Interpreting DMA curves, Part 1

The first part of this work introduces the technique of dynamic mechanical analysis (DMA) and deals with non-isothermal DMA measurements. The second part (UserCom16) will cover various aspects of isothermal measurements, concentrating primarily on frequency-dependent elasticity.

Introduction

By the term **elasticity** we mean the way in which materials change their shape through the action of external forces. The **modulus of elasticity** of a material is the ratio of the mechanical stress to the relative deformation. In **Dynamic Mechanical Analysis**, DMA, a sample is subjected to a sinusoidal mechanical deformation of frequency, \( f \), and the corresponding forces measured. Conversely, the sample can be subjected to a defined force amplitude and the resulting deformation measured.

Measurement modes

A number of different measurement modes are used:

- Shear for samples with a shear modulus in a very large range from about 1 kPa to 2 GPa. This allows viscous liquids and even solid samples, e.g. polymers in the glassy state, to be measured.
- Three-point bending for stiff samples with a modulus of elasticity of up to 1000 GPa.
- Single and dual cantilever bending for samples that deform too strongly with three-point bending.
- Tension for thin bars, films and fibers.
- Compression for samples with a modulus of elasticity of up to about 1 GPa.

![DMA/SDTA861 measurement modes](image)

Fig. 1. DMA/SDTA861 measurement modes: 1 shear; 2 three-point bending; 3 dual cantilever (similar to bending but the sample is fixed); 4 single cantilever; 5 tension for thin bars, films and fibers; 6 compression. The clamping assembly is colored black and the sample red. The hatched areas show the parts of the clamping assemblies that remain fixed in position.

![Force and displacement at a frequency (f) of 1 Hz](image)

Fig. 2. Force and displacement at a frequency \((f)\) of 1 Hz. The phase shift, \( \delta \), can be calculated from the time delay, \( \Delta \), using the equation \( \delta = 2\pi f \Delta \).
The quantities measured

The raw data, i.e. the measured force and displacement amplitudes, \( F_a \) and \( L_a \), and their phase shifts, \( \delta \), are used to calculate the desired material properties:

- Complex modulus (\( M^* \)): modulus of elasticity, Young’s modulus (\( E^* \)) or shear modulus (\( G^* \))
- Storage modulus, \( M' \), proportional to the energy stored elastically and reversibly
- Loss modulus, \( M'' \), proportional to the energy transformed into heat and irreversibly lost
- Loss factor, \( \tan \delta \). With completely elastic materials no phase shift, \( \delta \), occurs; completely viscous materials show a 90° phase shift. The loss factor of viscoelastic materials is between 0 and infinity (\( \delta = 90\degree \)). The term \( \tan \delta \) corresponds to the ratio of \( M'' \) to \( M' \).

The moduli are calculated according to the following formulas:

\[
|M^*| = \frac{F_a}{L_a} \quad M' = |M^*| \cos \delta
\]
\[
M'' = |M^*| \sin \delta \quad \tan \delta = \frac{M''}{M'}
\]

where \( g \) is known as the geometry factor calculated from the sample dimensions.

\( E \) and \( G \) are related by Poisson’s ratio, \( \mu \):
\[
E = 2 (1 + \mu) \times G
\]

For most isotropic materials, \( \mu \) lies between 0.2 and 0.5, and \( E \) is 2.4 to maximum 3 times greater than \( G \). In the rubbery-elastic region of unfilled materials, \( E = \frac{3}{2} G \) and in the glassy state \( E = 2.7 G \).

With anisotropic materials, e.g. unidirectional fiber reinforced plastics, \( E \) can be more than one hundred times larger than \( G \).

If a material is heated, the storage modulus decreases step-wise by several orders of magnitude. The step corresponds to a peak in the loss modulus. If the transitions are frequency-dependent, they are in fact relaxation transitions, which with increasing frequency shift to higher temperatures.

**Measurement details**

- Usually with DMA measurements, the measurement is performed at constant displacement amplitude, and a maximum force is set that should not be exceeded even with stiff samples. An unsuitable choice of the displacement or force amplitude can affect the measurement accuracy. Amplitudes greater than 1 µm and 10 mN are optimal, as long as the...
Commonly used thermoplastics such as polyvinylchloride and polystyrene have a modulus of elasticity of about 3 GPa. Their glass transition temperatures lie between room temperature and approx. 200 °C. At about 100 K above the glass transition, the polymers flow and can be plastically deformed (Fig. 6).

• Heating rates of $\leq 3$ K/min are usually used because of the low thermal conductivity of plastics and the relatively large samples – except for trial measurements. The same applies to cooling measurements.
• To determine the frequency dependence, measurements are performed with several frequencies. The frequencies can be either mixed (simultaneous multi-frequency mode) or applied individually one after the other (sequential frequency series).

Besides measurements with a dynamic temperature program, the DMA/SDTA861e can also perform isothermal measurements with increments of increasing or decreasing frequency, displacement amplitude and force amplitude.

The presentation of DMA curves
Since moduli can change by several orders of magnitude, a linear presentation cannot adequately display the measurement data (Fig. 3). For example, a step of 1 GPa to 10 MPa cannot be distinguished from a step of 1 GPa to 1 MPa. In the logarithmic display, however, such differences can be easily seen (Fig. 4).

Interpretation of DMA curves with a dynamic temperature program
The storage modulus of commonly used materials decreases with increasing temperature. The storage modulus of metals used for constructional purposes such as steel or aluminum alloys hardly changes up to temperatures of 400 °C (Fig. 5). Stepwise changes are caused by relaxation transitions (e.g. glass transition) or phase transitions (e.g. melting and crystallization). Peaks in the loss modulus and the loss factor, $\tan \delta$, correspond to the steps in the storage modulus.

Amorphous materials go through a glass transition on heating or cooling. The modulus changes by one to four decades. The same occurs when the crystallites of semicrystalline polymers melt. Such phase transitions do not of course exhibit the large frequency dependence of relaxation transitions.

Commonly used thermoplastics such as polyvinylchloride and polystyrene have a modulus of elasticity of about 3 GPa. Their glass transition temperatures lie between room temperature and approx. 200 °C. At about 100 K above the glass transition, the polymers flow and can be plastically deformed (Fig. 6).
Elastomers such as natural rubber, NR, exhibit a glass transition below room temperature and, because of chemical cross-linking, do not flow (Fig. 5). This low degree of cross-linking occurs during vulcanization of the originally thermoplastic rubber.

Thermosets such as epoxy resins are three-dimensionally cross-linked macromolecules. Their glass transition region is significantly above room temperature. Due to their three-dimensional cross-linking, they do not flow when the temperature is increased. The starting materials of thermosets consist of several different components, which are usually referred to as the “resin” and the “hardener” or “curing agent”. When the thermoplastic starting materials harden or cure, a three-dimensional network is produced and the glass transition temperature increases by 50 K to 300 K (Fig. 10).

If the macromolecules are mainly aligned as a result of processing, they are referred to as orientated polymers. They are then anisotropic, i.e. their properties are orientation-dependent. This also applies to fiber-reinforced polymers.

With amorphous and semicrystalline materials, several relaxation transitions are observed; the transition at the highest temperature is known as \( \alpha \)-relaxation or the glass transition. It is assigned to cooperative molecular movement over a range of several nanometers, while the weaker secondary relaxation or \( \beta \)-relaxation is due to the movement of short segments. Relaxation processes are frequency-dependent, in contrast to melting processes, crystallization and chemical reactions, and can therefore be easily identified. The glass transition shifts by 5 K to 10 K per frequency decade. \( \beta \)-relaxation (Fig. 7) is even more frequency-dependent with values of at least 10 K/decade.

Incompatible mixtures of amorphous polymers and block copolymers show the glass transitions of the individual components. Compatible mixtures and random copolymers exhibit only one glass transition between the glass transitions of the individual components (Fig. 8). The relative content of such samples can be estimated from the curves of pure polymers.
Semicrystalline thermoplastics have properties that depend on the crystallinity. Some plastics, e.g. polyethylene terephthalate, remain amorphous after shock cooling from the melt, and then crystallize when heated to above their $T_c$ (Fig. 9).

With thermosets, the main interest is in the behavior of the thermoplastic starting materials, the increase of the modulus on gelation, and the glass transition of the fully cured thermoset (Fig.10). Such measurements, which can cover a modulus range of more than 4 decades, can only be performed in the shear mode.

**Final comments**

DMA measurements provide an insight into temperature- and frequency-dependent molecular movement, and also supply the engineer with information on material properties regarding stiffness, damping behavior and the range of temperature in which materials can be used. DMA measurements show especially well how the glass transition depends on factors such as moisture or the degree of curing (see UserCom11, pages 8 to 13).

When unknown samples are measured with DMA, it is always a good idea to perform a DSC measurement at 20 K/min over a relative large temperature range. From the DSC curve one can often choose a reasonable temperature range for the DMA measurements to prevent the sample from melting completely or decomposing in the DMA. This also gives one the opportunity to perform a second measurement on the same sample, if need be, even with new sample geometry.

In general, DSC measurements aid the interpretation of DMA curves (and vice versa). DSC and DMA measurements provide different information and complement one another ideally; one technique cannot however replace the other.

**Publishing Note:**

This application has been published in the METTLER TOLEDO Thermal Analysis UserCom No. 15. See www.mt.com/ta-usercoms