Thermal Analysis

DMA evaluation

In general, the mechanical properties of materials depend on frequency. A good understanding of the influence of frequency on a material is therefore very important for its practical use. For example, a material appears hard under the action of a force at high frequency, but soft when the force is applied slowly. In the latter case, the molecules have much more time to adapt to the situation through relaxation processes.

The DMA evaluation software option is used for dynamic mechanical analysis. It allows you to study material behavior over a wide frequency range.

First of all, the software option allows you to program:
- Isothermal frequency sweeps, with linear or logarithmic increments;
- Multi-frequency measurements: This allows you to define 4 simultaneous frequencies with a fixed ratio of 1:2:5:10 for isothermal or heating/cooling measurements;
- Frequency series measurements: This allows you to define up to 10 frequencies for isothermal or heating/cooling measurements. The frequencies are processed sequentially and continuously during measurements.

Secondly, you can evaluate isothermal frequency sweeps by applying the Time-Temperature Superposition principle (called the TTS or master curve technique):
- Master curves of modulus and compliance (complex modulus, storage part, loss part and the loss factor, tan δ), over the frequency range of interest, can be constructed manually or automatically with predefined parameters for a reference temperature.
- The shift factor diagram or table at the reference temperature is generated automatically.
- The activation energy diagram can be calculated using a specified reference frequency.

The DMA evaluation software option offers a number of important advantages:
- Frequency-dependent effects such as glass transitions can be easily distinguished or separated from effects that do not depend on frequency, e.g. melting. This is very helpful for curve interpretation.
- Temperature gradients within a sample during isothermal frequency sweeps are minimal. This together with the direct measurement of sample temperature leads to master curves of high precision.
- The master curve technique extends the frequency range to beyond the range that can be directly measured of 0.001 Hz to 1000 Hz. This allows high quality mechanical spectroscopy to be performed. Mechanical properties can be characterized in much more detail and a much better insight is gained into molecular relaxation phenomena.
The Time-Temperature Superposition Principle

The behavior of viscoelastic materials like polymers depends on frequency and temperature. In general, there is equivalence between frequency and temperature behavior during transition processes. Since the frequency dependence is directly related to time dependence, the relationship is usually referred to as the Time-Temperature Superposition principle (TTS).

The TTS principle is the theoretical basis of the master curve technique. A master curve is often used to predict material performance at frequencies outside the range that can be measured with a dynamic mechanical analyzer. It is constructed by shifting isothermal frequency sweeps at different temperatures according to the TTS principle.

Various models have been developed to describe the shift behavior. In the DMA evaluation software option, the well-known Williams–Landel–Ferry (WLF) model is implemented for automatic master curve construction.

\[
\log \alpha_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)}
\]

Where,
- \( \alpha_T \): shift factor
- \( C_1, C_2 \): universal constants
- \( T_0 \): reference temperature in Kelvin
- \( T \): sample temperature in Kelvin

These parameters are well known for many materials. The software option provides a list of these parameters and also allows you to add your own ones.

As an example, the diagram shows master curves of the shear storage modulus, \( G' \), and shear loss modulus, \( G'' \), of a sample of vulcanized styrene-butadiene rubber (SBR) over a wide frequency range from \( 10^{-6} \) to \( 10^{10} \) Hz. The reference temperature is 0 °C. The glass transition takes place over a frequency range of about 8 decades. It is characterized by an increase of \( G' \) with increasing frequency and a maximum of \( G'' \) at about \( 10^3 \) Hz. Below \( 10^{-2} \) Hz, \( G' \) remains practically constant while \( G'' \) decreases continuously.

The wide frequency range (up to 1000 Hz) offered by the DMA/SDTA861 is very advantageous - the master curve can be constructed more quickly because less isothermal frequency sweeps need to be measured. For instance, 6 isothermal frequency sweeps in steps of 10 K or greater in shear mode were used to construct the master curves shown in the diagram. The isothermal sweep from 0.001 Hz to 1000 Hz at 0 °C (red) was selected as the reference measurement (shift factor 1) because it covers most of the transition process.

The shift factors are displayed as a function of reciprocal temperature values in a shift factor diagram. Multiplying the shift factor diagram by a reference frequency value (1 Hz) gives an activation energy diagram.
Elastomers exhibit excellent elastic and viscoelastic properties, i.e. both high deformability under applied stress and delayed but usually complete recovery after stress removal. The technological processes and applications in which elastomers are used often involve dynamic stress over a wide frequency range, e.g. rubber used for automobile tires. The characterization of the influence of frequency on the mechanical properties of elastomers at typical temperatures of use is therefore invaluable for material optimization or failure analysis. The DMA/SDTA861\textsuperscript{e} and the DMA evaluation software facilitate these types of studies and allow isothermal frequency sweep experiments to be performed and evaluated.

Frequency sweep measurements of 4 different samples of styrene-butadiene rubber (SBR) at –10 °C are shown in the diagram. The samples were prepared by vulcanization with different amounts of sulfur (phr, parts per hundred). This resulted in different degrees of cross-linking. The SBR vulcanized with 2 phr sulfur is used as an example to explain the material behavior. The storage modulus, G', shows a step change of about 3 decades through the relaxation range, while the tan δ curve (loss factor) displays a peak with a maximum of about 2.3 at 0.3 Hz. At high frequencies, the material appears hard and the value of G' is high; at low frequencies it appears soft and the G' value is low.

The influence of the degree of cross-linking is also clearly seen in the diagram. For example, at a frequency of 100 Hz, the storage modulus increases from 113.9 MPa for the non-vulcanized SBR to 658.9 MPa for SBR vulcanized with 4 phr sulfur. The step change of G' is shifted to lower frequencies with increasing sulfur content, and the tan δ peak maximum shifted from 10 Hz to about 0.01 Hz. This indicates that the elasticity of SBR increases with increasing degree of cross-linking.

The curing process of thermosets allows material performance to be predicted. Curing too slowly, for example, often results in a material that is weaker because network formation cannot be completed due to processes such as vitrification. Understanding the curing profile of thermosets is therefore very important for quality control and for process design and optimization. The DMA evaluation software together with the high sensitivity of the DMA/SDTA861\textsuperscript{e} is a powerful tool for studying the curing of thermoset systems.

The diagram shows the single cantilever measurement curves of a carbon-fiber reinforced prepreg measured in frequency series mode. The material shows a Young’s modulus, E’, of about 10 MPa at 130 °C, where the matrix resin is in the liquid state. The main contributor to E’ is the carbon fiber substrate. The curing process of the prepreg takes place in the range 130 °C to 200 °C and is independent of frequency. During this process, E’ increases and tan δ decreases, indicating that the material becomes harder. At the end of curing, the glass transition temperature of the prepreg reaches the processing temperature and vitrification occurs as a result of the slow heating rate of 2 K/min. This is clearly seen from the frequency-dependent step increase of E’ and the tan δ peaks.

Lower vitrification temperatures were measured at higher frequencies. Upon further heating, the system devitrified. This again is a frequency-dependent process.
Glass Transition of a PET Film

The glass transition is a major effect exhibited by many amorphous and semicrystalline polymers. It is frequently monitored for quality control and research purposes because a material's physical properties change drastically as it passes from a hard glassy state to a rubbery elastic state. The glass transition of films and fibers is often determined by DMA, in particular in cases where mechanical properties (e.g. modulus and damping) and frequency behavior are of great importance for the intended application.

A commercial transparency made of polyethylene terephthalate (PET) was measured with the DMA/SDTA861 by heating the sample through the glass transition range in tension mode. The figure shows the measurement curves of the film sample recorded at four simultaneous frequencies. The Young's modulus, $E'$, of the material is 2.93 GPa at 50 °C. A broad glass transition, with a gradual decrease of $E'$ of less than one decade, indicates that the material has a high degree of crystallinity. The frequency dependence of this transition is shown by the shift of $E'$ to higher temperature with increasing frequency. The same can be observed in the shifts of the loss modulus $E''$ or tan $\delta$ peaks.

The measurements illustrate the high frequency resolution of the DMA/SDTA861. For example, the shift of $E''$ and tan $\delta$ due to a very small frequency change from 1 Hz to 2 Hz (about 2 K at 75 °C) is clearly visible.

Characterization of a Toner

When polymeric materials containing additives are measured, thermal processes such as melting and the glass transition often overlap. This makes it difficult to interpret the different events that occur when an unknown material is measured. The example shows how the DMA evaluation software together with the wide frequency range (0.001 Hz to 1000 Hz) of the DMA/SDTA861 provides a powerful tool for separating and identifying overlapping effects by making use of different frequency behavior.

Toner consists of thermoplastic base material with different additives. The diagram shows the shear storage modulus, $G'$, as a function of temperature for a frequency series. A broad step in the modulus can be seen in the curve for 1 Hz. With increasing frequency, a second step becomes increasingly apparent. The first step shows approximately the same starting temperature independent of the frequency. It can therefore be attributed to the frequency-independent melting process of additives. The second step, which is shifted to higher temperatures with increasing frequency, corresponds to the frequency-dependent glass transition of the thermoplastic base material.

Literature

A detailed description of the use of thermal analysis techniques in elastomer analysis is given in the Collected Applications booklets Elastomers Volume 1 and Volume 2 (ME-51725067 and 51725068) and Thermoplastics (ME-51725002).