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TEST PROCEDURES
OF ELASTOMER COMPONENTS

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Physical Analytical Test Methods

Authors:
Bernd Sprenger
Dipl.-Ing. Bernhard Richter,
Dipl.-Ing. (FH) Ulrich Blobner

The following article presents the three most important methods of physical analysis for elastomers:

Thermogravimetric Analysis (TGA):

Description of Formulation Compositions and Rapid Detection of Formulation Consistency
Rubber compounds and elastomer finished parts are multi-component mixtures of processing aids, plasticizers, polymers, carbon blacks and fillers. They all play a role in the properties of use.
Even though it is extremely difficult to determine the original formulation from a vulcanized article, approximate methods have been established with which the quantitative proportions of the main components can be measured quickly and reproducibly.
In the TGA, a material sample (approx. 10 mg) is continuously heated up to max. 1000¬∞C and the relative weight loss is measured above the temperature. The evaluation allows the mixture components to be quantitatively determined as evaporable or volatile components

(predominantly plasticizers), pyrolysable components (predominantly polymers), oxidizable components (predominantly carbon black) and non-oxidizable components (fillers, primarily metal oxides), also referred to as ash residue.

Unfortunately, there is no universal TGA method to do the many different types of elastomers justice.

- **VDA 675 135** (2016-05): The old edition described an effective, simple method with a constant heating rate. The new edition of the 2016 standard has come closer to meeting ISO 9924.
- **ISO 9924-2** (2016-08): For polar and halogen-containing samples with long measuring time. Advantage: The carbon black produced during polymer pyrolysis is (usually) detected separately and not added to the carbon black quantity.
- **DIN EN ISO 11358** (2014-10): General description of the performance of a thermogravimetric analysis. The heating program is not defined.

The green curve of the following Fig. 1 shows the weight decrease over temperature (initial weight at RT = 100%) while the blue curve shows the first derivative of the relative weight over temperature. The latter is used to differentiate more precisely between the curves and the events.

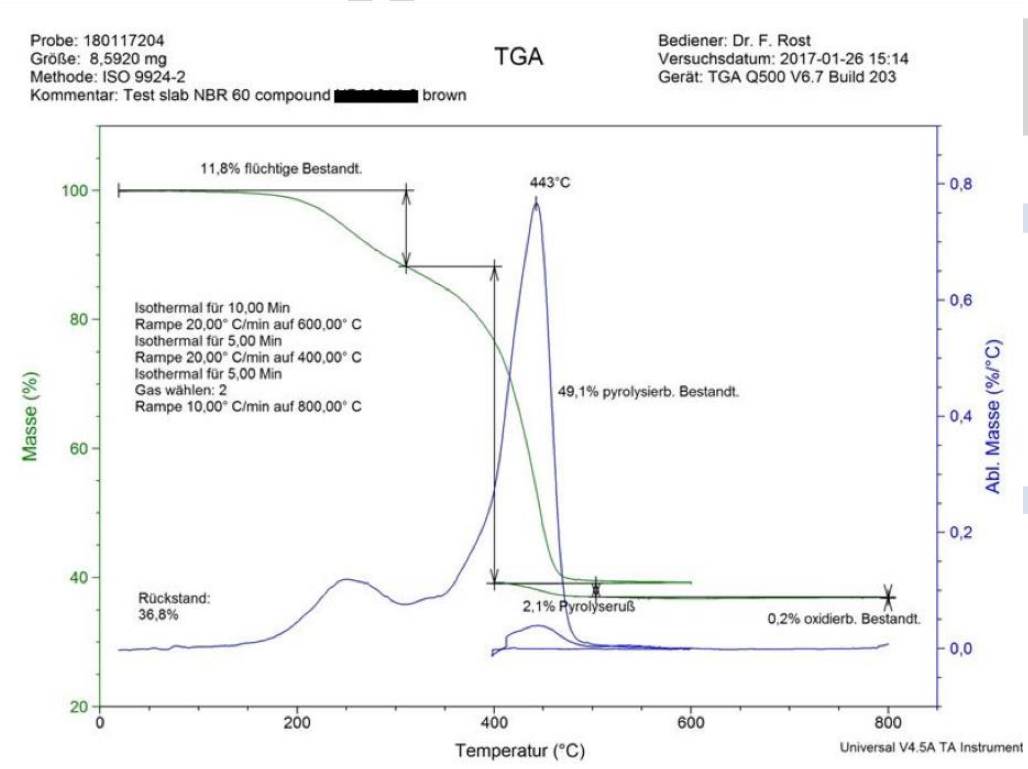

Fig. 1: Result Curves of a TGA Test

The method according to ISO 9924-2 shows that despite the 11.8% volatile components and the 49.1% pyrolysable components there are 2.1% pyrolysis carbon black. The high ash residue of 36.8% and the low oxidizable components of 0.2% are typical for a colored

compound without carbon black as filler.

2. Differential Scanning Calorimetry, better known as DSC:

The DSC method (Differential Scanning Calorimetry) measures changes in the specific heat capacity of samples as a function of temperature. The specific heat capacity indicates how much thermal energy a substance can store.
The most common and well-known application of the DSC method in the elastomer range is the determination of the glass transition. This is determined by the turning point of the heat flow over the temperature. The test method most frequently used in laboratories for this purpose is ISO 11357-2, which alternatively determines the glass transition point using the first derivative (Ti,g) or half the height of the tangents (T1/2,g), see Fig. 2. Further test standards for the DSC are VDA 675116, ASTM D3418 and ASTM D7426. However, the glass transition temperature determined according to a calorimetric measuring principle does not always correspond to the thermo-mechanical glass transition temperature. This means that the temperatures determined do not always represent reliable low-temperature limits for sealing applications where crystalline sequences in the polymer in particular can prevent resetting. This can occur particularly with EPDM and HNBR materials. Therefore, another method is recommended for EPDM and HNBR materials to determine the cryogenic limit (TR 10 according to ISO 2921, compression set at low temperatures according to ISO 815-2 or dynamic in DMA). In addition, DSC analysis offers the possibility of detecting and quantifying endothermic and exothermic reactions during heating and subsequent cooling, which can be helpful in particular to detect residual amounts of cross-linker in the elastomer.

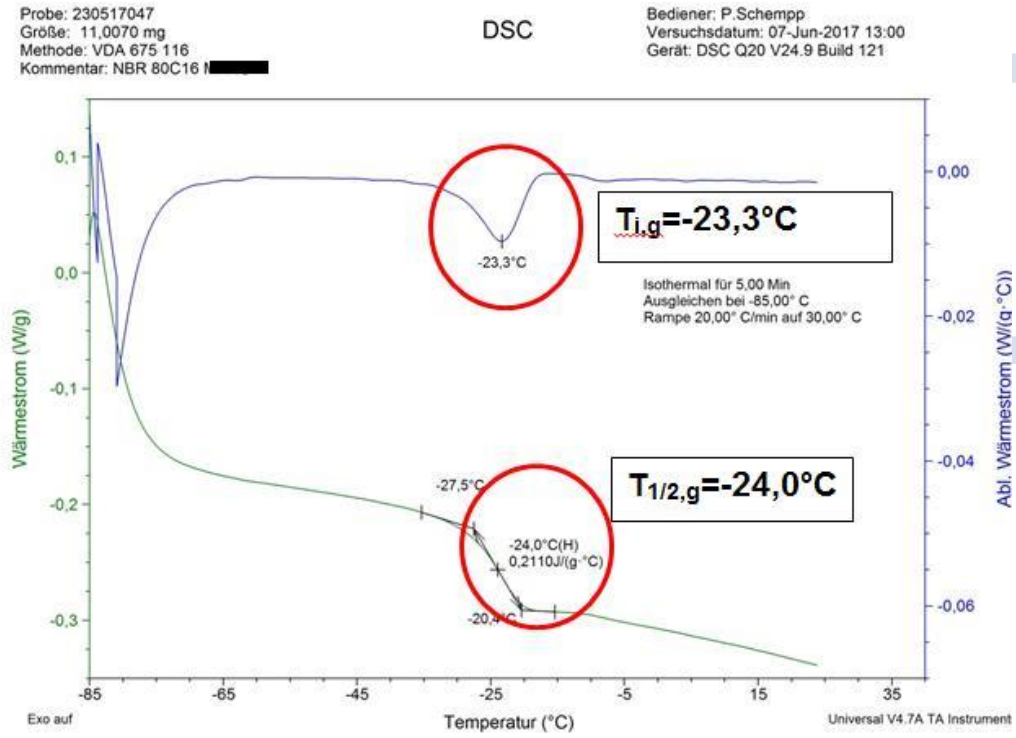

Fig. 2: Result curves of a DSC test for the determination of glass transition

3. Dynamic Mechanical Analysis (DMA):

An increasingly important test method, especially for determining characteristic values for numerical simulation.

In recent years, this process has become increasingly important and is no longer reserved for pure material research.
Elastomers are viscoelastic materials and combine viscous and elastic properties. These properties can be best measured in dynamic tests using DMA.

DMA measures quantitatively and qualitatively (at different deformations and frequencies):

- Viscoelastic behavior and damping properties, loss and memory module
- Flow and relaxation behavior as a function of temperature (-100°C to 600°C)

In contrast to older dynamic test methods, which usually require precisely standardized specimens, the DMA can easily analyze sections of finished parts, test plates or damaged parts. As is standard, the usual tensile specimens (S3A, S3 etc.) shortened in the clamping range are used in tensile mode. The compression and bending modes require plane-parallel specimens from test plates or finished parts. The most common test modes are:

- Cantilever (clamped bend, single or double)
- Tensile mode
- Pressure mode

Testing is carried out in accordance with defined standards, such as ISO 6721-1 or user specifications.
In contrast to the limited measurement possibilities with TGA and DSC, many possibilities are available with DMA:

- Path; different amplitudes
- Frequencies
- Force, static or dynamic
- Memory and loss module
- Angle of loss (tan δ)
- Glass transition (frequency-dependent)

All values are measured within a very small tolerance range:

- Force max. 18N (Resolution: 10-5 N)
- Path resolution 1nm
- Frequency (sinusoidal) up to max. 200Hz
- Usual temperature range for elastomers from -100°C to above the decomposition temperature of the polymer.
- Measurement duration per test: Usually longer than in the TGA or DSC. The DMA has

a larger sample chamber volume and a poor heat transition into the sample, therefore low cooling and heating rates are used.

Basically, two operating modes of the DMA can be distinguished:

1. Dynamic measurements at different frequencies, amplitudes or temperatures
2. Creep tests under constant load or constant deformation at consistent or linearly decreasing or increasing temperatures; measured at constant load are the resulting deformations, or at constant deformation the required changing force is measured.

The following **Fig. 3** shows the DMA test of an EPDM material at different frequencies (blue: 1Hz, red: 10Hz, green: 50Hz) in tensile stress test mode. The declining curves on the left of the diagram show the memory module. The higher the frequency, the faster it increases with decreasing temperatures. The curves in the middle show the tan Œ¥ (maximum = glass transition point). This increases with higher frequency (-35¬∞C at 1Hz, -26¬∞C at 50Hz).

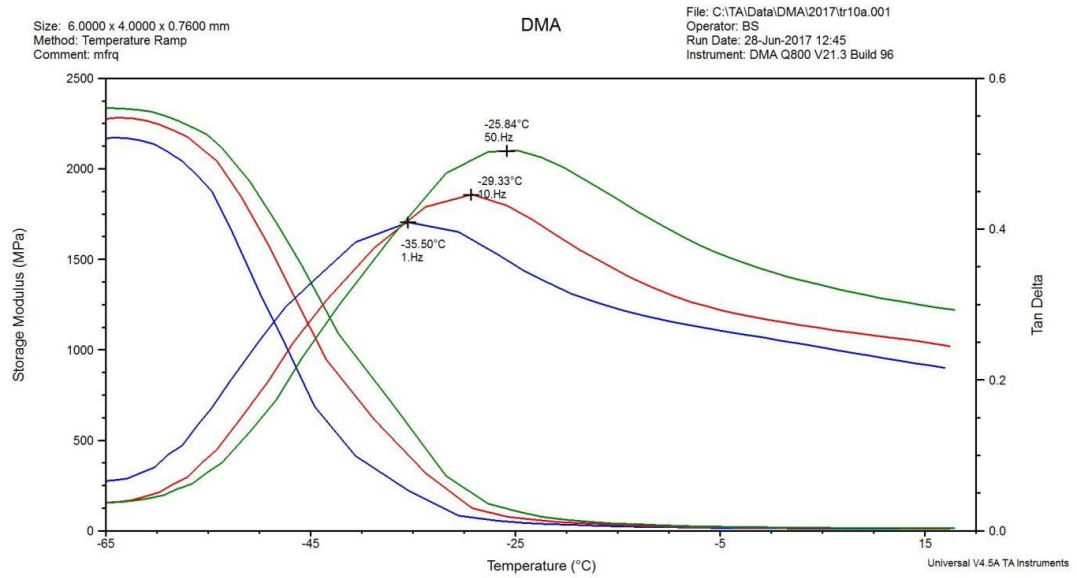

Fig. 3: Result curves of a DMA test at 3 different frequencies (memory module and tan δ)

DMA can be used to determine a large number of material properties, but a great deal of specialist knowledge and experience is required in order to be able to interpret and use the results in a practice-oriented manner for the user.

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