 minutes before starting the measurement.

## Choosing the sample geometry

Three main points should be considered when choosing sample geometry:

- In the bending and the shear modes, there are additional contributions from the other deformation mode. These contributions can be neglected if the following guidelines concerning sample geometry are observed (ISO 6721):
  - Shear mode:
    diameter > 3 x sample thickness.
  - 3-point bending mode:
    sample length > 8 x sample thickness;
    sample length > 3 x sample width.-
    Dual and single cantilever mode:
    sample length > 16 x sample thickness;
    sample length > 6 x sample width.
- From the physical point of view, the sample and sample holder represent two springs connected in series. The corresponding spring constants (stiffnesses) determine the displacement amplitude for a given force amplitude. To calculate the modulus, we are only interested in the part of the displacement amplitude that originates from the deformation of the sample. The DMA measures the total stiffness of the system, i.e. "sample + sample holder". The actual sample stiffness is calculated from the measured total stiffness and the stiffness of the sample holder.
  To avoid larger errors, the sample geometry should be chosen so that the stiffness of the sample is at least 5 times less than that of the sample holder.
- When thin samples are measured in tension, high stresses may result even with low applied forces; the samples are close to their elastic limit even before the start of the measurement.
  Example: 30-µm thick sample, 4 mm wide, tensile strength 10 MPa
  → maximum force is 1.2 N.
  It should be noted that this force is the sum of the offset and the dynamic force.

## Choosing the force and displacement amplitudes

Three different factors should be taken into account when choosing the force and displacement amplitudes:

1. Linearity of the sample (determines the maximum displacement amplitude)
2. Maximum stress that can be applied to the sample (determines the maximum force)
3. Resolution of the instrument

In general, DMA measurements are performed using displacement amplitudes at which the behavior of the material is still "linear". Deviation from linear behavior, i.e. the point at which the modulus depends on the displacement amplitude, defines the maximum deformation and therefore the maximum stress above which irreversible changes in the sample can occur. In tension experiments, the tear strength of the sample also represents an upper limit for the applied stress. Here you should be aware that high local tensional stresses arise at the clamping position if excessive force is used to fix the sample. This can lead to local changes in sample dimensions, e.g. the sample is thinner at the fixing point. Samples for measurement in tension should therefore be clamped so that as little deformation as possible occurs at the clamping position. With hard samples, sample deformation due to clamping can be reduced by wrapping the sample in aluminum foil at the clamping position – this improves contact and means that less force is necessary to fix the sample securely in place.

In the shear mode, the limits for force and displacement amplitudes are also largely determined by the properties of the sample. In addition, however, the frictional force use to fix the sample in the shear holder also limits the maximum stress that can be applied. The frictional force depends on the sample (coefficient of friction) and on the force used to clamp the sample. Clamping of the sample inevitably leads to its deformation. Basically samples should be clamped as weakly as possible and as strongly as necessary. For most samples, it is sufficient to hand-tighten the clamping screws of the shear sandwich holder. If the clamping screws are tightened with a torque wrench, the applied torque should not exceed 40 cNm. At higher torques, the shear sandwich holder could be damaged. If the start temperature for your experiment is significantly below the clamping temperature (usually room temperature), it is advisable to retighten the sample at the start temperature because of thermal shrinkage.

The maximum stress can be experimentally estimated by performing a displacement amplitude scan. An experiment illustrating this for a shear measurement is shown in Figure 1.
The linearity range of a sample is also measured using a displacement amplitude scan. DMA measurements should whenever possible be performed within the linear range of the sample. In the ex-

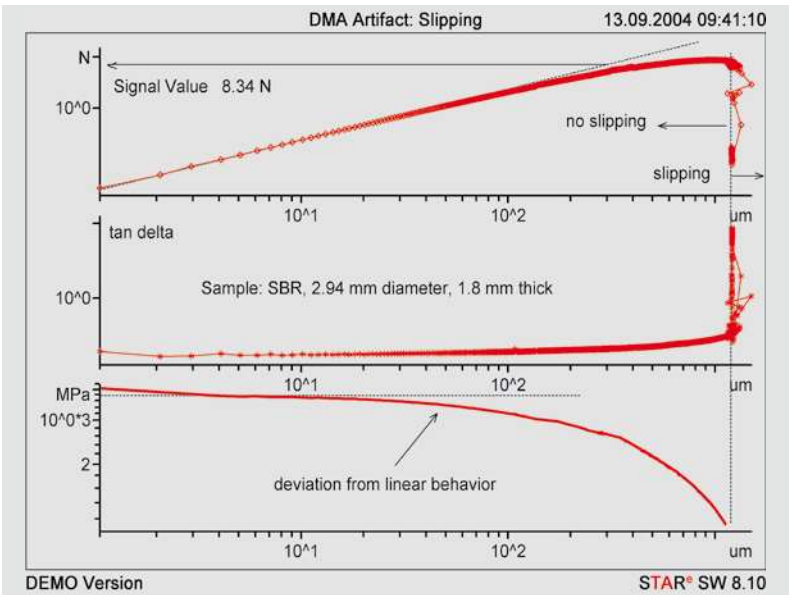



Figure 1.
A displacement amplitude scan in which the DMA successively increases the displacement amplitude and measures the necessary force allows you to estimate the maximum clamping stress. When this limit is reached, the sample begins to slip. This leads to very high tan δ values and erratic behavior of the force (and the modulus). In this example, the sample begins to slip at 8.33 N.

ample shown in Figure 1, this would be the case up to a displacement amplitude of about 10 µm. This value is typical for lightly filled elastomers.

Suitable values for the displacement and force amplitudes as a function of sample geometry can be obtained by using the "Modulus Calculator" (Figure 2) (see www.tiscalinet.ch/mschubnell/).

## Offsets

An offset force (i.e. pretension, precompression or predeformation) has to be applied to samples measured in the tension, compression and 3-point bending modes. Without this offset, the sample would only be under load during half the deformation cycle. The situation for 3-point bending is illustrated in Figure 3 as an example.

To subject the sample to a force throughout the entire deformation cycle, the offset must at least equal the force amplitude. The offset depends very much on the sample: Experience has shown that useful preliminary results can generally be obtained with an offset corresponding to about 150% of the force amplitude.

## Choosing the measurement frequency

To determine a DMA data point, the force on the sample and the deformation of the sample must be measured for at least one cycle (cycle [s] = 1/ frequency [Hz]). This means that at low frequencies the measurement of a data point takes significantly longer than at high frequencies (e.g. 10 Hz → 0.1 s, 0.1 Hz → 10 s). In principle, the stiffness of the sample should not change during the measurement of a data point.

In temperature scans, this condition is strictly speaking never fulfilled. In particular, at low frequencies and high heating rates, situations can arise in which the stiffness of the sample changes rapidly (such as during a glass transition). Heating rate and measurement frequency must therefore be matched so that adequate temperature resolution is always achieved.

The frequency at which a measurement is performed may also depend on the information required: For example, the **$\alpha_c$-relaxation** of polyolefines is best studied at frequencies of less than 1 Hz. With temperature scans, it is advisable to perform the measurements at different frequencies. This then yields information about the frequency dependence of the observed effects, which in turn simplifies their interpretation (for example, melting processes are not frequency dependent whereas relaxation processes usually exhibit marked frequency dependence).

The maximum frequency at which a sample can be mechanically stressed depends both on the deformation mode used and on the geometry and the modulus of the sample. In general, in a DMA, several more or less pronounced resonance regions occur that can quite possibly fall within the specified measurement range of the DMA. Table 2 shows the frequency limits for different sample holders. Above these frequencies, resonance effects can be expected due to the natural oscillation frequency of the sample (according to ISO 6721).

## Procedure with an unknown sample

It is of course difficult to recommend any general procedure for analyzing an unknown sample – in practice, samples are usually too "individual". This means that an appropriate method has to be developed for each sample.

Nevertheless, an attempt to define a standard approach is presented sche-

Figure 2.
To estimate the approximate sample dimensions and the force and displacement amplitudes, we recommend you the use a "Modulus Calculator" (see also www.tiscalinet.ch/mschubnell).

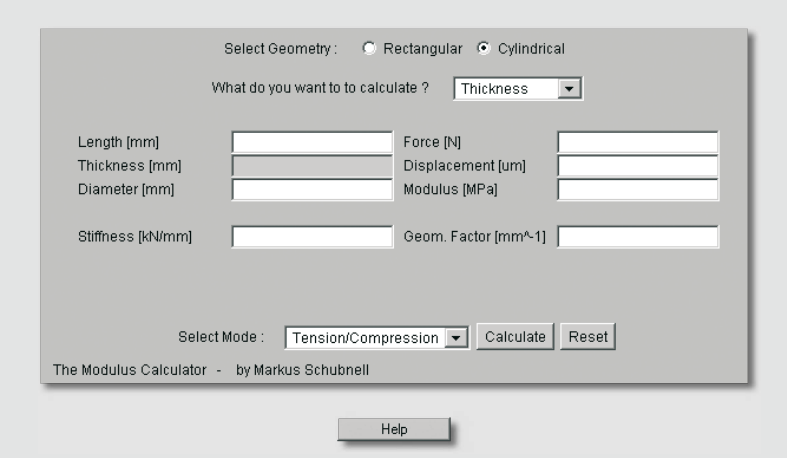



Figure 3.
Force amplitude with and without a force offset.

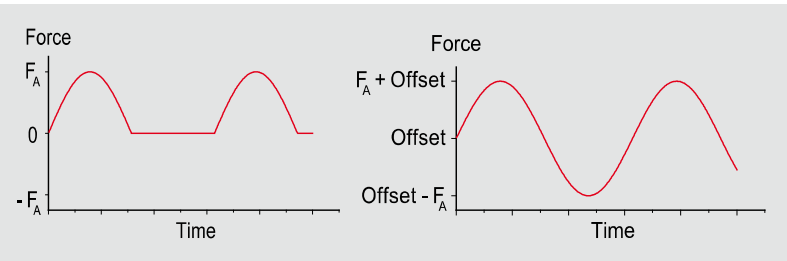



Table 2.
Limiting frequencies above which resonance effects due to natural oscillation of the sample are to be expected (ISO 6721). Here E′ or G′ is the storage modulus, δ the density, L the length of the sample and d the sample thickness (only in the bending mode).

| **Mode** | **Limiting frequency** due to natural oscillation of the sample (ISO 6721) | **Example** |
|---|---|---|
| 3-point bending | $f < 0.057 \frac{d}{L^2} \sqrt{\frac{E'}{\rho}}$ | E′ = 1 GPa, ρ = 1000 kg/m$^3$, L = 30 mm, d = 2 mm → f < 127 Hz |
| Dual cantilever<br>Single cantilever | $f < 0.082 \frac{d}{L^2} \sqrt{\frac{E'}{\rho}}$ | E′ = 1 GPa, ρ = 1000 kg/m$^3$, L = 30 mm, d = 2 mm → f < 182 Hz |
| Tension/ Compression | $f < \frac{0.04}{L} \sqrt{\frac{E'}{\rho}}$ | E′ = 1 GPa, ρ = 1000 kg/m$^3$, L = 10 mm → f < 3810 Hz |
| Shear | $f < \frac{0.04}{L} \sqrt{\frac{G'}{\rho}}$ | G′ = 1 MPa, ρ = 1000 kg/m$^3$, L = 2 mm → f < 663 Hz |

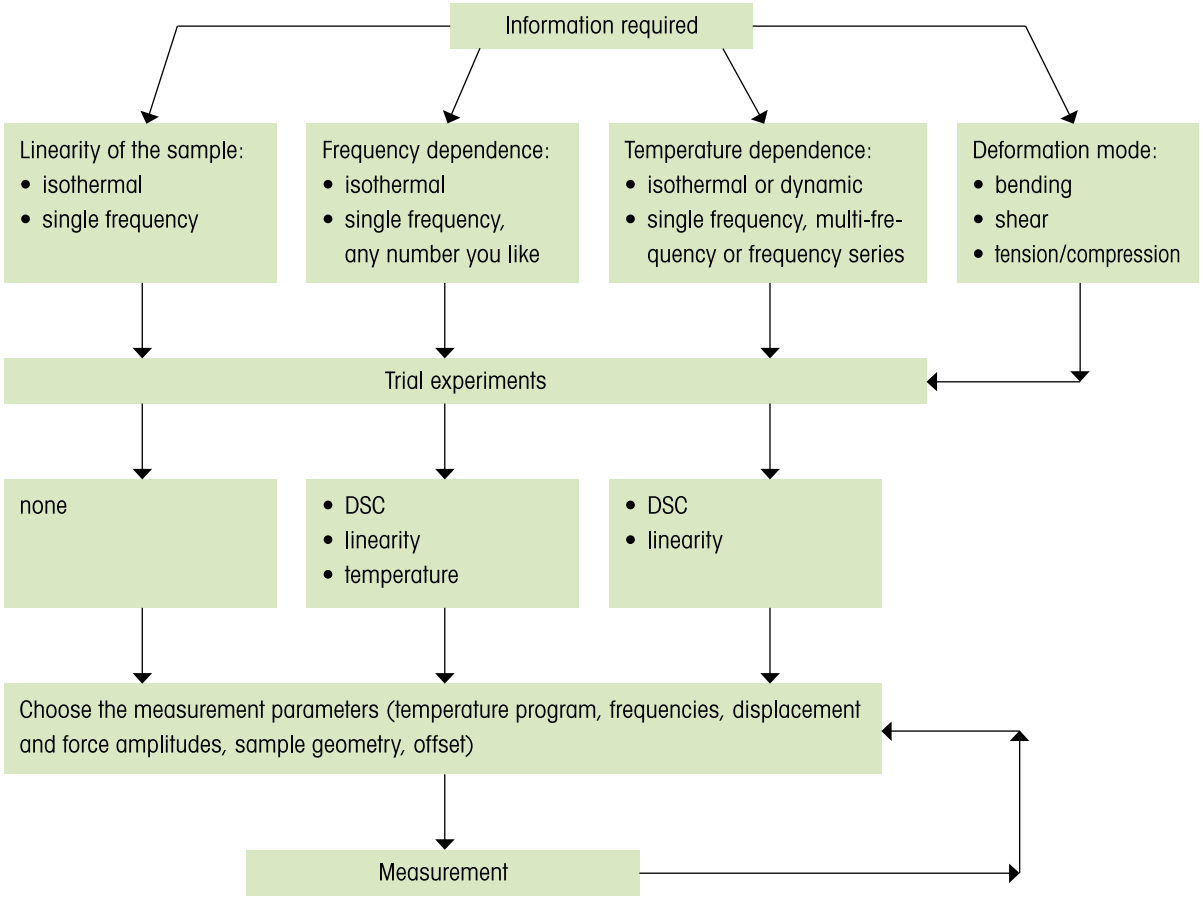



Figure 4.
General scheme for DMA measurements.

matically in Figure 4. The starting point with any unknown sample is to know exactly what information is required. This decides the deformation and measurement mode that is then used. Depending on the measurement mode chosen, it is advisable to perform one or more trial experiments. The purpose of these experiments is to determine the optimal mechanical measurement parameters so that the actual sample measurement can be successfully performed afterward.

## Conclusions

A DMA experiment begins with the choice of the right deformation mode for the measurements. This depends on the information you require, i.e. Young's modulus (bending, tension or compression) or shear modulus (shear), and on the type of sample. The next step is a trial experiment to determine the range in which deformation is linear and hence determine the maximum displacement amplitude. You can then use the "Modulus Calculator" to optimize the sample geometry and the force and displacement amplitudes so that the sample can be successfully measured in the expected modulus range with the DMA/SDTA861$^e$. Based on the measurement parameters, the offset parameters can then be set for 3-point bending, tension and compression. Table 3 summarizes approximate values for the sample geometry and force and displacement amplitudes for typical samples.

| Sample | Measurement mode | Typical sample geometry | Typical measurement parameters |
|---|---|---|---|
| Rubber, thermoplastics | Shear | diameter 4–6 mm<br>thickness 1–2 mm | max. force amplitude 5–15 N<br>max. displacement 3–10 µm |
| Composites, ceramics, metals | 3-point bending | length 6–10 cm<br>width 4–8 mm<br>thickness 1–3 mm | max. force amplitude 1–5 N<br>max. displacement 60 µm |
| Films (polymers) | Tension | length 10.5 mm<br>width 3–8 mm<br>thickness 10–100 µm | max. force amplitude 0.1–1 N<br>max displacement 10–100 µm |

Table 3.
Measurement mode, geometry and force or displacement amplitudes for samples typically investigated by DMA.